

Theoretical investigation of the nitrous oxide decomposition over iron zeolite catalysts

Vom Promotionsausschuss der
Technischen Universität Hamburg-Harburg
zur Erlangung des akademischen Grades
Doktor-Ingenieur
genehmigte Dissertation

von
Andreas Heyden
aus Pinneberg

2005

1. Gutachter: Prof. Dr. Dr. h.c. Frerich J. Keil

2. Gutachter: Prof. Dr. Joachim Werther

3. Gutachter: Prof. Dr. Alexis T. Bell

Tag der mündlichen Prüfung: 19.12.2005

Acknowledgments

This thesis is the result of my work as a Ph.D. student in the Department of Chemical Reaction Engineering at the Hamburg University of Technology in Germany. The project entailed joint work with the Department of Chemical Engineering at the University of California in Berkeley, USA.

First of all, I would like to thank my supervisors Professor Frerich J. Keil at the Hamburg University of Technology and Professor Alexis T. Bell at the University of California. Working under Professor Keil's and Bell's supervision has been an incredibly rewarding and enjoyable experience. I would like to thank Professor Keil particularly for his unfailing accessibility to discuss my work, for his consistent motivation to learn scientific fundamentals, and for opening up many possibilities to meet various researchers to discuss my work. To Professor Bell, I am thankful for giving me the opportunity to work on this exciting project, his enthusiasm towards my work, his discussions while I was in Berkeley and Hamburg, and for giving me words of encouragement whenever I needed them.

Next, my thanks go to Alexander Sasonov, Gamze Artug, Thore Oltersdorf, Ralf Renken, Tejinder Singh, Daniel Köpke, Jill Koglatis and Nasrat Kamal. They contributed to my thesis with their diploma thesis, Master thesis and project work. I also give special thanks to Jill Koglatis for revising parts of this thesis and making sure that I got healthy meals during the time I wrote this thesis.

I would like to thank my colleagues both in Hamburg and Berkeley for their friendship and support. In Hamburg, I would like to thank, in particular, Niels Hansen for revising this thesis and for helping me with some calculations presented in chapter 7. In Berkeley, my thanks go in particular, to Dr. Benjamin Wood for providing the experimental data used in this work and to Dr. Baron Peters for the fruitful discussions and for being such a great teacher and friend.

I would also like to thank all the other great researchers at various institutions for spending a significant amount of their time on discussing my work: Professor Arup K.

Chakraborty, Professor Martin Head-Gordon, Professor Volker Staemmler, Professor Albert Renken, Professor Joachim Sauer, Professor Matthias Scheffler, Dr. Liubov Kiwi-Minsker, Dr. Gerhard Pringruber, Dr. Jens Döbler and Dr. Bernd Kallies.

For providing the computer time necessary for this project the “Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen“ (HLRN) is acknowledged.

Finally, I like to thank Allison Hamada for her love, her encouragement and her always being there for me under all circumstances.

Schließlich möchte ich auch noch meinen Eltern und meiner Schwester danken, auf deren Unterstützung ich mich immer verlassen konnte.

Table of contents

1	Introduction	1
2	Control of nitrous oxide emissions.....	5
2.1	Kyoto process.....	5
2.2	Nitrous oxide emissions.....	6
2.3	Control of N ₂ O from nitric acid production.....	8
3	Theoretical background	13
3.1	Schrödinger equation	14
3.1.1	Born-Oppenheimer approximation	16
3.1.2	Variational principle and molecular orbitals.....	17
3.1.3	Hartree-Fock method	19
3.2	Density functional theory.....	20
3.2.1	Kohn-Sham equations	22
3.2.2	Exchange-correlation functionals.....	24
3.2.3	Hybrid exchange-correlation functionals.....	27
3.2.4	Basis sets	29
3.2.5	Basis set superposition error	31
3.3	Non-adiabatic effects	32
3.3.1	Spin surface crossing.....	34
3.3.2	Landau-Zener formula	35
3.4	Statistical methods	38
3.4.1	Potential energy surface	39
3.4.2	Transition state theory.....	45

3.4.3	Statistical mechanics and thermodynamic functions.....	47
3.4.4	Rates of reaction	50
4	Algorithms for finding transition states in chemical reactions	53
4.1	Interpolation methods.....	55
4.1.1	String method	57
4.1.2	Growing string method.....	60
4.2	Local saddle point search algorithms	63
4.2.1	Partitioned rational function optimization method.....	65
4.2.2	Dimer method	67
4.2.3	Improved dimer method	71
4.3	Comparison of improved dimer and P-RFO method	77
4.3.1	Details of calculations	78
4.3.2	Results	79
4.4	Algorithm for finding minimum energy crossing points.....	89
4.5	Conclusions	91
5	Comprehensive DFT study of the nitrous oxide decomposition over Fe-ZSM-5 .	93
5.1	N ₂ O decomposition over Fe-ZSM-5	94
5.1.1	Experimental characterization of Fe-ZSM-5	96
5.1.2	Theoretical characterization of Fe-ZSM-5	98
5.1.3	Conclusions	99
5.2	Computational model of the active site in Fe-ZSM-5	100
5.2.1	ZSM-5.....	101
5.2.2	Cluster models for extended systems	102
5.2.3	Limitations of the cluster model.....	105
5.3	Computational methodology	107

5.4	Computational results and discussion	109
5.4.1	Catalytic cycle on $Z[Fe]^+$	110
5.4.2	Catalytic cycle on $Z[FeO]^+$	126
5.4.3	Catalytic cycle on $Z[FeO_2]^+$	131
5.4.4	H_2O adsorption on $Z[FeO]^+$	132
5.4.5	Catalytic cycle on $Z[Fe(OH)_2]^+$	135
5.5	Comparison with experimental observation	137
5.6	Conclusions.....	141
6	Kinetic modeling of nitrous oxide decomposition on Fe-ZSM-5	143
6.1	Mechanism and kinetics of N_2O decomposition over Fe-ZSM-5.....	144
6.2	Effects of water vapor on the distribution of Fe species and the rate of N_2O decomposition	147
6.3	Simulation of temperature-programmed reaction experiments	149
6.4	Simulation of transient-response experiments	154
6.5	Oxygen adsorption and desorption from Fe-ZSM-5.....	158
6.6	Conclusions.....	161
7	Comprehensive DFT study of NO-assisted N_2O decomposition over Fe-ZSM-5	163
7.1	Experimental evidence of NO-assisted nitrous oxide decomposition	164
7.2	Computational methodology.....	168
7.3	Computational results and discussion.....	172
7.3.1	Interaction of nitric oxide with $Z[FeO]^+$, $Z[FeO_2]^+$ and $Z[OFeO]^+$	186
7.3.2	Catalytic cycle on $Z[FeONO]^+$	192
7.3.3	Catalytic cycle on $Z[FeO_2N]^+$	197
7.3.4	Catalytic cycle on $Z[FeO_2NO]^+$	201

7.3.5	Activation of poisoned $Z[Fe(OH)_2]^+$ sites	206
7.3.6	Catalytic cycle on $Z[FeOH]^+$	207
7.3.7	Formation of nitric oxide on single iron sites.....	212
7.4	Comparison with experimental observation.....	214
7.5	Conclusions	230
8	Summary.....	233
	List of acronyms.....	237
	List of symbols	241
	Literature cited	245
	Appendix	269
A	Convergence tests	271
A.1	Basis set.....	272
A.2	Cluster size	274
B	Apparent reaction rate constant for the N_2O decomposition on Fe-ZSM-5	281
B.1	System of rate equations.....	282
B.1.1	Gas species	282
B.1.2	Surface species	282
B.2	Pseudo-steady state approximation	283
B.3	Determination of main surface sites	285
B.4	Rate of change of nitrogen, oxygen and nitrous oxide.....	286

1 Introduction

The increasing concentration of greenhouse gases in the atmosphere and its consequences on global warming is an important environmental problem. The world's nitric acid plants represent the single greatest industrial source of nitrous oxide (N_2O) which is the third most important greenhouse gas following carbon dioxide (CO_2) and methane (CH_4). Having significant potential in contributing to the control of global warming, it has been found that the catalytic decomposition of nitrous oxide from industrial tail gas streams is an effective and cost efficient way of decreasing greenhouse gas emissions (Smit et al., 2001).

One peculiarity of the tail gas streams from nitric acid plants is the presence of both nitrous oxide and nitric oxide. Most catalytic systems active for nitrous oxide decomposition are inhibited by nitric oxide (e.g. those based on noble metals (Ru or Rh); see Oi et al. (1997) and Centi et al. (1997)). In contrast, for iron zeolite catalysts, it has been reported that nitric oxide significantly enhances the N_2O decomposition rate. As a result, iron zeolites have been proposed as possible catalysts for the stoichiometric decomposition of nitrous oxide into nitrogen and oxygen under industrial tail gas conditions (Kapteijn et al. (1996), Mul et al. (2001), Wood et al. (2002) and Zhu et al. (2004)).

Designing and optimizing catalysts that produce or decompose a specific product with a high yield and a high selectivity at low cost is a very demanding task. After having found a potential catalyst, a reaction network has to be established and kinetic measurements performed. Then, the new catalytic system must undergo testing for stability under industrial conditions and finally, scaled-up to a pilot plant level in order to study the interplay between reaction and diffusion under possibly non-isothermal conditions.

In order to speed-up the catalyst development process, researchers in catalysis and chemical reaction engineering would like to be able to predict the performance of a catalyzed reaction occurring in a reactor with knowledge only of feed composition, reaction conditions, reactor configuration, and catalyst composition and structure. Although accurate determinations of reactor performance given a set of rate parameters describing catalyst performance are possible, rate parameters must currently be obtained experimentally. Thus, a challenge is to develop theoretical methods to predict catalyst activity and selectivity from first principles (Bell, 2004).

Although comprehensive theoretical studies will probably not be able to substitute experimental studies to determine catalyst activity in the near future, combining theoretical studies to careful experiments can greatly improve the understanding of the catalyst system today, and hence, accelerate the development of better catalysts. Theoretical methods can help to determine reaction mechanisms, identify active sites, and possibly suggest methods to accelerate certain bottlenecks within the network of elementary reactions that the overall catalytic reaction is comprised of. These elementary reactions are usually undetectable in experiments. In some cases, spectroscopy or other surface science methods can shed some light on the nature of the most abundant reactive intermediates in the reaction network, but in many cases, only the overall rate and product distribution of the reaction network can be measured. As a result, if only overall kinetics are available, catalyst design is largely based on speculation about the nature of the rate limiting steps that determine the performance of the catalyst.

In this thesis, the nitrous oxide decomposition in the presence and absence of nitric oxide over iron zeolites is studied on a molecular level using density functional theory. The aim of this work was first to develop highly efficient algorithms for finding transition states on potential energy surfaces determined from quantum chemical calculations. Knowledge of transition states of chemical reactions is necessary to calculate rates of reactions from first principles. The next goal of this work was to determine the reaction mechanism of the nitrous oxide decomposition over iron zeolites,

identify the catalytically active sites, and explain apparently contradictory experimental observations. In particular, the role of water vapor and nitric oxide on the nitrous oxide decomposition over iron zeolites had to be elucidated.

The outline of this thesis is as follows. In chapter 2, some background information about the Kyoto protocol and nitrous oxide emissions, is presented. Some possibilities for controlling the nitrous oxide emissions from nitric acid production plants are summarized.

The different theoretical methods used to describe and understand chemical reactions on a molecular level are introduced in chapter 3. Molecular modeling of chemical reactions is based on quantum mechanics, statistical mechanics, and digital computation. To understand chemical reactions, the time-independent non-relativistic Schrödinger equation of a many-body system was solved. The density functional theory (DFT) approach for obtaining ground state properties was applied. To obtain thermodynamic functions and reaction rate constants from quantum mechanical data, standard statistical methods were used.

In chapter 4, three different types of algorithms for finding transition states in chemical reactions are presented. One of the major challenges in chemical kinetics continues to be the determination of transition states on potential energy surfaces obtained from quantum chemical calculations. An improved version of the dimer method has been developed. This algorithm is compared to both the original dimer method and the partitioned rational function optimization method for finding transition states. The improved dimer method in combination with the growing string method, an algorithm used to determine approximate intrinsic reaction coordinates, is found to be a highly efficient set of algorithms for finding first order saddle points in high dimensional quantum mechanical systems.

In chapter 5, the decomposition of nitrous oxide over iron zeolites is studied on a molecular level using density functional theory. The energetics and kinetics of the nitrous oxide decomposition are investigated on hydrated and dehydrated mononuclear iron sites in Fe-ZSM-5. An important part of this study is the determination of the effects of low concentrations of water vapor on the speciation of iron in Fe-ZSM-5. 63 elementary reactions are analyzed for their importance on the N_2O decomposition. The reaction mechanism and kinetic rate parameters obtained from first-principles are used to explain apparently contradictory experimental results. In particular, the large spread in rate parameters reported in the literature is discussed in this section.

To show that the mechanism and rate parameters determined from first principles can be used to provide insights into the effects of water vapor on experimental observations, macroscopic reactor simulation results are presented in chapter 6. Temperature-programmed reaction (TPR), transient response, and temperature-programmed desorption (TPD) experiments were simulated and compared with experimental data.

Chapter 7 presents studies of nitrous oxide decomposition over iron zeolites in the presence of nitric oxide on a molecular level using density functional theory. In total, 92 elementary reactions are investigated. A novel explanation of the promotional effect of nitric oxide on the nitrous oxide decomposition consistent with quantum chemical calculations and experimental findings is given.

Lastly, significant conclusions of this work are summarized in chapter 8.

2 Control of nitrous oxide emissions

The aim of this section is to give some background information about nitrous oxide emissions, the Kyoto protocol and nitric acid production, the single greatest industrial process source of N_2O emissions. The catalytic system studied in this work, Fe-ZSM-5, has been proposed as a possible catalyst for the catalytic decomposition of N_2O under nitric acid tail gas conditions (Kapteijn et al., 1996; Pérez-Ramírez, 2002; Pérez-Ramírez et al., 2002d; Melian-Cabrera et al., 2005). The decomposition of nitrous oxide over iron zeolite catalysts was found to be an effective and cost efficient way of decreasing the N_2O emissions from nitric acid plants (Smit et al., 2001).

In section 2.1, the Kyoto protocol, the main greenhouse gases and the concept of the global warming potential are reviewed. Nitrous oxide the third most important greenhouse gas and its emission sources are briefly discussed in section 2.2. Finally, some possibilities for controlling the nitrous oxide emissions from nitric acid production plants are summarized in section 2.3.

2.1 Kyoto process

To fight global climate change the Kyoto protocol and subsequent discussions within the European Union set objectives for the reduction of greenhouse gases to be realized in the period 2008-2012. The European Community committed itself to reduce its emissions of greenhouse gases by 8 % during this period in comparison with their levels in 1990. The focus of the Kyoto Protocol is on the following six gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6). All six greenhouse gases are weighted by their respective global warming potential (GWP). A GWP is a measure of

the relative effect of a substance in warming the atmosphere over a given period (100 years in the case of the Kyoto Protocol), compared with a value of one for carbon dioxide. Table 2.1 lists the six greenhouse gases and their global warming potential (Rodhe, 1990). Weighted by their respective global warming potential, CO₂ contributes about 85 % to the global greenhouse gas emissions; CH₄ contributes about 7 % and N₂O about 6 % (<http://unfccc.int/2860.php>; data from 2001). Due to a significantly higher cost efficiency of controlling non-CO₂ greenhouse gases, especially N₂O, PFCs, and HFCs, the contribution of these gases to the total reduction of greenhouse gases will in the near future be relatively high (Smit et al., 2001). Pérez-Ramírez (2002) reports for example that the cost of CO₂ reduction by changing coal-fired to gas-fired electricity plants is about 23 € per ton CO₂ equivalent; whereas, the cost effectiveness of de-N₂O technology has been reported to be a factor 5 to 50 higher (Smit et al., 2001).

TABLE 2.1: Global warming potential of greenhouse gases

Component	Global warming potential
CO ₂	1
CH ₄	21
N ₂ O	310
HFCs	140 - 11700
PFCs	6500 - 9200
SF ₆	23900

2.2 Nitrous oxide emissions

Nitrous oxide (N₂O) is an invisible, non-poisonous gas that is believed to contribute to the depletion of the ozone layer in the upper atmosphere (Crutzen, 1971; Crutzen and Howard, 1978) and is the third most important greenhouse gas after carbon dioxide (CO₂) and methane (CH₄). Due to its long life-time of approximately 150 years in the atmosphere, N₂O has a greenhouse potential that is calculated to be 310 times that of CO₂ (Rodhe, 1990). The atmospheric concentration of N₂O has been relatively constant for many centuries (~270 ppbv) and is increasing since industrialization to the present-day atmospheric concentration of about 316 ppbv. Figure 2.1 illustrates the global

increase of the N_2O concentration in the atmosphere in the last 25 years. This increase results from anthropogenic processes, especially during the second part of the 20th century. N_2O is produced by both natural (61 %) and anthropogenic (39 %) sources (AEA Technology Environment, 1998). Biological processes in soils and oceans are the primary natural sources of N_2O . Agriculture is the major anthropogenic source contributing about 64.5 % to the total anthropogenic N_2O emission. The control of N_2O emissions from agricultural sources is difficult due to its diffuse nature. N_2O emissions that can be reduced in the short term are associated with chemical production and the energy industry contributing about 31 % to the anthropogenic N_2O emissions in the European Union (<http://unfccc.int/2860.php>). This emission is concentrated in a limited number of large N_2O sources, which holds promise for an economic and efficient reduction strategy to fulfill the Kyoto commitment. The world's nitric acid plants represent the single greatest industrial process source of N_2O emissions. Currently, approximately 700 nitric acid plants are operated globally with an estimated amount of N_2O emissions of 400,000 t N_2O per year (corresponding to 125 Mio t CO_2 per year).

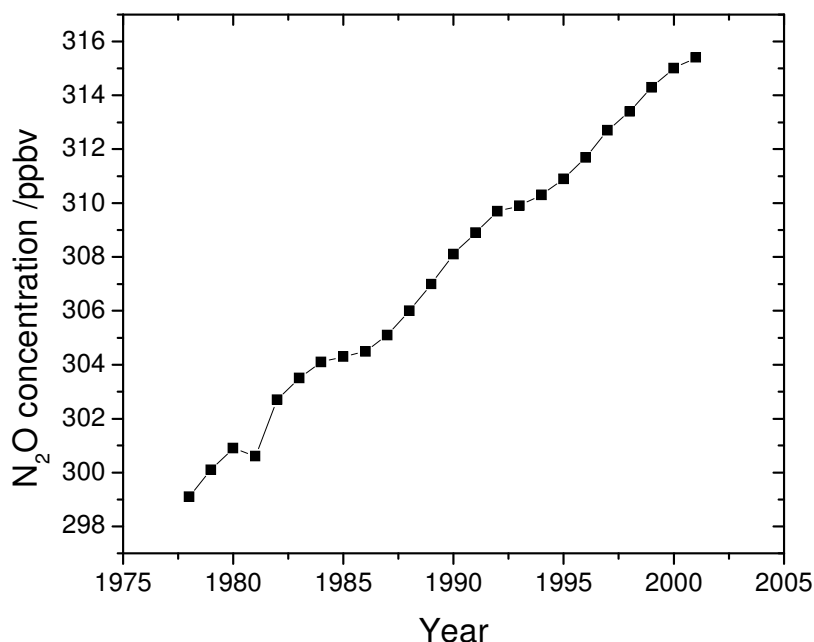


Figure 2.1: Evolution of the atmospheric N_2O concentration. Source: http://cdiac.ornl.gov/ftp/ale_gage_Agage/

N₂O is also produced during the manufacture of adipic acid (about 100,000 t N₂O per year), caprolactam, acrylonitrile, glycol, and in general organic syntheses using HNO₃ as the oxidant and reactions involving ammonia oxidation (Pérez-Ramírez et al., 2002d). Whereas, different thermal and catalytic abatement technologies have been successfully developed for adipic acid plants these are not applicable to nitric acid plants or combustion processes (Centi et al., 1999 and 2000). In adipic acid plants, the N₂O concentration in the tail gas is 25-40 vol.%. As a result, the exothermic N₂O decomposition leads to temperatures of over 900 K. At this temperature a large number of catalysts exhibit a considerable activity. In nitric acid plants, N₂O concentrations in the tail gas are in the range of 300 to 3500 ppmv and tail gas temperatures are relatively low, typically below 800 K. Due to the presence of catalyst inhibitors like O₂, H₂O, SO₂, and NO_x the N₂O decomposition under nitric acid tail gas conditions is found to be challenging.

2.3 Control of N₂O from nitric acid production

Nitric acid is mostly produced as a weak acid (50-65 %) for the production of nitrogen fertilizers like ammonium nitrate and super phosphates, but also as an oxidizing agent for the production of adipic acid and other organic compounds. A smaller amount is produced as concentrated nitric acid (> 70 %) for the production of explosives, use in the metallurgy industry, and for the production of rocket fuel (Smit et al., 2001). As the production of concentrated nitric acid by either concentrating weak acid or direct synthesis from air does not significantly contribute to the N₂O formation, this section focuses on the production of N₂O in weak nitric acid plants.

The production of weak nitric acid is based on the Oswald process and takes place in three process steps. The first step constitutes the catalytic oxidation of ammonia with air over platinum-rhodium gauzes in a converter to form nitric oxide, $4 \text{ NH}_3 + 5 \text{ O}_2 \rightleftharpoons 4 \text{ NO} + 6 \text{ H}_2\text{O}$. At a temperature of 1073 to 1223 K and pressures between 1 to 13 bar, an ammonia conversion of about 96 % is achieved. The remainder of the ammonia is

either converted to nitrogen or nitrous oxide. After formation of nitric oxide, the gases are cooled to promote further oxidation to nitrogen dioxide, $2 \text{NO} + \text{O}_2 \rightleftharpoons 2 \text{NO}_2$. NO reacts non-catalytically with the residual oxygen to form NO₂ and its liquid dimer, N₂O₄. After being cooled, the nitrogen dioxide / dimer mixture is introduced into an absorption column, where nitrogen dioxide reacts with water and oxygen to form weak nitric acid, $4 \text{NO}_2 + \text{O}_2 + 2 \text{H}_2\text{O} \rightleftharpoons 4 \text{HNO}_3$. Figure 2.2 illustrates a schematic flow sheet of a nitric acid plant.

The nitrous oxide produced in the first step of the nitric acid production (the catalytic oxidation of ammonia) is passed through the rest of the process unchanged and is usually emitted to the atmosphere in the tail gas. The tail gas at the outlet of the NO₂ absorber consists of N₂ and 100-3500 ppm NO_x, 300-3500 ppm N₂O, 1-4 % O₂, and 0.3 to 2 % H₂O (Pérez-Ramírez, 2002).

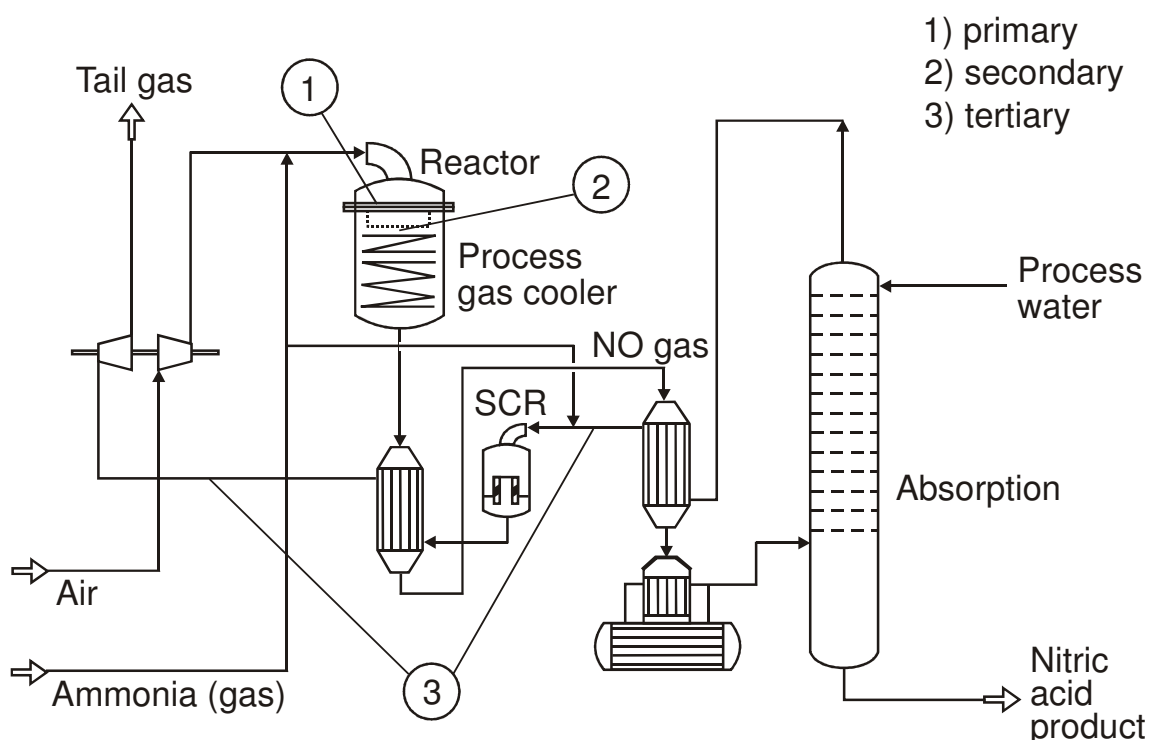


Figure 2.2: Schematic flow sheet of a nitric acid plant. Indicated are the three main possible positions for de-N₂O technology. Source: Uhde GmbH.

A number of promising de-N₂O techniques have been developed that can be classified into three groups according to their position in the process. Primary abatement measures aim at preventing N₂O from being formed in the ammonia burner. This involves modification of the ammonia oxidation catalyst, e.g., by modifying the Pt-Rh gauzes or by replacing the Pt-Rh gauzes by a Co₃O₄ catalyst to increase the NO yield and consequently decrease the N₂O production. As the conversion of this process is well optimized any further prevention of unwanted N₂O production is expected to be limited (Pérez-Ramírez, 2002).

Secondary abatement measures focus on the decomposition of N₂O, either by thermal decomposition or by catalytic decomposition, in the high-temperature zone immediately downstream of the ammonia burner. Kongshaug et al. from Norsk Hydro (1990) suggested extending the reactor chamber to thermally decompose N₂O in the hot zone downstream of the ammonia combustion Pt-Rh gauzes at temperatures ranging from 1023 to 1223 K. This involves a novel design of the ammonia oxidation unit so that the residence time of the process gas in the burner is extended (1-2 s) and the metastable N₂O is decomposed. The disadvantages of this technology are a high investment cost, limited N₂O conversion (70 %) and possible nitric acid production losses due to NO_x decomposition in the extended reactor chamber (Smit et al., 2001). Schumacher et al. (1998) proposed a selective catalytic N₂O decomposition unit directly after the Pt-Rh catalyst where the temperature is higher than 773 K. A Cu-Zn-Al spinel catalyst is currently used at this position by BASF in Antwerp (Belgium) and Ludwigshaven (Germany). N₂O conversions of 70 to 80 % have been reported.

Implementation of N₂O abatement measures between the NO₂ absorption section and the tail-gas expander (see Figure 2.2) offer the advantage of not influencing the heart of the nitric acid plant, i.e., the ammonia burner and the absorber, and can be combined with the de-NO_x SCR unit. Tertiary measures are more flexible with respect to the size of the reactor than secondary measures and enable the achievement of high levels of N₂O removal greater 99 %. Technologies that can in principle be applied at this level of the plant are thermal decomposition, non-selective catalytic reduction, selective

catalytic reduction, and catalytic decomposition. The pressure and especially the temperature of the tail gas are essential parameters to determine the optimal process option for tertiary N₂O abatement. In general the optimum position for a tertiary N₂O destruction facility is at the hottest position in the tail gas stream. Non-selective catalytic reduction (NSCR) has been developed by GIAP for NO_x removal and has been shown to be capable of reducing nitrous oxide as well. A reducing agent like hydrogen, natural gas, or naphtha is added to the tail gas. First the O₂ and then the NO_x and N₂O in the tail gas are consumed in this process. Due to the high fuel consumption levels and high secondary emissions this option is probably not viable in the future any more (Smit et al., 2001). SCR of N₂O with hydrocarbons and direct N₂O decomposition has been extensively investigated over Fe-based zeolites. Addition of hydrocarbons to the tail gas mixture reduces the temperature for N₂O decomposition over Fe-ZSM-5 catalysts by approximately 100 K with respect to direct N₂O decomposition, leading to operation temperatures of 573 to 648 K for high N₂O decomposition rates. For low tail gas temperatures, Schwefer (2005) suggested the use of oxidic cobalt compounds mixed with oxidic magnesium compounds. Uhde GmbH applies a tertiary N₂O abatement technology based on iron zeolites.

To summarize, the catalytic decomposition inside the reaction chamber and upstream the tail gas expander are probably the most effective and cost efficient ways of decreasing the N₂O emissions from nitric acid plants (Smit et al., 2001). Iron zeolite catalysts, similar to the Fe-ZSM-5 catalyst studied theoretically in this work, have been proposed as a catalyst for the direct catalytic decomposition and the selective catalytic reduction (SCR) upstream the tail gas expander, giving an additional incentive to understand the catalytically active site and their interaction with N₂O and NO in these materials.

3 Theoretical background

In this chapter, the different theoretical methods that are used in the present work to describe and understand chemical reactions on a molecular level are introduced. Molecular modeling of chemical reactions is based on three developments: quantum mechanics, statistical mechanics, and digital computation. Section 3.1 introduces the Schrödinger equation and gives a brief description of the most common *ab initio* approach, the Hartree-Fock method, to solve the non-relativistic time-independent Schrödinger equation (*ab initio* = generating solutions without reference to experimental data). In principle, all materials and properties can be studied theoretically by solving the Schrödinger equation. In section 3.2, the density functional theory (DFT) approach for obtaining ground state properties like the energy is presented. Here, the hybrid functional, B3LYP, and the basis sets used, are introduced and their limitations described. Section 3.3 discusses non-adiabatic effects and the approximate way they are dealt with in this work. Finally, in section 3.4, the statistical methods that are used to obtain thermodynamic functions like the enthalpy and reaction rate constants from quantum mechanical data are summarized. All algorithms developed and programmed in this work are presented in section 4.

In the present work, the determination of chemical reaction rates is restricted to classical statistical methods, so that time-dependent *ab initio* methods or quantum scattering methods are not discussed. An introduction to time-dependent *ab initio* methods can e.g. be found in the papers from Simons (2003), and Makri (1999). A recent review of the quantum scattering methods was written by Althorpe and Clary (2003).

3.1 Schrödinger equation

If the electron distribution in materials or molecules is of central importance, as it is in chemical reactions, there is no substitute for quantum mechanics. Electrons are very light particles, that cannot be described even qualitatively correct by classical mechanics. The Schrödinger equation is the fundamental equation of non-relativistic quantum mechanics. It describes the temporal evolution of a state of a physical system. The time-independent non-relativistic Schrödinger equation of a many-body system can be written as:

$$H(\mathbf{R}, \mathbf{r})\Psi(\mathbf{R}, \mathbf{r}) = E \Psi(\mathbf{R}, \mathbf{r}), \quad (3.1)$$

where E is the total energy of the system and Ψ is the wave function of the $3n$ electronic coordinates, $\mathbf{r}$, and the $3N$ coordinates of the nuclei, $\mathbf{R}$. N is the number of nuclei and n is the number of electrons in the system. H is the many-body Hamiltonian operator. The only fundamental interactions of concern, in solid state physics and most of quantum chemistry, are the electrostatic interactions. In principle, relativistic effects and magnetic effects should be included, but for simplicity these effects are not considered in this work. The Hamiltonian operator for a system of n electrons and N nuclei can be written as:

$$H = T_{el} + T_{nucl} + V_{nucl-nucl} + V_{nucl-el} + V_{el-el}, \quad (3.2)$$

where T_{nucl} and T_{el} represent the kinetic energy operator of the nuclei and electrons, respectively, and are given by:

$$T_{nucl} = - \sum_{I=1}^N \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2, \quad T_{el} = - \sum_{i=1}^n \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_i}^2. \quad (3.3)$$

The Laplacian operators $\nabla_{\mathbf{R}_I}^2$ and $\nabla_{\mathbf{r}_i}^2$ involve differentiation with respect to the I -th nuclei coordinates, at position $\mathbf{R}_I$ and the i -th electron coordinates, at position $\mathbf{r}_i$, while M_I and m_i denote the nuclei and electronic masses. $\hbar$ is the Planck's constant divided by 2π . The repulsive Coulomb interactions between the nuclei are represented by

$$V_{nucl-nucl} = \sum_{I=1}^{N-1} \sum_{J=I+1}^N \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\mathbf{R}_I - \mathbf{R}_J|}, \quad (3.4)$$

where Z_I and Z_J are the atomic number of nuclei I and J , e is the charge on the electron and ϵ_0 is the vacuum permittivity. The electrostatic potential energy due to the interactions between electrons and nuclei and the repulsion between electrons are given by:

$$V_{nuc-el} = -\sum_{i=1}^n \sum_{I=1}^N \frac{Z_I e^2}{4\pi\epsilon_0 |\mathbf{R}_I - \mathbf{r}_i|}, \quad V_{el-el} = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}. \quad (3.5)$$

In general Eqn. (3.1), which is an eigenvalue equation, has many acceptable eigenfunctions, Ψ , for a given molecule, each characterized by a different (or equivalent in the case of degenerate eigenfunctions) associated eigenvalue E . The whole physical information except for the symmetry of the wave functions is contained in the Hamiltonian operator. The only further information needed are the appropriate quantum statistics and, especially for heavier elements relativistic corrections. Heavy elements have very localized wave functions for the core electrons. As a result, the core electrons have a very high kinetic energy and move with a velocity close to the speed of light. Since chemical reactions involve usually just a change in the valence electron distribution, relativistic effects are often, as a first approximation, neglected for reactions involving atoms up to krypton (36). The heaviest element studied in this work is iron (26). While relativistic effects are present in systems containing iron these effects on energy differences are considered small and are as a first approximation neglected in this work.

Unfortunately, a closed form solution of the Schrödinger equation is not possible for more than two particles owing to the correlation of all particles with each other. In order to simplify the eigenvalue problem a number of approximations like the Born-Oppenheimer approximation, the introduction of one-electron equations, the concept of orbitals, and the basis sets used to construct them are common to most *ab initio* methods and will be described in the next sections.

An introduction to quantum mechanics and solutions of the Schrödinger equation can be, for example, found in the books of Levine (2000), Sakurai (1994) and Cohen-

Tannoudji, Diu and Laloë (1977). Further details of the implementation of electronic structure theory are given e.g. in the books of Szabo and Ostlund (1996), Yarkony (1995) and Helgaker et al. (2002). Elementary review articles for chemical engineers are written by Keil (2004) and Santiso and Gubbins (2004).

3.1.1 Born-Oppenheimer approximation

One difficulty in solving Eqn. (3.1) arises from the large number of variables the many-body wave function, Ψ , depends on. For a system consisting of n electrons and N nuclei there are $3n + 3N$ degrees of freedom, i.e. three spatial coordinates for each electron and for each nucleus. A first simplification can be achieved by taking into account the large difference in masses between the electrons and the nuclei (nuclei are approximately 10^3 to 10^5 times heavier than electrons). Since the nuclei are much heavier than the electrons, their motion will be much slower, i.e. the characteristic time scales of processes involving the electrons are much smaller. Hence, it is supposed that the electrons follow the motion of the nuclei instantaneously. In other words, the electronic wave functions can be found by assuming that the nuclei are fixed in space. The nuclei coordinates are just parameters in the electronic Schrödinger equation and as a first approximation the motions of the electrons and nuclei are decoupled. As a result, the full Hamiltonian is split. The electronic Hamiltonian, H_{el} , for fixed nuclear coordinates, $\mathbf{R}$, can be written as

$$H_{el} = T_{el} + V_{nucl-el} + V_{el-el} \quad (3.6)$$

and the Schrödinger equation for the electrons, for a fixed given configuration of the nuclei, is

$$H_{el} \psi_{el} = E_{el} \psi_{el} \quad (3.7)$$

The nuclei, in turn, are assumed to move according to the atomic Schrödinger equation:

$$(T_{nucl} + V_{nucl-nucl} + E_{el}) \psi_{nucl} = E_{nucl} \psi_{nucl} \quad (3.8)$$

The potential energy surface (PES) or Born-Oppenheimer (BO) energy surface,

$$V^{BO} = V_{nuc1-nuc1} + E_{el} , \quad (3.9)$$

is taken to be the potential energy for the nuclear motion. Strictly speaking, this nuclear motion should be treated quantum mechanically. In practice, it is sufficient to solve a classical equation of motion for the nuclei, as quantum-mechanical effects, such as zero point vibrations or tunneling, can be corrected for in an ad hoc way if necessary. To summarize, within the BO approximation first the electronic eigenvalue equation, Eqn. (3.7), has to be solved, and then Eqn. (3.9) is applied to obtain the potential energy surface (PES). It is noted that the eigenvalue equation, Eqn. (3.7), has an infinite number of solutions. In many cases one is just interested in the solution with the lowest energy, which corresponds to the ground state of the electronic system.

Most *ab initio* methods make use of the here described Born-Oppenheimer (and adiabatic) approximation, proposed by Born and Oppenheimer in 1927. A detailed mathematical description of the Born-Oppenheimer and adiabatic approximation can e.g. be found in the books from Jensen (1999) and Hirst (1985). It is important to note that the adiabatic and Born-Oppenheimer approximation breaks down when two or more solutions of the electronic Schrödinger equation come energetically close together. If non-adiabatic effects are important it is possible to include corrections after a BO calculation has been made using surface-hopping methods developed by Tully (Preston (1971), Tully (1971) and Tully (1990)). Alternatively, very sophisticated quantum scattering or semiclassical approaches have to be used. Section 3.3 discusses non-adiabatic effects and how they are dealt with approximately in this work.

3.1.2 Variational principle and molecular orbitals

Many *ab initio* methods are based on the Rayleigh-Ritz variational principle. Given any normalized electronic wave function, $\Phi_e(\mathbf{r})$, which need not be the true solution to the Schrödinger equation, Eqn. (3.7), the expectation value of the Hamiltonian:

$$E[\Phi_e] = \int d\mathbf{r} \Phi_e^* H \Phi_e , \quad (3.10)$$

corresponding to $\Phi_e(\mathbf{r})$ will always be greater than or equal to the ground state energy E_0 of the electronic Schrödinger equation, i.e.:

$$E[\Phi_e] \geq E_0 \quad \text{for all } \Phi_e. \quad (3.11)$$

Since the Hamiltonian is a Hermitian operator the proof of this principle is simple and can be found in any elementary quantum chemistry text book. Hence, finding the ground state energy and wave function of a many-body system can be formulated as a variational minimization problem:

$$\delta E[\Phi_0] = 0. \quad (3.12)$$

The wave function appearing in the electronic problem (3.7) depends on the coordinates of all electrons. As a next approximation the trial molecular wave functions are chosen as combinations of single electron functions, so called Slater determinants, see Slater (1929):

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix} \quad (3.13)$$

The single electron functions are called molecular spin orbitals, χ_i , and consist of a product of a spatial orbital $\psi_i(\mathbf{r})$ and the spin of the electron, σ (α or β). Single electron functions are arranged in Slater determinants to ensure that the many-electron wave function is antisymmetric upon electron interchange and obey the Pauli exclusion principle that in a system of identical fermions (e.g. a multi-electron system) two particles can never occupy the same quantum state. The spatial orbitals are usually expressed in terms of a set of basis functions $\phi_\mu(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^K C_{\mu i} \phi_\mu(\mathbf{r}) \quad (3.14)$$

These basis functions are often (and always in this work) centered at the nuclei. When functions centered at different nuclei in a molecule are combined linearly as in Eqn. (3.14), the spatial orbitals are called LCAO-MO (Linear Combinations of Atomic Orbitals - Molecular Orbitals). Once a set of basis functions is chosen, the “best”

electronic wave function within the basis is obtained by minimizing the energy with respect to the expansion coefficients $C_{\mu i}$. The shape and kind of the basis functions used in this work will be described in section 3.2.4.

3.1.3 Hartree-Fock method

The idea to replace the complicated many-electron problem (Eqn. 3.7) by a one-electron problem in which electron-electron repulsion is treated in an average way is called Hartree-Fock (HF) approximation. The Hartree-Fock method (see Hartree (1928) and Fock (1930)) is based on the following assumptions: 1) the Born-Oppenheimer approximation, 2) the many-electron Hamiltonian is replaced by a sum of effective one-electron Hamiltonians which act on one-electron wave functions (a single Slater determinant) and 3) the Coulomb repulsion between electrons is represented in an averaged way. The matrix elements of the effective Hamiltonian depend on the wave function, i.e. the Schrödinger equation becomes non-linear and requires a self-consistency procedure. All self-consistent mean-field (SCF) theories like the Hartree-Fock method lead to equations of the form:

$$f(i)\chi(\mathbf{r}_i, \sigma) = \epsilon\chi(\mathbf{r}_i, \sigma), \quad (3.15)$$

where the Fock operator $f(i)$ can be written as:

$$f(i) = -\frac{\hbar^2}{2m_i}\nabla_i^2 + v^{eff}(i). \quad (3.16)$$

Here $\mathbf{r}_i$ are the spatial coordinates of the i^{th} electron, χ are the spin orbitals and v^{eff} is the effective potential “seen” by the i^{th} electron which depends on the spin orbitals of the other electrons. Using an atomic orbital (AO) basis the so-called Roothaan matrix equations (Roothaan (1951)) have to be solved iteratively in the SCF procedure for closed shell molecules, where all electron spins are paired:

$$\mathbf{FC}_k = \epsilon_k \mathbf{SC}_k. \quad (3.17)$$

For unrestricted open shell calculations separate spatial orbitals for α and β spin are used and the Pople-Nesbet equations (Pople and Nesbet (1954)) have to be solved:

$$\mathbf{F}^\alpha \mathbf{C}_k^\alpha = \boldsymbol{\varepsilon}_k^\alpha \mathbf{S} \mathbf{C}_k^\alpha \text{ and } \mathbf{F}^\beta \mathbf{C}_k^\beta = \boldsymbol{\varepsilon}_k^\beta \mathbf{S} \mathbf{C}_k^\beta \quad (3.18)$$

Here $\mathbf{F}$ is the Fock matrix, $\mathbf{C}$ is a square matrix of molecular orbital coefficients, $\mathbf{S}$ is the overlap matrix and $\boldsymbol{\varepsilon}$ is the diagonal matrix of the orbital energies. The larger and more complete the set of basis functions in the Hartree-Fock method is, the greater is the degree of flexibility in the expansion for the spin orbitals and the lower will be the expectation value of the ground state energy. The lowest energy value achievable in this way is called the Hartree-Fock limit, E_{tot}^{HF} .

The representation of the wave function by a single Slater determinant function includes Fermi statistics (“exchange” effects), but does not account for all correlation effects. Electronic screening and instantaneous electron-electron correlations are not described properly. Electron correlation effects, $E_c = E_{tot} - E_{tot}^{HF}$, are commonly included in post HF methods, such as Møller-Plesset perturbation theory, configuration-interaction (CI) or coupled-cluster (CC) theory. Such methods are, however, computationally very demanding and are currently limited to a rather small number of atoms and are not applied in this work. A good review of *ab initio* methods for electron correlation in molecules can e.g. be found by Knowles et al. (2000).

3.2 Density functional theory

Over the last fifteen years density functional theory (DFT) has strongly influenced the evolution of quantum chemistry. In contrast to the Hartree-Fock picture, which begins conceptually with a description of individual electrons interacting with the nuclei and all other electrons in the system, density functional theory allows one to replace the complicated n -electron wave function, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$, and the associated Schrödinger equation by the much simpler electron density, $\rho(\mathbf{r})$, and its associated calculation

scheme. It is important to note that the charge density is a function of only three variables, while the wave function contains for an n -electron system $3n$ coordinates. The rigorous foundation of density functional theory is given by Hohenberg and Kohn (1964) who proved that in essence an exact representation of the ground state properties of a stationary, non-relativistic many-body system in terms of the ground state density is possible. The theorem ensures that the exact ground state density can be calculated without resort to the Schrödinger equation from a variational principle involving only the electron density. Viz, the electron correlation energy is at least in principle included in density-functional theory. For a given system of Coulomb-interacting particles moving in an external potential, $V^{ext}(\mathbf{r})$, the exact ground state density and energy are obtained by minimization of the energy functional:

$$E[\rho] = T[\rho] + V_{el-el}[\rho] + \int d^3\mathbf{r} V^{ext}(\mathbf{r})\rho(\mathbf{r}), \quad (3.19)$$

where $T[\rho]$ is the kinetic contribution and $V_{el-el}[\rho]$ is the electron-electron interaction functional of the electron density. These two functionals do not depend on the external potential $V^{ext}(\mathbf{r})$ of the system and are therefore universal (e.g. the same functional can be used for Br_2 , H_2O , Cu or Fe). The problem of DFT is that although it has been proven that each different density yields a different ground-state energy, the Hohenberg-Kohn functional, $F_{HK}[\rho] = T[\rho] + V_{el-el}[\rho]$, connecting these two quantities is not known.

While more accurate forms of the Hohenberg-Kohn functional are constantly being developed there is no systemic way to improve the functional to achieve an arbitrary level of accuracy. Thus, the traditional wave function approaches offer, using post HF methods, the possibility of achieving an arbitrary level of accuracy, but can be computationally very demanding. DFT approaches, on the other hand, offer a practical route but the theory is currently incomplete. A detailed description of density functional theory can, for example, be found in the books of Dreizler and Gross (1990) and Parr and Yang (1989). Recent review articles were written by Geerlings et al. (2003), Perdew and Kurth (2003), Hafner (2000) and Bickelhaupt and Baerends (2000).

A more practical guide to density functional theory was published by Koch and Holthausen (2001).

3.2.1 Kohn-Sham equations

The Hohenberg-Kohn theorems set the foundations of density functional theory, but owing to the unknown Hohenberg-Kohn functional, in particular the kinetic energy functional, $T[\rho]$, an efficient scheme to obtain the ground state density and energy was missing. Kohn and Sham (1965) turned DFT from a theory to a practical tool for quantum chemical calculations by the introduction of the concept of a non-interacting reference system. Kohn and Sham invented an indirect approach to the kinetic energy functional, $T[\rho]$, by separating it into the kinetic energy T_S of a system of non-interacting electrons, which can be calculated exactly using orbitals:

$$T_S = \sum_{i=1}^n \int d\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) \phi_i(\mathbf{r}), \quad (3.20)$$

and a small unknown component T_C , which contains the corrections resulting from the electronic interaction. The single-particle Kohn-Sham orbitals ϕ_i , in Eqn. (3.20) are determined under the constraint to reproduce the density of the fully interacting many-body system in a self-consistent way from the Kohn-Sham equations,

$$f_{KS} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (3.21)$$

The Kohn-Sham operator f_{KS} is an effective one-electron operator and is given by

$$f_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + V^{ext}[\rho] + E_H[\rho] + V_{XC}[\rho]. \quad (3.22)$$

$V^{ext}[\rho]$ is the external potential due to the nuclei, $E_H[\rho]$ is the classical Hartree potential, which is essentially the known classical part of the universal electron-electron interaction functional:

$$E_H[\rho] = V_{el-el}[\rho] - E_{non-classical}[\rho] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.23)$$

and $V_{xc}[\rho]$ is the exchange-correlation potential. The density constructed from the Kohn-Sham orbitals ϕ_i is the same as the density of the interacting system:

$$\rho(\mathbf{r}) = \sum_{i=1}^n |\phi_i(\mathbf{r})|^2 \quad (3.24)$$

The ϕ_i are functionals of the density, ρ , and hence, the kinetic energy, Eqn. (3.20), is also given as a functional of the density. The remaining kinetic energy part owing to the electron interaction T_C is combined with the non-classical contributions to the electron-electron interaction in the exchange-correlation functional $E_{xc}[\rho]$. As a result, the exchange-correlation functional contains everything unknown. The exchange-correlation functional is related to the exchange-correlation potential V_{xc} in Eqn. (3.22) in that the latter is the exchange-correlation functional's derivative with respect to the density:

$$V_{xc}[\rho(\mathbf{r})] = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (3.25)$$

In summary, the essence of the Kohn-Sham scheme is the existence of an auxiliary system of a non-interacting classical electron gas, with kinetic energy T_S , subject to two external potentials: one due to the nuclei, V^{ext} , and one due to the exchange and correlation effects, V_{xc} , such that the ground-state density, $\rho(\mathbf{r})$, of the interacting system equals the ground-state density of the auxiliary system. The price to be paid for this scheme is the appearance of orbitals instead of just the ground-state density, $\rho(\mathbf{r})$. The Kohn-Sham equations, Eqn. (3.22), are one-electron equations, just as the Hartree-Fock equations, that have to be solved iteratively. The incorporation of electron correlation in these equations appears with the exchange correlation potential, $V_{xc}[\rho(\mathbf{r})]$, the form of which is unknown and for which no systematic strategy for improvement is available.

3.2.2 Exchange-correlation functionals

With the introduction of the Kohn-Sham formalism most contributions to the total energy can be calculated exactly. The remaining unknown parts are assembled in the exchange-correlation functional. Good approximations to $E_{xc}[\rho]$ are crucial to obtain reliable results in a DFT calculation. The first attempt to find an expression for $E_{xc}[\rho]$ was based on the homogeneous electron gas for which the exact exchange-correlation energy is known. In this local density approximation (LDA) the exchange-correlation energy for the homogeneous electron gas is used for the non-homogeneous system. The basic assumption is that exchange and correlation depend only on the local value of the density. One approximates the real inhomogeneous electron density as a sum of small cells each of which has a homogeneous electron density. It is assumed that $E_{xc}[\rho(\mathbf{r})]$ at position $\mathbf{r}$ is identical to $E_{xc}^{LDA}[\rho(\mathbf{r})]$ of the homogeneous electron gas of the same density. The exchange-correlation functional is then given by

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})), \quad (3.26)$$

where ε_{xc} is the exchange-correlation energy per particle of the homogeneous electron gas. $E_{xc}^{LDA}[\rho(\mathbf{r})]$ can be split into an exchange and a correlation contribution E_x^{LDA} and E_c^{LDA} . The exchange part can be given analytically:

$$E_x^{LDA}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} \rho^{4/3}, \quad (3.27)$$

while the correlation energy is only known numerically from quantum Monte Carlo calculations from Ceperley and Alder (1980). The correlation part was parameterized by Vosko et al. (1980) and by Perdew and Wang (1992). Both parameterizations give usually very similar results.

Although the local density approximation is a rather unrealistic model for real systems, it gives for slowly varying electron densities as in simple crystalline metals very accurate results. Even for other systems it is, due to a fortunate error cancellation, often comparable to the Hartree-Fock method. However, the LDA approximation typically

overestimates binding energies and underestimates bond lengths. An improvement on LDA can be achieved by including the first derivative of the electron density, $\nabla\rho$, in the exchange-correlation functional. The exchange-correlation functional can then be written in this generalized gradient approximation (GGA) as:

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int d\mathbf{r} f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})). \quad (3.28)$$

One generalized gradient exchange functional used in this work was presented by Becke (1988), two popular generalized gradient correlation functionals, also used, are the LYP correlation functional of Lee, Yang and Parr (1988) and Perdew's 1986 correlation functional. Various other generalized gradient exchange-correlation functionals have been developed and can be found, e.g., in the book from Jensen (1999). In most cases GGA functional energies are more reliable than LDA results, but due to their ambiguous definition there is a certain variation in the energies obtained from different GGA functionals. In addition, most GGA calculations are strictly spoken not an *ab initio* calculation, as some experimental information is used in there construction. Both LDA and GGA calculations can fail badly if the Kohn-Sham non-interacting wave function is not a single Slater determinant, or when the non-interacting energies are nearly degenerate (Perdew and Kurth, 2003).

It should be noted that even if the real wave function cannot be described with a single Slater determinant, DFT is still often able to calculate the energy of such a system provided that the electron density can be fitted to a single determinant ansatz for the Kohn-Sham orbitals and that an exact exchange-correlation functional is known (Gritsenko and Baerends, 1997). Such cases are termed non-interacting pure state V_s representable. On the other hand, Schipper et al. (1998) demonstrated that for some systems (e.g., for the $^1\Sigma_g^+$ state of the C_2 molecule) it is not possible to fit the electron density to a single Slater determinant. For these systems the non-interacting ground state density cannot be represented by a single Kohn-Sham determinant even if the exact exchange-correlation functional is known.

Many systems of interest possess an odd number of electrons or have to be treated even with an even number of electrons as radicals. If the exact exchange-correlation functional is available, the Kohn-Sham formalism is in principle suitable for any kind of atom or molecule, regardless of closed-shell or open-shell character. Even if a system with an odd number of electrons is considered, the basic variable remains the total density which can be constructed from the individual α and β spin densities, $\rho = \rho^\alpha + \rho^\beta$. In practice, the current exchange-correlation functionals cannot account for open-shell problems in a realistic manner, and an unrestricted ansatz is commonly used. Spin-density functionals for exchange and correlation are employed that explicitly depend on the α and β spin densities. This unrestricted Kohn-Sham (UKS) approach can capture more of the essential physics in open-shell systems than the spin-independent functionals. However, the use of UKS has some drawbacks. The spatial symmetry of the total wave function (charge density) is often lower than the symmetry of the system. This unphysical phenomenon is termed spatial symmetry breaking and the resulting wave functions are often termed broken symmetry solutions. Additionally, spin unrestricted wave functions are not eigenfunctions of the total spin angular momentum operator $\hat{S}^2$ anymore. The deviation of the expectation value $\langle \hat{S}^2 \rangle$ from the correct value $S(S + 1)$ is taken as a measure for the “contamination” of the wave function with wave functions of other spin multiplicities. From a fundamental point of view, it is to be noted that the Kohn-Sham determinant in DFT does not represent the true wave function of the real system, but only the wave function of the fictitious non-interacting reference system. The true wave function is not available with DFT. Thus, the deviation of $\langle \hat{S}^2 \rangle$ is not necessarily a probe for the quality of the UKS energies. This is in contrast to the unrestricted Hartree-Fock formalism, where the unrestricted Slater determinant is actually meant to represent the true wave function. In practice, however, the performance of the UKS approach depends on the system under consideration, and some severe failures have been noted, see e.g. Bauschlicher et al. (1999) and Alcamí et al. (2000). In summary, the broken symmetry solutions obtained by the UKS scheme provide in many cases with strong non-dynamical correlation effects surprisingly good results, at the price of unphysical spin densities. Nevertheless the performance of UKS should be evaluated against reliable reference data, and its applicability remains a case-by-case decision.

Using an atomic orbital (AO) basis for the Kohn-Sham orbitals in Eqn. (3.21), just as in the Hartree-Fock scheme, similar equations to the Roothaan matrix equations (Eqn. (3.17)) for closed shell molecules and the Pople–Nesbet equations (Eqn. (3.18)) for open shell molecules can be derived.

3.2.3 Hybrid exchange-correlation functionals

For the purpose of describing many chemical aspects of molecules, the accuracy of the gradient corrected spin-density schemes is insufficient. Hybrid exchange-correlation functionals, self-interaction correlation and meta-generalized gradient approximation functionals are three general ways to improve the accuracy of density functional theory. Self-interaction correlation methods that reduce the self-interaction energy and meta-generalized gradient approximation functionals that take more semi-local information into account are not used in this work and will not be discussed further. All computational results presented in this work have been obtained with the B3LYP hybrid exchange-correlation functional. Hybrid density functional theory is based on the adiabatic connection theory which states that more accurate results can be obtained by replacing some DFT exchange by Hartree-Fock exchange. Hartree-Fock exchange does not suffer from the self-interaction error of DFT, but does not include static and dynamic correlation which is inseparable from the DFT exchange. As a result, a fraction of the Hartree-Fock exchange is added to the exchange-correlation functional. The hybrid B3LYP density functional (Stephens et al., 1994) can be written as:

$$E_{xc} = (1 - a_0)E_x^{LSDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} + E_c^{LSDA} + a_c \Delta E_c^{PW91} \quad (3.29)$$

Here ΔE_x^{B88} is Becke's (1988) gradient correction to the exchange functional, ΔE_c^{PW91} is the Perdew-Wang gradient correction to the correlation functional (Perdew, 1991), E_x^{HF} is the exact Hartree-Fock exchange, and E_x^{LSDA} and E_c^{LSDA} are the local spin density approximation to the exchange and correlation functional, respectively. The coefficients $a_0 = 0.2$, $a_x = 0.72$, and $a_c = 0.81$ were fitted to heats of formation of small molecules.

The B3LYP functional has proven successful in a number of reported applications. In particular, reactions of hydrocarbons with FeO^+ molecules in the gas phase are well described with the B3LYP functional (Koch and Holthausen, 2001, Yoshizawa et al., 1999). Following the work of Zilberberg et al. (2002), who showed that despite some spin contamination the relative energies and geometries of different states of $\text{OFe}(\text{OH})_2$ calculated with DFT-B3LYP are in good agreement with predictions of very accurate multi-reference CASSCF-MCQDPT2 calculations, it is concluded that a DFT-B3LYP approach can also be used successfully for the nitrous oxide decomposition on an iron zeolite catalyst model (see also Zygmunt et al., 1998).

However, since B3LYP contains Hartree-Fock exchange it is computationally more expensive than pure DFT functionals. In addition, all density functionals, including hybrid density functionals are less accurate for kinetics than for thermochemistry and can in general not reproduce van der Waals interaction energies. Zhao et al. (2004) showed that the first generation GGA functionals and the B3LYP functional calculate atomization energies usually within 2 kcal/mol, which can be considered “chemical accuracy”. Reaction barriers on the other hand are on average underestimated by GGA functionals by 7 - 10 kcal/mol. For heavy atom transfer reactions Zhao et al. (2005) observed in his test set that reaction barriers were underestimated by up to 15 kcal/mol (and 23 kcal/mol for the LSDA functional). The Hartree-Fock method on the other hand overestimates barrier heights by about 8 kcal/mol and in heavy atom transfer reactions by about 15 kcal/mol. As a result, the B3LYP functional which mixes some Hartree-Fock exchange underestimates barrier heights by about 4 - 5 kcal/mol. For heavy atom transfer reactions, B3LYP reaction barriers are underestimated by as much as 8 kcal/mol.

It has to be noted that the latter numbers are just average values for a relatively small test set, and that it is in general much more difficult to compare reaction barriers than atomization energies with experimental data.

New second and third generation density functionals have been developed in the last couple of years. Examples are the BB1K hybrid functional from Zhao et al. (2004b) or the new “optimized” exchange functional OPTX from Handy and Cohen (2001), which is combined with the LYP correlation functional to the OLYP functional or the O3LYP hybrid functional. While these functionals show a significantly better performance on the test set they were optimized on, there is, until now, not enough experience on more complicated systems to prove their superiority to the well established B3LYP functional. In particular, Baker and Pulay (2003) showed that the OLYP density functional performs worse than the B3LYP functional and that the O3LYP hybrid functional is also not superior to the B3LYP hybrid functional on first-row transition metals. As a result, they concluded that there is no real incentive to use either OLYP or O3LYP in place of B3LYP for calculations involving first-row transition metals.

In general, DFT calculations proceed in the same way as Hartree-Fock calculations, with the addition of the evaluation of the extra term, E_{XC} . Integrals involving the exchange-correlation functional cannot be evaluated analytically and are therefore computed numerically. For the systems studied in this work the numerical quadrature was performed for all final structures with the very fine grid m5 described by Treutler and Ahlrichs (1995) and as implemented in the TURBOMOLE V5.6 and V5.7 program package (Ahlrichs et al., 1989 and 1995)) to always ensure convergence. All DFT calculations were performed in C_1 symmetry (no symmetry used).

3.2.4 Basis sets

In section 3.1.2 linear combinations of atomic orbitals (LCAO-MO) were introduced as basis functions for the spatial part of the molecular orbitals in Slater determinants.

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu}(\mathbf{r}) \quad (3.14)$$

One of the approximations inherent in all *ab initio* methods is the introduction of a basis set for the atomic orbitals. Expanding an unknown function, such as an atomic orbital,

in a set of known functions is not an approximation, if the basis is complete. However, a complete basis means that an infinite number of functions must be used. When a finite basis is used, only the components of the atomic orbital along those coordinate axes corresponding to the selected basis can be represented. A smaller basis automatically means a poorer representation of the molecular orbitals. The type of basis functions used also influences the accuracy. The better a single basis function is able to reproduce the unknown function, the fewer basis functions are necessary for achieving a given level of accuracy. Two types of commonly used basis functions are Slater type orbitals (STO) and Gaussian type orbitals (GTO). While STOs mirror the exact orbitals for the hydrogen atom and are therefore a natural choice, the calculation of three and four center two electron integrals cannot be performed analytically. As a result STOs are primarily used for small systems where high accuracy is required and in semi-empirical methods where all three and four center integrals are neglected.

Integrals involving Gaussian type orbitals can always be evaluated analytically. Gaussian type orbitals centered at atom A can be written as a sum of Gaussian primitives in terms of Cartesian coordinates as:

$$\phi_A(\mathbf{r}) = \sum_i d_i \cdot N_i (x - x_A)^k (y - y_A)^l (z - z_A)^m e^{-\eta_i (\mathbf{r} - \mathbf{r}_A)^2}, \quad (3.30)$$

where N_i , k , l , m and η_i are constants and the sum of k , l , m determines the type of orbital. A maximum amount of flexibility can be achieved by optimizing the d_i of every atomic Gaussian primitive in any SCF iteration. Since the computational effort of a SCF iteration scales formally as M^4 , where M is the number of basis functions, a number of Gaussian primitives are usually contracted to a so called contracted Gaussian type orbital (CGTO). A CGTO is a linear combination of Gaussian primitives, e.g. with fixed values of d_i . The number of CGTOs used to represent a single Slater type orbital is a measure of the quality of the basis, e.g. a triple zeta (TZ) basis set uses three CGTOs to represent a single Slater type orbital. In this work, the fully optimized TZVP Gaussian type orbitals from Schäfer et al. (1994) were used in all calculations. As a split-valence basis set of triple zeta quality, the core orbitals are represented with a single CGTO, while the valence orbitals, required for the accurate description of

chemical bonding, use three CGTOs. In addition, polarization functions have been added to improve the reproducibility of the chemical bonding. Polarization functions have a higher angular momentum than the occupied atomic orbitals for the corresponding atom. A comparison of different basis sets for a few sample systems is shown in appendix A. It is found that the TZVP basis is an efficient and accurate all electron basis for the systems studied in this work.

3.2.5 Basis set superposition error

One problem associated with all finite basis set descriptions of quantum chemical systems is the so called basis set superposition error (BSSE) of adsorbing or desorbing processes. The interaction energy of a complex AB can be defined as the difference

$$\Delta E = E^{AB} - E^A - E^B. \quad (3.31)$$

Even if in principle a size-consistent method like DFT is used, i.e. for large separations the energy of AB, E^{AB} , reduces to the sum $E^A + E^B$, the interaction energy ΔE is too negative. As the distance between A and B decreases, the interaction is not only switched on but also the monomers present in AB start using the one-electron basis set of their partner in the complex and thereby provide an additional stabilization that has physically nothing to do with the interaction energy one is interested in. In other words the basis set used for each monomer increases owing to the presence of the other monomer, and because of the variational principle the resulting energy is reduced. The size of this basis set superposition error increases with increasing basis set and when electron correlation is included.

It is emphasized that the usage of the partner basis is not in itself an error, for it actually improves the wave function of each monomer. Rather, the error in the above procedure is a matching or balancing error, resulting from the fact that one compares the energy of AB, E^{AB} , at distances where usage of partner orbitals plays a role, to E^{AB} at infinity, where it does not. This matching error can be avoided by calculating the interaction energy from

$$\Delta E = E^{AB} - E^{A\{AB\}} - E^{B\{AB\}}, \quad (3.32)$$

where $E^{A\{AB\}}$ and $E^{B\{AB\}}$ are monomer energies obtained using the full dimer basis $\{AB\}$ at the particular AB geometry one is studying. The basis-set matching embodied in Eqn. (3.32) has been termed function counterpoise by Boys and Bernardi (1970), who originally proposed the use of this counterpoise (CP) method. Two good reviews about the basis set superposition error and the counterpoise theory are written by Kestner and Combariza (1999) and van Duijneveldt et al. (1994).

Correcting for BSSE with the counterpoise method requires the calculation of the energy of every monomer with the full dimer basis. This essentially means that every quantum chemical calculation of every reactant and transition state has to be performed twice (one time for the adsorbed product and after that for each reactant). Since the size of the BSSE is usually small (around 2 kcal/mol) and the computational cost associated with the counterpoise method is very high, the basis set superposition error is neglected in this work.

3.3 Non-adiabatic effects

In most quantum mechanical descriptions of chemical reactions, the adiabatic and Born-Oppenheimer (BO) approximation is invoked that separates the motion of light electrons and heavy nuclei (see section 3.1.1). Thereby, the motion of the nuclei is restricted to a single adiabatic electronic state. While the Born-Oppenheimer approximation has been widely tested for gas-phase reactions and its limitations are known, the situation for reactions at surfaces is less clear (Sitz, 2005). Experiments conducted by White et al. (2005) on the interaction of highly excited nitric oxide molecules with metal surfaces indicate a strong coupling between nuclear motion and electronic excitations and therefore shows that the Born-Oppenheimer approximation is invalid in these reactions. In general, it is known that intersections between neighboring electronic states are common in molecular systems of interest to chemistry and biology.

Even if electronic states do not intersect, non-adiabatic couplings become significant between energetically close electronic states. These couplings allow for the motion of nuclei on multiple coupled adiabatic electronic states. The non-adiabatic couplings give rise to electronic transitions and can be classified into two categories: (a) Radial couplings, which arise due to translational, vibrational and angular motions of the atomic or molecular species involved in the chemical process and (b) rotational couplings, which arise as a result of a transformation of molecular coordinates from a space-fixed frame to a body fixed one due to the conservation of the total electron plus nuclear angular momentum. If non-adiabatic effects are important, the Born-Oppenheimer approximation breaks down and the problem becomes very demanding. The electronic Schrödinger equation needs to be solved for two or more electronic states. In addition, calculation of the off-diagonal (non-adiabatic) interactions that promote transitions between different electronic potential energy surfaces is required. The treatment of nuclear motion is also more difficult. Four approaches for calculating the electronically non-adiabatic dynamics are: (1) accurate quantum mechanical scattering calculations, (2) approximate wave packet methods, (3) surface hopping, and (4) semiclassical approaches. In this work non-adiabatic effects are not considered in the quantum chemical calculations. All spin constrained DFT calculations are done assuming the Born-Oppenheimer approximation is valid. Instead, it is tried to estimate the possible influence of non-adiabatic effects on the reaction dynamics. In all cases, it was found that corrections for non-adiabatic effects will most likely only slightly increase the error bars of the DFT calculations. Even more important; reactions for which non-adiabatic effects are most important were never found to be rate limiting for the whole reaction network.

Some good recent reviews about chemical reaction dynamics beyond the Born-Oppenheimer approximation are written by Worth and Cederbaum (2004), Jasper et al. (2004), Nikitin (1999), Drukker (1999), and Nakamura (1997). An older but very detailed review was published by Tully (1976). Butler (1998) reviewed what classes of chemical reactions are particularly susceptible to a breakdown of the Born-Oppenheimer approximation.

3.3.1 Spin surface crossing

Reactions on transition metal surfaces or on single transition metal atoms occur often on multiple electronic spin surfaces. The spin-constrained energy levels of the interaction between the transition metal and the reactants are often just a few kcal/mol apart so that in principle non-adiabatic effects can play a significant role. In particular, during the decomposition of two nitrous oxide molecules into an oxygen and two nitrogen molecules the total electron spin moment of the system changes from all spins are paired to two spins are unpaired. (N_2O and N_2 are singlet molecules; O_2 is a triplet molecule.) Consequently, during the decomposition reaction of nitrous oxide the electronic spin of the ground state has to change. At least once during the catalytic decomposition reaction cycle of nitrous oxide in Fe-ZSM-5 two spin-constrained potential energy surfaces have to cross. While these spin inversions are “forbidden” in the sense that the rate of spin inversion can be very low, Plattner (1999), Schröder et al. (2000), and Schwarz (2004) showed that if a spin inversion leads to a reduced activation barrier for the reaction, the overall reaction rate can be significantly increased. The low spin inversion probability is overcompensated by a reduced activation barrier. Figure 3.1 illustrates a qualitative energy profile for such a spin-accelerated reaction.

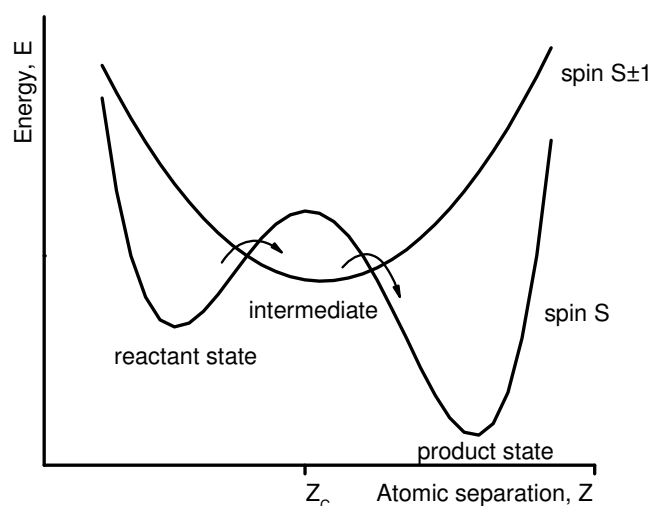


Figure 3.1: Qualitative energy profile for a spin-accelerated reaction. Both spin restricted potential energy surfaces are calculated within the Born-Oppenheimer approximation.

In particular, these authors observe a spin-accelerated reaction or “two-state reactivity” for the oxidation of hydrogen and methane with FeO^+ molecules in the gas phase ($\text{FeO}^+ + \text{H}_2 \rightleftharpoons \text{Fe}^+ + \text{H}_2\text{O}$, and $\text{FeO}^+ + \text{CH}_4 \rightleftharpoons \text{Fe}^+ + \text{CH}_3\text{OH}$). Since spin-accelerated reactions seem to be possible for reactions involving iron (high spin and low spin iron), all reactions studied in this work were investigated on multiple spin-constrained potential energy surfaces.

3.3.2 Landau-Zener formula

Whenever two spin-constrained potential energy surfaces cross, nonadiabatic effects become important and the transmission coefficient for spin inversion can become low. It is therefore necessary to understand the factors influencing the spin inversion probability and to be able to estimate the transmission coefficient for spin inversion. The first studies of surface crossing or surface hopping between two interacting one-dimensional potential energy curves (collision of two atoms) were performed by Landau (1932), Zener (1932 and 1933), and Stückelberg (1932). When two atoms collide a charge transfer from one atom to the other can occur below a certain distance Z_c if the energy of an ion pair becomes lower than the energy of the two neutral atoms. The neutral and the ionic potential energy surface form two diabatic states ψ_1^d and ψ_2^d of the system that cross at the atomic separation Z_c , see Figure 3.2. For an interatomic distance smaller than Z_c the state ψ_2^d is lower in energy, and for a distance larger than Z_c the state ψ_1^d is energetically favorable. By a combination of ψ_1^d and ψ_2^d the adiabatic ground state ψ_1^a can be constructed, if the coupling $H_{12} = \int \psi_1^d H \psi_2^d d\tau$ of the two diabatic states is known. The adiabatic ground state has the lowest energy for all interatomic separations and approaches the diabatic states asymptotically for large and small distances. A second combination of the diabatic states yields the excited adiabatic state ψ_2^a , which forms an upper bound to the diabatic energies. Both adiabatic states do not cross, they have an “avoided crossing”, and the energy difference of both adiabatic states at Z_c is twice the coupling constant H_{12} of the two diabatic states. The energies

$E_{1,2}^a$ of the adiabatic states are related to the diabatic energies $E_{1,2}^d$ by (see Darling and Holloway, 1994):

$$E_{1,2}^a = \frac{E_1^d + E_2^d}{2} \pm \frac{1}{2} \sqrt{(E_1^d - E_2^d)^2 + 4H_{12}^2} \quad (3.33)$$

Both, the adiabatic and the diabatic states, are able to describe a two-state system. For an increasing interatomic distance both representations become identical due to the absence of coupling. The Hamiltonian $\mathbf{H}'$ in the adiabatic representation is diagonal, while the Hamiltonian $\mathbf{H}$ in the diabatic representation contains the off-diagonal coupling matrix elements H_{12} and H_{21} , which are complex conjugate numbers.

$$\mathbf{H}' = \begin{pmatrix} H'_{11} & 0 \\ 0 & H'_{22} \end{pmatrix} \quad \mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \quad (3.34)$$

If the atoms move infinitely slow, the diabatic potential energy curves are nearly parallel, or the energy difference between the adiabatic states is high, the system will follow the adiabatic ground state. The extent of the separation of the two curves at the “crossing” point in Figure 3.2 depends on the symmetry properties of the two states.

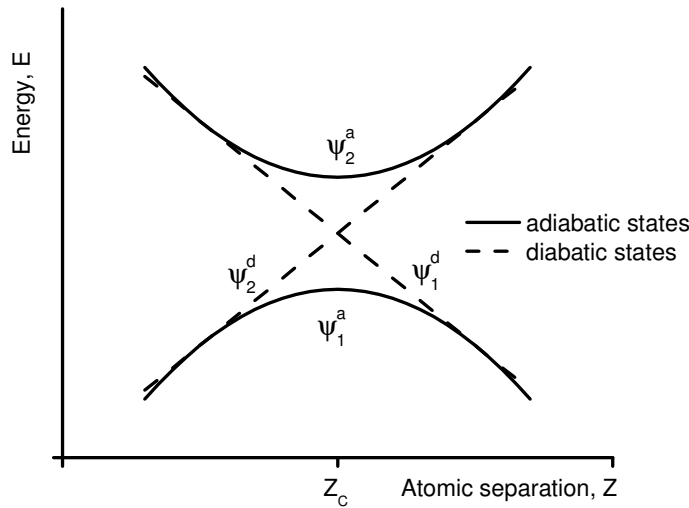


Figure 3.2: General two-state curve crossing problem.

If the states have different symmetry, e.g. different spin quantum numbers, then the resonance separation, equal to the matrix element H_{12} , is small. For a small resonance splitting, the spin inversion probability is low, and the adiabatic curves behave as though they are really crossed. For states of different symmetry, the resonance splitting depends on spin-spin and spin-orbital interactions. For an exact treatment of spin-surface crossing, especially the spin-orbit coupling energies have to be calculated, $H_{12} \approx \int \psi_1^d H_{so} \psi_2^d d\tau$. However, in view of the computational expense necessary for these calculations, spin-orbit coupling energies are not calculated in this work. Instead, the adiabatic approximation (and Born-Oppenheimer approximation) was used to calculate approximately the diabatic energy levels of different spin states and the spin-orbit coupling energies are assumed to be in the range between 395 to 825 J/mol. Danovich and Shaik (1997) calculated spin-orbit coupling energies in this range for the oxidative activation of H_2 by FeO^+ . Since spin-orbit coupling energies could not be calculated for the N_2O Fe-ZSM-5 system, the error in the rates of spin-surface crossing can be significantly larger than the error in calculated rates of reaction on one spin-constrained potential energy surface. With a given spin-orbit coupling energy H_{12} it is possible to estimate if low spin inversion probabilities could result in a significant reduction of the rates of spin-surface crossing. Thermally averaged spin transition probabilities are calculated with the Landau-Zener formula (see Stern and Eyring, 1935):

$$\bar{P}_{12} = \int_0^\infty dv \left(1 - \exp \left\{ - \frac{4\pi^2 H_{12}^2}{h v \|grad(E_1) - grad(E_2)\|} \right\} \right) \cdot \frac{\exp(-v^2/2k_B T)}{\int_0^\infty dv \exp(-v^2/2k_B T)} \quad (3.35)$$

Here H_{12} is the spin-orbit coupling energy, v is the mass-weighted velocity of the system at the crossing point, T is the absolute temperature, and $\|grad(E_1) - grad(E_2)\|$ is the absolute value of the mass-weighted difference in directional derivatives perpendicular to the seam at the point of crossing (in one-dimension this corresponds to the crossing point depicted in Figure 3.2). Here, it is supposed that the velocity of the system is at the crossing point Maxwell-Boltzmann distributed. The transmission coefficient for spin inversion can be calculated in most cases studied in this work as:

$$\kappa = 2\bar{P}_{12} - \bar{P}_{12}^2. \quad (3.36)$$

It is important to note that the necessary correction for the reaction rates, owing to a spin inversion probability smaller one, is comparable to the error inherent in the DFT calculations of activation energies. In addition, the rates of spin-surface crossing were never rate limiting in this work and, hence, spin-surface crossing should not have an influence on the overall kinetics of the reaction network studied.

More accurate but computationally slightly more demanding formulas than the Landau-Zener formula for nonadiabatic transitions between two electronic states are given by Zhu and Nakamura (1994 and 1995).

3.4 Statistical methods

In this section, some theoretical methods are explained that help to transform quantum chemical data of energy, gradient and second derivative matrix at specific molecule configurations into data that are comparable to experimentally measurable quantities. In particular, we like to study chemical reactions on catalyst surfaces on a molecular level to understand chemical reaction mechanisms, identify catalytically active sites, and calculate elementary reaction rate constants and heats of reaction. These microscopic kinetic and thermodynamic data of complicated elementary reaction networks can be scaled up and compared to macroscopic experimental results.

Section 3.4.1 introduces important concepts of the potential energy surface like the minimum energy pathway, transition states, and minima on the seam of two potential energy surfaces. These concepts are important to understand elementary reaction mechanisms and help to distinguish catalytically active from inactive sites. In fact, the potential energy surface and the temperature entirely determine the rate of reaction, so that potential energy surfaces are of central importance in chemical kinetics (Laidler, 1987). In section 3.4.2 classical transition state theory is reviewed. All elementary reaction rate constants presented in this work are calculated within the harmonic

approximation of conventional transition state theory. Some key ideas of statistical mechanics are presented in section 3.4.3. In particular the partition function of an ideal polyatomic gas is given. With this partition function it is possible to bridge the gap between a molecule moving on a potential energy surface to thermodynamic functions like the enthalpy and entropy. Finally, in section 3.4.4 all formulas used in the present work to calculate rates of adsorption, desorption, chemical reaction, and rates for non-adiabatic processes are summarized.

3.4.1 Potential energy surface

Within the Born-Oppenheimer approximation (see section 3.1.1) the nuclei move on a potential energy surface (PES) following Newton's equations of motion. For a molecular system with N atoms, the PES is generally a function of the $3N$ nuclear Cartesian coordinates, $\mathbf{x} = (x_1, y_1, z_1, \dots, x_N, y_N, z_N)$. Several alternative coordinate systems are in use (see Pulay and Fogarasi, 1992 and Baker et al., 1996). Another particularly useful coordinate system uses mass weighted Cartesian coordinates $\mathbf{x}_{\text{MWC}} = (M_1^{1/2} x_1, M_1^{1/2} y_1, M_1^{1/2} z_1, \dots, M_N^{1/2} z_N)$, where M_k is the mass of the k^{th} nuclei (Wilson et al., 1955). In mass weighted coordinates Newton's equations of motion simplify to $d^2 \mathbf{x} / dt^2 = -\nabla V_{\text{MWC}}^{\text{BO}}$, where $\nabla V_{\text{MWC}}^{\text{BO}} = \mathbf{M}^{-1/2} \nabla V^{\text{BO}}$ is the gradient of the Born-Oppenheimer potential in mass weighted coordinates ($\mathbf{M} = \text{diag}(M_1, M_1, M_1, \dots, M_N, M_N, M_N)$). All reference to the masses of the nuclei has disappeared in these equations. In general it is important to note that the potential energy surface is fully specified by $3N-6$ linearly independent coordinates ($3N-5$ for a linear molecule), since the Hamiltonian is invariant to a translation and rotation of the whole system. Figure 3.3 illustrates a PES for a H_2 molecule adsorbing on a platinum surface. If a full potential energy surface of a chemical system is available scattering calculations and molecular dynamics simulations can be performed to accurately calculate the rate of reaction from one potential energy minimum to another potential energy minimum. Unfortunately, mapping an entire PES is not practicable for larger systems. As the size of a molecular system increases, the number of electronic structure calculations required

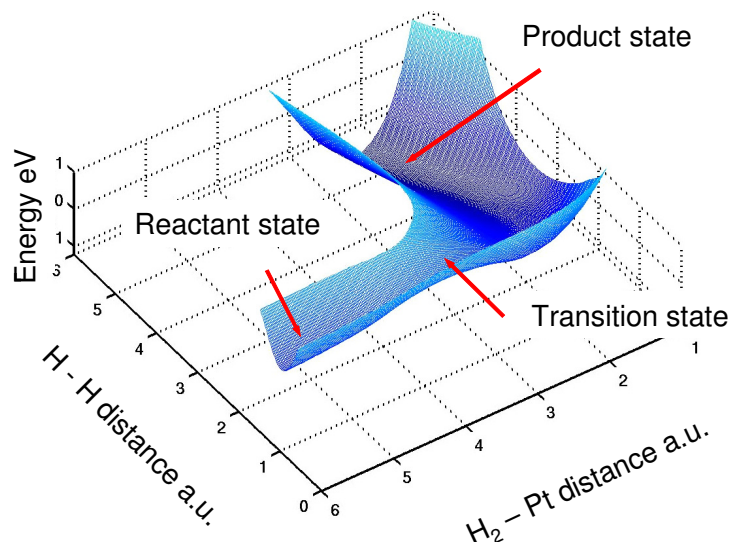


Figure 3.3: Potential energy surface of H₂ adsorbing on a Pt surface.

to create a complete map increases exponentially. Assuming that at least 10 energy calculations per coordinate axis have to be performed to fit a PES, 10^{3N-6} quantum chemical calculations are necessary for a system of N nuclei. For more than three atoms more than a million energy calculations are necessary to map such a complete potential energy surface.

Fortunately, small variations in the geometry of a molecule usually result in significant energy differences. The Boltzmann distribution determines the relative importance of configurations on the PES. The Boltzmann distribution gives the unnormalized probability of finding a system at a position $\mathbf{x}$ on the PES as $\exp[-V(\mathbf{x})/k_B T]$ (Chandler, 1987). Configurations with high potential energy are less likely to occur than configurations of low energy. The disparity becomes especially pronounced for low temperatures T , where the system possesses low kinetic energy and just structures near a potential energy minimum configuration are observed. For most chemical reactions even at a temperature of 1000 K changes in the geometry (different chemical species) result in changes in the potential energy that are significantly larger than the thermal energy, $\Delta V(\mathbf{x}) \gg k_B T$. As a result, just configurations close to PES minima are observed for chemical reaction systems. The minimum energy configuration within

a basin of attraction can be viewed as an approximate average molecular structure around which a molecule vibrates. Each distinct basin of attraction can be viewed as a region corresponding to a distinct chemical species identifiable by its average structure and vibrational spectrum. At a potential energy minimum, the gradient is zero and the second derivative matrix is positive definite (all eigenvalues greater zero). Close to a minimum energy configuration, $\mathbf{x}_{MWC}^{\min}$, the potential can be expanded in a Taylor series with vanishing gradient of the potential:

$$V(\mathbf{x}_{MWC}) = V(\mathbf{x}_{MWC}^{\min}) + \overset{0}{(\nabla V_{MWC}^{\min})^T} (\mathbf{x}_{MWC} - \mathbf{x}_{MWC}^{\min}) + \frac{1}{2} (\mathbf{x}_{MWC} - \mathbf{x}_{MWC}^{\min})^T \mathbf{H}_{MWC}^{\min} (\mathbf{x}_{MWC} - \mathbf{x}_{MWC}^{\min}) + \dots \quad (3.37)$$

Here $\mathbf{H}_{MWC}^{\min}$, $\mathbf{H}_{MWC}^{\min} = \mathbf{M}^{-1/2} \mathbf{H}^{\min} \mathbf{M}^{-1/2}$, is the mass weighted second derivative matrix of the potential energy at the minimum. Truncating the Taylor expansion at the second order, the equations of motion of configurations close to the minimum can be written as:

$$\frac{d^2(\mathbf{x}_{MWC} - \mathbf{x}_{MWC}^{\min})}{dt^2} = \mathbf{H}_{MWC}^{\min} (\mathbf{x}_{MWC} - \mathbf{x}_{MWC}^{\min}). \quad (3.38)$$

The eigenvectors and eigenvalues of this system of ordinary differential equations are the vibrational modes and squared angular vibrational frequencies of the system. If λ_i are the eigenvalues of the matrix $\mathbf{H}_{MWC}$ then the harmonic vibrational frequencies can be obtained in wavenumbers:

$$\tilde{\nu}_i = \sqrt{\frac{\lambda_i}{4\pi^2 c^2}}, \quad (3.39)$$

where c is the speed of light. Wavenumbers obtained in this way are often used to interpret experimental IR spectra (Wilson et al., 1955).

If a molecular configuration stays most of the time close to a PES minimum, then only certain features of the PES are important in determining rates of reactions between two basins of attraction. By efficiently locating and describing the important features of the PES the problems associated with mapping out a high dimensional potential energy surface can be circumvented. The basins of attraction on a PES are separated by a

dividing surface. This convention establishes a natural definition for reaction events as the crossing of a dividing surface. The Boltzmann distribution dictates the relative importance of states on the dividing surface. It is common practice to place the dividing surface in a way that the lowest energy point on a dividing surface is a first order saddle point on the PES (Jensen, 1999). All elementary reactions on one PES possess a saddle point connecting reactant and product states. A first order saddle point is a stationary point with zero gradient. All but one eigenvalue of the second derivative matrix $\mathbf{H}_{\text{MWC}}$ are positive (maximum in one direction; minimum in all other directions). The negative eigenvalue (imaginary frequency) corresponds to an unstable mode oriented perpendicular to the dividing surface. A steepest descent calculation started from the saddle point forward and backward along the unstable mode on the PES will reach the minima in the basins of attraction on either side of the dividing surface (Schlegel, 2003). The path followed by such a steepest descent calculation is known as the minimum energy path (MEP). Figure 3.4 shows for a model potential energy surface, reactant and product states (minima), a saddle point, and a minimum energy pathway connecting these states. The first order saddle point is the highest energy point on the MEP. Close to the MEP there is no other pathway that has a lower highest energy point on the pathway from the reactant to the product state than the first order saddle point.

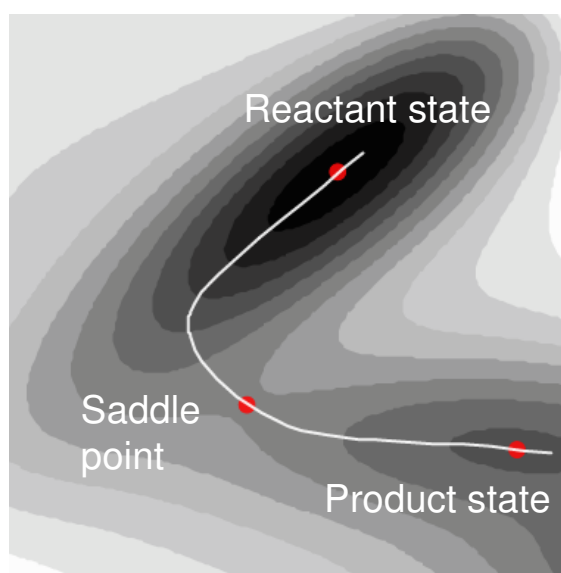


Figure 3.4: Model potential energy surface with reactant and product minima, saddle point, and minimum energy pathway (white).

An ensemble of reactive trajectories sampled from a Boltzmann distribution reveals that most reactive trajectories cross the dividing surface in the vicinity of the saddle point, see Laidler (1987). Consequently, to a first approximation only properties of the saddle point in relation to the reactant state will determine the kinetics of a reaction that requires surmounting a significant energy barrier to go from a reactant to a product state. In principle, all species on the dividing surface are called transition states; in practice just the first order saddle point is usually meant by a transition state.

In section 3.3 non-adiabatic effects and the breakdown of the Born-Oppenheimer approximation have been discussed. If two potential energy surfaces cross along the pathway from a reactant to a product state, the highest energy point on the minimum energy pathway is not necessarily a first order saddle point. Figure 3.5 illustrates two cases where the minimum energy pathway from a reactant to a product state involves a change of spin potential energy surface. In Figure 3.5a) the highest energy point along the reaction coordinate is a first order saddle point. The two potential energy surfaces involved in this chemical reaction cross before or after the saddle point. In this case it is again convenient to choose a dividing surface between reactant and product states that passes through the saddle point. Similarly to reactions on one PES, properties of the saddle point in relation to the reactant state will mainly determine the kinetics of the reaction. (Strictly speaking the rate of spin surface crossing can have a significant influence on the rate of reaction, see section 3.3). Figure 3.5b) illustrates a reaction coordinate without saddle point. The highest energy state along the reaction coordinate is a minimum on the seam of two potential energy surfaces, also called minimum energy crossing point, MECP (see Yarkony, 1995). The dividing surface between reactant and product states is conveniently placed in a way that it passes through the MECP (Jensen, 1992 and Bearpark et al., 1994). Locally, no pathway from a reactant state to a product state passes through a lower highest energy point on the pathway than the one passing through the MECP. It is noted that a minimum on the seam of two potential energy surfaces is not a stationary point on any potential energy surface.

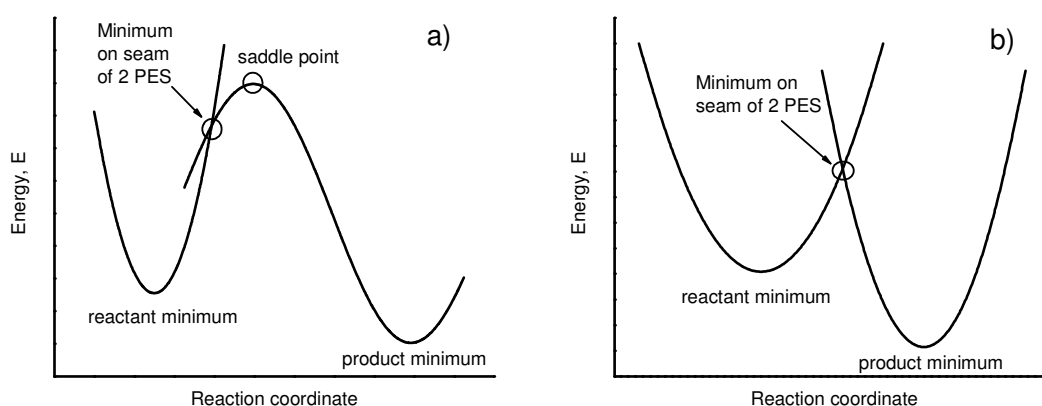


Figure 3.5: Energy profile along a reaction coordinate. Reactant and product states are on different spin potential energy surfaces. a) First order saddle point is highest energy state along reaction coordinate. b) Minimum on the seam of two potential energy surfaces is highest energy state along reaction coordinate.

Instead, it is the lowest energy configuration on one PES under the constraint that the other PES has the same energy at this configuration (minimum in $3N-7$ dimensional space). Here the rate of spin surface crossing together with the probability of reaching the point of spin surface crossing determines the rate of reaction.

In all of this work, it is assumed that the potential energy surface is in the relevant length scale a smooth function, i.e. a second order Taylor series approximation of the potential energy is useful over a significant region and the number of potential energy minima and first order saddle points is not too large to handle individually. This is usually the case for gas phase reactions and reactions on surfaces. For reactions in solutions where solvent-solvent and solvent-reactant interactions are relevant, the potential energy surface is often rugged and the methods described in this and the next sections to calculate thermodynamic functions and reaction rate constants are not applicable. Bolhuis et al. (2002) and Dellago et al. (2002) have written excellent reviews on how to calculate macroscopic rate constants for rough potential energy surfaces.

3.4.2 Transition state theory

Chemical reaction rates are usually expressed in terms of reaction rate constants, $k(T)$. After having recognized the saddle point as the bottleneck for reactive trajectories Eyring (1935) and Evans and Polanyi (1935) developed a transition state theory (TST) to determine absolute reaction rate constants:

$$k_{TST} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R}. \quad (3.40)$$

Here k_B is the Boltzmann constant, h is the Planck constant, Q_R is the reactant basin partition function and $Q^\ddagger$ is the dividing surface partition function. The factor $(k_B T/h)$ is a frequency factor for crossing the transition state. For a system at constant temperature and pressure the conventional TST rate constant can be written as (Wynne-Jones and Eyring, 1935):

$$k_{TST} = \frac{k_B T}{h} \exp(-\Delta G^\ddagger / k_B T) \quad (3.41)$$

where $\Delta G^\ddagger$ is the standard-state quasi-thermodynamic free energy of activation, i.e., the difference between the standard-state free energy of the transition state and that of the reactants.

A number of assumptions are made to derive the TST rate expression. First, it is assumed that a separation of nuclear and electronic motion is possible (Born-Oppenheimer approximation) and that the reactant molecules are distributed among their states in accordance with the Maxwell-Boltzmann distribution. Second, it is assumed that even in the absence of an equilibrium between reactant and product molecules, species close to the transition state that are becoming products are distributed among their states according to the Maxwell-Boltzmann distribution. The third assumption is that close to the transition state, motion along the reaction coordinate can be separated from the other motions and is treated classically as a translation. Finally, it is assumed that molecular species that have crossed the transition state in the direction of products cannot turn around and reform reactant species again.

In principle the calculation of the free energy of activation, $\Delta G^\ddagger$, requires a difficult integration over a high dimensional dividing surface. In practice, nearly all applications of TST use a hyperplane dividing surface with a harmonic approximation applied at the reactant minimum and the first order saddle point on the PES (Wert and Zener, 1949 and Vineyard, 1957). In the harmonic approximation, the hyperplane dividing surface is oriented perpendicular to the unstable vibrational mode at the saddle point. Though conventional TST contains seemingly severe assumptions the theory works surprisingly well as long as barrier crossing events are fast in comparison to the time between barrier crossings, i.e. when $\Delta V^\ddagger/k_B T \gg 1$ (see Hänggi et al., 1990). This condition is met for the absolute majority of chemical reactions. By defining the reaction rate constant by free energy differences, detailed balance is obeyed and the equilibrium constant for a chemical reaction is the ratio of the forward and reverse reaction rate constant:

$$K_{RP}^{eq} = \exp\left(-\frac{\Delta G_{RP}}{k_B T}\right) = \frac{k_{R \rightarrow P}}{k_{P \rightarrow R}}. \quad (3.42)$$

Shortly after conventional transition state theory was developed, generalized transition state theory emerged to improve the theory (Eyring and Stern, 1939, Truhlar et al., 1983 and 1996, Anderson, 1995). Generalized TST defines the rate constant for a reaction at temperature T as:

$$k(T) = \gamma(T) \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger(T)}{k_B T}\right), \quad (3.43)$$

where a generalized transmission coefficient, $\gamma(T)$, is introduced that relates the actual rate for the reaction to that obtained from the conventional transition state theory with $\gamma(T)$ equal to unity. The generalized transmission coefficient, $\gamma(T)$, can be expressed as a product of three contributions (Truhlar et al. 1996):

$$\gamma(T) = \Gamma(T) \kappa(T) g(T) \quad (3.44)$$

$\Gamma(T)$ arises from dynamical recrossing. It takes into account that some trajectories that cross the dividing surface in the direction of products recross and return to the reactant region (Shizgal and Karplus, 1970). $\Gamma(T)$ is smaller than 1. $\kappa(T)$ arises from quantum mechanical tunneling. Tunneling is a quantum mechanical effect most important for

light particles at low temperatures. $\kappa(T)$ is greater or equal to 1. $g(T)$ takes deviations of the equilibrium distribution in phase space into account. $g(T)$ can be either less than or greater than 1. In principle, with the help of the factor $\gamma(T)$ generalized TST can also be used to describe rates of reactions that cross multiple spin surfaces along the reaction coordinate. In this work transition state theory was used with a generalized transmission coefficient of unity. Although, transmission coefficients can be as small as 0.1 (and even smaller if spin surface crossings occurs), uncertainties in the rate constants are dominated by errors in the height of the activation barrier calculated with an unknown exchange-correlation functional (see section 3.2).

3.4.3 Statistical mechanics and thermodynamic functions

All macroscopic thermodynamic functions can be calculated in statistical mechanics with the help of the partition function (McQuarrie, 1976). The partition function, q , for a single molecule is defined as a sum of exponential terms involving all possible quantum energy states:

$$q = \sum_i^{\text{all states}} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad (3.45)$$

For N non-interacting identical particles the partition function of the whole system, Q , can be written as:

$$Q = \frac{q^N}{N!} \quad (3.46)$$

All thermodynamic functions can be calculated if the partition function of a system is known. In the following the relationship between the partition function and the Helmholtz free energy F , the enthalpy H , and the entropy S is given:

$$F = -k_B T \ln Q \quad (3.47)$$

$$H = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (3.48)$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B \ln Q \quad (3.49)$$

In order to calculate Q all possible quantum states are needed. It is usually assumed that the energy of a molecule can be approximated as a sum of terms involving translational, rotational, vibrational, and electronical states. This approximation is usually very good except for “floppy” molecules and cases where the Born-Oppenheimer approximation breaks down. Writing the energy in a sum of terms implies that the partition function can be written as a product of terms:

$$q = q_{trans} q_{rot} q_{vib} q_{el} \quad (3.50)$$

The translational partition function is given by:

$$q_{trans} = \left(\frac{2\pi k_B T \sum_i M_i}{h^2} \right)^{3/2} V, \quad (3.51)$$

where V is the volume and M_i is the i^{th} nuclei mass. A good approximation to the rotational partition function of a polyatomic molecule is given by:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \sqrt{I_1 I_2 I_3}. \quad (3.52)$$

Here σ is the symmetry index of the molecule and I_i are the three moments of inertia. For a diatomic molecule like O_2 or N_2 the rotation partition function becomes:

$$q_{rot} = \frac{8\pi^2 I k_B T}{h^2 \sigma}. \quad (3.53)$$

For calculating the vibrational partition function the harmonic approximation is used for potential energy minima and first order saddle points. Within this approximation the vibrational partition function is given by:

$$q_{vib} = \prod_{i=1}^{3N-6(7)} \frac{\exp\left(-\frac{h\nu_i}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_B T}\right)}. \quad (3.54)$$

Here ν_i are the vibrational frequencies of the molecule. The product in the vibrational partition function goes over all real frequencies. Consequently, for a PES minimum there are $3N-6$ terms and $3N-7$ terms for a first order saddle point (where N is the number of nuclei).

The electronic partition function involves a sum over electronic quantum states. The energy difference between the ground and excited states is usually much larger than the thermal energy, $k_B T$, so that the electronic partition function can be written as:

$$q_{el} = g \exp(-E_0/k_B T), \quad (3.55)$$

where g is the electronic degeneracy and E_0 is the ground state energy (not zero point corrected).

With these partition functions the connection between quantum chemical calculations of PES minima and first order saddle points, and thermodynamic functions and reaction rate constants becomes apparent. The mass of the molecule determines the translational partition function. The geometry of the molecule at the PES minimum and first order saddle point defines the appropriate moments of inertia and symmetry index in the rotational partition function. The harmonic vibrational frequencies in the vibrational partition function are obtained from a second derivative calculation at the stationary points with the help of Eqn. (3.39). Finally, the electronic degeneracy and the ground state energy in the electronic partition function are the solutions of the Schrödinger equation, Eqn. (3.7).

Vibrational frequencies determined by *ab initio* computational methods are typically larger than the fundamental frequencies observed experimentally (Hehre et al. 1986). As a result, there has been some effort in the last decade to scale down theoretical harmonic vibrational frequencies to match experimental frequencies and thermodynamic functions of enthalpy and entropy. Typical scaling factors for DFT-B3LYP are about 0.96 to match experimental frequencies and 0.97 to 1.0 to match thermodynamic functions (Wong, 1996, Halls et al., 2001, Scott and Radom, 1996). In

the present work frequency scaling was not used. To simulate reactions on solid surfaces with the help of a cluster model some surface atoms are fixed in space (see section 5). To obtain reasonable vibrational frequencies the flexible part of the second derivative matrix $\mathbf{H}_{\text{MWC}}$ has to be carved out of the full matrix and the vibrational analysis has to be performed for the flexible part of the second derivative matrix only. Since vibrational relaxation beyond fixed atoms is not possible, the uncertainty in calculated harmonic frequencies is larger than for molecules in the gas phase. Given that DFT-B3LYP frequency scaling factors are very close to one and that only ratios of vibrational partition functions appear in thermodynamic functions, very accurate vibrational frequencies are not important to obtain accurate thermodynamic functions.

3.4.4 Rates of reaction

One of the most important parts of the present work is the calculation of a large number of reaction rates of elementary processes on a catalyst surface. This section summarizes the formulas used to calculate the elementary reaction rate constants. As stated above, overall equilibrium constants and reaction rate constants were computed using standard statistical mechanics and conventional TST in the harmonic approximation. To calculate the partition function of all gaseous species participating in the reaction, translational, rotational, vibrational, and electronic contributions of the partition function were considered. For the zeolite cluster, representing the catalyst active site, only the vibrational and electronic contributions of the partition function were included. Since the zeolite cluster is part of a solid, translational and rotational partition functions for the zeolite were assumed to be equal in the reactant, transition, and product state. For a reaction on one spin potential energy surface the reaction rate constant is given as:

$$k = \frac{k_B T}{h} \frac{\tilde{Q}^\ddagger}{\tilde{Q}_R}, \quad (3.56)$$

where $\tilde{Q}$ is the partition function without contributions from solid translation and rotation.

The procedure described above is not able to determine rates of spin-surface crossing. The minimum-energy structure on the seam of two PESs is not a stationary point. As a result, the partition function of the dividing surface cannot be calculated using the equations presented in section 3.4.3. Since the species with low spin multiplicity in this work is usually an adsorbed species (e.g. adsorbed O₂), the framework of absolute rate theory is used under the assumption that the partition functions of the hypothetical transition state (minimum on the seam of two PES) and the reactant state (minimum on PES with lower spin multiplicity) are identical (except for the energy). Consequently,

$$k_{low \rightarrow high} = \frac{k_B T}{h} \exp\left(-\frac{\Delta E}{k_B T}\right); \quad k_{high \rightarrow low} = k_{low \rightarrow high} \cdot K_{equil}, \quad (3.57)$$

where ΔE is the difference in the electronic energy of the minimum on the seam of the two PESs and the reactant state. This corresponds to an energy barrier of ΔE and an escape attempt probability of $(k_B T/h)$. This procedure completely neglects a low spin surface crossing probability (see section 3.3) or rather assumes that the probability of spin surface crossing times the partition function of the transition state equals the partition function of the reactant state. Since the partition function of a transition state is indeed usually larger than that of an adsorbed state, the procedure is reasonable as a zeroth order approximation. To estimate if very low spin surface crossing probabilities could result in very different reaction rate constants, thermally averaged spin transition probabilities are calculated with the Landau-Zener formula (see section 3.3.2):

$$\bar{P}_{12} = \int_0^\infty dv \left(1 - \exp\left\{ -\frac{4\pi^2 H_{12}^2}{h v \|grad(E_1) - grad(E_2)\|} \right\} \right) \cdot \frac{\exp(-v^2/2k_B T)}{\int_0^\infty dv \exp(-v^2/2k_B T)}, \quad (3.35)$$

where the spin-orbit coupling energy H_{12} is assumed to be in the range between 395 and 825 J/mol, as calculated by Danovich and Shaik (1997).

It is important to note that the necessary correction for the reaction rates, owing to a spin inversion probability smaller one, is in this work found to be comparable to the error inherent in the DFT calculations of activation energies. In addition, the rates of spin-surface crossing were never rate limiting in this work and, hence, spin-surface

crossing should not have an influence on the overall kinetics of the reaction network studied.

Recently, Okuno and Mashiko (2005) presented an approximate expression for the calculation of the partition function of the dividing surface for non-adiabatic transitions that just requires the calculation of one complicated integral.

The same approach as for spin surface crossing was also used for the computation of rates of desorption on one PES when the adsorption process is barrierless (Laidler, 1987):

$$k_{des} = \frac{k_B T}{h} \exp\left(-\frac{\Delta E}{k_B T}\right); \quad k_{ads} = k_{des} \cdot K_{equil} \quad (3.58)$$

In principle, it is questionable to use transition state theory for a process like adsorption that is not an activated process. For such a process the separation of time scales between the activation process and the relaxation of the local system is not fulfilled (Hänggi et al. 1990). As a result, it is common to introduce a sticking coefficient to describe adsorption and desorption (Behler, 2004). Nevertheless, adsorption and desorption are usually fast equilibrium processes, so that the absolute value of the rate process is not important as long as the absolute rate is high enough. Since the partition function of the dividing surface is most likely larger than the partition function of the adsorbed state, Eqn. (3.58) is a conservative estimate of the absolute rate of adsorption and desorption. However, adsorption and desorption processes without an activation barrier for adsorption were always found to be equilibrium processes in this work, justifying the use of Eqn. (3.58).

4 Algorithms for finding transition states in chemical reactions

The calculation of rates of reaction usually requires the determination of the reactant minimum energy configuration and the highest energy configuration along the reaction path. For reactions on one spin potential energy surface the highest energy configuration connecting reactant and product states is a first order saddle point. For reactions on two spin potential energy surfaces a minimum energy crossing point (MECP) is often the highest energy state along the reaction coordinate. While locating potential energy minima can routinely be done, finding transition states on potential energy surfaces determined from quantum chemical calculations can be extremely difficult, and remains one of the major challenges in chemical kinetics for medium to large systems. Three different types of algorithms for finding these transition states in chemical reactions have been developed and programmed in the present work.

The algorithms for finding first order saddle points on one spin potential energy surface can be divided into two groups, those based on interpolation between a reactant and a product minimum, and those using only local information. A combination of both algorithms is probably the most efficient way of finding first order saddle points. Section 4.1 explains interpolation methods such as the string method and the growing string method. Peters et al. (2004) showed that the growing string method is superior to the other common interpolation algorithms. The growing string method was programmed and used throughout this work. Interpolation methods are able to find an approximation to the minimum energy pathway (MEP) and thereby provide a good initial guess for a transition state and imaginary mode connecting both reactant and product states. Since interpolation methods employ usually just a small number of configurations and converge slowly close to the minimum energy pathway, local methods such as partitioned rational function optimization (P-RFO) methods (Baker, 1986) using either exact or approximate Hessians or minimum mode following methods

like the dimer (Henkelman and Jónsson, 1999) or the Lanczos method (Malek and Mousseau, 2000) have to be used to converge to the transition state. Such local saddle point search algorithms are discussed in section 4.2. In particular, a modification to the original dimer method proposed by Henkelman and Jónsson (1999) is presented, reducing the number of gradient calculations per cycle from six to four gradients or three gradients and one energy, and significantly improve the overall performance of the algorithm on quantum chemical potential energy surfaces (PES), where forces are subject to numerical noise. The P-RFO methods from Baker (1986) and various dimer methods have been programmed and used in the present work. In section 4.3 a comparison is made between the dimer methods and the well-established P-RFO methods for finding transition states after the use of interpolation methods. Results for 24 different small to medium sized chemical reactions covering a wide range of structural types demonstrate that the improved dimer method is an efficient alternative saddle point search algorithm on medium sized to large systems and is often even able to find transition states when P-RFO methods fail to converge (Heyden et al., 2005). Finally, in section 4.4, an algorithm for finding minimum energy crossing points based on a multiplier penalty function algorithm from Powell (1969) is presented. The multiplier penalty function approach was found to be very robust and efficient for quantum chemical constraint optimization problems.

It has to be stressed that every algorithm used in connection with a QM program package has to consider certain particularities of QM calculations:

- 1.) Converging the wave function, i.e. calculating the system energy, is a computationally very demanding task. The computed energies, forces and Hessians are subject to significant numerical noise.
- 2.) Once the wave function is known, the gradient of the energy can be calculated readily utilizing the Hellmann-Feynman theorem and calculating the Pulay forces (Springborg, 2000).
- 3.) Efficient parallelized routines are often available in commercial QM program systems for energy and gradient calculations. A parallelized analytical second

derivative calculation is not possible with most QM program systems like e.g. the TURBOMOLE V5.5-5.7 program package used in this work.

As a result, every algorithm used in connection with a QM program system should make massive use of gradient calculations and should preferably not need to calculate any second derivative matrix of the potential energy.

4.1 Interpolation methods

Interpolation methods generate a sequence of approximate minimum energy pathways by interpolating between a reactant and a product state. The highest energy configuration along the MEP is a first order saddle point. Both, reactant and product states must be known, so that these methods cannot reveal unexpected chemical pathways with multiple intermediates. Furthermore, if multiple pathways exist only the one nearest to the interpolated guess will be found (Peters, 2004). Nevertheless, interpolating algorithms are powerful methods for calculating saddle points and minimum energy pathways as the system size increases. These algorithms convert a saddle point search in configuration space to a minimization problem in discretized path space (Jensen, 1999). The solution of a fully converged interpolation algorithm in mass-weighted coordinates is the intrinsic reaction coordinate (IRC). In this way, interpolation methods guarantee that the saddle point found connects both reactant and product states. Furthermore, unlike saddle point searches, minimization problems in path space can easily handle large numbers of low-frequency modes; a significant challenge for most local surface-walking algorithms. Since the dimensionality of the discretized path space is significantly larger than that of the configurational space the computational cost of interpolation methods per iteration is significantly larger than for most surface-walking algorithms. Henkelman and Jónsson (2000) have suggested that an interpolation scheme should only be used to generate a good initial guess for the saddle point and the minimum energy pathway. This guess is then refined using a local surface-walking algorithm. In this way, a good guess for the saddle point and the

imaginary mode connecting both reactant and product states is generated from the interpolation algorithm, and the saddle point found by the surface-walking algorithm is most likely a transition state connecting reactant and product states.

Interpolation algorithms include methods such as the linear synchronous transit (Halgren and Lipscomb, 1977), conjugate peak refinement (Fischer and Karplus, 1992), self penalty walk (Elber and Karplus, 1987), nudged elastic band (NEB) (Mills and Jónsson, 1994; Henkelman and Jónsson, 2000), and the string method (E et al., 2002). While especially the NEB and the string method are highly effective for many problems, these methods initiate the search for a transition state by assuming that the MEP is a straight line in multidimensional space connecting the reactant and product states. Figure 4.1 illustrates the initial guess of the MEP and the converged MEP for the Müller-Brown potential energy surface (Müller and Brown, 1979). Depending on the coordinate system, a straight line guess for the MEP is often adequate, but in some reactions it may be far from the correct path. A bad guess for the MEP can result in slow convergence or worse in a failure of the electronic structure calculation (electronic structure calculations fail to converge for configurations with significant atomic overlap).

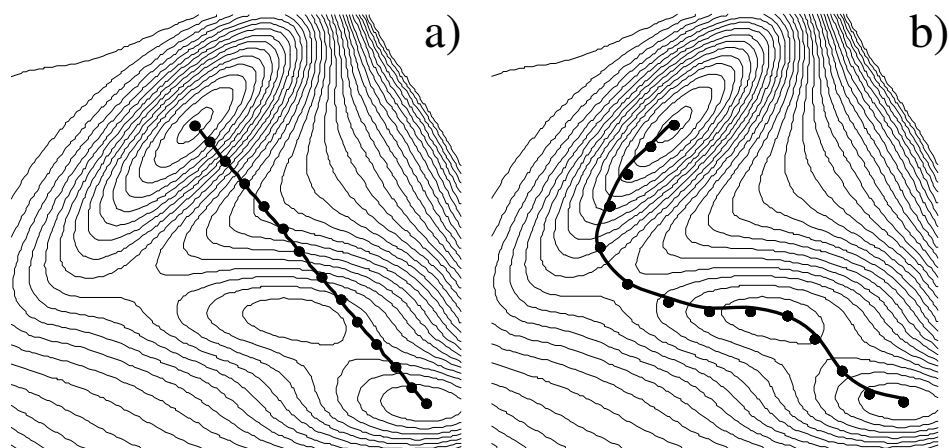


Figure 4.1: Interpolation method on the Müller-Brown potential energy surface. Panel a) shows the initial string with nodes as black dots. Panel b) shows the converged string.

Peters et al. (2004) have shown that the growing string method, an interpolation method that does not require an initial guess for the initial pathway, needs significantly fewer gradient calculations to find a saddle point than the zero temperature string method of Ren (2002) and the NEB. A version of the growing string method developed in this work and the zero temperature string method upon which the growing string method is based, are explained in the next sections.

4.1.1 String method

In this section the zero temperature string method from Ren (2002) and E et al. (2002) is described. The string is a path, $\varphi(\sigma)$, connecting the reactant and product configurations. The parameterization variable, σ , is some monotonic function of the normalized arc length, s , measured from one end of the string. The actual function $\sigma(s)$ is determined from a parameterization density, and is normalized so that $\varphi(0)$ is the reactant state, and $\varphi(1)$ is the product state. A simple way to find the minimum energy pathway is to evolve the string, φ , according to the velocity, u , given by:

$$u = -(\nabla V)^\perp(\varphi), \quad (4.1)$$

where $(\nabla V)^\perp$ denotes the projection of the gradient of the potential into the hyperplane normal to the path φ :

$$(\nabla V)^\perp(\varphi) = \nabla V(\varphi) - \mathbf{t}(\sigma)^T \nabla V(\varphi) \mathbf{t}(\sigma), \quad (4.2)$$

where $\mathbf{t}$ is the normalized tangent vector of the path. The stationary solution of Eqn. (4.1) satisfies

$$(\nabla V)^\perp(\varphi) = 0, \quad (4.3)$$

which defines the MEP of the potential V . The problem of finding the MEP can be reformulated (Peters, 2004). The MEP is the global minimum of the functional F :

$$F[\varphi] = \int_0^1 d\sigma \left((\nabla V)^\perp(\varphi(\sigma)) \right)^T (\nabla V)^\perp(\varphi(\sigma)) \quad (4.4)$$

over all paths connecting the reactant and product state. In practice the string is represented by a series of discrete configurations, uniformly spaced in the variable σ , so that the objective function becomes:

$$F(\varphi(\sigma_0), \varphi(\sigma_1), \dots, \varphi(\sigma_n)) = \sum_{k=0}^n \left| (\nabla V)^\perp(\varphi(\sigma_k)) \right|^2. \quad (4.5)$$

Moving discrete configurations on the path to find the minimum of the objective function F , results in a non-uniform spacing in the variable σ . As a result, the iteration scheme of the string method consists of two steps, an evolution step that guides the string towards the MEP, and a reparameterization step that enforces the prescribed parameterization density.

4.1.1.1 Evolution step

In the evolution step the string is moved towards the MEP. There are a number of numerical methods for minimizing functions like $F[\varphi]$. In the present work a steepest descent, conjugate gradient, and BFGS quasi-Newton algorithm (Nocedal and Wright, 1999) have been programmed. A BFGS algorithm with an initial unit inverse second derivative matrix (in electronic units) of the energy of each configuration and an inexact line search, as suggested by Fletcher (1987), performed best and was used throughout this work. One particular problem in minimizing $F[\varphi]$ is the determination of the path tangent used to calculate the gradient of the potential perpendicular to the path φ . A centered-difference scheme grows kinks and becomes unstable if the spacing between the configurations becomes smaller than $|(\nabla V)^T \mathbf{t}|/2\lambda$, where λ is the smallest eigenvalue of the second derivative matrix in the hyperplane normal to the path (Peters, 2004). In the present work an essentially non-oscillatory scheme (ENO) as described by Ren (2003) was implemented. The first order ENO scheme resembles the upwind difference scheme for defining the path tangent at each configuration:

$$\mathbf{t}(\sigma_i) = \begin{cases} \text{forward differences} & \text{if } V(\varphi_{i+1}) > V(\varphi_i) > V(\varphi_{i-1}) \\ \text{backward differences} & \text{if } V(\varphi_{i+1}) < V(\varphi_i) < V(\varphi_{i-1}) \end{cases} \quad (4.6)$$

If $V(\varphi)$ achieves a local minimum or maximum at φ_i , the tangent is approximated by potential weighted finite differences to avoid an abrupt change of the tangent vector. Alternatively, Peters (2004) suggested the use of cubic splines to fit the path, φ , and to obtain the tangents of the path.

4.1.1.2 Reparameterization

The second step of the string method is the reparameterization of the string in order to enforce a prescribed parameterization density. In other words, the nodes that constitute the discretized string are redistributed along the string according to the chosen parameterization density. The function $\sigma(s)$ disperses nodes along the string at uniform intervals in s , i.e., at $\sigma = 0, 1/n, 2/n, \dots, 1$ for a string discretized in $n+1$ nodes, such that the density of nodes as a function of the normalized arc length, s , is consistent with a chosen parameterization density, $\rho(s)$. The inverse function $s(\sigma)$ is determined by solving the differential equation (Ren, 2002):

$$\frac{d}{d\sigma} \left(\rho(s) \frac{ds}{d\sigma} \right) = 0 \quad (4.7)$$

with the boundary conditions, $s(0) = 0$ and $s(1) = 1$. Integrating Eqn. (4.7) twice from zero to one normalizes the parameterization density.

$$c = \int_0^1 \rho(s) ds \quad (4.8)$$

Integrating the density until the integral reaches a fraction $\sigma_k = k/n$ of c gives the new normalized arc length $s_k = s(\sigma_k)$ along the previous evolved string.

$$\int_0^{s_k} \rho(s) ds = c \sigma_k \quad (4.9)$$

The reparameterized position $\varphi_k = \varphi(s_k)$ is then determined by following along the evolved string to an arc length $s_k S$, where S is the true non-normalized arc length of the string (Peters, 2004). In the present work, the zero temperature string method was used

with a uniform parameterization density, $\rho(s)$, and the string was reparameterized whenever the true arc length between nodes was more than 20 % off the desired arc length between nodes.

4.1.2 Growing string method

The growing string method is based on the “zero temperature string method” of Ren (2002) explained in the last section. The basic idea of the growing string method is that the parameterization density, $\rho(s)$, need not be continuous and can even change between iterations. The growing string method uses an initially discontinuous parameterization density with a varying number of nodes on the string, n , between iterations. These properties allow a systematic evolution of the parameterization density so that the string grows from its endpoints as it evolved until eventually the two ends join to form one continuous string. In this way, no initial MEP has to be assumed, fewer calculations have to be performed on initial approximate MEPs that are far away from the true MEP and the string can avoid rugged regions of the PES where electronic structure calculations may fail. A flow sheet for the growing string algorithm is shown in Figure 4.2.

The string ends grow into the unknown interior of the reaction pathway whenever the normal force at a frontier node of a string fragment is smaller a preset value. In the present work a new node was added to a string fragment (i.e., the parameterization density evolves by $1/n$, where $n+1$ is the number of nodes on the converged string), if the force on the node at the end of a string fragment, from which the tangential component is projected out, is smaller than $0.02 E_h/\text{bohr}$. In this way, the string fragments of the growing string method merge relatively rapidly and an approximation of the MEP is generated. The tangent vector of the string at a frontier node is not calculated the usual way using the ENO scheme (Ren, 2003). Instead, the tangent vector is always calculated by finite differencing on the respective string side. As a result, nodes far away from the frontier node do not influence its movement to the MEP.

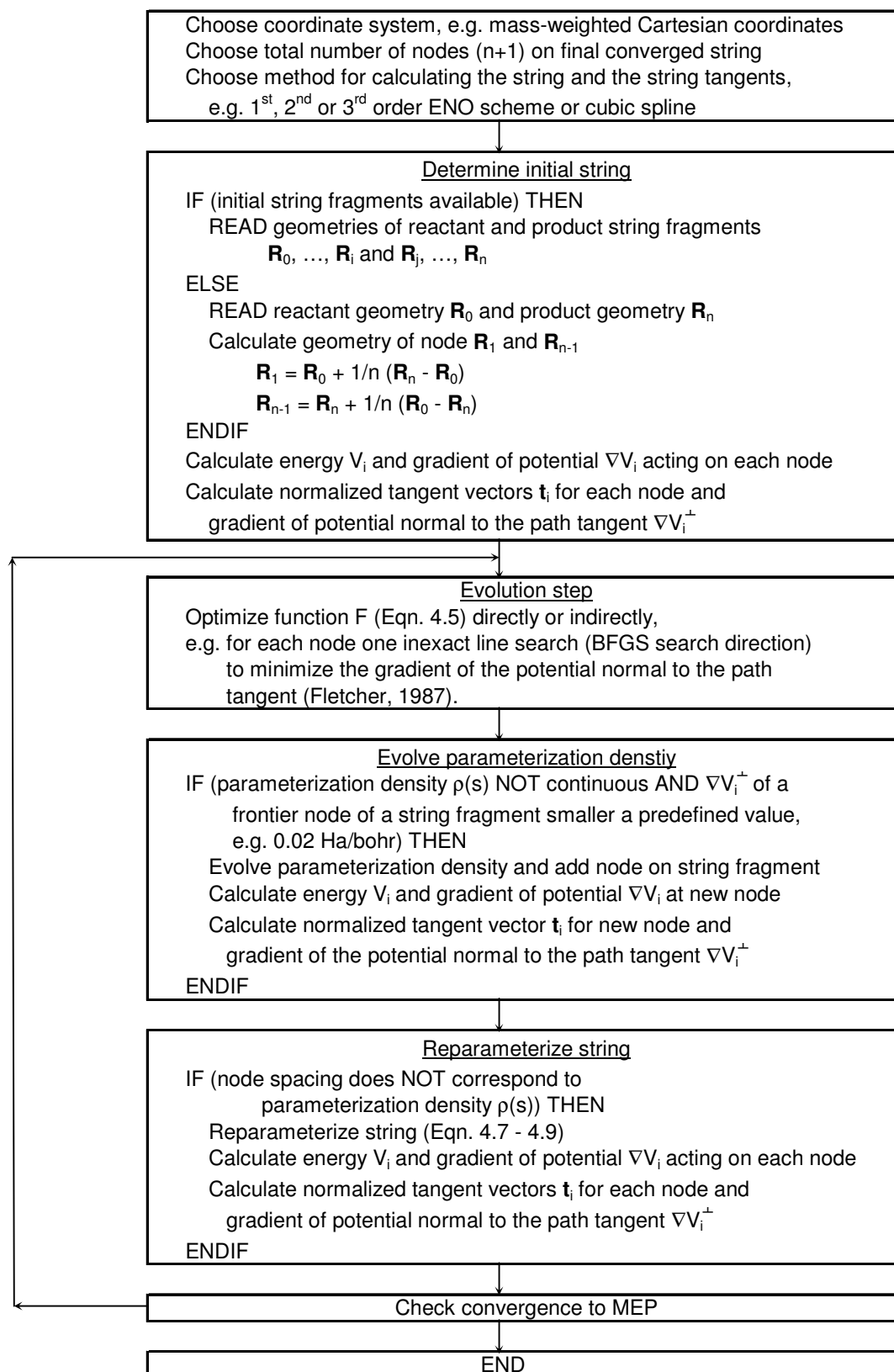


Figure 4.2: Flow sheet of the growing string algorithm as it was implemented in the present work.

Figure 4.3 illustrates the mechanism of the growing string method by showing four snapshots of the growing string with 18 nodes on the Müller-Brown potential. Initially, the string fragments, bound either to the reactant or to the product potential energy minimum, consist of two nodes. One node fixed in the potential energy minimum, the second pointing in the direction of the frontier node of the opposite string fragment. Each node on the string fragments is moved according to minimize Eqn. (4.5).

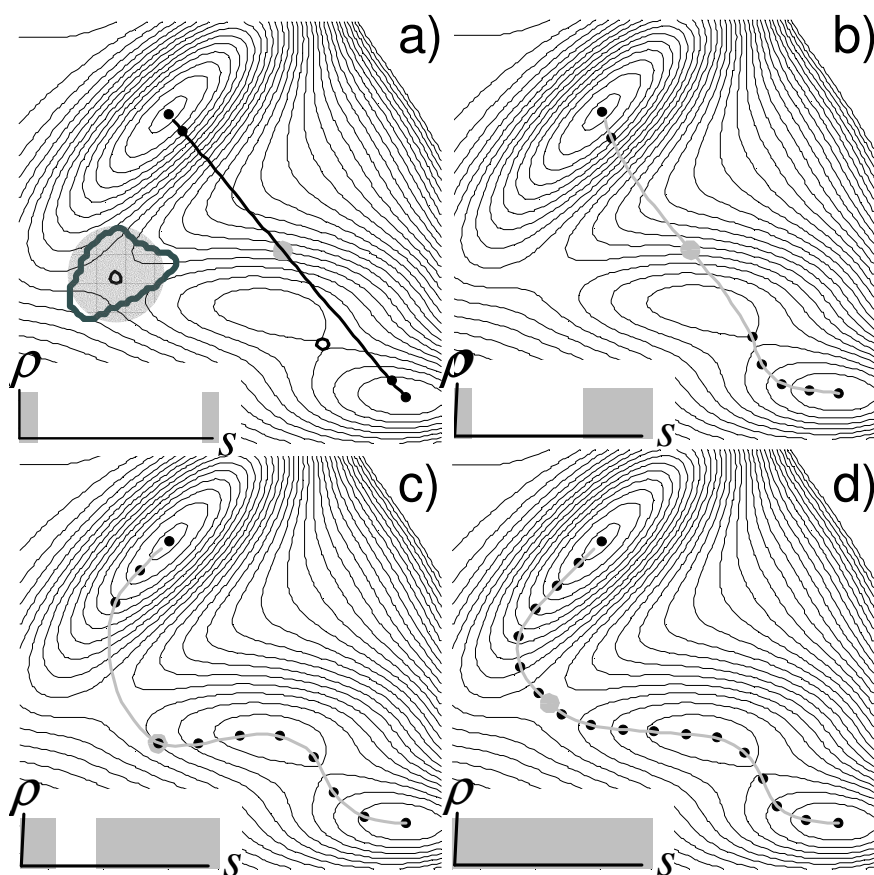


Figure 4.3: Four snapshots of a growing string on the Müller-Brown potential energy surface. Panels (a), (b), (c) and (d) show iterations 0, 4, 8, and 12, respectively. The nodes are shown as black dots, and the splined string is shown between the nodes as a gray curve. The parameterization density $\rho(s)$ is shown in the lower left of each panel. The gray dot on each string is the interpolated point of maximum energy. (a) shows the two saddle points on the potential energy surface as small open circles. The gray outline around the highest energy saddle point is its Newton-Raphson basin of attraction. The large shaded circle has radius 0.25 and approximately covers the basin of attraction. Figure from Peters et al. (2004).

If the true arc length between nodes is more than 20 % off the desired arc length given by the parameterization density, the string is reparameterized, i.e. the nodes are redistributed along the string. Whenever, the gradient of a frontier node, from which the tangential component is projected out, is smaller than a preset value, e.g. $0.02 E_h/\text{bohr}$, the string fragment is nearly converged to the minimum energy pathway and a new node is added to the string fragment pointing in the direction of the frontier node of the opposite string fragment, i.e. the parameterization density evolved. This procedure is repeated until the string fragments merge and an approximation to the MEP is found. In the present work, the growing string method was always used in mass-weighted coordinates so that the computed MEP corresponds to the intrinsic reaction coordinate.

Recently, Quapp (2005) proposed a combination of the Newton projector (Quapp, 2004) and the growing string method. On the test set used by the author this combination was shown to be superior to the original growing string method from Peters et al. (2004).

4.2 Local saddle point search algorithms

Local surface-walking algorithms explore the potential energy surface (PES) using local gradient and usually second derivative information. These methods can be initiated anywhere on the PES and when close to a saddle point converge rapidly. Unfortunately, surface-walking algorithms perform poorly for systems with several low-frequency vibrational modes or for searches started far from a transition state. Therefore, one of the major challenges in the use of surface-walking algorithms for large systems is to find a good initial guess of the transition state. An intuitive guess of the transition state configuration often results in a second derivative matrix that has several unstable modes, none of which resemble the motion along the reaction coordinate. Furthermore, even if a transition state is found it is possible that the transition state does not connect reactant and product states. Consequently, an interpolation algorithm like the growing string method described in the last section was

always used in the present work before the local surface walking algorithm to generate a good starting configuration of the transition state.

The most common surface-walking algorithms are quasi-Newton methods introduced by Cerjan and Miller (1981) and later modified by Simons et al. (1983), Banerjee et al. (1985), Nichols et al. (1990) and Wales (1989). One of these methods widely used for *ab initio* molecular calculations is the partitioned rational function optimization algorithm of Baker (1986), which utilizes either an approximate or an exact Hessian matrix. For large systems with a starting geometry far from the saddle point exact Hessians have to be calculated regularly even if a Hessian matrix updating scheme is used. If the Hessian matrix cannot be determined analytically, the second derivative matrix has to be determined numerically. For large systems this step often becomes prohibitively expensive.

Recently, minimum mode finding algorithms, such as the dimer (Henkelman and Jónsson, 1999) and Lanczos methods (Malek and Mousseau, 2000) have been developed. Instead of calculating the full Hessian matrix these algorithms calculate only the lowest eigenvalue and the corresponding eigenvector. The dimer method, developed by Henkelman and Jónsson, was designed to determine which activated transitions can occur from a given initial state at a finite temperature. In this way the algorithm is intended to find a set of low-lying saddle points at the boundary of the potential energy basin associated with the initial state.

In the following the P-RFO algorithm from Baker (1986), the original dimer method from Henkelman and Jónsson (1999) and a modification of the dimer method developed in this work are explained. All three surface-walking algorithms were programmed and used in this work for finding transition states on quantum chemical potential energy surfaces.

4.2.1 Partitioned rational function optimization method

Surface-walking algorithms for finding stationary points are usually based on a local quadratic approximation of the potential energy surface. The fastest step $\Delta \mathbf{x}$ to reach a stationary point is then the Newton-Raphson (NR) step:

$$\Delta \mathbf{x} = \sum_i (\mathbf{u}_i^T \mathbf{f}) \mathbf{u}_i / \lambda_i \quad (4.10)$$

Here $\mathbf{u}_i$ is the eigenvector, λ_i is the eigenvalue of the second derivative matrix of the energy E , and $\mathbf{f}$ is the force at the current configuration. Cerjan and Miller (1981) introduced a shift parameter γ to the Hessian eigenvalues λ_i to ensure that the surface-walking algorithm moves uphill along the lowest Hessian eigenvector and downhill along all other eigenvectors.

$$\Delta \mathbf{x} = \sum_i (\mathbf{u}_i^T \mathbf{f}) \mathbf{u}_i / (\lambda_i - \gamma) \quad (4.11)$$

Banerjee et al. (1985) showed that the above equation can be obtained when a rational function optimization (RFO) approach is used to approximate the potential energy surface. The shift parameter γ can then be found iteratively from the relationship:

$$\sum_i (\mathbf{u}_i^T \mathbf{f})^2 / (\gamma - \lambda_i) = \gamma \quad (4.12)$$

For finding first order transition states Banerjee et al. (1985) suggested separating the principle mode to be maximized and the $(n - 1)$ modes to be minimized by partitioning the RFO matrix into two smaller P-RFO matrices and solving each problem separately. Hence there are two shift parameters, γ_p and γ_n . For maximization along the k th mode, γ_p is the largest eigenvalue of

$$\begin{pmatrix} \lambda_k & -\mathbf{u}_k^T \mathbf{f} \\ -\mathbf{u}_k^T \mathbf{f} & 0 \end{pmatrix} \begin{pmatrix} \Delta x_k \\ 1 \end{pmatrix} = \gamma_p \begin{pmatrix} \Delta x_k \\ 1 \end{pmatrix} \quad (4.13)$$

and γ_n is the lowest eigenvalue of

$$\begin{pmatrix}
\lambda_1 & & & & & & & & \\
& \ddots & & & & & & & \\
& & \lambda_{k-1} & & & & & & \\
& & & \lambda_{k+1} & & & & & \\
& & & & \ddots & & & & \\
& & & & & \lambda_n & & & \\
-\mathbf{u}_1^T \mathbf{f} & \cdots & -\mathbf{u}_{k-1}^T \mathbf{f} & -\mathbf{u}_{k+1}^T \mathbf{f} & \cdots & -\mathbf{u}_n^T \mathbf{f} & 0 & &
\end{pmatrix}
\begin{pmatrix}
\Delta x_1 \\
. \\
\Delta x_{k-1} \\
\Delta x_{k+1} \\
. \\
\Delta x_n \\
1
\end{pmatrix}
= \gamma_n
\begin{pmatrix}
\Delta x_1 \\
. \\
\Delta x_{k-1} \\
\Delta x_{k+1} \\
. \\
\Delta x_n \\
1
\end{pmatrix} \quad (4.14)$$

The step $\Delta \mathbf{x}$ then has the form:

$$\Delta \mathbf{x} = \sum_{j=1}^n \Delta \mathbf{x}_j, \Delta \mathbf{x}_k = \mathbf{u}_k^T \mathbf{f} \mathbf{u}_k / (\lambda_k - \gamma_p), \Delta \mathbf{x}_{i, i \neq k} = \mathbf{u}_i^T \mathbf{f} \mathbf{u}_i / (\lambda_i - \gamma_n) \quad (4.15)$$

The mode k is generally chosen to correspond to the lowest eigenvalue, whereas in a mode following procedure, the mode k followed is the one having the greatest overlap with the mode followed in the previous cycle or the initial path guess from the growing string method. Care is taken in the present work to always ensure that the total step length does not exceed $\Delta x_{\max} = 0.1$ bohr, i.e. the step goes not far outside the local quadratic approximation of the PES.

Recalculation of the Hessian matrix for every cycle is very time consuming, and hence, for larger systems the second derivative matrix is calculated at predefined intervals and Hessian updating schemes are used between these intervals. The Bofill (1994) Hessian updating scheme, $\mathbf{H}_{j+1} = \mathbf{H}_j + \Delta \mathbf{H}_j$, was used in the present study, which combines the updating scheme of Powell (1970) with the symmetric, rank-one (SR1) updating scheme of Murtagh and Sargent (1970).

$$\begin{aligned}
\Delta \mathbf{H}_j^{\text{Bofill}} &= \phi^{\text{Bofill}} \Delta \mathbf{H}_j^{\text{SR1}} + (1 - \phi^{\text{Bofill}}) \Delta \mathbf{H}_j^{\text{Powell}} \\
\Delta \mathbf{H}_j^{\text{SR1}} &= \frac{(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)^T}{(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)^T \Delta \mathbf{x}_j} \\
\Delta \mathbf{H}_j^{\text{Powell}} &= \frac{(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j) \Delta \mathbf{x}_j^T + \Delta \mathbf{x}_j (\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)^T}{\Delta \mathbf{x}_j^T \Delta \mathbf{x}_j} \\
&\quad - \frac{(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)^T \Delta \mathbf{x}_j (\Delta \mathbf{x}_j \Delta \mathbf{x}_j^T)}{(\Delta \mathbf{x}_j^T \Delta \mathbf{x}_j)^2}
\end{aligned} \quad (4.16)$$

with $\Delta \mathbf{f}_{j+1} = \mathbf{f}(\mathbf{x}_j) - \mathbf{f}(\mathbf{x}_{j+1})$, and the Bofill factor given by

$$\phi^{Bofill} = \frac{\left[(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)^T \Delta \mathbf{x}_j \right]^2}{(\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j)^T (\Delta \mathbf{f}_{j+1} - \mathbf{H}_j \Delta \mathbf{x}_j) \Delta \mathbf{x}_j^T \Delta \mathbf{x}_j}. \quad (4.17)$$

4.2.2 Dimer method

The original dimer method, developed by Henkelman and Jónsson (1999), is a local saddle-point search algorithm that uses only first derivatives of the potential energy and is, therefore, especially appropriate for large systems. The dimer method uses two points in $3n$ dimensional space, which are slightly displaced by a fixed distance, $2 \Delta R$, (see Figure 4.4). The term n represents the number of atoms. The locations of the dimer end points, $\mathbf{R}_1$ and $\mathbf{R}_2$, are defined by

$$\mathbf{R}_1 = \mathbf{R}_0 + \Delta R \mathbf{N} \quad \text{and} \quad \mathbf{R}_2 = \mathbf{R}_0 - \Delta R \mathbf{N} \quad (4.18)$$

where $\mathbf{N}$ is a unit vector along the dimer axis and $\mathbf{R}_0$ is the dimer midpoint. The saddle-point search algorithm involves two steps. In the first step the dimer axis is rotated into the lowest curvature mode of the potential energy at the midpoint of the dimer, $\mathbf{R}_0$, and then the dimer is translated for a certain step length on the potential energy surface thereby moving it towards a saddle point.

In significant contrast to quasi-Newton-Raphson algorithms, where the Hessian, $\mathbf{H}$, is updated, the curvature of the PES, C_x , is calculated numerically along one direction (dimer axis) and therefore is more accurate than a curvature calculated with an updated Hessian.

$$C_N = \mathbf{N}^T \mathbf{H} \mathbf{N} \approx \frac{(\mathbf{f}_2 - \mathbf{f}_1)^T \cdot \mathbf{N}}{2 \Delta R} \approx \frac{E_1 + E_2 - 2E_0}{\Delta R^2} \quad (4.19)$$

Here $\mathbf{f}_1$ and $\mathbf{f}_2$ are the forces acting on configuration 1 and 2 and E_i is the energy at the corresponding configuration. From Eqn. (4.19) it can be seen that during a rotation of

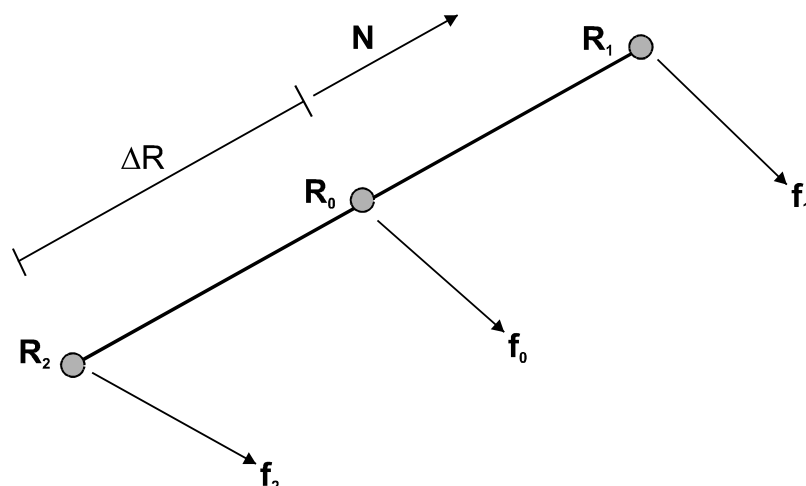


Figure 4.4: Definition of various points in $3n$ dimensional space used by the dimer method.

the dimer axis (the first step of the algorithm), the minimum of the curvature in the rotation plane is equivalent to the minimum of the dimer energy, $E = E_1 + E_2$ (assuming the dimer axis is small enough that the energy varies quadratically). The rotational plane is spanned by the dimer axis and a normalized vector Θ (to be determined) that is orthogonal to the dimer axis. The optimal direction for Θ is that which leads to a maximum overlap (scalar product) with the eigenvector corresponding to the lowest eigenvalue. The steepest descent direction for rotation can be calculated as:

$$\frac{\partial E}{\partial \varphi} = \frac{\partial E_1}{\partial \varphi} + \frac{\partial E_2}{\partial \varphi} = -\mathbf{f}_1^T \frac{\partial \mathbf{R}_1}{\partial \varphi} - \mathbf{f}_2^T \frac{\partial \mathbf{R}_2}{\partial \varphi} \quad (4.20)$$

with

$$\mathbf{R}_{1/2}(\varphi) = \mathbf{R}_0 \pm \Delta R (\mathbf{N} \cos \varphi + \Theta \sin \varphi) \quad (4.21)$$

and

$$\frac{\partial \mathbf{R}_{1/2}}{\partial \varphi} = \pm \Delta R \Theta \quad (4.22)$$

and consequently

$$\frac{\partial E}{\partial \varphi} = -\Delta R \cdot (\mathbf{f}_1 - \mathbf{f}_2)^T \Theta. \quad (4.23)$$

It is easily seen from Eqn. (4.23) that the steepest descent direction, Θ , has to be parallel to $(\mathbf{f}_1 - \mathbf{f}_2)$. Θ is then made orthogonal to the dimer axis $\mathbf{N}$. An improvement to the steepest descent direction can be obtained with a modified conjugate gradient approach as described by Henkelman and Jónsson (1999). The efficiency of the dimer algorithm relies heavily on an efficient algorithm for rotating the dimer into the lowest curvature mode spanned by $\mathbf{N}$ and Θ . Henkelman and Jónsson (1999) showed that within a second order Taylor series expansion of the energy the rotational force F on the dimer can be expressed as

$$-\frac{\partial E}{\partial \varphi} = F \approx A \sin(2\varphi) \quad (4.24)$$

where A is a constant. Then the lowest curvature mode is found by rotating the dimer axis by

$$\varphi_{\min} = -\frac{1}{2} \arctan\left(\frac{2F}{F'}\right) - \delta\varphi/2, \quad (4.25)$$

where the rotational force F and the rotational curvature F' are found by doing gradient calculations at a dimer configuration rotated by a small angle $\delta\varphi$. One obtains:

$$F = \frac{[(\mathbf{f}_1 - \mathbf{f}_2)^T \cdot \Theta]_{\varphi=\delta\varphi} + [(\mathbf{f}_1 - \mathbf{f}_2)^T \cdot \Theta]_{\varphi=0}}{2} \quad (4.26)$$

$$F' = \frac{[(\mathbf{f}_1 - \mathbf{f}_2)^T \cdot \Theta]_{\varphi=\delta\varphi} - [(\mathbf{f}_1 - \mathbf{f}_2)^T \cdot \Theta]_{\varphi=0}}{\delta\varphi} \quad (4.27)$$

Olsen et al. (2004) suggested that after rotation, if the rotational force F does not lie below a chosen threshold δF , the rotational procedure is repeated multiple times until convergence is achieved or a maximum number of allowed rotations is reached. Thus, at least four gradient calculations are necessary for every rotation.

In the second step of the dimer method, the dimer midpoint is translated along a modified force $\mathbf{f}^\dagger$, where the force component along the dimer axis is inverted. In convex regions of the PES, where the curvature along the dimer axis is positive, the

modified force is simply the negative of the force component along the dimer axis. This procedure forces the dimer to leave the convex region faster.

$$\mathbf{f}^\dagger = \begin{cases} -(\mathbf{f}_0^T \cdot \mathbf{N}) \cdot \mathbf{N} & \text{if } C_N > 0 \\ \mathbf{f}_0 - 2(\mathbf{f}_0^T \cdot \mathbf{N}) \cdot \mathbf{N} & \text{if } C_N < 0 \end{cases} \quad (4.28)$$

In the original dimer method the force at the midpoint is calculated as the arithmetic mean of the force at position 1 and 2. Next, the length of the step is determined by doing a Newton step with maximum step length $\Delta x_{\max}$.

$$\Delta x = -\frac{F^\dagger}{C^\dagger} = -\frac{(\mathbf{f}^\dagger|_{x=\delta x} + \mathbf{f}^\dagger|_{x=0})^T \cdot \mathbf{N}^\dagger / 2}{(\mathbf{f}^\dagger|_{x=\delta x} - \mathbf{f}^\dagger|_{x=0})^T \cdot \mathbf{N}^\dagger / \delta x} + \frac{\delta x}{2} \quad (4.29)$$

Here the curvature along the modified force direction $\mathbf{N}^\dagger = \mathbf{f}^\dagger / \|\mathbf{f}^\dagger\|$ is calculated by first doing a small step with step length δx , calculating gradients and then finite differencing. A conjugate gradient approach for determining the search direction for dimer translation has been suggested in order to improve the performance of the dimer method (Henkelman and Jónsson, 1999). To conclude, two gradient calculations have to be done for every dimer translation, and, therefore, altogether every dimer cycle involves at least six gradient calculations.

The original algorithm of Henkelman and Jónsson (1999) was developed for use with an analytical potential energy surface, for which energies and gradients can be calculated with double precision accuracy. Quantum chemical SCF calculations cannot be done efficiently with the same accuracy. As a result, small dimer separations of $\Delta R = 10^{-3}$ Å and small displacements during rotations (10^{-3} rad) and translations (10^{-3} Å) as suggested by Henkelman and Jónsson (1999) should not be used because of the numerical noise in quantum chemical potential energy surfaces. At the same time molecular coordinates have to be converged to $3 \cdot 10^{-4}$ bohr, and consequently an algorithm in which the forces are not calculated at the dimer midpoint does not converge efficiently to the saddle point with chemical precision. A modification to the original dimer method has recently been suggested by Heyden and Keil (2003) and Olsen et al. (2004). Instead of calculating the gradient at $\mathbf{R}_2$ the gradient is calculated at $\mathbf{R}_0$ and the force at $\mathbf{R}_2$ is approximated by $\mathbf{f}_2 = 2\mathbf{f}_0 - \mathbf{f}_1$ (linear extrapolation). This

decreases the accuracy of the curvature calculation from $O(\Delta R^2)$ to $O(\Delta R)$ but also decreases the minimum number of gradient calculations for rotation to two (twice at $\mathbf{R}_1$) and translation to two (twice at $\mathbf{R}_0$). In addition, the energy and gradient is calculated in this algorithm at the dimer midpoint, so that convergence to a saddle point can be achieved with a significant dimer separation, ΔR .

4.2.3 Improved dimer method

A further improvement to the dimer method, which is well suited for potential energy surfaces determined from quantum chemical calculations has been developed in the present work. A flow sheet for this algorithm is shown in Figure 4.5. Instead of working with two points in configuration space as in the original dimer method, the algorithm utilizes the position of the dimer midpoint $\mathbf{R}_0$ and, depending on whether the curvature along the dimer axis is calculated by central difference or forward difference, energies and gradients are calculated at $\mathbf{R}_1$ and $\mathbf{R}_2$. The distance between $\mathbf{R}_1$ and $\mathbf{R}_2$ (central differences) or $\mathbf{R}_1$ and $\mathbf{R}_0$ (forward differences) is chosen to be as small as possible in order to increase the accuracy of the calculated curvature, Eqn. (4.19), and at the same time large enough to avoid numerical noise. For standard quantum chemical SCF accuracies a value of $\Delta R = 10^{-2}$ bohr is found to be appropriate. If the true Hessian matrix is known, the curvature along any direction $\mathbf{x}$ during rotation is given by:

$$C_x = \mathbf{x}^T \mathbf{H} \mathbf{x} \quad (4.30)$$

Expanding the direction vector $\mathbf{x}$ in an orthonormal eigenvector basis of the Hessian, $\mathbf{u}_i$, and using

$$\mathbf{x} = \mathbf{N} \cos \varphi + \mathbf{\Theta} \sin \varphi, \quad (4.31)$$

it follows that the curvature during a rotation can always be expressed exactly by a short Fourier series:

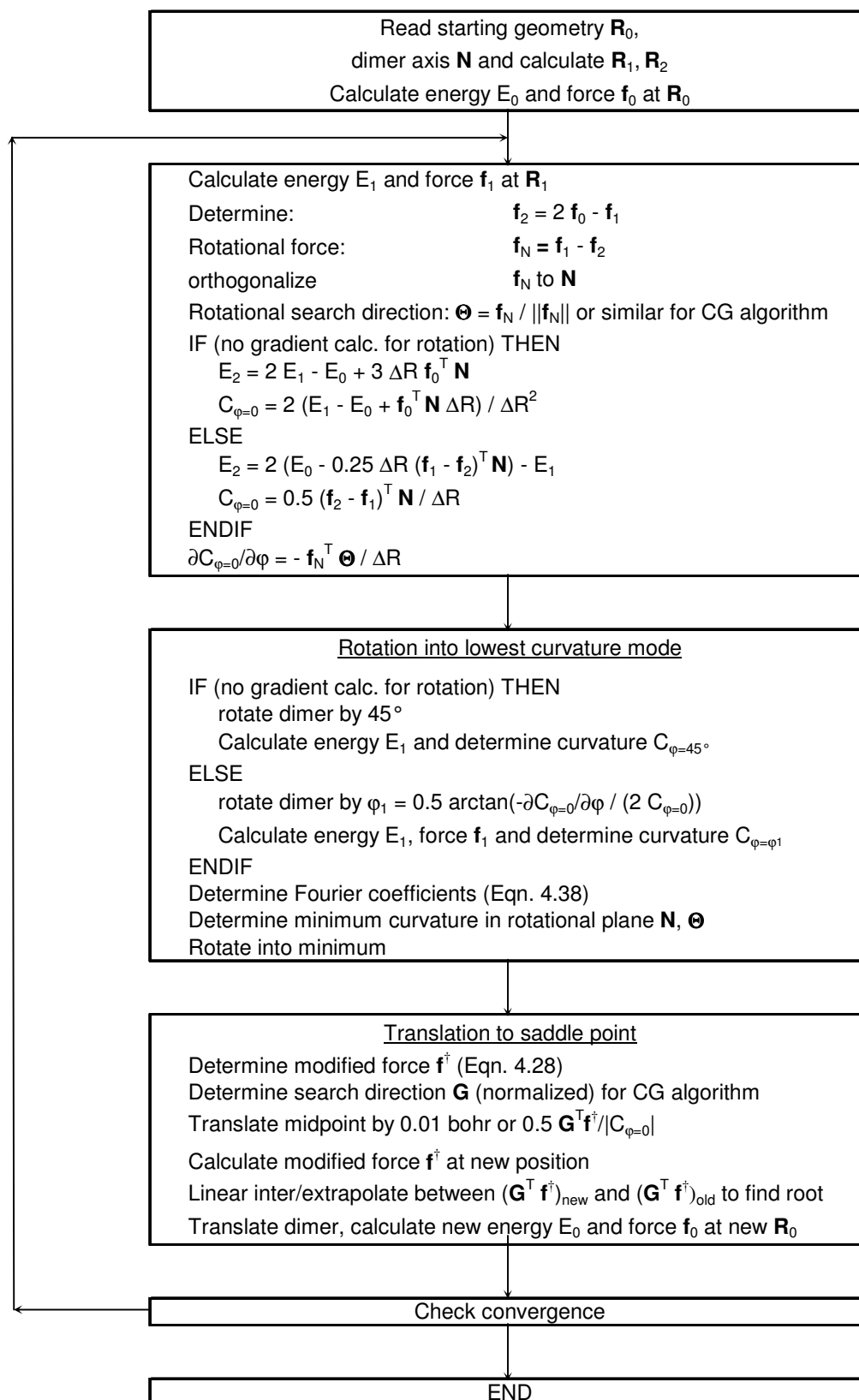


Figure 4.5: Flow sheet of the improved dimer method.

$$\begin{aligned}
C_x &= \cos^2 \varphi \left(\sum_i \lambda_i (\mathbf{N}^T \mathbf{u}_i)^2 \right) + 2 \sin \varphi \cos \varphi \left(\sum_i \lambda_i (\mathbf{N}^T \mathbf{u}_i)(\Theta^T \mathbf{u}_i) \right) \\
&\quad + \sin^2 \varphi \left(\sum_i \lambda_i (\Theta^T \mathbf{u}_i)^2 \right) \\
&= \frac{a_0}{2} + a_1 \cos(2\varphi) + b_1 \sin(2\varphi)
\end{aligned} \tag{4.32}$$

Here λ_i is the eigenvalue corresponding to the eigenvector $\mathbf{u}_i$ of the exact Hessian and a_0 , a_1 and b_1 are constants that are determined by the eigenvalues and eigenvectors of the Hessian. The minimum curvature in the plane spanned by $\mathbf{N}$ and Θ can therefore be found exactly by rotating the dimer by:

$$\varphi_{\min} = \frac{1}{2} \arctan \left(\frac{b_1}{a_1} \right) \tag{4.33}$$

Substitution of $\varphi_{\min}$ into Eqn. (4.32) gives the minimum curvature without the need for additional energy or gradient calculations. If the curvature after rotation is larger than before rotation a maximum curvature is found and the rotation angle has to be increased by 90° .

The coefficients a_0 , a_1 and b_1 appearing in Eqns. (4.32) and (4.33) are calculated as accurately and as efficiently as possible. It follows from Eqn. (4.19) that the total dimer energy E and the rotational force $-\partial E/\partial \varphi$ vary approximately during rotation like a Fourier series:

$$E \approx 2E_0 + \Delta R^2 \cdot \left(\frac{a_0}{2} + a_1 \cos(2\varphi) + b_1 \sin(2\varphi) \right) \tag{4.34}$$

$$\begin{aligned}
-\frac{\partial E}{\partial \varphi} &= \Delta R \cdot (\mathbf{f}_1 - \mathbf{f}_2)^T \cdot \Theta \\
&\approx \Delta R^2 \cdot (2a_1 \sin(2\varphi) - 2b_1 \cos(2\varphi)) = -\Delta R^2 \cdot \frac{\partial C_x}{\partial \varphi}
\end{aligned} \tag{4.35}$$

Here a_0 , a_1 and b_1 are the same coefficients as those appearing in Eqn. (4.32). Before rotation, the curvature along $\varphi = 0$ and the derivative of the curvature with respect to the angle φ is known, so that just one more piece of information is needed in order to

determine the curvature along any direction in the rotational plane spanned by $\mathbf{N}$ and Θ . One way is to rotate the dimer by a fixed rotation angle φ , e.g. 45° and then calculate the curvature (one energy calculation if forward differences are used) or the derivative of the curvature (one force calculation if forward differences are used), Eqns. (4.36) and (4.37).

$$C_x(\varphi_1) \approx \frac{2(E_1(\varphi_1) - E_0 + \Delta R \cdot \mathbf{f}_0^T \cdot \mathbf{N}(\varphi_1))}{\Delta R^2} \quad (4.36)$$

$$\left. \frac{\partial C_x}{\partial \varphi} \right|_{\varphi=\varphi_1} \approx \frac{1}{\Delta R} \cdot (\mathbf{f}_2(\varphi_1) - \mathbf{f}_1(\varphi_1))^T \cdot \Theta(\varphi_1) \quad (4.37)$$

In case of forward differentiation $\mathbf{f}_2$ is again approximated as $\mathbf{f}_2 = 2\mathbf{f}_0 - \mathbf{f}_1$. Thus, ultimately, a_0 , a_1 and a_2 are given by:

$$\begin{aligned} a_1 &= \frac{C_x|_{\varphi=0} - C_x|_{\varphi=\varphi_1} + 0.5 \cdot \left. \frac{\partial C_x}{\partial \varphi} \right|_{\varphi=0} \sin(2\varphi_1)}{1 - \cos(2\varphi_1)} \quad or \\ &= \frac{\left. \frac{\partial C_x}{\partial \varphi} \right|_{\varphi=0} \cos(2\varphi_1) - \left. \frac{\partial C_x}{\partial \varphi} \right|_{\varphi=\varphi_1}}{2 \sin(2\varphi_1)} \\ b_1 &= 0.5 \cdot \left. \frac{\partial C_x}{\partial \varphi} \right|_{\varphi=0} \\ a_0 &= 2 \cdot (C_x|_{\varphi=0} - a_1) \end{aligned} \quad (4.38)$$

It is important to note here that due to the numerical noise associated with any quantum chemical SCF calculation it is not recommended to take a small step and then extrapolate the curvature as suggested by Henkelman and Jónsson (1999) and Olsen et al. (2004), but, rather, to execute a large rotational step and then interpolate. Figure 4.6 illustrates the effects of initial dimer orientation on the curvature and predicted rotation angle required to achieve minimum curvature in the rotation plane for the isomerization reaction $\text{HCN} \leftrightarrow \text{HNC}$. Depending on the initial direction of the dimer axis the original dimer method predicts a minimum curvature at a rotation angle between 12° to 24° almost independent of the accuracy used in the SCF calculation. Using a SCF accuracy of $10^{-6} E_h$ the improved dimer method presented here predicts the minimum curvature

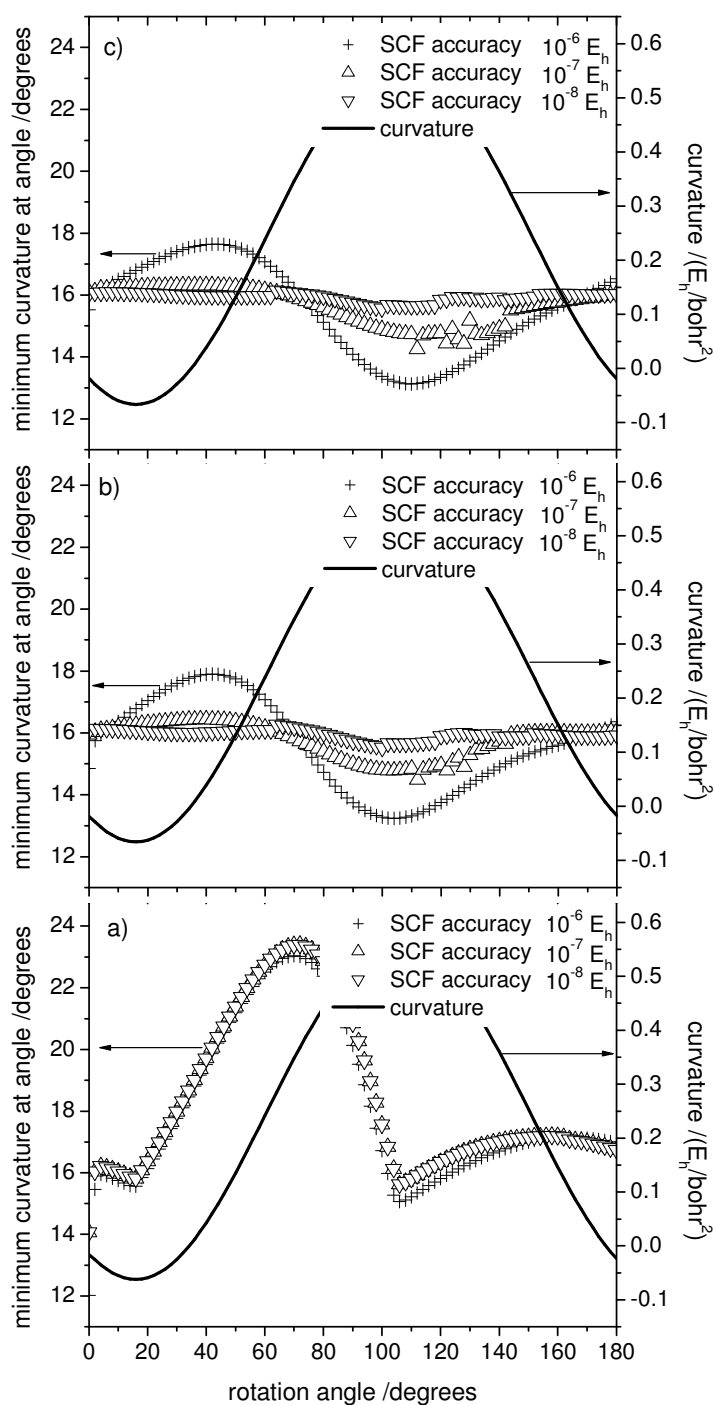


Figure 4.6: Effects of initial dimer orientation on the curvature and predicted rotation angle required to achieve minimum curvature in the rotation plane for the isomerization reaction $\text{HCN} \leftrightarrow \text{HNC}$. a) Original dimer method; rotation angle of minimum curvature predicted with Eqn. (4.25). $\delta\phi = 0.01$ rad, $\Delta R = 0.01$ bohr. b) Improved dimer method with gradient calculation for rotation. c) Improved dimer method with energy calculation for rotation. In b) and c) the rotation angle of minimum curvature was predicted with Eqn. (4.33), $\Delta R = 0.01$ bohr; initial fixed rotation angle of 45° . Forward differences were used in all cases. For an SCF accuracy of $10^{-8} E_h$ a very fine numerical quadrature grid (m5) was used for the DFT calculation.

at a rotation angle between 13° to 18° . This range of predicted rotation angles required to achieve minimum curvature can be reduced significantly by raising the accuracy of the SCF calculation. Using the algorithm proposed here, the dimer axis is always very close to the minimum curvature mode after rotation and the curvature after rotation is determined by Eqn. (4.32). In order to increase the performance of dimer rotation somewhat, the rotational curvature before rotation is approximated and used to determine the initial rotation angle φ_l :

$$\begin{aligned}
 \frac{\partial^2 C_x}{\partial \varphi^2} \Delta R^2 &\approx \frac{\partial^2 E}{\partial \varphi^2} = \frac{\partial^2 E_1}{\partial \varphi^2} + \frac{\partial^2 E_2}{\partial \varphi^2} \\
 &\approx \frac{\partial \mathbf{R}_1^T}{\partial \varphi} \mathbf{H}_1 \frac{\partial \mathbf{R}_1}{\partial \varphi} + \frac{\partial \mathbf{R}_2^T}{\partial \varphi} \mathbf{H}_2 \frac{\partial \mathbf{R}_2}{\partial \varphi} - \mathbf{f}_1^T \frac{\partial^2 \mathbf{R}_1}{\partial^2 \varphi} - \mathbf{f}_2^T \frac{\partial^2 \mathbf{R}_2}{\partial^2 \varphi} \\
 &\approx \Delta R^2 (\Theta^T \mathbf{H}_1 \Theta + \Theta^T \mathbf{H}_2 \Theta - 2C_x) \\
 &\propto \Delta R^2 4|C_x|
 \end{aligned} \tag{4.39}$$

$$\varphi_l = \frac{1}{2} \arctan \left(- \frac{2 \frac{\partial C_x}{\partial \varphi} \Big|_{\varphi=0}}{\frac{\partial^2 C_x}{\partial \varphi^2} \Big|_{\varphi=0}} \right) \approx \frac{1}{2} \arctan \left(\frac{(\mathbf{f}_1(0) - \mathbf{f}_2(0))^T \cdot \Theta(0)}{2 \Delta R |C_x|_{\varphi=0}} \right) \tag{4.40}$$

If φ_l is smaller than 0.01 (or a different predefined value) no rotation and no SCF calculation is necessary, the dimer axis is aligned with the lowest curvature mode in the plane spanned by $\mathbf{N}$ and Θ .

The translational step of the dimer method is also slightly modified by using a different line search. A step with a predefined step length of 0.01 bohr or $\Delta x = 0.5 (\mathbf{G}^T \mathbf{f}^\dagger) / |C_x|$ is chosen ($\mathbf{G}$ is the normalized search direction), the modified force is calculated and then a linear inter/extrapolation is done to find the root of the modified force. It is noted that C_x is not the curvature along the modified force but along the dimer axis, so that a Newton step is not chosen. To summarize, the improved dimer method proposed here requires three gradient calculations and one energy calculation, or four gradient calculations, instead of six gradient calculations as proposed by Henkelman and Jónsson (1999) and at least four gradient calculations as suggested by Olsen et al. (2004). In addition, the improved dimer method is significantly more accurate for calculating the

minimum curvature mode and therefore much more robust than the original dimer methods when energies and forces are subject to numerical noise.

In the present work, the initial position for the midpoint of the dimer is always taken as that of the highest energy point determined by the interpolation algorithm. The dimer axis is initially aligned along the tangent to the approximate minimum energy pathway at the highest energy point. Even if this dimer axis is not aligned in the direction of the lowest curvature mode (the initial guess might have multiple unstable modes), it is most likely aligned with the direction of the reaction coordinate. As in the P-RFO algorithm, the maximum dimer displacement for translation is set to 0.1 bohr.

4.3 Comparison of improved dimer and P-RFO method

The aim of this section is to identify the factors affecting the performance of the dimer method and compare the improved dimer method developed in this work with the original dimer algorithm. The improved dimer method is then compared with the well-established partitioned rational function optimization methods for finding transition states. In particular, the performance of these local surface walking algorithms is studied after the use of an interpolation algorithm (growing string method) to obtain the initial guess for the position of the transition state and an approximate imaginary mode connecting reactant and product states. The performance of different methods for refining the initial guess for the transition state was tested for 24 different chemical reactions involving small to medium sized reactants and covering a wide range of structural types (Baker and Chan, 1996).

4.3.1 Details of calculations

In the following some computational details about the comparison of the different local surface-walking algorithms are given. All quantum chemical calculations were performed using nonlocal, gradient-corrected density-functional theory (DFT) (Parr and Yang, 1989) in C_1 symmetry. The effects of exchange and correlation were described by Becke's 3-parameter hybrid exchange-correlation functional, B3LYP (Stephens et al., 1994). Unless otherwise stated a SCF convergence criterion of 10^{-7} hartree and the standard grid (m3) for numerical quadrature is used (Treutler and Ahlrichs, 1995). The triple- ζ basis set with polarization functions (TZVP) was used for all atoms to mimic a realistic level of theory (Schäfer et al., 1994). All energy and gradient calculations were carried out using the TURBOMOLE V5.7 suite of programs (Ahlrichs et al., 1989; Ahlrichs and v. Armin, 1995). Convergence was considered to have been achieved for the standard defaults of $3 \cdot 10^{-4}$ hartree per bohr on the maximum gradient component and either an energy change from the previous cycle of less than 10^{-6} hartree or a maximum predicted displacement of less than $3 \cdot 10^{-4}$ bohr per coordinate (Baker and Chan, 1996). The growing string method described in section 4.1.2 was used to find approximations to the minimum energy pathway and the transition state. For the present study a uniform distribution of nodes at both ends, starting with two nodes on each side, was used. The fully converged string consisted of either 9 or 13 nodes. 13 nodes were used only if none of the local saddle point search algorithms used subsequently was able to locate the correct transition state starting from an initial configuration generated using a string with 9 nodes. A new node was added to a string fragment (i.e., the parameterization density evolves), if the force on the node at the end of a string fragment, from which the tangential component is projected out, is smaller than $0.02 E_h/\text{bohr}$. In this way, the string fragments of the growing-string method merge relatively rapidly and an approximation of the MEP is generated. Once the parameterization density becomes continuous, the string is not converged further to the MEP, the algorithm is stopped, and a local saddle-point search algorithm is started. The initial guess for the transition state is the geometry of the node with the highest energy and the initial path guess is the path tangent at the highest energy node. It is noted that this procedure does not lead to the exact MEP; however, the MEP can be determined

from the converged saddle point by following the gradient down to the neighboring minima (Page and McIver, 1988; Gonzalez and Schlegel, 1991; Sun and Ruedenberg, 1993). Converging the string to the MEP with high accuracy is unnecessary if only saddle points which connect reactant and product states are needed. All saddle point searches were performed in Cartesian coordinates.

4.3.2 Results

The performance of the original dimer method developed by Henkelman and Jónsson (1999) and later modified by Olsen et al. (2004) is compared with the improved dimer method proposed in this work. This comparison is done for the standard suit of test reactions given by Baker and Chan (1996) and presented in Table 4.1. Table 4.2 shows the number of cycles and the number of gradient calculations necessary to converge from the starting configuration generated by the growing string method to the transition state connecting reactant and product states. If a gradient calculation is done during the rotational step of the improved dimer method, independent of the line search algorithm used, the improved dimer method always converges to the right transition state and needs fewer cycles and gradients than the original dimer method. This speed-up is especially pronounced if a SCF convergence criterion of $10^{-6} E_h$ is used for the DFT calculation. In this case, virtually all saddle point searches fail using the original dimer method, whereas all but one (reaction 19 which has a very loose transition state) of the searches is successful using the improved dimer method. Pre-optimizations with a reduced SCF accuracy are often helpful, since a SCF calculation with a convergence criterion of $10^{-7} E_h$ requires about 40 % more SCF cycles to converge than a SCF calculation with a convergence criterion of $10^{-6} E_h$. The significant speed-up and robustness of the improved dimer method comes from the improved rotational step. In the improved dimer method the minimum curvature in the plane spanned by $\mathbf{N}$ and $\mathbf{\Theta}$ is always found within the accuracy of the curvature calculation. In the original dimer method the minimum curvature is not always found. Owing to the finite difference approximation used to calculate the second derivative of the total dimer energy E and

TABLE 4.1: List of investigated reactions and properties of initial starting configuration

Reaction investigated	# of atoms	# of neg. Eigenvalues in starting Hessian	mode with max. overlap with path	overlap of initial path with imag. mode at TS
1 HCN $\leftrightarrow$ HNC	3	1	1	0.97
2 HCCH $\leftrightarrow$ CCH ₂	4	0	1	0.92
3 H ₂ CO $\leftrightarrow$ H ₂ + CO	4	1	1	0.94
4 CH ₃ O $\leftrightarrow$ CH ₂ OH	5	1	1	0.98
5 cyclopropyl ring opening	8	1	2	0.62
6 bicyclo[1.1.0] butane ring opening TS 2	10	6	5	0.88
7 1,2-migration -(formyloxy) ethyl	10	1	6	0.21
8 cis-butadiene + ethylene $\leftrightarrow$ cyclohexene	16	7	5	0.53
9 s-tetrazine $\leftrightarrow$ 2 HCN + N ₂	8	2	1	0.96
10 trans-butadiene $\leftrightarrow$ cis-butadiene	10	3	1	0.72
11 [†] CCH ₃ CH ₃ $\leftrightarrow$ CH ₂ CH ₂ + H ₂	8	1	1	0.94
12 CH ₃ CH ₂ F $\leftrightarrow$ CH ₂ CH ₂ + HF	8	1	1	0.88
13 vinyl alcohol $\leftrightarrow$ acetaldehyde	7	1	1	0.98
14 HCOCl $\leftrightarrow$ HCl + CO	4	1	1	0.85
15 H ₂ PO ₄ ⁻ $\leftrightarrow$ H ₂ O + PO ₃ ⁻	7	3	1	0.84
16 CH ₂ CHCH ₂ -O-CHCH ₂ $\leftrightarrow$ CH ₂ CHCH ₂ CH ₂ CHO	14	2	1	0.16
17 SiH ₃ CH ₂ CH ₃ $\leftrightarrow$ SiH ₂ + CH ₃ CH ₃	11	2	1	0.98
18 HNCCS $\leftrightarrow$ HNC + CS	5	1	1	0.74
19 HCONH ₃ ⁺ $\leftrightarrow$ NH ₄ ⁺ + CO	7	1	1	0.71
20 rotational TS in acrolein	8	3	1	0.74
21 OCHNHOH $\leftrightarrow$ HOCHNOH	7	2	1	1.00
22 H ₂ CNH $\leftrightarrow$ HNC + H ₂	5	3	1	0.83
23 H ₂ CNH $\leftrightarrow$ HCNH ₂	5	2	1	0.96
24 [†] HCNH ₂ $\leftrightarrow$ HCN + H ₂	5	1	1	0.86

[†] Growing string method with 13 nodes

TABLE 4.2: Comparison of various dimer methods for finding saddle points in chemical reactions[§]

System	Improved Dimer Method gradient calculation for dimer rotation								Original Dimer Method with modifications from Olsen et al. ²⁹	
	Variable rotational angle		Fixed rotational angle of 45°		Fixed rotational angle 45°		Variable rotational angle			
	Fixed translational step of 0.01 a.u.		Variable translational step		Fixed translational step of 0.01 a.u.		Variable translational step			
	# of cycles*	# of gradient calc.*	# of cycles*	# of gradient calc.*	# of cycles*	# of gradient calc.*	# of cycles*	# of gradient calc.*	# of cycles*	# of gradient calc.*
1	10 (8)	42 (34)	12 (7)	50 (30)	9 (7)	38 (30)	11 (7)	46 (30)	12 (9)	50 (38)
2	11 (9)	46 (38)	11 (19)	46 (78)	12 (9)	50 (38)	14 (22)	58 (90)	24 (failed)	98 (failed)
3	23 (16)	93 (66)	22 (23)	90 (94)	20 (21)	82 (86)	26 (29)	100 (117)	29 (70)	118 (282)
4	14 (10)	56 (40)	13 (13)	54 (54)	15 (13)	62 (54)	14 (10)	57 (40)	15 (failed)	62 (failed)
5	37 (66)	148 (266)	36 (44)	146 (178)	40 (31)	162 (126)	49 (42)	196 (169)	40 (failed)	162 (failed)
6	44 (42)	175 (169)	49 (40)	198 (162)	43 (44)	174 (178)	48 (40)	192 (161)	48 (failed)	194 (failed)
7	42 (101)	161 (400)	46 (64)	186 (258)	49 (42)	198 (170)	48 (57)	184 (227)	50 (failed)	202 (failed)
8	97 (96)	387 (383)	100 (87)	402 (348)	100 (94)	402 (378)	97 (89)	384 (355)	150 (failed)	602 (failed)
9	19 (17)	77 (69)	18 (17)	74 (70)	20 (17)	82 (70)	18 (17)	74 (69)	26 (failed)	106 (failed)
10	48 (126)	194 (550)	88 (178)	354 (714)	102 (90)	410 (362)	108 (170)	434 (682)	62 (failed)	250 (failed)
11 [†]	25 (29)	96 (114)	24 (19)	98 (78)	25 (16)	102 (66)	25 (19)	99 (77)	25 (failed)	102 (failed)
12	25 (24)	101 (97)	26 (21)	106 (86)	26 (21)	106 (86)	24 (23)	94 (93)	26 (failed)	106 (failed)
13	14 (14)	56 (55)	15 (12)	62 (50)	14 (12)	58 (50)	14 (15)	55 (61)	13 (failed)	54 (failed)
14	15 (11)	61 (46)	11 (35)	46 (142)	14 (12)	58 (50)	15 (10)	61 (41)	15 (failed)	62 (failed)
15	37 (28)	148 (112)	39 (32)	158 (130)	38 (31)	154 (126)	38 (28)	152 (114)	42 (failed)	170 (failed)
16	32 (41)	129 (166)	32 (42)	130 (170)	32 (20)	130 (82)	32 (53)	130 (213)	38 (failed)	154 (failed)
17	42 (16)	163 (66)	30 (16)	122 (66)	43 (15)	174 (62)	38 (14)	144 (58)	50 (failed)	202 (failed)
18	20 (15)	82 (62)	31 (20)	126 (82)	24 (59)	98 (238)	22 (48)	68 (193)	28 (failed)	114 (failed)
19	38 (failed)	154 (failed)	46 (failed)	186 (failed)	34 (failed)	138 (failed)	43 (failed)	174 (failed)	42 (failed)	170 (failed)
20	39 (58)	158 (234)	124 (102)	498 (410)	51 (103)	206 (414)	114 (71)	457 (286)	failed to converge	
21	31 (17)	121 (70)	32 (19)	130 (78)	33 (19)	134 (78)	35 (19)	136 (77)	27 (failed)	110 (failed)
22	23 (24)	91 (96)	25 (22)	102 (90)	24 (25)	98 (102)	27 (26)	110 (105)	28 (failed)	114 (failed)
23	26 (8)	97 (34)	26 (7)	106 (30)	26 (8)	106 (34)	26 (8)	101 (33)	28 (failed)	114 (failed)
24 [†]	20 (29)	81 (117)	23 (23)	94 (94)	24 (19)	98 (78)	24 (24)	95 (98)	29 (failed)	118 (failed)

[†] Growing string method with 13 nodes. [§] A conjugate gradient algorithm was used for dimer rotation and translation.

* In brackets: # of cycles and gradients to reduce maximum gradient component to $< 10^{-3} E_h/\text{bohr}$. DFT calculation done with a SCF convergence criterion of $10^{-6} E_h$.

the numerical noise in the SCF calculation, the dimer axis is sometimes rotated in arbitrary directions. This results in significantly more cycles required to converge the initial estimate of the transition state to its final configuration and sometimes even to a failure to converge to the transition state. (An algorithm is considered “failed to converge” to a transition state, if it did not converge within 500 cycles.) This situation was encountered with a SCF accuracy of $10^{-7} E_h$ in the DFT calculation, for example, for the Diels-Alder reaction (reaction 8) and the rotational isomerization of acrolein (reaction 20).

It is important to note that the improved dimer method always converged to the correct transition state even if the initial dimer axis was not aligned with the eigenvector of the imaginary mode at the transition state. Table 4.1 shows that for the ring opening reactions 7 and 16, the overlap of the dimer axis $\mathbf{N}$ and the eigenvector for the imaginary mode at the transition state is 0.21 and 0.16 respectively. Nevertheless, the improved dimer method identifies the reaction coordinate relatively rapidly and converges to the saddle point. Table 4.2 shows that the performance of the improved dimer method with gradient calculations for dimer rotation is more or less independent of the line search algorithm used.

Table 4.3 illustrates the performance of the improved dimer method if an energy calculation is done to determine the Fourier coefficients in Eqn. (4.32). Using an energy calculation instead of a gradient calculation saves one gradient calculation per cycle but also reduces the accuracy of the curvature calculation. The performance of the algorithm depends on the method used to determine the Fourier coefficients in Eqn. (4.32). If a large enough angular rotation, e.g. 45° , is done, the Fourier coefficients in Eqn. (4.32) are found with high accuracy. On the other hand, if a variable rotation of the dimer axis is done, Eqn. (4.40), a small rotation angle is sometimes chosen, resulting in a curvature calculation that is not sufficiently accurate to determine the Fourier coefficients and the curvature minimum. The dimer separation, ΔR , then has to be reduced, but this is not possible because it increases the impact of the numerical noise in the SCF calculation.

TABLE 4.3: Comparison of different line searches in the improved dimer method if no extra gradient calculation is done during rotation[§]

	Fixed rotational angle of 45°			Variable rotational angle			Fixed rotational angle of 45°			Variable rotational angle		
	Fixed translational step of 0.01 a.u.			Fixed translational step of 0.01 a.u.			Variable translational step			Variable translational step		
System	# of cycles	# of gradient calc.	extra energy calc.	# of cycles	# of gradient calc.	extra energy calc.	# of cycles	# of gradient calc.	extra energy calc.	# of cycles	# of gradient calc.	extra energy calc.
1	10	32	10	16	50	15	13	41	13	14	44	14
2	16	50	16	22	68	22	15	47	15	17	53	17
3	22	68	22	86	260	81	22	68	22	31	98	31
4	15	47	15	42	128	42	14	44	14	53	161	
5	converged to wrong TS			converged to wrong TS			31	95	31	102	308	98
6	45	137	45	72	218	69	50	152	50	69	209	68
7	48	146	48	232	698	217	45	137	45	157	473	150
8	100	302	100	352	1058	334	99	299	99	failed to converge		
9	19	59	19	21	65	20	18	56	18	20	62	20
10	272	818	272	failed to converge			81	245	81	46	140	46
11 [†]	25	77	25	66	200	64	26	80	26	50	152	46
12	24	74	24	74	224	73	26	80	26	82	248	78
13	14	44	14	32	98	32	15	47	15	37	113	37
14	14	44	14	13	41	12	13	41	13	19	59	18
15	37	113	37	83	251	77	37	113	37	75	227	69
16	29	89	29	198	596	192	31	95	31	45	137	44
17	42	128	42	95	287	88	42	128	42	123	371	119
18	20	62	20	29	89	29	25	77	25	21	65	20
19	37	113	37	48	146	47	40	122	40	44	134	42
20	109	329	109	52	158	52	50	152	50	89	269	89
21	32	98	32	65	197	60	29	89	29	62	188	60
22	28	86	28	96	290	90	27	83	27	38	116	38
23	33	101	33	138	416	129	26	80	26	58	176	55
24 [†]	25	77	25	119	359	110	22	68	22	36	110	34

[†] Growing string method with 13 nodes. [§] A conjugate gradient algorithm was used for dimer rotation and translation.

As a result, the improved dimer method with variable rotation angle rotates the dimer axis in a manner similar to that used in the original dimer method proposed by Henkelman and Jónsson (1999), which can sometimes result in the selection of arbitrary directions and the requirement of more than twice as many cycles to converge to the transition state. The improved dimer method without gradient calculation during rotation, but using a fixed rotation angle of 45° in the rotational step, performs similarly to the improved dimer method with gradient calculation. For a level of theory where the gradient of the potential energy can be obtained very rapidly with a well-converged wave function using the generalized Hellmann-Feynman theorem, this modification to the improved dimer method is not recommended. The reduction in the number of gradient calculations per iteration cycle is outweighed by the reduced accuracy in curvature calculation and the corresponding risk of not finding the minimum curvature mode in the plane spanned by $\mathbf{N}$ and $\mathbf{Q}$. On the other hand, if the gradient calculation has to be performed numerically, this modification to the improved dimer method is recommended.

Henkelman and Jónsson (1999) suggested the use of a conjugate gradient (CG) algorithm for the translational and rotational step in the original dimer method. Table 4.4 illustrates the benefit of using such an algorithm. Use of the CG algorithm of Polak-Ribière (Polak and Ribière, 1969) for the translational step greatly improves the dimer method by more than halving the number of cycles and gradient calculations needed to converge to a saddle point. The conjugate gradient algorithm for the rotational step (Henkelman and Jónsson, 1999) on the other hand does not significantly improve the performance of the dimer method over a steepest descent (SD) step. The reason for the lack of improvement in the CG algorithm originates from not generating a set of conjugate directions. After every rotation a translational step is done such that the coordinates $\mathbf{R}_0$, $\mathbf{R}_1$, $\mathbf{R}_2$ change and no set of conjugate directions for rotation can be generated. This problem does not occur for the translational step, since the dimer midpoint is not moved during the rotational step.

TABLE 4.4: Comparison of improved dimer methods with steepest descent or with conjugate gradient algorithm for dimer rotation and translation^{§*}

System	CG for rotation		SD for rotation		SD for rotation		CG for rotation	
	SD for translation		SD for translation		CG for translation		CG for translation	
	# of cycles	# of gradient	# of cycles	# of gradient	# of cycles	# of gradient	# of cycles	# of gradient
		calc.		calc.		calc.		calc.
1	24	97	27	110	8	34	10	42
2	25	102	17	70	12	50	11	46
3	27	103	30	122	20	81	23	93
4	37	129	33	127	12	49	14	56
5	50	191	converged to wrong TS		28	114	37	148
6	85	336	85	342	43	174	44	175
7	110	404	115	456	42	170	42	161
8	202	781	206	826	107	430	97	387
9	48	189	44	178	16	66	19	77
10	145	581	149	598	68	274	48	194
11 [†]	52	183	45	179	24	97	25	96
12	57	222	49	198	28	113	25	101
13	31	117	26	105	18	73	14	56
14	32	130	32	130	17	70	15	61
15	69	274	121	485	41	166	37	148
16	72	290	77	310	29	118	32	129
17	58	226	62	248	38	154	42	163
18	37	150	39	158	17	70	20	82
19	134	536	124	498	32	130	38	154
20	123	494	84	338	48	194	39	158
21	58	228	62	250	30	122	31	121
22	50	200	50	202	24	98	23	91
23	79	316	111	446	27	109	26	97
24 [†]	43	165	44	178	29	118	20	81

[†] Growing string method with 13 nodes. [§] A gradient calculation was done during rotation.

* The improved dimer method was used with a variable initial rotation angle and a fixed initial translational step of 0.01 bohr.

Table 4.5 compares the number of cycles and the time (for a single processor on an Opteron 848, 2.2 GHz computer) necessary to converge to a saddle point connecting reactant and product states using the improved dimer method and the P-RFO method. A saddle point is found with the P-RFO algorithm if only one Hessian calculation (analytical or numerical) is done for the starting configuration and the Hessian updating scheme of Bofill (1994) is used thereafter. A regular calculation of the second derivative matrix is not required. If the P-RFO method converges to a transition state it needs on average 25 – 30 % fewer cycles and about 35 % (numerical Hessian calculation) to 55 % (analytical Hessian calculation) less time than the improved dimer method. The dimer method is not quadratic convergent close to the saddle point as is

TABLE 4.5: Comparison of improved dimer method with P-RFO algorithm for finding saddle points in chemical reactions

System	P-RFO Method				Improved Dimer Method [¶]			
	Hessian matrix updating formula from Bofill				gradient calc. for rotation		no gradient calc. for rotation	
	follow lowest mode				Variable rotational angle		Fixed rotational angle of 45°	
	analytical Hessian		numerical Hessian		Fixed translational step of 0.01 a.u.		Variable translational step	
	# of cycles*	time /s	# of cycles*	time /s	# of cycles*	time /s	# of cycles*	time /s
1	5 (4)	35	5 (4)	72	10 (7)	81	13 (10)	100
2	7 (6)	66	7 (6)	118	11 (9)	126	15 (12)	160
3	13 (12)	87	13 (12)	141	23 (19)	270	22 (18)	249
4	7 (6)	113	7 (6)	191	14 (11)	250	14 (11)	254
5	converged to wrong TS [§]		converged to wrong TS [§]		37 (28)	2802	31 (27)	2319
6	89 (81)	4185	96 (92)	5449	44 (41)	5587	50 (42)	5904
7	30 (27)	3336	28 (23)	4864	42 (30)	8148	45 (27)	9611
8	failed to converge [§]		failed to converge [§]		97 (89)	42201	99 (91)	43263
9	12 (9)	1594	12 (10)	2445	19 (17)	3268	18 (15)	3236
10	27 (19)	1777	21 (15)	2219	48 (34)	5543	81 (48)	9061
11 [†]	16 (14)	428	16 (14)	658	25 (18)	922	26 (18)	992
12	19 (15)	691	20 (15)	1001	25 (21)	1510	26 (22)	1499
13	7 (6)	353	7 (6)	579	14 (11)	681	15 (11)	725
14	8 (7)	128	8 (7)	212	15 (9)	338	13 (9)	294
15	29 (26)	1392	29 (24)	1806	37 (31)	3560	37 (34)	3517
16	15 (11)	4862	11 (10)	7681	32 (21)	11445	31 (20)	11308
17	13 (10)	1155	15 (9)	1929	42 (14)	3712	42 (14)	3862
18	8 (6)	268	7 (6)	399	20 (16)	902	25 (18)	1104
19	39 (30)	653	23 (21)	637	38 (26)	1380	40 (28)	1438
20	28 (26)	1202	failed to converge		39 (23)	3310	50 (26)	4095
21	10 (9)	552	11 (9)	877	31 (17)	1902	29 (18)	1835
22	24 (22)	183	23 (22)	256	23 (21)	371	27 (23)	418
23	11 (8)	128	11 (8)	206	26 (8)	390	26 (8)	401
24 [†]	20 (17)	171	20 (17)	248	20 (19)	343	22 (18)	367

[†] Growing string method with 13 nodes. * In brackets: number of cycles to reduce maximum gradient component to $< 10^{-3} E_h/\text{bohr}$.

[§] Reaction 5 and 8 failed to converge to right TS even if Hessian is calculated in every cycle. [¶] CG for translation, CG for rotation

the P-RFO method, which uses the second derivative matrix of the potential energy. If the convergence criterion to find a transition state is relaxed to a maximum gradient component of $10^{-3} E_h/\text{bohr}$, the improved dimer method requires 10 – 20 % more cycles to converge to the transition state. The P-RFO method is superior to the improved dimer method for problems in which the starting Hessian matrix has one and only one negative eigenvalue and this eigenvector for this mode is aligned with the reaction coordinate (see Table 4.1). However, the P-RFO method has problems finding the correct transition state if an eigenvector not corresponding to the lowest eigenvalue is aligned with the reaction coordinate. Table 4.6 illustrates that this problem does not fully disappear if a mode following type algorithm is used and the Hessian matrix is calculated regularly. The P-RFO method failed to converge to the right transition state for Reactions 5 and 8. The improved dimer method, on the other hand, has fewer problems with multiple negative eigenvalues and a reaction coordinate not corresponding to the eigenvector with the lowest eigenvalue. As long as the initial dimer orientation has significant overlap with the reaction coordinate the improved dimer method has a larger convergence radius than the P-RFO method and is therefore more robust.

In saddle point searches involving heavy atoms, in particular transition metals, the potential energy surface is often shallow and the second derivative matrix has to be calculated regularly in the P-RFO algorithm. Under these circumstances, it is possible to determine approximately the system size above which the improved dimer method outperforms the P-RFO method for problems where both algorithms converge to the correct transition state. Assuming the Hessian matrix is calculated every X cycles, a Hessian calculation takes about as much time as $3n$ gradient calculations (C_1 symmetry), where n is the number of atoms in the system, and the improved dimer method needs α % (about 35 to 45 % using a tight convergence criteria and about 10 to 20 % for a loose convergence criteria; in fact α is also a function of X) more cycles to converge, the improved dimer method is superior if:

TABLE 4.6: Performance of a mode following P-RFO algorithm where the mode followed uphill is the one that has greatest overlap with the mode followed uphill in the previous step[§]

System	analytical Hessian					numerical Hessian				
	1 Hessian calc.		every 5th cycle Hessian calc.			1 Hessian calc.		every 5th cycle Hessian calc.		
	# of cycles	# of gradient	# of cycles	# of gradient	# of Hessian	# of cycles	# of gradient	# of cycles	# of gradient	# of Hessian
	calc.	calc.	calc.	calc.	calc.	calc.	calc.	calc.	calc.	calc.
5	failed to converge		failed to converge			converged to wrong TS		74	74	15
6	114	114	converged to wrong TS			failed to converge		failed to converge		
7	failed to converge		converged to wrong TS			failed to converge		converged to wrong TS		
8	failed to converge		failed to converge			failed to converge		failed to converge		

[§] Data just illustrated if the mode followed uphill is at least one time not the one with the lowest eigenvalue.

$$\begin{aligned}
 X + 3n &> 4 \times X \times \left(1 + \frac{\alpha}{100}\right) \\
 n &> X \times \left(1 + \frac{4}{3} \frac{\alpha}{100}\right) \\
 n &> 1.5 X \quad (\text{tight convergence criteria}) \\
 n &> 1.2 X \quad (\text{loose convergence criteria})
 \end{aligned}
 \tag{4.41}$$

E.g., if the Hessian matrix is calculated every 10th cycle the improved dimer method should be used for systems with more than 15 atoms (tight convergence criteria) or 12 atoms (loose convergence criteria). It is also noted that the improved dimer method has a larger convergence radius if a reasonable initial path tangent guess is available. This is especially relevant for problems with many negative eigenvalues in the Hessian matrix at the initial configuration.

For all of the test calculations reported here, the algorithm spends more than 99.9 % of the time in the QM program package. The determination of the eigenvalues and eigenvectors of the Hessian matrix in the P-RFO algorithm is never rate limiting. For very large systems with an analytical (cheap) potential this step can become rate limiting and the dimer methods will always outperform algorithms based on a second derivate matrix (Olsen et al., 2004).

4.4 Algorithm for finding minimum energy crossing points

The third type of algorithm programmed in the present work for finding transition states is a constrained minimization routine. The highest energy configuration along the intrinsic reaction coordinate involving configurations on multiple spin potential energy surfaces is often a minimum potential energy structure on the seam of two potential energy surfaces. To calculate these minimum energy crossing points (MECP), a number of algorithms have been developed (Fletcher, 1987; Jensen, 1992 and Bearpark et al., 1994). Most algorithms used in quantum chemistry transform the constrained optimization to an unconstrained optimization with the help of a Lagrange multiplier

and / or a penalty function. In the present work the MECP was determined with a multiplier penalty function algorithm by Powell (1969). The function F was minimized

$$F(\mathbf{R}; M_{Si}, M_{Sj}, \lambda, \mu) = E(\mathbf{R}, M_{Si}) + E(\mathbf{R}, M_{Sj}) - \lambda \cdot (E(\mathbf{R}, M_{Si}) - E(\mathbf{R}, M_{Sj})) + \frac{1}{2} \mu (E(\mathbf{R}, M_{Si}) - E(\mathbf{R}, M_{Sj}))^2 \quad (4.42)$$

for the coordinates $\mathbf{R}$ with fixed parameters M_{Si} , M_{Sj} , λ and μ using the quasi-Newton algorithm of Broyden, Fletcher, Goldfarb and Shanno (BFGS) with an inexact line search (Fletcher, 1987). M_{Si} and M_{Sj} are the spin multiplicities, λ is the Lagrange multiplier and μ the penalty function parameter. When the energy of the structure on the two PESs differs by less than 75 % (or another to be set value) between two minimizations the Lagrange multiplier λ is updated:

$$\lambda^{k+1} = \lambda^k - \mu \cdot (E(\mathbf{R}, M_{Si}) - E(\mathbf{R}, M_{Sj})). \quad (4.43)$$

Otherwise, the penalty function parameter μ is multiplied by 10. The optimization is repeated with the updated parameters until the minimization results in an energy difference of the structure on the two PESs of 10^{-6} Ha. With λ initially set to zero and μ initially set to 10^3 1/Ha fast convergence to the minimum energy crossing point was usually observed. Indeed, finding a minimum energy crossing point was usually not difficult; finding a MECP that is on the reaction coordinate was in some cases more challenging. The function F has a number of local minima. In these cases, approximate minimum energy pathways were determined on each spin PES using the growing string method (see section 4.1.2). With the help of these pathways an intrinsic reaction coordinate can usually be visualized and a good starting configuration for the minimum potential energy configuration on the seam of two PESs can be obtained.

After every constrained minimization the second derivative matrix $\mathbf{H}$ of the electronic energy was calculated on both PESs. To confirm that the optimized structure is a minimum on the seam of two PESs the vector $\mathbf{v}$:

$$\mathbf{v} = \text{grad}(E(\mathbf{R}, M_{Si})) - \text{grad}(E(\mathbf{R}, M_{Sj})) \quad (4.44)$$

is projected out of the matrix $\nabla_{\mathbf{x}}^2 \mathbf{L}$:

$$\nabla_x^2 L = \mathbf{H}(\mathbf{R}, M_{Si}) \cdot (1 - \lambda) + \mathbf{H}(\mathbf{R}, M_{Sj}) \cdot (1 + \lambda) \quad (4.45)$$

and it is verified that the eigenvalues of this projected matrix are all positive.

4.5 Conclusions

In this chapter, three classes of algorithms for finding transition states in chemical reactions were presented that require only the evaluation of the system energy and force. Using these routines no Hessian matrix calculation is necessary for finding transition states making these algorithms especially suitable for use with the TURBOMOLE V5.5-5.7 program system that has efficient parallelized routines for computing the system energy and gradient, but no parallelized routine for calculating the analytical second derivative matrix.

For chemical reactions on one spin potential energy surface, the transition state is usually chosen to be a first order saddle point on the minimum energy pathway connecting reactant and product states. For finding approximations to the MEP and the first order saddle point a version of the growing string method was developed. In the growing string method no initial MEP has to be assumed, only few calculations have to be performed on initial approximate MEPs that are far away from the true MEP and the algorithm automatically avoids rugged regions of the PES where electronic structure calculations may fail.

For finding saddle points, after the use of an interpolation algorithm to obtain a reasonable guess for the transition state and the path tangent at the starting configuration, a number of dimer methods and the partitioned rational function optimization method were illustrated. In particular, an improved dimer method for finding transition states was presented and compared with the original dimer method of Henkelman and Jonsson (1999) as modified by Olsen et al. (2004) and with the well-established partitioned rational function optimization method (Baker, 1986). The

improved dimer method with gradient calculation during rotation requires significantly fewer cycles and is much more robust than the original dimer method when energies and forces are subject to numerical noise. If a gradient calculation takes significantly longer than an energy calculation, e.g. the gradient has to be calculated numerically, the gradient calculation during the rotational step can be replaced with an energy calculation. A conjugate gradient algorithm for the translational step in the dimer method improves its performance; however, a conjugate gradient approach for the rotational step does not significantly improve the algorithm over a steepest descent direction for rotation. After every rotation a translation is done and no set of conjugate directions for rotation is generated. Depending how tight the convergence criterion is chosen the improved dimer method requires about 1.10 to 1.45 more cycles to converge to a saddle point than a P-RFO algorithm using a Hessian updating scheme. As a result of the better scaling with system size, the improved dimer method is recommended relative to the P-RFO method for systems with more than $1.5 \times X$ atoms ($1.2 \times X$ atoms for a loose convergence criterion), where the Hessian matrix is calculated in the P-RFO method every X cycle. If efficient parallelized routines for energy and gradient calculations are available, but not for Hessian calculations the improved dimer method is recommended even for smaller system sizes. A mode-following algorithm based on the P-RFO can fail to find the right transition state if the reaction coordinate does not correspond to the eigenvector with the lowest eigenvalue. Under similar circumstances, the improved dimer method converges to the correct transition state, provided a good initial guess for the path tangent is available.

Finally, a constrained optimization algorithm was presented for calculating the minimum potential energy structure on the seam of two potential energy surfaces. For chemical reactions involving configurations on multiple spin potential energy surfaces, the minimum energy crossing point is often the highest energy configuration along the intrinsic reaction coordinate and can therefore be considered the transition state of the reaction. A simple multiplier penalty function algorithm from Powell (1969) was found to be efficient and reliable for calculating minimum energy crossing points.

5 Comprehensive DFT study of the nitrous oxide decomposition over Fe-ZSM-5

In this section, the decomposition of nitrous oxide in iron zeolites is studied on a molecular level using density functional theory. With the help of the algorithms for finding transition states on quantum chemical potential energy surfaces, developed in the present work and described in the last chapter, the energetics and kinetics of the nitrous oxide decomposition are analyzed on hydrated and dehydrated mononuclear iron sites in Fe-ZSM-5. In total, 46 different surface species with different spin states (spin multiplicity $M_S = 4$ and 6) and 63 elementary reactions are considered.

The aim of chapter 5 and 6 is to determine the reaction mechanism of the nitrous oxide decomposition over iron zeolites, identify the rate limiting step and catalytically active sites, and explain apparently contradictory experimental observations. In particular, the activity of single iron sites for N_2O decomposition is investigated. A rate limiting step in the reaction mechanism on single iron sites is identified under steady state conditions. The observed rate limiting step differs from the previously assumed rate limiting step proposed by various authors. It is shown that the previously proposed reaction mechanism is not able to explain some experimental findings that can be explained with the here proposed reaction mechanism. An important part of this investigation is the determination of the effects of low concentrations of water on the speciation of Fe in Fe-ZSM-5. This part of the investigation was stimulated by the work of Wood et al. (2004), Kiwi-Minsker et al. (2003), and Bulushev et al. (2004), who proposed that low concentrations of water vapor could alter the concentration of active Fe species. It is observed in the present work that water impurities in the gas stream have a strong inhibiting effect. In the concentration range of 1 to 100 ppb the presence of water vapor influences the surface composition and the apparent rate coefficient. This is especially relevant in the temperature range of 600 to 700 K where most experimental kinetic studies are performed. Apparent activation barriers determined over this temperature

range vary from 28.4 kcal/mol (1 ppb H₂O) to 54.8 kcal/mol (100 ppb H₂O). These results give an explanation why different research groups and different catalyst pretreatments result often in very different activation barriers and preexponential factors.

In section 5.1, various experimental and theoretical studies about the nitrous oxide decomposition on iron zeolite systems are summarized. The state of iron in Fe-ZSM-5 is found to be strongly dependent on the method of iron exchange in the zeolite pore system, the level of Fe exchange (i.e., the Fe/Al ratio), and the pretreatment of the as-exchanged material. The computational model of the active site in Fe-ZSM-5 used in the present work is explained in section 5.2. In particular, the limitations of the chosen cluster model are discussed. In section 5.3, the computational methodology used for all quantum chemical calculations is outlined. More details about the methodology can be found in chapter 3 and 4 of this work. A discussion of the computational results of this study is presented in section 5.4. Finally, section 5.5 compares the computational results with some experimental findings. A more in depth comparison between computational and experimental data is done in section 6.

5.1 N₂O decomposition over Fe-ZSM-5

Iron-exchanged ZSM-5 is an active catalyst for the stoichiometric decomposition of N₂O to N₂ and O₂ (e.g., Panov et al., 1990 and 1998; Kapteijn et al., 1997; Sang and Lund, 2000 and 2001; El-Malki et al., 2000 and 2000b; Wood et al., 2002; Zhu et al., 2002; Pérez-Ramírez et al., 2003; Kiwi-Minsker et al., 2003). Figure 5.1 shows some temperature-programmed N₂O decomposition experiments from Panov et al. (1990) on Fe-ZSM-5 with various amounts of iron. An increasing amount of iron in the zeolite matrix increases the amount of N₂O decomposition at low temperatures.

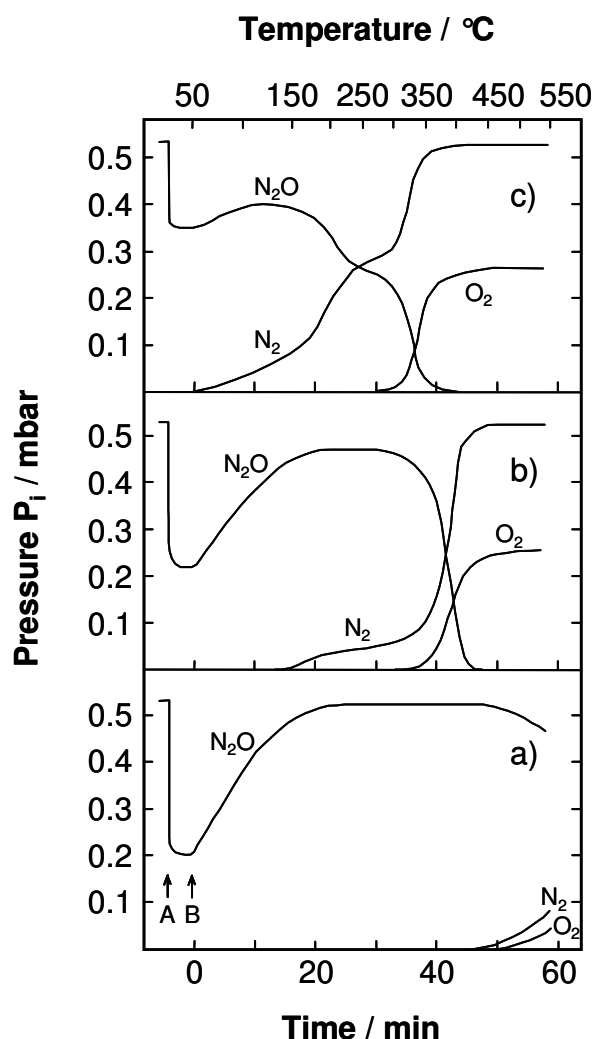


Figure 5.1: Temperature-programmed decomposition of N₂O over Fe-0.004 (a); Fe-0.08 (b) and Fe-0.5 (c) ZSM-5. Data from Panov et al. (1990).

Figure 5.2 compares N₂O decomposition activities of various catalysts as a function of temperature. Li and Armor (1992) found that various transition metal exchanged zeolites with MFI structure are active catalysts for N₂O decomposition. But while Cu-ZSM-5 and other transition metal exchanged zeolites are shown to be more active for N₂O decomposition than Fe-ZSM-5, these catalysts were shown to be very sensitive to water vapor, an ubiquitous and inevitable component in all industrial processes (Kögel, 2001). Iron containing catalysts, however, are reported to be remarkable insensitive to water vapor and are therefore potentially useful for the abatement of N₂O emissions from industrial waste streams, such as those occurring in nitric acid plants (Pérez-Ramírez et al., 2001 and 2002b; Melián-Cabrera et al., 2005). These findings have

stimulated an interest in identifying the nature of the active site for N_2O decomposition and the mechanism via which this reaction occurs.

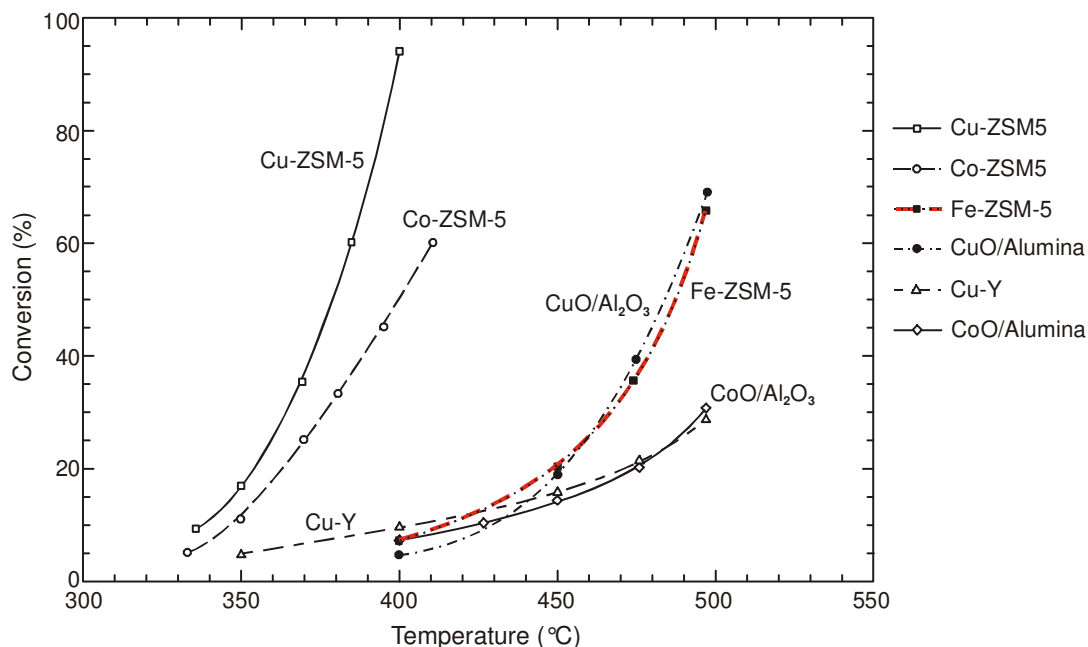


Figure 5.2: Comparison of N_2O decomposition activities of various catalysts as a function of temperature. The reactions were run on a 0.1 g sample with a total flow-rate of $100 \text{ cm}^3/\text{min}$ and $[\text{N}_2\text{O}] = 990 \text{ ppm}$. Data from Li and Armor (1992).

5.1.1 Experimental characterization of Fe-ZSM-5

A number of surface science methods and kinetic measurements of the N_2O decomposition over differently prepared and pretreated iron MFI catalysts have been performed to characterize the state of iron in Fe-ZSM-5. The state of iron is found to be strongly dependent on the method of iron exchange, the level of Fe exchange (i.e., the Fe/Al ratio), and the pretreatment of the as-exchanged material (e.g. Zhu et al., 2002; Kiwi-Minsker, 2004; Wąclaw et al., 2004).

EXAFS characterization of Fe-ZSM-5 prepared by aqueous ion exchange of H-ZSM-5 conducted by Joyner and Stockenhuber (1999) showed the presence of isolated iron

cations, large clusters of Fe₃O₄, as well as Fe₄O₄ nanoclusters. The disordered nature of the abundantly present iron oxide aggregates and the possibility of a minority species responsible for catalysis have been reported more recently by van Santen and coworkers (Zhu et al., 2004; Hensen et al., 2004). Careful preparation of Fe-ZSM-5 by dry exchange of H-ZSM-5 minimizes the formation of Fe₃O₄ and enhances the dispersion of Fe as well-defined species. EXAFS data by Battiston et al. (2000, 2003, 2003b, 2003c), Marturano et al. (2000 and 2001), and Jia et al. (2002) of fully exchanged H-ZSM-5 (Fe/Al = 1) shows evidence for diferric oxo/hydroxyl-bridged clusters. Marturano et al. (2000) have also shown that the distribution of iron in Fe-ZSM-5 is strongly dependent on the source of the parent ZSM-5, and have noted that, with some ZSM-5 samples, particles of Fe₂O₃ can form after calcination of the as-exchanged material.

Mössbauer spectroscopy has also been used to provide evidence for di-iron sites in studies reported by Dubkov et al. (2002). On the other hand, Perez-Ramirez et al. (2002) and Doménech et al. (2002, 2002b) have observed isolated iron cations and small oligonuclear oxo-iron complexes in the zeolite channels by Mössbauer spectroscopy and voltammetry. Overweg et al. (2004) concluded from ⁵⁷Fe Mössbauer data that there cannot be a similarity between the active Fe species and the binuclear clusters in methane monooxygenase (MMO) as claimed by Dubkov et al. (2002).

Evidence for isolated Fe sites in partially exchanged samples of ZSM-5 has been obtained in several recent studies. Lobree et al. (1999) and similarly Kucherov and Shelef (2000) have reported that for Fe/Al ratios below ~ 0.6, Fe³⁺ cations exchange on a one to one basis with Brønsted acid protons in H-ZSM-5. EXAFS analyses conducted by Choi et al. (2003 and 2004) have confirmed that for Fe/Al < 1.0 isolated Fe³⁺ cations associated with single charge-exchange sites are present in Fe-ZSM-5 prepared by solid-state exchange of H-ZSM-5 with FeCl₃ and by high temperature pretreatment of Fe/Al-MFI. In a related work, Berlier et al. (2002 and 2005), Ferretti et al. (2002), Pérez-Ramírez et al. (2003b and 2004) and Pirngruber et al. (2004) have demonstrated that isolated iron ions in extra-framework positions have the highest activity per mole of iron for N₂O decomposition in the presence of a reducing agent.

5.1.2 Theoretical characterization of Fe-ZSM-5

Several quantum chemical studies have been reported aimed at identifying the mechanism by which N_2O decomposes to form N_2 and O_2 . Yakovlev et al. (2001) and Kachurovskaya et al. (2003) have investigated the decomposition of N_2O on an active single iron site modeled as $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2$ and on a Fe^{2+} ion stabilized by interaction with four oxygen atoms from two intersecting five-membered zeolite rings. These authors have also investigated the N_2O decomposition on binuclear Fe complexes in ZSM-5 (Yakovlev, 2001b). In the study the zeolite was represented by a pair of 5T rings sharing an edge and the Fe complex was represented as either $[(\text{HO})\text{FeOFe}(\text{OH})]^{2+}$ or $[\text{FeOFe}]^{2+}$ (5T rings designate the presence of five tetrahedral (Si, Al) atoms). Neither activation energies nor rates of N_2O decomposition were reported in the latter two studies. Yoshizawa et al. (2000 and 2000b) investigated the decomposition of N_2O on mononuclear iron sites. In their study a fully relaxed 3T cluster with a bare iron site $\text{Z}[\text{Fe}]^+$ was used. An activation energy of 2.4 kcal/mol was calculated for the decomposition of N_2O . Ryder et al. (2002) investigated the full cycle of the N_2O decomposition on a constrained 5T zeolite cluster $\text{Z}[\text{FeO}]^+$. Although their calculated apparent activation energy is in reasonable agreement with experiments, the value of the preexponential factor is an order of magnitude smaller than that observed.

Mononuclear and dinuclear iron sites have been suggested to be the main active site in Fe-ZSM-5. For dinuclear iron sites to be stable, two Al sites in close proximity are required in the zeolite framework to charge balance the active di-iron site. Lewis et al. (1995), Feng and Hall (1997), Rice et al. (1999 and 2000) and Goodman et al. (2000) tried to test, by statistical analysis of the Al distribution and metal ion pairing probabilities in zeolites of typical Si/Al ratios, if such a close proximity of Al sites in the zeolite framework is possible for a significant fraction of Al atoms. Since Han et al. (2002) showed in a recent NMR study that the Al distribution in the ZSM-5 framework might be nonrandom and kinetically controlled a statistical analysis of the Al distribution was not able to prove that the formation of stable dinuclear iron sites is likely or improbable.

5.1.3 Conclusions

It can be summarized that it is agreed that tetragonally coordinated iron in the zeolite framework and iron oxide particles at the external surface of the zeolite crystal are inactive for N₂O decomposition. Careful preparation of Fe-ZSM-5 by dry exchange of H-ZSM-5 minimizes the formation of Fe₃O₄ nanoparticles and enhances the dispersion of iron. Al favors the dispersion of extraframework iron species. Divalent iron species with one or two Al atoms in the immediate vicinity are active sites in partial oxidation reactions (Berlier et al., 2003; Hensen et al., 2003). The nuclearity of the active site in Fe-ZSM-5 is unclear. EXAFS characterization of such materials has provided evidence for both diferric oxo/hydroxyl-bridged clusters (or oligonuclear iron species) and isolated ferric oxo species. Since the catalytically active site might be a minority species it is very difficult to clearly identify the most active site in Fe-ZSM-5. While it was proposed that different preparation and pretreatment methods produce different active sites, Pirngruber et al. (2004) have suggested that since differently prepared zeolites lead to different types of iron species but show qualitatively similar catalytic behavior in N₂O decomposition, the same iron species might be present in all samples, but in different concentrations.

However, iron cations can also be incorporated into the zeolite framework during synthesis. If the resulting framework also contains tetrahedrally coordinated Al atoms, then upon high-temperature pretreatment Fe atoms leave the zeolite framework and are stabilized as extra-framework FeO species at cation exchange positions associated with the framework Al (Choi et al., 2004; Taboada et al., 2005). EXAFS characterization of Fe-ZSM-5 prepared by dry exchange of H-ZSM-5 and high-temperature treatment of Fe/Al-MFI shows that the environment of Fe is effectively the same and is best described as isolated Fe cations (Choi et al., 2004). Consequently, single iron sites in cation exchange position are active for N₂O decomposition and a second iron atom in the immediate vicinity seems to be not necessary for N₂O decomposition.

A number of recent kinetic studies of the N_2O decomposition in the presence of a reducing agent like, e.g. nitric oxide or carbon monoxide, have been performed by Mul et al. (2001), Pérez-Ramírez et al. (2002, 2003, 2004) and Pérez-Ramírez (2004). Apparently, these experiments show the need for oligonuclear iron species to explain a fast N_2O decomposition in the absence of a reducing agent. A detailed discussion of these experiments and a novel explanation for the observations is given in chapter 7.

5.2 Computational model of the active site in Fe-ZSM-5

One of the most important tasks in studying complex systems like the N_2O decomposition over Fe-ZSM-5 with theoretical methods like density functional theory is to choose a reasonable model system and an appropriate level of theory. The model system and level of theory should be as simple as possible and as complex as necessary to get meaningful results in a reasonable period of time.

Macroscopic systems are complex systems that are usually ill-defined. When studying systems in the solid state on a molecular level it is often not obvious which component of a macroscopic system needs to be considered and what can be neglected. Even an apparently pure gas cylinder of N_2O contains a number of impurities like e.g. NO , NO_2 and H_2O . Zeolites like ZSM-5 are crystalline materials that contain mainly silicon, aluminum, oxygen, sodium and water. Industrially used zeolites consist of many small single crystals that possess a large number of surface defects. Owing to the preparation method, some transition metals that might be catalytically active can be found in all zeolites. Even a perfect ZSM-5 crystal possesses 12 different T sites each with a different local environment. The incorporation of iron atoms in the ZSM-5 pore system further complicates the situation.

In the following, the zeolite ZSM-5 is briefly explained. Then the cluster model used in this work to mimic the active site in Fe-ZSM-5 is presented. Finally, the limitations of the cluster model used in the present work are discussed.

5.2.1 ZSM-5

Zeolites are crystalline, highly porous natural or synthetic aluminosilicates formed from edge-sharing $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra. The microporous structure of the zeolite ZSM-5 allows penetration of its small pores by small molecules only. This results in a selective effect that depends on the structure of the penetrating molecule. Trivalent aluminum introduces an overall negative charge in the silicon oxide matrix. Counter ions, such as H^+ or metal ions, bind to the oxygen sites local to the aluminum atom and balance this negative charge. Figure 5.3 illustrates the three dimensional pore structure of ZSM-5 (**Z**eoelite **S**ocony **M**obil - **f**ive). The pore system of ZSM-5 consists of straight pores with a diameter of 5.4 to 5.6 Å and interconnecting zigzag pores with a diameter of 5.1 to 5.5 Å. The chemical composition of a unit cell of ZSM-5 can be described as $[\text{Na}^+_n (\text{H}_2\text{O})_{16}] [\text{Al}_n \text{Si}_{96-n} \text{O}_{192}]$ -MFI with $n < 27$ (Baerlocher et al. 2001).

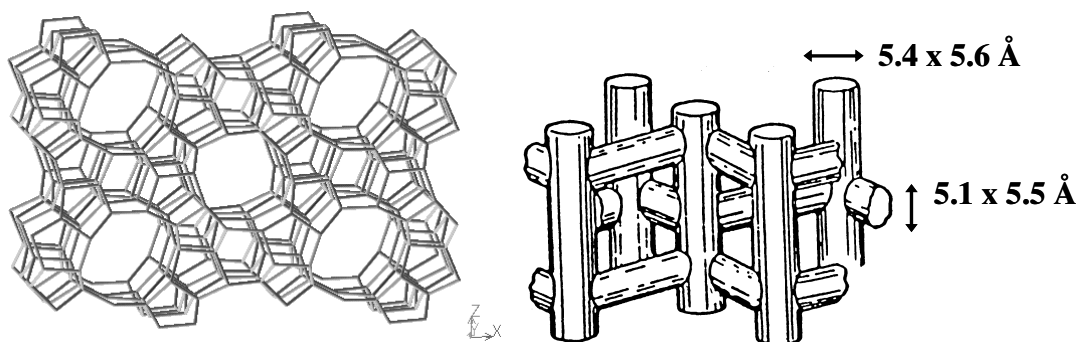


Figure 5.3 Crystallographic structure of MFI (ZSM-5). On the left panel, all silicon and aluminum atoms are depicted as crossing points. Oxygen atoms are placed on the connecting lines. On the right panel, the characteristic pore system of ZSM-5 of interconnecting straight and zigzag pores is schematically illustrated.

5.2.2 Cluster models for extended systems

There are three different techniques that are currently used to model the structure of a catalytically active site in a solid. These are known as the cluster (van Santen and Neurock, 1995; van Santen and Kramer, 1995; van Santen, 1997, Staemmler, 2005), embedded-cluster (Whitten and Yang, 1996; Sauer, 1989 and 1994; Sauer et al, 1994; Sierka and Sauer, 2000, Sierka, 2000), and periodic technique approach (Hammer and Norskov, 2000; Payne et al., 1992), respectively. Each of these methods has its advantages and disadvantages.

In the periodic approach, a unit cell is defined to represent the system that is subsequently repeated in three dimensions to model the bulk material. The smallest possible unit cell of ZSM-5 consists of at least 288 atoms. With a high level of theory like B3LYP/TZVP necessary to accurately model reactions on transition metals these systems are up to now too large to handle.

Embedded-cluster methods use two levels of theory to model the catalytically active site and the external electronic environment. The catalytically active site is modeled with a rigorous quantum mechanical method. The outer environment is usually treated with an empirical force field to reduce the computational expense. The difficulties with this approach involve accurately matching the electronic structure at the interface between the inner cluster and the outer system. Depending on the treatment of the electrostatic interaction between the inner and the outer system mechanical embedding and electrostatic embedding can be distinguished. Mechanical embedding treats the interactions between the inner and outer system on a molecular mechanics level. These schemes have the disadvantage that an accurate set of electrostatic molecular mechanics parameters is often not available for the inner system (e.g. Fe atoms) and that it ignores the potential perturbation of the electronic structure of the inner system by the charge distribution of the outer system. In electrostatic embedding the QM computation for the inner system is carried out in the presence of the outer system by including terms that describe the electrostatic interaction between the inner and outer system as one-electron

operators that enter the QM Hamiltonian. The electrostatic embedding schemes are computationally more expensive. In addition, it is often difficult to construct an appropriate representation of the charge distribution in the outer system.

In this work, the most common cluster approach for studying heterogeneous catalytic reactions was employed. The catalytically active center and a portion of the zeolite framework are represented by a 23 to 27 atom cluster. As shown in Figure 5.4, the portion of the cluster describing the zeolite contains an Al atom in the T12 site of the framework surrounded by shells of O- and Si-atoms. The terminal Si-atoms are fixed in their crystallographic positions as reported by Olson et al. (1981). Dangling bonds are terminated by H-atoms located 1.48 Å from each terminal Si-atom oriented in the direction of the next O-atom. This corresponds to the Si-H distance in SiH₄.

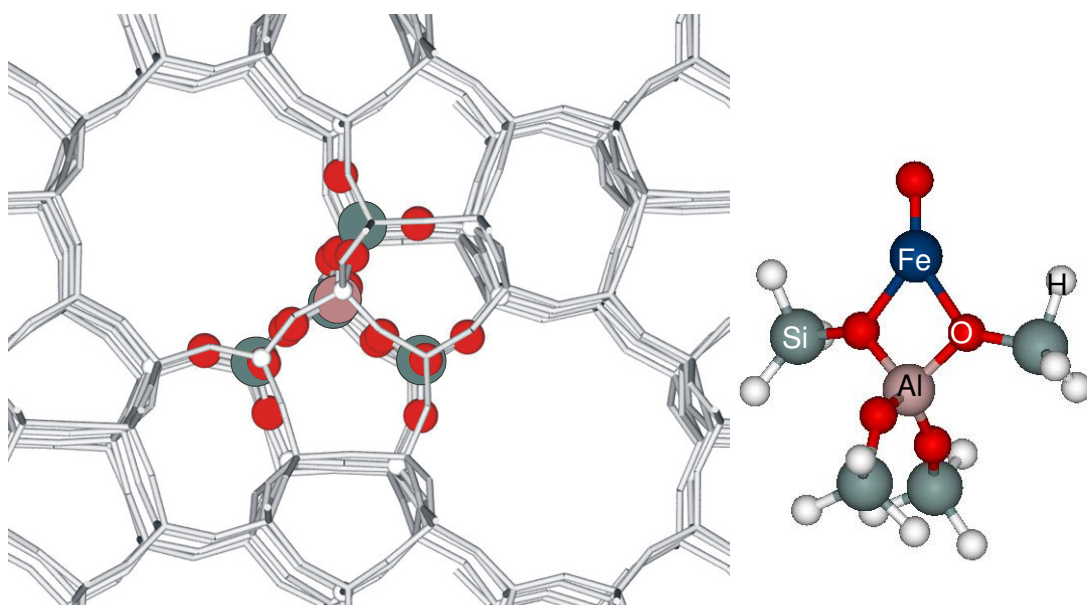


Figure 5.4: Left: Section of the crystal structure of ZSM-5. Colored spheres are atoms used to form the active site model. Al is in T12 position. Right: Active site model ($Z[FeO]^+$) for the N₂O decomposition in Fe-ZSM-5. Si-atoms are fixed in the crystallographic positions of ZSM-5. Dangling bonds are terminated by H-atoms located 1.48 Å from each terminal Si-atom oriented in the direction of the next O-atom.

The anionic cluster is charge-compensated by a metal or metal-oxo species, $[\text{Fe}]^+$, $[\text{FeO}]^+$, $[\text{FeO}_2]^+$, $[\text{OFeO}]^+$, $[\text{O}_2\text{FeO}]^+$, $[\text{O}_2\text{FeO}_2]^+$, $[\text{Fe}(\text{OH})_2]^+$, $[\text{OFe}(\text{OH})_2]^+$ or $[\text{O}_2\text{Fe}(\text{OH})_2]^+$, placed between two of the four O atoms surrounding the Al atom. Using such a variety of hydrated and dehydrated metal-oxo species on top of the anionic cluster permits a full investigation of the N_2O decomposition over all stable mononuclear iron species that can be formed in the presence of N_2O and H_2O . Figure 5.5 illustrates the bonding and atomic distances of the most abundant mononuclear surface species $\text{Z}[\text{FeO}]^+$, $\text{Z}[\text{FeO}_2]^+$ and $\text{Z}[\text{Fe}(\text{OH})_2]^+$. The choice of $\text{Z}[\text{FeO}]^+$ and $\text{Z}[\text{Fe}(\text{OH})_2]^+$ sites as possible active centers is guided by experimental observation (Lobree et al., 1999). One possible preparation route of Fe-ZSM-5 involves dry exchange of H-ZSM-5 with FeCl_3 . This results in the release of HCl and replacement of each Brønsted acid proton by $[\text{FeCl}_2]^+$. The Cl-atoms associated with iron are removed by washing the catalyst in water. Consequently, the charge-exchange positions in Fe-ZSM-5 are now occupied by $[\text{Fe}(\text{OH})_2]^+$. The catalyst is then heated, water is liberated and the charge compensating unit becomes possibly $[\text{FeO}]^+$.

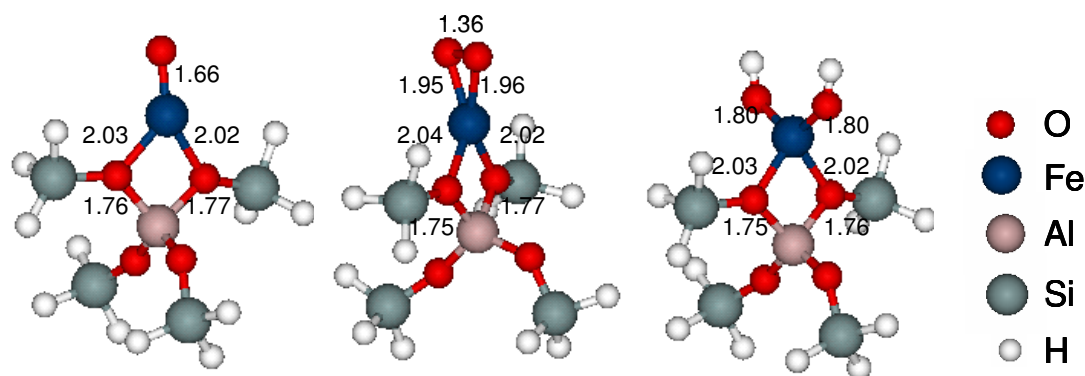


Figure 5.5: Iron oxo/hydroxo zeolite cluster of most abundant surface species. Structures are potential energy minima on the potential energy surface with spin multiplicity $M_s = 6$. Left: Active site for N_2O decomposition. Middle: Possible α -oxygen site. Right: Deactivated iron hydroxo site. Atomic distances in Å are indicated.

5.2.3 Limitations of the cluster model

Heterogeneous catalytic reactions occur on solid surfaces. It may seem that the surface chemistry that is the basis to heterogeneous catalysis cannot be properly described by heterogeneous catalytic site models based on clusters. Clearly those aspects of the reaction that intrinsically relate to the presence of the extended lattice or micropore network cannot be described by cluster models but require full consideration of the three-dimensional geometry, e.g., in zeolites the shape and size of the micropore cavities may prevent particular reaction pathways when transition states are too bulky. In contrast, if reactant, transition, and product states just involve a few atoms, as in the N_2O decomposition, space constraints on the transition state are unlikely even in a zeolite. Hence, it is important to discriminate between those aspects of the reaction that depend on local properties that can be treated using a cluster approach and those aspects of the reaction that are not. In fact, when the surface-chemical bond is localized, there is no significant charge transfer, and boundary effects are well understood, one often finds very similar reaction energies and barrier heights from cluster models and QM/MM embedding schemes. This does not mean that the outer system does not affect the inner system. Instead, the effect is roughly the same for the reactant, transition, and product state, and cancellation leads to small net effects (van Santen, 1997; Bates and van Santen (1998)).

In general, cluster calculations do not account for the long-range interaction, an interrupted charge transfer and a missing structure constraint. The long-range interactions originating from the environment are most important for adsorption and desorption processes and for charged molecules or molecules with a high multipole moment. Here, the long-range effects are different for the reactant, transition and product state and consequently do not cancel.

The missing structure constraint of the cluster approach does not just pose a problem if there are space constraints on the transition state geometry. If the cluster model representing the active site is treated as a gas phase molecule with no structural

constraints these models can gain (for small cluster sizes) an internal stabilization by direct interaction between remote groups (e.g., formation of hydrogen bonds). Such stabilization is not possible in real systems and has to be avoided by constraints on the cluster coordinates. If the coordinates of every atom of the cluster are fixed at positions derived from experimental diffraction data, a stabilization of the transition state of chemical reactions by considerable motion of the surface atoms is not possible and hence, calculated reaction barriers are too high. As a result, constrained optimizations have been performed in this work where the outer atoms of the cluster are fixed at experimental positions of the extended system, and the remaining internal atoms are optimized. Adopting such a procedure introduces some artificial strain since the atomic positions of the outer atoms are not exactly known and may even change along the reaction coordinate in the true extended system. Still, for a small but not too small cluster size such a procedure introduces the smallest errors in the energy along the reaction coordinate.

Formation of a chemical bond is connected with charge transfer or charge separation between the atoms forming the bond. Overlap between the orbitals of the two atoms forming the bond creates the energy splitting between the occupied and virtual states. If bonds are cut on definition of the cluster, charge transfer is interrupted and the number of electrons in the cluster will be different from that in the corresponding piece of the extended system. Moreover, orbitals at the outer atoms miss one partner orbital to interact with. These dangling bond states are artificial radical states and show up in the gap between the occupied and virtual orbitals (Sierka, 2000). As a result, hydrogen atoms were added in this work to terminate the dangling bonds of the cluster. The terminating H-atoms play the role of one half of an oxygen atom (for Si-H terminated clusters). The electronegativity of H is between that of Si and O. H accepts electrons from Si as O does. As a result, if the cluster is large enough to allow for all significant charge delocalization effects, terminal H-atoms approximately simulate the electronic effect of the bulk of the solid. A detailed theoretical study of the cluster size is presented in appendix A.

When metal cations, like iron-oxo species, are exchanged into the zeolite pore system, the zeolite framework acts as a ligand and alters the catalytic properties of the cation. As a result, different exchange sites show different catalytic behavior and the choice and size of the zeolite cluster used, can have a significant effect on the catalytic properties of the site (Pabchanda et al., 2004). In this work, mononuclear iron sites exchanged on a T12 site were investigated. The T12 site in ZSM-5 is readily accessible so that an exchange of a Brønsted acid proton by an iron-oxo species can readily occur. While it was not tested in this work, if different exchange sites show a different catalytic activity, it is believed by the author that a variation in the exchange site does not alter the energies along the reaction coordinate by more than a few kcal/mol. Considering all approximations inherent in the model and the calculations such a variation in the energies can be considered small and does not change conclusions drawn from mononuclear iron sites exchanged on a T12 site.

5.3 Computational methodology

Following the work from Yoshizawa et al. (1999 and 2000b) and Shaik et al. (1995 and 1998), who proposed that more than one spin potential energy surface should be involved in reactions catalyzed by organometallic iron systems (“two-state reactivity”), multiple spin states were analyzed. Quantum chemical calculations of the geometry and energies of potential energy minima, transition-state structures and minimum energy structures on the seam of two PES were performed for spin surfaces with spin multiplicity $M_S = 4$ and $M_S = 6$, using non-local, gradient-corrected density-functional theory (DFT). PES minima were also calculated for $M_S = 2$ and 8. To represent the effects of exchange and correlation, Becke’s 3-parameter exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) were used with a very fine grid size (m5) (see section 3.2.3). To speed up the calculation of PES minima, all structures were pre-optimized with the pure density functional RI-BP (Becke’s 1988 generalized gradient exchange functional together with Perdew’s 1986 correlation functional) using the resolution of identity approach for computing the electronic coulomb interaction

(Eichkorn et al., 1995 and 1997). SCF calculations with the RI-BP functional are about ten times faster than B3LYP calculations and optimized configurations of PES minima were found to be most of the time very similar to B3LYP structures. Basis sets at the triple-zeta level with polarization functions were used for all atoms, including Fe (TZVP). No corrections were made for basis set superposition error (BSSE). All calculations and reported values were carried out using the TURBOMOLE V5.6 suite of programs (Ahlich et al., 1989 and 1995).

Calculations on different spin surfaces revealed that only the PESs with spin multiplicity $M_S = 4$ and 6 need to be considered. Consequently, just these results are reported in this chapter. Spin contamination was negligible for ground state structures on the spin surface $M_S = 6$. Some spin contamination was observed for transition states, minimum structures on a seam of two PESs, and for minimum energy structures on the $M_S = 4$ surface. In all cases it was still possible to distinguish clearly between states of different spin multiplicities.

TURBOMOLE V5.6 does not allow fixing specific atoms in a molecular cluster. As a result, the TURBOMOLE V5.6 optimization script was changed. The Cartesian gradient component of fixed atoms was set to zero and the coordinates of every fixed atom were reset after each cycle. Fast convergence properties were observed for minimizations with an energy convergence criterion of at least 10^{-7} Ha and a gradient norm convergence criterion of 10^{-4} Ha/bohr. At the end of all minimizations or saddle point searches a frequency calculation was done to confirm that for minima all frequencies are positive and for saddle points exactly one frequency is imaginary.

In order to accelerate the search for transition states a combination of interpolation and local methods described in section 4 was used. The growing string method was used in mass-weighted coordinates with a maximum of 11 to 15 nodes. After the two separate ends join, the growing string method was terminated and an approximate saddle point was obtained. To refine the position of the saddle point the modified dimer method was employed. A convergence criterion of the gradient norm of 5×10^{-4} Ha/bohr was used

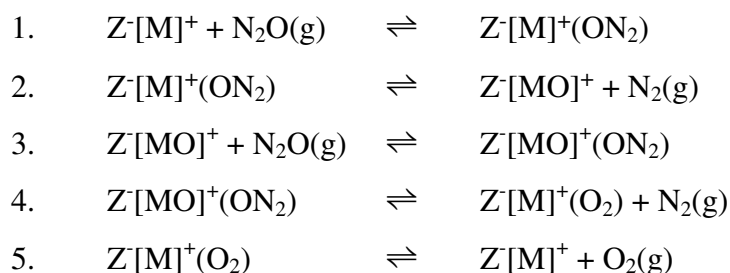
for transition states, and, as described above, first-order saddle points were identified with a frequency calculation. Owing to the use of mass-weighted coordinates in the growing string method an approximation to the minimum energy path (MEP) was obtained, which could be used to determine that reactant and product states are linked by the transition structure found.

Minimum potential energy structures on the seam of two potential energy surfaces were determined with a multiplier penalty function algorithm described in section 4.4. Converged minimum energy crossing point structures had a maximum energy difference on both PESs of less than 10^{-6} Ha.

Overall equilibrium constants and reaction rate constants were computed using standard statistical mechanics and absolute rate theory. To calculate rates of spin surface crossing, e.g., desorption rates of oxygen, the framework of absolute rate theory is used under the assumption that the partition functions of the hypothetical transition state (minimum on the seam of two PESs) and the minimum on the PES with lower spin multiplicity (adsorbed state) are identical except for the electronic energy (Eq. (3.57)). This procedure completely neglects a low probability for spin surface crossing (see section 3.3). To estimate if very low spin surface crossing probabilities could result in very different reaction rate constants, thermally averaged spin transition probabilities are calculated with the Landau-Zener formula (Eq. (3.35)) with a spin-orbit coupling energy H_{I2} of 395 and 825 J/mol, as calculated by Danovich and Shaik (1997) for the oxidative activation of H_2 by FeO^+ . More details about the calculation of rate parameters can be found in section 3.4.4.

5.4 Computational results and discussion

The decomposition of N_2O on a mononuclear iron oxo/hydroxo site can be envisioned to proceed via the following sequence of steps:



In this sequence, $[\text{M}]^+$ represents either $[\text{Fe}]^+$, $[\text{FeO}]^+$, $[\text{FeO}_2]^+$, or $[\text{Fe}(\text{OH})_2]^+$. Reactions 1 and 3 involve the adsorption of gas-phase N_2O from its O-end. Reactions 2 and 4 describe the dissociation of adsorbed N_2O to give N_2 and an adsorbed O-atom. Reaction 5 represents the desorption of molecular O_2 . The sum of these five steps constitutes a complete catalytic cycle. In what follows, first the calculations on the energetics and structures for a complete catalytic cycle on all three mononuclear iron oxo sites are presented. Then the consequences of water adsorption are demonstrated and the calculations of the energetics and structures for the catalytic cycle on a mononuclear iron hydroxo site presented. For all cases, the results for the PESs with spin multiplicity $M_S = 4$ and 6 are given. All quantum chemical calculations are summarized in Table 5.1(a)-(i). Thermally averaged Landau-Zener transition probabilities are summarized for a spin-orbit coupling energy of 395 J/mol and 825 J/mol for several temperatures in Table 5.2. All spin inversion transmission coefficients are larger than 0.05. As a result, not correcting reaction rates for spin inversion probabilities smaller one creates errors smaller than an error in the activation barrier of 4 kcal/mol (at 700 K).

5.4.1 Catalytic cycle on $\text{Z}^-\text{[Fe]}^+$

Yoshizawa et al. (2000 and 2000b) have proposed that bare iron sites ($\text{Z}^-\text{[Fe]}^+$) are responsible for N_2O decomposition. The catalytic cycle on $\text{Z}^-\text{[Fe]}^+$ is illustrated in Figure 5.6 for the quartet PES and in Figure 5.7 for the sextet PES. N_2O adsorbs from the N-end with an enthalpy of adsorption of $\Delta H_{\text{ads}}(M_S = 4) = -21.8$ kcal/mol or

TABLE 5.1a: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
1. $Z[Fe]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[Fe]^+(N_2O) \{M=4\}$	$\Delta H_1 = -21.8$ $E_1^\ddagger = 0.0$ $E_{-1}^\ddagger = 23.1$	K_1, bar^{-1} $A_1, \text{s}^{-1} \text{bar}^{-1}$ $k_1, \text{s}^{-1} \text{bar}^{-1}$ A_{-1}, s^{-1} k_{-1}, s^{-1}	6.35E+01 2.54E+06 2.54E+06 1.25E+13 4.01E+04	4.57E+00 3.49E+06 3.49E+06 1.46E+13 7.64E+05	6.54E-01 4.64E+06 4.64E+06 1.67E+13 7.10E+06
2. $Z[FeO]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[FeO]^+(N_2O) \{M=4\}$	$\Delta H_2 = -7.5$ $E_2^\ddagger = 0.0$ $E_{-2}^\ddagger = 8.4$	K_2, bar^{-1} $A_2, \text{s}^{-1} \text{bar}^{-1}$ $k_2, \text{s}^{-1} \text{bar}^{-1}$ A_{-2}, s^{-1} k_{-2}, s^{-1}	5.15E-05 5.71E+05 5.71E+05 1.25E+13 1.11E+10	2.06E-05 7.28E+05 7.28E+05 1.46E+13 3.53E+10	1.06E-05 9.11E+05 9.11E+05 1.67E+13 8.56E+10
3. $Z[FeO_2]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[FeO_2]^+(N_2O) \{M=4\}$	$\Delta H_3 = 0.3$ $E_3^\ddagger = 0.0$ $E_{-3}^\ddagger = 1.5$	K_3, bar^{-1} $A_3, \text{s}^{-1} \text{bar}^{-1}$ $k_3, \text{s}^{-1} \text{bar}^{-1}$ A_{-3}, s^{-1} k_{-3}, s^{-1}	6.70E-05 2.30E+08 2.30E+08 1.25E+13 3.44E+12	6.84E-05 3.30E+08 3.30E+08 1.46E+13 4.82E+12	7.14E-05 4.52E+08 4.52E+08 1.67E+13 6.33E+12
4. $Z[OFeO]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[OFeO]^+(N_2O) \{M=4\}$	$\Delta H_4 = 4.5$ $E_4^\ddagger = 2.8$ $E_{-4}^\ddagger = 0.0$	K_4, bar^{-1} $A_4, \text{s}^{-1} \text{bar}^{-1}$ $k_4, \text{s}^{-1} \text{bar}^{-1}$ A_{-4}, s^{-1} k_{-4}, s^{-1}	3.54E-08 4.57E+06 4.43E+05 1.25E+13 1.25E+13	5.95E-08 6.42E+06 8.68E+05 1.46E+13 1.46E+13	9.04E-08 8.68E+06 1.51E+06 1.67E+13 1.67E+13
5. $Z[O_2FeO]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[O_2FeO]^+(N_2O) \{M=4\}$	$\Delta H_5 = 0.7$ $E_5^\ddagger = 0.0$ $E_{-5}^\ddagger = 0.6$	K_5, bar^{-1} $A_5, \text{s}^{-1} \text{bar}^{-1}$ $k_5, \text{s}^{-1} \text{bar}^{-1}$ A_{-5}, s^{-1} k_{-5}, s^{-1}	4.63E-07 3.36E+06 3.36E+06 1.25E+13 7.26E+12	4.96E-07 4.54E+06 4.54E+06 1.46E+13 9.15E+12	5.37E-07 5.95E+06 5.95E+06 1.67E+13 1.11E+13
6. $Z[Fe(OH)_2]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[Fe(OH)_2]^+(N_2O) \{M=4\}$	$\Delta H_6 = -0.2$ $E_6^\ddagger = 0.0$ $E_{-6}^\ddagger = 1.8$	K_6, bar^{-1} $A_6, \text{s}^{-1} \text{bar}^{-1}$ $k_6, \text{s}^{-1} \text{bar}^{-1}$ A_{-6}, s^{-1} k_{-6}, s^{-1}	2.30E-04 6.30E+08 6.30E+08 1.25E+13 2.74E+12	2.21E-04 8.77E+08 8.77E+08 1.46E+13 3.97E+12	2.20E-04 1.17E+09 1.17E+09 1.67E+13 5.33E+12
7. $Z[OFe(OH)_2]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[OFe(OH)_2]^+(N_2O) \{M=4\}$	$\Delta H_7 = -5.5$ $E_7^\ddagger = 0.0$ $E_{-7}^\ddagger = 6.2$	K_7, bar^{-1} $A_7, \text{s}^{-1} \text{bar}^{-1}$ $k_7, \text{s}^{-1} \text{bar}^{-1}$ A_{-7}, s^{-1} k_{-7}, s^{-1}	1.64E-03 1.13E+08 1.13E+08 1.25E+13 6.89E+10	8.34E-04 1.41E+08 1.41E+08 1.46E+13 1.69E+11	5.13E-04 1.73E+08 1.73E+08 1.67E+13 3.37E+11

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1b: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
8. $Z[Fe]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[FeO]^+ \{M=4\} + N_2(g)$	$\Delta H_8 = -62.2$ $E_8^\ddagger = 0.0$ $E_8^\ddagger = 63.6$	$K_8, -$ $A_8, s^{-1} bar^{-1}$ $k_8, s^{-1} bar^{-1}$ $A_8, s^{-1} bar^{-1}$ $k_8, s^{-1} bar^{-1}$	1.61E+23 7.25E+04 7.25E+04 6.80E+04 4.50E-19	9.29E+19 3.81E+04 3.81E+04 3.02E+04 4.10E-16	3.49E+17 2.26E+04 2.26E+04 1.57E+04 6.48E-14
9. $Z[FeO]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[FeO]^+(ON_2) \{M=4\}$	$\Delta H_9 = -1.0$ $E_9^\ddagger = 0.0$ $E_9^\ddagger = 2.7$	K_9, bar^{-1} $A_9, s^{-1} bar^{-1}$ $k_9, s^{-1} bar^{-1}$ A_9, s^{-1} k_9, s^{-1}	9.12E-06 1.16E+07 1.16E+07 1.25E+13 1.28E+12	7.92E-06 1.63E+07 1.63E+07 1.46E+13 2.06E+12	7.32E-06 2.20E+07 2.20E+07 1.67E+13 3.01E+12
10. $Z[FeO_2]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[FeO_2]^+(ON_2) \{M=4\}$	$\Delta H_{10} = 0.7$ $E_{10}^\ddagger = 0.0$ $E_{10}^\ddagger = 1.3$	K_{10}, bar^{-1} $A_{10}, s^{-1} bar^{-1}$ $k_{10}, s^{-1} bar^{-1}$ A_{10}, s^{-1} k_{10}, s^{-1}	4.52E-06 1.91E+07 1.91E+07 1.25E+13 4.22E+12	4.85E-06 2.79E+07 2.79E+07 1.46E+13 5.75E+12	5.25E-06 3.88E+07 3.88E+07 1.67E+13 7.38E+12
11. $Z[OFeO]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[OFeO]^+(ON_2) \{M=4\}$	$\Delta H_{11} = 4.5$ $E_{11}^\ddagger = 2.8$ $E_{11}^\ddagger = 0.0$	K_{11}, bar^{-1} $A_{11}, s^{-1} bar^{-1}$ $k_{11}, s^{-1} bar^{-1}$ A_{11}, s^{-1} k_{11}, s^{-1}	1.60E-08 2.08E+06 2.00E+05 1.25E+13 1.25E+13	2.69E-08 2.92E+06 3.92E+05 1.46E+13 1.46E+13	4.09E-08 3.95E+06 6.83E+05 1.67E+13 1.67E+13
12. $Z[O_2FeO]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[O_2FeO]^+(ON_2) \{M=4\}$	$\Delta H_{12} = -0.2$ $E_{12}^\ddagger = 0.0$ $E_{12}^\ddagger = 1.6$	K_{12}, bar^{-1} $A_{12}, s^{-1} bar^{-1}$ $k_{12}, s^{-1} bar^{-1}$ A_{12}, s^{-1} k_{12}, s^{-1}	7.24E-07 2.33E+06 2.33E+06 1.25E+13 3.21E+12	6.95E-07 3.16E+06 3.16E+06 1.46E+13 4.55E+12	6.92E-07 4.16E+06 4.16E+06 1.67E+13 6.02E+12
13. $Z[Fe(OH)_2]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[Fe(OH)_2]^+(ON_2) \{M=4\}$	$\Delta H_{13} = -0.5$ $E_{13}^\ddagger = 0.0$ $E_{13}^\ddagger = 2.1$	K_{13}, bar^{-1} $A_{13}, s^{-1} bar^{-1}$ $k_{13}, s^{-1} bar^{-1}$ A_{13}, s^{-1} k_{13}, s^{-1}	9.41E-05 2.02E+08 2.02E+08 1.25E+13 2.15E+12	8.70E-05 2.81E+08 2.81E+08 1.46E+13 3.23E+12	8.42E-05 3.75E+08 3.75E+08 1.67E+13 4.45E+12
14. $Z[OFe(OH)_2]^+ \{M=4\} + N_2O(g) \leftrightarrow Z[OFe(OH)_2]^+(ON_2) \{M=4\}$	$\Delta H_{14} = -5.4$ $E_{14}^\ddagger = 0.0$ $E_{14}^\ddagger = 6.1$	K_{14}, bar^{-1} $A_{14}, s^{-1} bar^{-1}$ $k_{14}, s^{-1} bar^{-1}$ A_{14}, s^{-1} k_{14}, s^{-1}	3.91E-04 3.06E+07 3.06E+07 1.25E+13 7.82E+10	2.01E-04 3.79E+07 3.79E+07 1.46E+13 1.88E+11	1.25E-04 4.62E+07 4.62E+07 1.67E+13 3.71E+11

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1c: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T,K		
			600	700	800
15. $Z[Fe]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[Fe]^+(N_2O) \{M=6\}$	$\Delta H_{15} = -13.3$ $E_{15}^\ddagger = 0.0$ $E_{-15}^\ddagger = 14.7$	K_{15}, bar^{-1} $A_{15}, \text{s}^{-1} \text{bar}^{-1}$ $k_{15}, \text{s}^{-1} \text{bar}^{-1}$ A_{-15}, s^{-1} k_{-15}, s^{-1}	3.63E-02 1.16E+07 2.06E+06 1.25E+13 5.68E+07	7.25E-03 1.63E+07 2.78E+06 1.46E+13 3.84E+08	2.23E-03 2.20E+07 3.66E+06 1.67E+13 1.64E+09
16. $Z[FeO]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[FeO]^+(N_2O) \{M=6\}$	$\Delta H_{16} = -10.1$ $E_{16}^\ddagger = 0.0$ $E_{-16}^\ddagger = 11.7$	K_{16}, bar^{-1} $A_{16}, \text{s}^{-1} \text{bar}^{-1}$ $k_{16}, \text{s}^{-1} \text{bar}^{-1}$ A_{-16}, s^{-1} k_{-16}, s^{-1}	5.74E-03 4.06E+06 4.06E+06 1.25E+13 7.07E+08	1.67E-03 5.57E+06 5.57E+06 1.46E+13 3.34E+09	6.79E-04 7.38E+06 7.38E+06 1.67E+13 1.09E+10
17. $Z[FeO_2]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[FeO_2]^+(N_2O) \{M=6\}$	$\Delta H_{17} = -2.3$ $E_{17}^\ddagger = 0.0$ $E_{-17}^\ddagger = 3.8$	K_{17}, bar^{-1} $A_{17}, \text{s}^{-1} \text{bar}^{-1}$ $k_{17}, \text{s}^{-1} \text{bar}^{-1}$ A_{-17}, s^{-1} k_{-17}, s^{-1}	5.69E-06 3.05E+06 3.05E+06 1.25E+13 5.36E+11	4.25E-06 4.17E+06 4.17E+06 1.46E+13 9.81E+11	3.50E-06 5.50E+06 5.50E+06 1.67E+13 1.57E+12
18. $Z[OFeO]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[OFeO]^+(N_2O) \{M=6\}$	$\Delta H_{18} = -3.2$ $E_{18}^\ddagger = 0.0$ $E_{-18}^\ddagger = 4.7$	K_{18}, bar^{-1} $A_{18}, \text{s}^{-1} \text{bar}^{-1}$ $k_{18}, \text{s}^{-1} \text{bar}^{-1}$ A_{-18}, s^{-1} k_{-18}, s^{-1}	1.42E-05 3.57E+06 3.57E+06 1.25E+13 2.52E+11	9.53E-06 4.89E+06 4.89E+06 1.46E+13 5.13E+11	7.26E-06 6.47E+06 6.47E+06 1.67E+13 8.91E+11
19. $Z[O_2FeO]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[O_2FeO]^+(N_2O) \{M=6\}$	$\Delta H_{19} = 1.4$ $E_{19}^\ddagger = 0.0$ $E_{-19}^\ddagger = 0.2$	K_{19}, bar^{-1} $A_{19}, \text{s}^{-1} \text{bar}^{-1}$ $k_{19}, \text{s}^{-1} \text{bar}^{-1}$ A_{-19}, s^{-1} k_{-19}, s^{-1}	1.32E-06 1.41E+07 1.41E+07 1.25E+13 1.06E+13	1.53E-06 1.94E+07 1.94E+07 1.46E+13 1.27E+13	1.76E-06 2.59E+07 2.59E+07 1.67E+13 1.47E+13
20. $Z[Fe(OH)_2]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[Fe(OH)_2]^+(N_2O) \{M=6\}$	$\Delta H_{20} = 0.4$ $E_{20}^\ddagger = 0.0$ $E_{-20}^\ddagger = 1.2$	K_{20}, bar^{-1} $A_{20}, \text{s}^{-1} \text{bar}^{-1}$ $k_{20}, \text{s}^{-1} \text{bar}^{-1}$ A_{-20}, s^{-1} k_{-20}, s^{-1}	7.32E-05 3.39E+08 3.39E+08 1.25E+13 4.63E+12	7.52E-05 4.68E+08 4.68E+08 1.46E+13 6.23E+12	7.86E-05 6.23E+08 6.23E+08 1.67E+13 7.92E+12
21. $Z[OFe(OH)_2]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[OFe(OH)_2]^+(N_2O) \{M=6\}$	$\Delta H_{21} = -0.2$ $E_{21}^\ddagger = 0.0$ $E_{-21}^\ddagger = 1.7$	K_{21}, bar^{-1} $A_{21}, \text{s}^{-1} \text{bar}^{-1}$ $k_{21}, \text{s}^{-1} \text{bar}^{-1}$ A_{-21}, s^{-1} k_{-21}, s^{-1}	1.56E-04 4.76E+08 4.76E+08 1.25E+13 3.05E+12	1.50E-04 6.54E+08 6.54E+08 1.46E+13 4.36E+12	1.50E-04 8.67E+08 8.67E+08 1.67E+13 5.79E+12

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1d: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
22. $Z[Fe]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[Fe]^+(ON_2) \{M=6\}$	$\Delta H_{22} = 1.9$	K_{22}, bar^{-1}	2.10E-04	2.60E-04	3.13E-04
	$E_{22}^\ddagger = 0.03$	$A_{22}, \text{s}^{-1} \text{bar}^{-1}$	2.69E+09	3.86E+09	5.30E+09
		$k_{22}, \text{s}^{-1} \text{bar}^{-1}$	2.63E+09	3.79E+09	5.21E+09
	$E_{-22}^\ddagger = 0.0$	A_{-22}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-22}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
23. $Z[FeO]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[FeO]^+(ON_2) \{M=6\}$	$\Delta H_{23} = -4.8$	K_{23}, bar^{-1}	9.55E-05	5.28E-05	3.48E-05
	$E_{23}^\ddagger = 0.0$	$A_{23}, \text{s}^{-1} \text{bar}^{-1}$	5.75E+06	7.95E+06	1.06E+07
		$k_{23}, \text{s}^{-1} \text{bar}^{-1}$	5.75E+06	7.95E+06	1.06E+07
	$E_{-23}^\ddagger = 6.4$	A_{-23}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-23}, s^{-1}	6.02E+10	1.51E+11	3.05E+11
24. $Z[FeO_2]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[FeO_2]^+(ON_2) \{M=6\}$	$\Delta H_{24} = -1.2$	K_{24}, bar^{-1}	1.73E-06	1.47E-06	1.33E-06
	$E_{24}^\ddagger = 0.0$	$A_{24}, \text{s}^{-1} \text{bar}^{-1}$	2.19E+06	3.01E+06	3.99E+06
		$k_{24}, \text{s}^{-1} \text{bar}^{-1}$	2.19E+06	3.01E+06	3.99E+06
	$E_{-24}^\ddagger = 2.7$	A_{-24}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-24}, s^{-1}	1.27E+12	2.05E+12	2.99E+12
25. $Z[OFeO]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[OFeO]^+(ON_2) \{M=6\}$	$\Delta H_{25} = -3.0$	K_{25}, bar^{-1}	5.35E-06	3.66E-06	2.82E-06
	$E_{25}^\ddagger = 0.0$	$A_{25}, \text{s}^{-1} \text{bar}^{-1}$	1.51E+06	2.07E+06	2.74E+06
		$k_{25}, \text{s}^{-1} \text{bar}^{-1}$	1.51E+06	2.07E+06	2.74E+06
	$E_{-25}^\ddagger = 4.5$	A_{-25}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-25}, s^{-1}	2.82E+11	5.66E+11	9.71E+11
26. $Z[O_2FeO]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[O_2FeO]^+(ON_2) \{M=6\}$	$\Delta H_{26} = 0.3$	K_{26}, bar^{-1}	1.32E-06	1.35E-06	1.41E-06
	$E_{26}^\ddagger = 0.0$	$A_{26}, \text{s}^{-1} \text{bar}^{-1}$	5.98E+06	8.24E+06	1.09E+07
		$k_{26}, \text{s}^{-1} \text{bar}^{-1}$	5.98E+06	8.24E+06	1.09E+07
	$E_{-26}^\ddagger = 1.2$	A_{-26}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-26}, s^{-1}	4.52E+12	6.10E+12	7.77E+12
27. $Z[Fe(OH)_2]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[Fe(OH)_2]^+(ON_2) \{M=6\}$	$\Delta H_{27} = 0.2$	K_{27}, bar^{-1}	8.31E-05	8.35E-05	8.59E-05
	$E_{27}^\ddagger = 0.0$	$A_{27}, \text{s}^{-1} \text{bar}^{-1}$	3.42E+08	4.70E+08	6.23E+08
		$k_{27}, \text{s}^{-1} \text{bar}^{-1}$	3.42E+08	4.70E+08	6.23E+08
	$E_{-27}^\ddagger = 1.3$	A_{-27}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-27}, s^{-1}	4.12E+12	5.63E+12	7.25E+12
28. $Z[OFe(OH)_2]^+ \{M=6\} + N_2O(g) \leftrightarrow Z[OFe(OH)_2]^+(ON_2) \{M=6\}$	$\Delta H_{28} = -0.5$	K_{28}, bar^{-1}	2.95E-05	2.72E-05	2.62E-05
	$E_{28}^\ddagger = 0.0$	$A_{28}, \text{s}^{-1} \text{bar}^{-1}$	6.64E+07	9.12E+07	1.21E+08
		$k_{28}, \text{s}^{-1} \text{bar}^{-1}$	6.64E+07	9.12E+07	1.21E+08
	$E_{-28}^\ddagger = 2.0$	A_{-28}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-28}, s^{-1}	2.25E+12	3.36E+12	4.61E+12

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1e: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
29. $Z[Fe]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + N_2 (g)$	$\Delta H_{29} = -67.9$ $E_{29}^\ddagger = 2.8$ $E_{29}^\ddagger = 70.0$	K_{29}, bar A_{29}, s^{-1} k_{29}, s^{-1} $A_{29}, s^{-1} \text{ bar}^{-1}$ $k_{29}, s^{-1} \text{ bar}^{-1}$	2.81E+28 6.28E+09 6.24E+08 7.43E+05 2.22E-20	8.35E+24 6.36E+09 8.77E+08 7.94E+05 1.05E-16	1.85E+22 6.43E+09 1.14E+09 8.54E+05 6.14E-14
30. $Z[FeO]^+(ON_2) \{M=4\} \leftrightarrow$ $Z[FeO_2]^+ \{M=4\} + N_2 (g)$	$\Delta H_{30} = -25.7$ $E_{30}^\ddagger = 29.0$ $E_{30}^\ddagger = 53.7$	K_{30}, bar A_{30}, s^{-1} k_{30}, s^{-1} $A_{30}, s^{-1} \text{ bar}^{-1}$ $k_{30}, s^{-1} \text{ bar}^{-1}$	2.18E+14 3.77E+12 1.04E+02 1.79E+07 4.79E-13	1.02E+13 4.12E+12 3.67E+03 2.15E+07 3.60E-10	1.00E+12 4.43E+12 5.34E+04 2.55E+07 5.32E-08
31. $Z[FeO]^+(ON_2) \{M=4\} \leftrightarrow$ $Z[OFeO]^+ \{M=4\} + N_2 (g)$	$\Delta H_{31} = -17.5$ $E_{31}^\ddagger = 27.5$ $E_{31}^\ddagger = 43.9$	K_{31}, bar A_{31}, s^{-1} k_{31}, s^{-1} $A_{31}, s^{-1} \text{ bar}^{-1}$ $k_{31}, s^{-1} \text{ bar}^{-1}$	3.27E+11 1.00E+13 9.83E+02 3.11E+07 3.00E-09	4.09E+10 1.15E+13 3.03E+04 3.96E+07 7.41E-07	8.38E+09 1.28E+13 4.00E+05 4.91E+07 4.78E-05
32. $Z[FeO_2]^+(ON_2) \{M=4\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=4\} + N_2 (g)$	$\Delta H_{32} = -16.8$ $E_{32}^\ddagger = 24.0$ $E_{32}^\ddagger = 40.3$	K_{32}, bar A_{32}, s^{-1} k_{32}, s^{-1} $A_{32}, s^{-1} \text{ bar}^{-1}$ $k_{32}, s^{-1} \text{ bar}^{-1}$	2.61E+12 8.44E+13 1.49E+05 2.86E+07 5.71E-08	3.53E+11 9.88E+13 3.10E+06 3.49E+07 8.78E-06	7.72E+10 1.12E+14 3.06E+07 4.19E+07 3.96E-04
33. $Z[OFeO]^+(ON_2) \{M=4\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=4\} + N_2 (g)$	$\Delta H_{33} = -28.8$ $E_{33}^\ddagger = 42.9$ $E_{33}^\ddagger = 71.5$	K_{33}, bar A_{33}, s^{-1} k_{33}, s^{-1} $A_{33}, s^{-1} \text{ bar}^{-1}$ $k_{33}, s^{-1} \text{ bar}^{-1}$	4.92E+17 6.63E+13 1.58E-02 3.72E+06 3.22E-20	1.59E+16 7.88E+13 3.21E+00 4.41E+06 2.02E-16	1.19E+15 9.07E+13 1.74E+02 5.18E+06 1.47E-13
34. $Z[Fe(OH)_2]^+(ON_2) \{M=4\} \leftrightarrow$ $Z[OFe(OH)_2]^+ \{M=4\} + N_2 (g)$	$\Delta H_{34} = 5.75$ $E_{34}^\ddagger = 54.4$ $E_{34}^\ddagger = 48.4$	K_{34}, bar A_{34}, s^{-1} k_{34}, s^{-1} $A_{34}, s^{-1} \text{ bar}^{-1}$ $k_{34}, s^{-1} \text{ bar}^{-1}$	4.93E+02 1.92E+11 2.86E-09 2.60E+06 5.79E-12	9.95E+02 1.96E+11 1.98E-06 2.69E+06 1.99E-09	1.66E+03 1.99E+11 2.68E-04 2.81E+06 1.62E-07
35. $Z[OFe(OH)_2]^+(ON_2) \{M=4\} \leftrightarrow$ $Z[O_2Fe(OH)_2]^+ \{M=4\} + N_2 (g)$	$\Delta H_{35} = 30.4$ $E_{35}^\ddagger = 52.2$ $E_{35}^\ddagger = 21.8$	K_{35}, bar A_{35}, s^{-1} k_{35}, s^{-1} $A_{35}, s^{-1} \text{ bar}^{-1}$ $k_{35}, s^{-1} \text{ bar}^{-1}$	1.15E-07 7.61E+11 6.90E-08 5.29E+07 6.00E-01	4.45E-06 8.46E+11 4.03E-05 5.84E+07 9.05E+00	6.82E-05 9.22E+11 4.82E-03 6.42E+07 7.07E+01

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1f: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
36. $Z[FeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[FeO_2]^+ \{M=6\} + N_2 (g)$	$\Delta H_{36} = -20.0$ $E_{36}^\ddagger = 30.4$ $E_{36}^\ddagger = 50.0$	K_{36}, bar A_{36}, s^{-1} k_{36}, s^{-1} $A_{36}, s^{-1} \text{bar}^{-1}$ $k_{36}, s^{-1} \text{bar}^{-1}$	1.78E+13 5.40E+13 4.48E+02 4.19E+07 2.52E-11	1.65E+12 6.22E+13 1.97E+04 4.97E+07 1.20E-08	2.71E+11 6.98E+13 3.41E+05 5.82E+07 1.26E-06
37. $Z[FeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[OFeO]^+ \{M=6\} + N_2 (g)$	$\Delta H_{37} = -11.8$ $E_{37}^\ddagger = 30.7$ $E_{37}^\ddagger = 41.9$	K_{37}, bar A_{37}, s^{-1} k_{37}, s^{-1} $A_{37}, s^{-1} \text{bar}^{-1}$ $k_{37}, s^{-1} \text{bar}^{-1}$	6.69E+09 1.58E+14 1.06E+03 2.97E+08 1.58E-07	1.64E+09 1.84E+14 4.87E+04 3.67E+08 2.97E-05	5.61E+08 2.09E+14 8.71E+05 4.43E+08 1.55E-03
38. $Z[FeO_2]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=6\} + N_2 (g)$	$\Delta H_{38} = -12.0$ $E_{38}^\ddagger = 20.1$ $E_{38}^\ddagger = 31.5$	K_{38}, bar A_{38}, s^{-1} k_{38}, s^{-1} $A_{38}, s^{-1} \text{bar}^{-1}$ $k_{38}, s^{-1} \text{bar}^{-1}$	3.84E+05 5.91E+09 2.75E+02 2.12E+08 7.17E-04	2.10E+05 1.56E+10 8.11E+03 2.63E+08 3.87E-02	1.24E+05 3.12E+10 9.88E+04 3.19E+08 7.95E-01
39. $Z[OFeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=6\} + N_2 (g)$	$\Delta H_{39} = -18.3$ $E_{39}^\ddagger = 16.5$ $E_{39}^\ddagger = 34.4$	K_{39}, bar A_{39}, s^{-1} k_{39}, s^{-1} $A_{39}, s^{-1} \text{bar}^{-1}$ $k_{39}, s^{-1} \text{bar}^{-1}$	1.44E+13 2.35E+14 2.27E+08 5.47E+07 1.57E-05	1.63E+12 2.81E+14 1.96E+09 6.75E+07 1.20E-03	3.12E+11 3.25E+14 1.00E+10 8.16E+07 3.21E-02
40. $Z[O_2FeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[O_2FeO_2]^+ \{M=6\} + N_2 (g)$	$\Delta H_{40} = -25.5$ $E_{40}^\ddagger = 41.1$ $E_{40}^\ddagger = 66.9$	K_{40}, bar A_{40}, s^{-1} k_{40}, s^{-1} $A_{40}, s^{-1} \text{bar}^{-1}$ $k_{40}, s^{-1} \text{bar}^{-1}$	5.67E+16 4.42E+13 4.48E-02 1.99E+06 7.91E-19	2.71E+15 5.14E+13 7.22E+00 2.19E+06 2.66E-15	2.73E+14 5.81E+13 3.30E+02 2.42E+06 1.21E-12
41. $Z[Fe(OH)_2]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[OFe(OH)_2]^+ \{M=6\} + N_2 (g)$	$\Delta H_{41} = 16.7$ $E_{41}^\ddagger = 42.8$ $E_{41}^\ddagger = 25.1$	K_{41}, bar A_{41}, s^{-1} k_{41}, s^{-1} $A_{41}, s^{-1} \text{bar}^{-1}$ $k_{41}, s^{-1} \text{bar}^{-1}$	1.35E-03 2.02E+10 5.01E-06 5.09E+06 3.70E-03	1.01E-02 2.13E+10 8.99E-04 6.05E+06 8.89E-02	4.47E-02 2.25E+10 4.44E-02 7.09E+06 9.93E-01
42. $Z[OFe(OH)_2]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[O_2Fe(OH)_2]^+ \{M=6\} + N_2 (g)$	$\Delta H_{42} = 19.4$ $E_{42}^\ddagger = 61.7$ $E_{42}^\ddagger = 41.2$	K_{42}, bar A_{42}, s^{-1} k_{42}, s^{-1} $A_{42}, s^{-1} \text{bar}^{-1}$ $k_{42}, s^{-1} \text{bar}^{-1}$	1.72E-04 6.02E+14 1.90E-08 1.11E+11 1.10E-04	1.79E-03 7.79E+14 4.03E-05 1.63E+11 2.25E-02	1.02E-02 9.58E+14 1.28E-02 2.23E+11 1.25E+00

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1g: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
43. $Z[Fe]^+ \{M=4\} \leftrightarrow$ $Z[Fe]^+ \{M=6\}$	$\Delta H_{43} = 0.1$ $E_{43}^\ddagger = 0.3$	$K_{43}, -$ A_{43}, s^{-1} k_{43}, s^{-1}	1.49E+00 1.25E+13 9.52E+12	1.51E+00 1.46E+13 1.15E+13	1.53E+00 1.67E+13 1.36E+13
	$E_{43}^\ddagger = 0.3$	A_{43}, s^{-1} k_{43}, s^{-1}	7.94E+12 6.39E+12	9.20E+12 7.64E+12	1.05E+13 8.89E+12
44. $Z[FeO]^+ \{M=4\} \leftrightarrow$ $Z[FeO]^+ \{M=6\}$	$\Delta H_{44} = -3.7$ $E_{44}^\ddagger = 2.3$	$K_{44}, -$ A_{44}, s^{-1} k_{44}, s^{-1}	5.47E+01 1.25E+13 1.77E+12	3.53E+01 1.46E+13 2.73E+12	2.54E+01 1.67E+13 3.85E+12
	$E_{44}^\ddagger = 5.9$	A_{44}, s^{-1} k_{44}, s^{-1}	4.65E+12 3.24E+10	5.47E+12 7.74E+10	6.30E+12 1.52E+11
45. $Z[FeO_2]^+ \{M=4\} \leftrightarrow$ $Z[FeO_2]^+ \{M=6\}$	$\Delta H_{45} = -1.7$ $E_{45}^\ddagger = 2.9$	$K_{45}, -$ A_{45}, s^{-1} k_{45}, s^{-1}	4.68E+01 1.25E+13 1.07E+12	3.81E+01 1.46E+13 1.77E+12	3.26E+01 1.67E+13 2.63E+12
	$E_{45}^\ddagger = 5.0$	A_{45}, s^{-1} k_{45}, s^{-1}	1.54E+12 2.28E+10	1.72E+12 4.65E+10	1.90E+12 8.07E+10
46. $Z[O_2FeO]^+ \{M=4\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=6\}$	$\Delta H_{46} = 1.2$ $E_{46}^\ddagger = 21.6$	$K_{46}, -$ A_{46}, s^{-1} k_{46}, s^{-1}	1.15E-01 1.25E+13 1.63E+05	1.32E-01 1.46E+13 2.54E+06	1.47E-01 1.67E+13 2.03E+07
	$E_{46}^\ddagger = 20.2$	A_{46}, s^{-1} k_{46}, s^{-1}	3.25E+13 1.41E+06	3.91E+13 1.92E+07	4.59E+13 1.38E+08
47. $Z[FeO_2]^+ \{M=4\} \leftrightarrow$ $Z[Fe]^+ \{M=4\} + O_2 (g)$	$\Delta H_{47} = 50.3$ $E_{47}^\ddagger = 50.9$	K_{47}, bar A_{47}, s^{-1} k_{47}, s^{-1}	2.09E-11 1.25E+13 3.53E-06	8.86E-09 1.46E+13 1.84E-03	8.05E-07 1.67E+13 2.04E-01
	$E_{47}^\ddagger = 0.0$	$A_{47}, s^{-1} \text{ bar}^{-1}$ $k_{47}, s^{-1} \text{ bar}^{-1}$	1.69E+05 1.69E+05	2.08E+05 2.08E+05	2.54E+05 2.54E+05
48. $Z[O_2FeO]^+ \{M=4\} \leftrightarrow$ $Z[FeO]^+ \{M=4\} + O_2 (g)$	$\Delta H_{48} = 4.2$ $E_{48}^\ddagger = 21.6$	K_{48}, bar A_{48}, s^{-1} k_{48}, s^{-1}	2.85E+05 1.25E+13 1.63E+05	4.80E+05 1.46E+13 2.54E+06	6.92E+05 1.67E+13 2.03E+07
	$E_{48}^\ddagger = 16.7$	$A_{48}, s^{-1} \text{ bar}^{-1}$ $k_{48}, s^{-1} \text{ bar}^{-1}$	7.14E+05 5.70E-01	8.91E+05 5.29E+00	1.10E+06 2.93E+01
49. $Z[O_2Fe(OH)_2]^+ \{M=4\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=4\} + O_2 (g)$	$\Delta H_{49} = -68.8$ $E_{49}^\ddagger = 13.1$	K_{49}, bar A_{49}, s^{-1} k_{49}, s^{-1}	3.20E+33 1.72E+13 2.94E+08	8.56E+29 1.83E+13 1.50E+09	1.74E+27 1.92E+13 5.10E+09
	$E_{49}^\ddagger = 81.5$	$A_{49}, s^{-1} \text{ bar}^{-1}$ $k_{49}, s^{-1} \text{ bar}^{-1}$	4.70E+04 9.18E-26	5.11E+04 1.75E-21	5.60E+04 2.93E-18

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1h: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
50. $Z[FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[Fe]^+ \{M=4\} + O_2 (g)$	$\Delta H_{50} = 52.0$ $E_{50}^\ddagger = 53.0$ $E_{50}^\ddagger = 0.0$	K_{50}, bar A_{50}, s^{-1} k_{50}, s^{-1} $A_{50}, s^{-1} \text{ bar}^{-1}$ $k_{50}, s^{-1} \text{ bar}^{-1}$	4.47E-13 1.25E+13 6.14E-07 1.37E+06 1.37E+06	2.33E-10 1.46E+13 4.11E-04 1.76E+06 1.76E+06	2.47E-08 1.67E+13 5.50E-02 2.23E+06 2.23E+06
51. $Z[FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[Fe]^+ \{M=6\} + O_2 (g)$	$\Delta H_{51} = 52.1$ $E_{51}^\ddagger = 54.2$ $E_{51}^\ddagger = 1.1$	K_{51}, bar A_{51}, s^{-1} k_{51}, s^{-1} $A_{51}, s^{-1} \text{ bar}^{-1}$ $k_{51}, s^{-1} \text{ bar}^{-1}$	6.66E-13 1.25E+13 2.28E-07 8.73E+05 3.43E+05	3.52E-10 1.46E+13 1.76E-04 1.11E+06 5.00E+05	3.77E-08 1.67E+13 2.62E-02 1.40E+06 6.94E+05
52. $Z[O_2FeO]^+ \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=4\} + O_2 (g)$	$\Delta H_{52} = 3.0$ $E_{52}^\ddagger = 6.9$ $E_{52}^\ddagger = 3.5$	K_{52}, bar A_{52}, s^{-1} k_{52}, s^{-1} $A_{52}, s^{-1} \text{ bar}^{-1}$ $k_{52}, s^{-1} \text{ bar}^{-1}$	2.48E+06 1.25E+14 3.69E+11 2.76E+06 1.49E+05	3.63E+06 1.39E+14 9.43E+11 3.17E+06 2.60E+05	4.72E+06 1.51E+14 1.91E+12 3.61E+06 4.04E+05
53. $Z[O_2FeO]^+ \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + O_2 (g)$	$\Delta H_{53} = -0.6$ $E_{53}^\ddagger = 8.0$ $E_{53}^\ddagger = 8.1$	K_{53}, bar A_{53}, s^{-1} k_{53}, s^{-1} $A_{53}, s^{-1} \text{ bar}^{-1}$ $k_{53}, s^{-1} \text{ bar}^{-1}$	1.36E+08 1.25E+13 1.56E+10 1.02E+05 1.15E+02	1.28E+08 1.46E+13 4.72E+10 1.24E+05 3.68E+02	1.20E+08 1.67E+13 1.11E+11 1.51E+05 9.23E+02
54. $Z[O_2FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[FeO_2]^+ \{M=4\} + O_2 (g)$	$\Delta H_{54} = 1.5$ $E_{54}^\ddagger = 11.4$ $E_{54}^\ddagger = 8.3$	K_{54}, bar A_{54}, s^{-1} k_{54}, s^{-1} $A_{54}, s^{-1} \text{ bar}^{-1}$ $k_{54}, s^{-1} \text{ bar}^{-1}$	6.55E+04 2.10E+13 1.52E+09 2.51E+07 2.32E+04	8.00E+04 2.24E+13 6.33E+09 3.16E+07 7.91E+04	9.02E+04 2.35E+13 1.84E+10 3.85E+07 2.04E+05
55. $Z[O_2FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[FeO_2]^+ \{M=6\} + O_2 (g)$	$\Delta H_{55} = -0.2$ $E_{55}^\ddagger = 5.8$ $E_{55}^\ddagger = 4.9$	K_{55}, bar A_{55}, s^{-1} k_{55}, s^{-1} $A_{55}, s^{-1} \text{ bar}^{-1}$ $k_{55}, s^{-1} \text{ bar}^{-1}$	3.07E+06 1.25E+13 9.30E+10 1.84E+06 3.03E+04	3.04E+06 1.46E+13 2.18E+11 2.42E+06 7.18E+04	2.94E+06 1.67E+13 4.22E+11 3.11E+06 1.43E+05
56. $Z[O_2Fe(OH)_2]^+ \{M=6\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=4\} + O_2 (g)$	$\Delta H_{56} = -60.2$ $E_{56}^\ddagger = 16.0$ $E_{56}^\ddagger = 76.2$	K_{56}, bar A_{56}, s^{-1} k_{56}, s^{-1} $A_{56}, s^{-1} \text{ bar}^{-1}$ $k_{56}, s^{-1} \text{ bar}^{-1}$	3.99E+30 3.48E+13 5.00E+07 7.62E+04 1.26E-23	2.97E+27 3.89E+13 3.82E+08 8.37E+04 1.28E-19	1.31E+25 4.23E+13 1.76E+09 9.25E+04 1.34E-16

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.1i: Computed rate parameters for elementary steps in nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
57. $Z[O_2Fe(OH)_2]^+ \{M=6\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=6\} + O_2(g)$	$\Delta H_{57} = -74.3$ $E_{57}^\ddagger = 15.8$ $E_{57}^\ddagger = 90.9$	K_{57}, bar A_{57}, s^{-1} k_{57}, s^{-1} $A_{57}, \text{s}^{-1} \text{bar}^{-1}$ $k_{57}, \text{s}^{-1} \text{bar}^{-1}$	1.17E+37 1.25E+13 2.12E+07 2.52E+03 1.81E-30	1.61E+33 1.46E+13 1.65E+08 2.62E+03 1.02E-25	2.01E+30 1.67E+13 7.83E+08 2.81E+03 3.90E-22
58. $Z[FeO_2]^+ \{M=4\} \leftrightarrow$ $Z[OFeO]^+ \{M=4\}$	$\Delta H_{58} = 8.2$ $E_{58}^\ddagger = 30.5$ $E_{58}^\ddagger = 22.3$	$K_{58}, -$ A_{58}, s^{-1} k_{58}, s^{-1} A_{58}, s^{-1} k_{58}, s^{-1}	1.50E-03 1.26E+14 9.60E+02 8.24E+13 6.38E+05	4.01E-03 1.40E+14 4.13E+04 9.23E+13 1.03E+07	8.35E-03 1.52E+14 6.97E+05 1.01E+14 8.35E+07
59. $Z[FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[OFeO]^+ \{M=6\}$	$\Delta H_{59} = 8.1$ $E_{59}^\ddagger = 22.5$ $E_{59}^\ddagger = 14.1$	$K_{59}, -$ A_{59}, s^{-1} k_{59}, s^{-1} A_{59}, s^{-1} k_{59}, s^{-1}	3.77E-04 7.68E+12 4.91E+04 1.86E+13 1.30E+08	9.96E-04 8.11E+12 7.68E+05 2.02E+13 7.71E+08	2.07E-03 8.46E+12 6.05E+06 2.15E+13 2.93E+09
60. $Z[FeO]^+ \{M=4\} + H_2O(g) \leftrightarrow$ $Z[FeO]^+(OH_2) \{M=4\}$	$\Delta H_{60} = -8.8$ $E_{60}^\ddagger = 0.0$ $E_{60}^\ddagger = 10.5$	K_{60}, bar^{-1} $A_{60}, \text{s}^{-1} \text{bar}^{-1}$ $k_{60}, \text{s}^{-1} \text{bar}^{-1}$ A_{60}, s^{-1} k_{60}, s^{-1}	1.53E-03 2.75E+06 2.75E+06 1.25E+13 1.79E+09	4.80E-04 3.56E+06 3.56E+06 1.46E+13 7.41E+09	2.08E-04 4.54E+06 4.54E+06 1.67E+13 2.19E+10
61. $Z[FeO]^+ \{M=6\} + H_2O(g) \leftrightarrow$ $Z[FeO]^+(OH_2) \{M=6\}$	$\Delta H_{61} = -15.6$ $E_{61}^\ddagger = 0.0$ $E_{61}^\ddagger = 17.3$	K_{61}, bar^{-1} $A_{61}, \text{s}^{-1} \text{bar}^{-1}$ $k_{61}, \text{s}^{-1} \text{bar}^{-1}$ A_{61}, s^{-1} k_{61}, s^{-1}	2.58E-01 1.58E+06 1.58E+06 1.25E+13 6.14E+06	3.56E-02 2.03E+06 2.03E+06 1.46E+13 5.71E+07	8.32E-03 2.57E+06 2.57E+06 1.67E+13 3.09E+08
62. $Z[FeO]^+(OH_2) \{M=4\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=4\}$	$\Delta H_{62} = -23.5$ $E_{62}^\ddagger = 1.9$ $E_{62}^\ddagger = 24.6$	$K_{62}, -$ A_{62}, s^{-1} k_{62}, s^{-1} A_{62}, s^{-1} k_{62}, s^{-1}	5.74E+06 1.47E+11 3.00E+10 4.89E+12 5.23E+03	3.42E+05 1.30E+11 3.34E+10 4.77E+12 9.75E+04	4.14E+04 1.19E+11 3.62E+10 4.67E+12 8.74E+05
63. $Z[FeO]^+(OH_2) \{M=6\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=6\}$	$\Delta H_{63} = -27.1$ $E_{63}^\ddagger = 9.2$ $E_{63}^\ddagger = 36.4$	$K_{63}, -$ A_{63}, s^{-1} k_{63}, s^{-1} A_{63}, s^{-1} k_{63}, s^{-1}	1.83E+09 2.28E+12 1.03E+09 1.08E+13 5.63E-01	7.10E+07 2.18E+12 2.97E+09 1.02E+13 4.18E+01	6.26E+06 2.13E+12 6.60E+09 9.69E+12 1.05E+03

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 5.2: Norm of the gradient difference at the point of spin surface crossing and thermally averaged Landau-Zener Transition probabilities at temperatures of 600, 700 and 800 K^a

Reaction ^b	grad(E ₁) - grad(E ₂) (kJ/mol/Å)	P _{LZ} (H ₁₂ = 395 J/mol)			P _{LZ} (H ₁₂ = 825 J/mol)		
		T, K			T, K		
		600	700	800	600	700	800
43. Z[Fe] ⁺ {M=4} ↔ Z[Fe] ⁺ {M=6}	113	0.096	0.090	0.086	0.270	0.257	0.246
44. Z[FeO] ⁺ {M=4} ↔ Z[FeO] ⁺ {M=6}	37	0.185	0.176	0.168	0.462	0.443	0.427
45. Z[FeO ₂] ⁺ {M=4} ↔ Z[FeO ₂] ⁺ {M=6}	264	0.048	0.045	0.043	0.148	0.140	0.133
46. Z[O ₂ FeO] ⁺ {M=4} ↔ Z[O ₂ FeO] ⁺ {M=6}	405	0.033	0.031	0.029	0.105	0.099	0.094
47. Z[FeO ₂] ⁺ {M=4} ↔ Z[Fe] ⁺ {M=4} + O ₂ (g)	264	0.048	0.045	0.043	0.148	0.140	0.133
48. Z[O ₂ FeO] ⁺ {M=4} ↔ Z[FeO] ⁺ {M=4} + O ₂ (g)	405	0.033	0.031	0.029	0.105	0.099	0.094
49. Z[O ₂ Fe(OH) ₂] ⁺ {M=4} ↔ Z[Fe(OH) ₂] ⁺ {M=4} + O ₂ (g)	102	0.089	0.084	0.080	0.254	0.242	0.231
51. Z[FeO ₂] ⁺ {M=6} ↔ Z[Fe] ⁺ {M=6} + O ₂ (g)	113	0.095	0.090	0.085	0.269	0.256	0.245
53. Z[O ₂ FeO] ⁺ {M=6} ↔ Z[FeO] ⁺ {M=6} + O ₂ (g)	366	0.035	0.033	0.031	0.111	0.105	0.100
55. Z[O ₂ FeO ₂] ⁺ {M=6} ↔ Z[FeO ₂] ⁺ {M=6} + O ₂ (g)	173	0.068	0.064	0.061	0.201	0.190	0.182
57. Z[O ₂ Fe(OH) ₂] ⁺ {M=6} ↔ Z[Fe(OH) ₂] ⁺ {M=6} + O ₂ (g)	512	0.029	0.027	0.025	0.092	0.086	0.082

(a) Landau-Zener probabilities are calculated for a spin-orbit coupling energy of H₁₂ = 395 and 825 J/mol

(b) Reaction numbers are the same as in Table 5.1

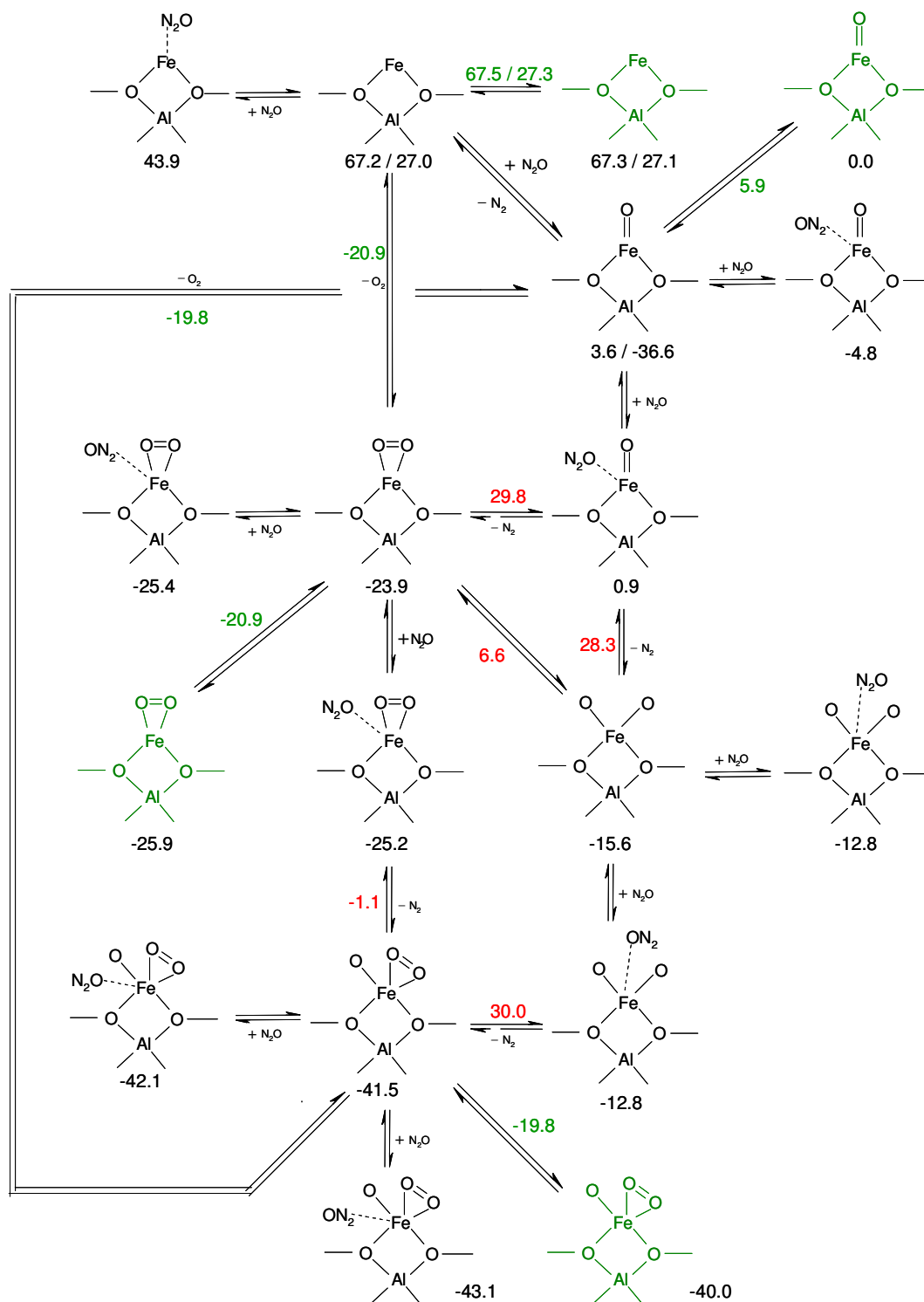
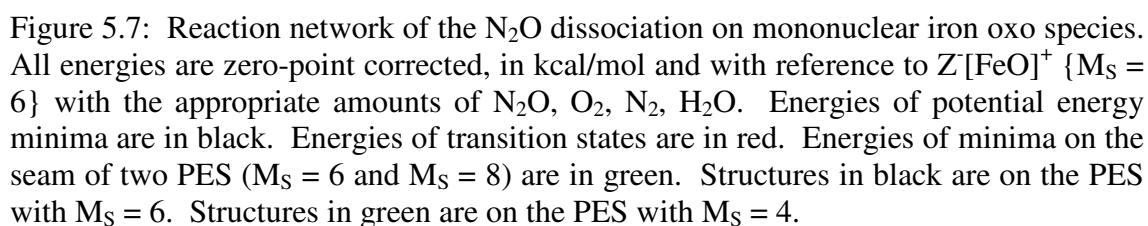


Figure 5.6: Reaction network of the N_2O dissociation on mononuclear iron oxo species. All energies are zero-point corrected, in kcal/mol and with reference to $\text{Z}[\text{FeO}]^+ \{M_S = 6\}$ with the appropriate amounts of N_2O , O_2 , N_2 , H_2O . Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PES ($M_S = 4$ and $M_S = 6$) are in green. Structures in black are on the PES with $M_S = 4$. Structures in green are on the PES with $M_S = 6$.



$\Delta H_{\text{ads}}(M_S = 6) = -13.3$ kcal/mol (see Table 5.1a and c). The large difference in the enthalpy of adsorption on both spin surfaces follows from the fact that N_2O cannot adsorb linearly on the sextet surface as it does on the quartet surface. Until a N_2O molecule gets closer than $2.5 \text{ \AA}$ to the iron atom, the electron configuration of the iron is on the sextet surface $4s^1 3d^6$ and we have Pauli repulsion. For the nitrous oxide to adsorb, the electron configurations of iron and N_2O have to change. N_2O adsorbs bent on the sextet surface. The N-N-O angle is 133.7° and the N-N bond distance increases from $1.12 \text{ \AA}$ to $1.23 \text{ \AA}$. Figure 5.8 illustrates the adsorbed N_2O species on bare iron sites. The adsorption process on both spin surfaces is barrierless and both adsorption and desorption are rapid. The zero-point-corrected energy of bare iron sites is nearly identical on the quartet and sextet PESs, and the spin change barrier is approximately $E^\ddagger = 0.3$ kcal/mol. As a result, if bare iron sites are present both spin states of iron would be populated and N_2O would preferentially adsorb through the N-end on the $M_S = 4$ surface. N_2O should not adsorb through its O-end, $\Delta H_{\text{ads}}(M_S = 6) = 1.9$ kcal/mol, but if N_2O approaches a bare iron site from with its O-end the site can be oxidized readily.

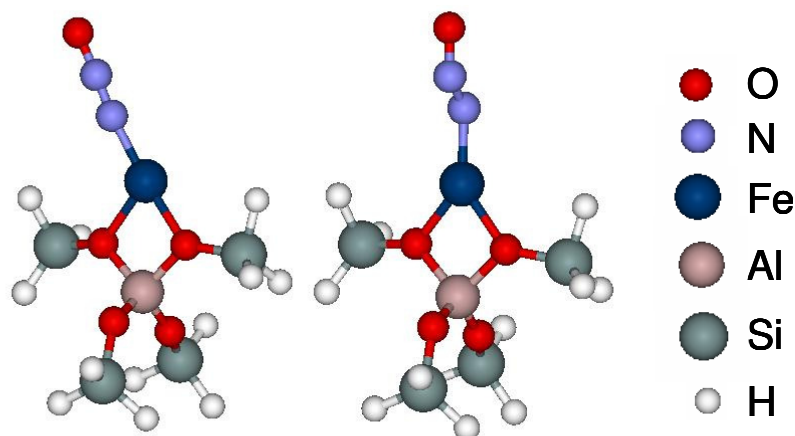


Figure 5.8: Adsorbed N_2O on bare iron sites. On the left $M_S = 4$, on the right $M_S = 6$

An activation barrier does not exist for $M_S = 4$, $E^\ddagger = 0$ kcal/mol, and is very low for $M_S = 6$, $E^\ddagger = 2.8$ kcal/mol (compared to 2.4 kcal/mol from Yoshizawa et al., 2000). The imaginary frequency associated with the transition state mode is $220i \text{ cm}^{-1}$ ($M_S = 6$).

The major difference between the transition state and the adsorbed state is the bending of the N-N'-O'' bond angle from 180° in the adsorbed state to 162.9° in the transition state. In the product state the surface oxygen is located 1.68 Å ($M_S = 4$) or 1.66 Å ($M_S = 6$) apart from the Fe atom. The calculated vibrational mode associated with the Fe-O stretch in $Z[FeO]^+$ is 700 cm⁻¹ on the quartet PES and 878 cm⁻¹ on the sextet PES. Taking into account that the enthalpy of reaction is $\Delta H_R(M_S = 4) = -62.2$ kcal/mol or $\Delta H_R(M_S = 6) = -67.9$ kcal/mol, it follows that the reverse reaction is very slow. As a result, bare iron sites are unlikely to exist under reaction conditions in the presence of N₂O. It is worthwhile noting that for bare iron sites the quartet PES ($M_S = 4$) is preferred to the sextet PES ($M_S = 6$), but for oxidized mononuclear iron $Z[FeO]^+$, the reverse is true.

$Z[FeO]^+$ sites are also catalytically active for N₂O dissociation. N₂O adsorbs from the N-end in a barrierless fashion with an enthalpy of adsorption of $\Delta H_{ads}(M_S = 4) = -7.5$ kcal/mol or $\Delta H_{ads}(M_S = 6) = -10.1$ kcal/mol. The zero-point corrected energy of $Z[FeO]^+$ in the sextet state is 3.6 kcal/mol lower than in the quartet state. Since the barrier for transition from the sextet to the quartet state is 6.9 kcal/mol, both spin surfaces should be populated under reaction conditions, but the sextet state should dominate. N₂O adsorption from the O-end is weaker than from the N-end: $\Delta H_{ads}(M_S = 4) = -1.0$ kcal/mol or $\Delta H_{ads}(M_S = 6) = -4.8$ kcal/mol.

Two reaction pathways for N₂O dissociation from $Z[FeO]^+(ON_2)$ sites were found on the quartet and sextet PESs. One reaction pathway leads to $Z[FeO_2]^+$ in which the two O-atoms form either a superoxide O₂⁻ or a peroxide O₂²⁻ anion attached to a Fe²⁺ or Fe³⁺ cation. The other reaction path leads to a dioxo $Z[OFeO]^+$ species. In this section just the reaction pathway leading to $Z[FeO_2]^+$ is discussed. The second pathway is considered in the context of the catalytic cycle occurring on $Z[FeO]^+$. The transition state from $Z[FeO]^+(ON_2)$ to $Z[FeO_2]^+$ is characterized by a bending of the N₂O molecule from 180° in the adsorbed state to 139.8° ($M_S = 4$)/144.5° ($M_S = 6$) in the transition state. In addition, the N'-O'' bond length of the N₂O molecule is increased from 1.20 Å to 1.45 Å ($M_S = 4$) or 1.56 Å ($M_S = 6$) in the transition state. The

activation barrier for the decomposition is $E^\ddagger(M_S = 4) = 29.0$ kcal/mol or $E^\ddagger(M_S = 6) = 30.4$ kcal/mol. The imaginary frequency associated with the transition state mode is $864i$ cm^{-1} ($M_S = 4$) or $825i$ cm^{-1} ($M_S = 6$). Figure 5.9 illustrates the transition state structures on both PESs. Because of an enthalpy of reaction of $\Delta H_R(M_S = 4) = -25.7$ kcal/mol or $\Delta H_R(M_S = 6) = -20.0$ kcal/mol, the reverse reaction has a very high barrier and should not occur readily. Ryder et al. (2002) found for the same reaction an activation barrier with respect to the gas phase of 31.0 kcal/mol. The agreement with the value of 24.0 kcal/mol (on the sextet PES) calculated in this work is reasonable (see Figure 5.7), considering that different basis sets and different quantum packages were used in the two studies.

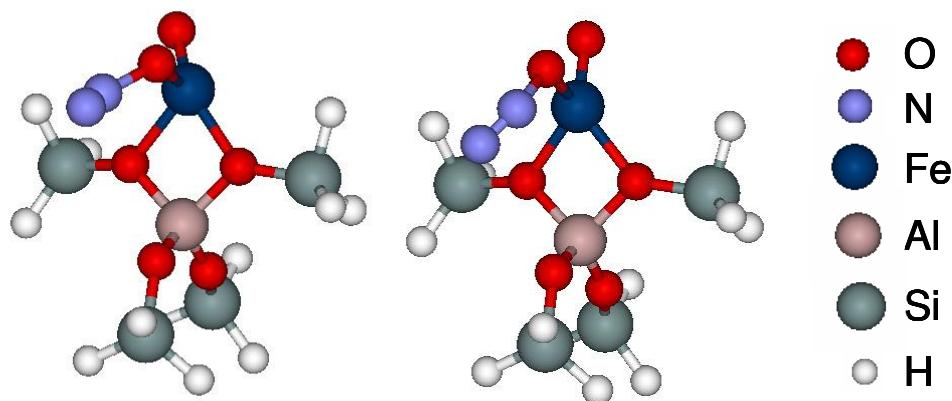


Figure 5.9: Transition state structures for N_2O decomposition on $\text{Z}[\text{FeO}]^+$. On the left $M_S = 4$, on the right $M_S = 6$

Figure 5.6 illustrates that the zero-point corrected energy of $\text{Z}[\text{FeO}_2]^+$ on the quartet PES is approximately 2 kcal/mol higher than on the sextet PES. Since the barrier for the transition from the sextet to the quartet state of this species is 5 kcal/mol, both states are populated with a small preference for the sextet state. The O-O bond length in the $\text{Z}[\text{FeO}_2]^+$ species is calculated to be 1.40 Å ($M_S = 4$) or 1.36 Å ($M_S = 6$). The corresponding Fe-O bond distances are 1.81 Å ($M_S = 4$) or 1.95 Å ($M_S = 6$). Spectroscopic observations made on Fe-ZSM-5 confirm the presence of a stable form of diatomic oxygen associated with Fe. Based on ESR studies of Fe-ZSM-5, Chen et al. (2000) suggested the presence of superoxide ions, O_2^- , at 77 K. On the other hand, Gao et al. (2001) have reported evidence for peroxide, O_2^{2-} , species using UV-Raman

spectroscopy. The calculated vibrational modes associated with O_2 in $Z[FeO_2]^+$ are 969 cm^{-1} and 1015 cm^{-1} on the quartet PES and 1092 cm^{-1} and 1103 cm^{-1} on the sextet PES. Based on the work of Che and Tench (1983) the O-O bond length and the vibrational frequency of $Z[FeO_2]^+$ on the sextet PES suggest a superoxide species, whereas the longer bond length and lower O-O frequency stretches on the quartet PES suggest a species somewhere between a peroxide and a superoxide anion.

Oxygen can desorb from $Z[FeO_2]^+$. The ground state of the oxygen molecule is a triplet $^3\Sigma_g^-$ state with two unpaired electrons. As a result, the O_2 desorption process is accompanied by a change in the spin of the zeolite cluster. If both reactant and product states are on the sextet PES, the barrier for a spin-change is calculated to be 54.1 kcal/mol (sextet/octet PES). In case the reactant is on the sextet PES and the product is on the quartet PES there is no spin change and the energy barrier can be calculated as the energy difference between the desorbed O_2 state minus the adsorbed O_2 state, 52.9 kcal/mol (no transition state was found). If the reactant and product states are on the quartet PES, the calculated spin-surface crossing energy (quartet/sextet PES) is lower than the product-state energy, so that the effective barrier can again be calculated as the energy difference of the product and the reactant state, 50.9 kcal/mol . To conclude, the O_2 desorption barrier is larger than 50 kcal/mol . Therefore, regeneration of an active $Z[Fe]^+$ site is unlikely to happen under reaction conditions, and a $Z[Fe]^+$ site should not be considered as the active site for the nitrous oxide decomposition on Fe-ZSM-5.

5.4.2 Catalytic cycle on $Z[FeO]^+$

As shown in the last section $Z[FeO]^+$ sites are catalytically active. Parts of the catalytic cycle on $Z[FeO]^+$ were discussed above and will not be repeated. As noted above, one reaction pathway for the N_2O dissociation leads to $Z[FeO_2]^+$, whereas another leads to dioxo $Z[OFeO]^+$ species. The transition state for the reaction of $Z[FeO]^+(ON_2)$ to form $Z[OFeO]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 140.5° ($M_S = 4$) or 143.6° ($M_S = 6$) in the transition state, whereas the

length of the N'-O'' bond of the N₂O molecule increases from 1.20 Å to 1.44 Å ($M_S = 4$) or 1.54 Å ($M_S = 6$). The activation barrier for the decomposition is $E^\ddagger(M_S = 4) = 27.5$ kcal/mol or $E^\ddagger(M_S = 6) = 30.7$ kcal/mol. The imaginary frequency associated with the transition state mode is $810i$ cm⁻¹ ($M_S = 4$) or $892i$ cm⁻¹ ($M_S = 6$). Both the transition state structures and the energetics are very similar for the reaction pathways leading to Z[FeO₂]⁺ and Z[OFeO]⁺. Figure 5.10 illustrates the transition state structures on both PESs. The zero-point corrected energy of Z[OFeO]⁺ on the quartet PES is approximately 2 kcal/mol higher than on the sextet PES. The surface O-atoms are located 1.59 Å ($M_S = 4$) or 1.68 Å ($M_S = 6$) from the Fe atom. The O-O bond length is 2.71 Å ($M_S = 4$) or 2.32 Å ($M_S = 6$). There is no chemical bond between the two oxygen atoms. The surface oxygen atoms are much closer to the iron atom in the Z[OFeO]⁺ structure than in the Z[FeO₂]⁺ structure and, therefore, much more similar to Z[FeO]⁺, for which the Fe-O bond length is 1.68 Å ($M_S = 4$) or 1.66 Å ($M_S = 6$). The calculated vibrational modes associated with the Fe-O stretch in Z[OFeO]⁺ are 955 cm⁻¹ and 1012 cm⁻¹ on the quartet PES and 643 cm⁻¹ and 868 cm⁻¹ on the sextet PES. Figures 5.6 and 5.7 illustrate that the Z[OFeO]⁺ species is 8.3 kcal/mol higher in energy than the Z[FeO₂]⁺ species. A reaction pathway connecting Z[OFeO]⁺ and Z[FeO₂]⁺ was found. The activation energy for this reaction is $E^\ddagger(M_S = 4) = 22.2$ kcal/mol or $E^\ddagger(M_S = 6) = 14.2$ kcal/mol (starting from Z[OFeO]⁺). The imaginary frequency associated with the transition state mode is $702i$ cm⁻¹ ($M_S = 4$) or $636i$ cm⁻¹ ($M_S = 6$). Both Z[OFeO]⁺ and Z[FeO₂]⁺, should be present under reaction conditions with Z[FeO₂]⁺ as the dominant species.

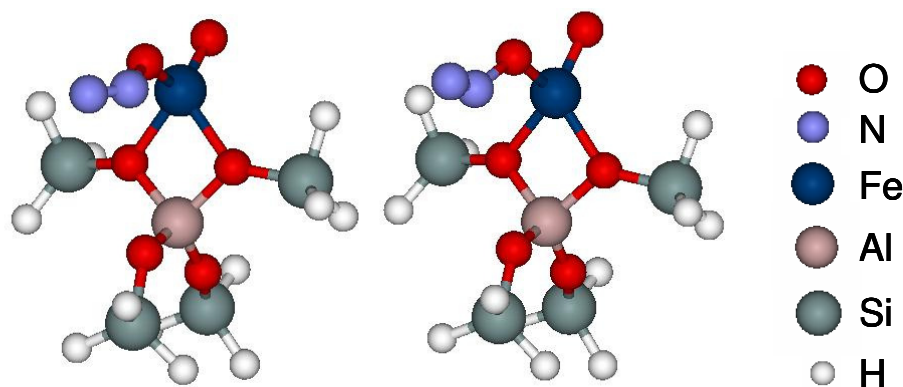


Figure 5.10: Transition state structures for N₂O decomposition on Z[FeO]⁺. On the left $M_S = 4$, on the right $M_S = 6$

Both $Z[\text{OFeO}]^+$ and $Z[\text{FeO}_2]^+$ sites are catalytically active for the N_2O dissociation. N_2O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{\text{ads}}(M_S = 4) = 4.5$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = -3.2$ kcal/mol on $Z[\text{OFeO}]^+$, and with an enthalpy of adsorption of $\Delta H_{\text{ads}}(M_S = 4) = 0.3$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = -2.3$ kcal/mol on $Z[\text{FeO}_2]^+$. N_2O adsorption through the O-end is as weak as through the N-end: $\Delta H_{\text{ads}}(M_S = 4) = 4.5$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = -3.0$ kcal/mol on $Z[\text{OFeO}]^+$ and $\Delta H_{\text{ads}}(M_S = 4) = 0.7$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = -1.2$ kcal/mol on $Z[\text{FeO}_2]^+$. Taking into account the loss of entropy associated with the adsorption process, it follows that N_2O does not adsorb on the quartet PES and only weakly on the sextet PES.

One reaction pathway was found for N_2O dissociation from $Z[\text{OFeO}]^+(\text{ON}_2)$ and one for $Z[\text{FeO}_2]^+(\text{ON}_2)$, yielding $Z[\text{O}_2\text{FeO}]^+$. The transition state for the reaction leading from $Z[\text{OFeO}]^+(\text{ON}_2)$ to $Z[\text{O}_2\text{FeO}]^+$ is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 149.7° ($M_S = 4$) or 139.7° ($M_S = 6$) in the transition state. In addition, the $\text{N}'\text{-O}''$ bond length of the N_2O molecule increases from $1.20 \text{ \AA}$ to $1.68 \text{ \AA}$ ($M_S = 4$) or $1.42 \text{ \AA}$ ($M_S = 6$) in the transition state. The activation barrier for the decomposition is $E^\ddagger(M_S = 4) = 42.9$ kcal/mol and $E^\ddagger(M_S = 6) = 16.5$ kcal/mol. The imaginary frequency associated with the transition state mode is $790i \text{ cm}^{-1}$ ($M_S = 4$) and $716i \text{ cm}^{-1}$ ($M_S = 6$). On the sextet PES the transition state involves first the formation of a superoxide species on top of the iron atom. From the activation barriers it follows that the quartet PES is non-reactive while the sextet PES is very reactive. Figure 5.11 illustrates the transition state structures on both PES. From the heats of reaction, $\Delta H_R(M_S = 4) = -28.8$ kcal/mol or $\Delta H_R(M_S = 6) = -18.3$ kcal/mol, it can be concluded that the reverse reaction is very slow and that decomposition is essentially irreversible.

The transition state for the reaction leading from $Z[\text{FeO}_2]^+(\text{ON}_2)$ to $Z[\text{O}_2\text{FeO}]^+$ is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 140.8° ($M_S = 4$) or 139.9° ($M_S = 6$) in the transition state. In addition, the $\text{N}'\text{-O}''$ bond length of the N_2O molecule is increased from $1.20 \text{ \AA}$ to $1.44 \text{ \AA}$ ($M_S = 4$) or $1.42 \text{ \AA}$ ($M_S = 6$) in the transition state. The activation barrier for decomposition is

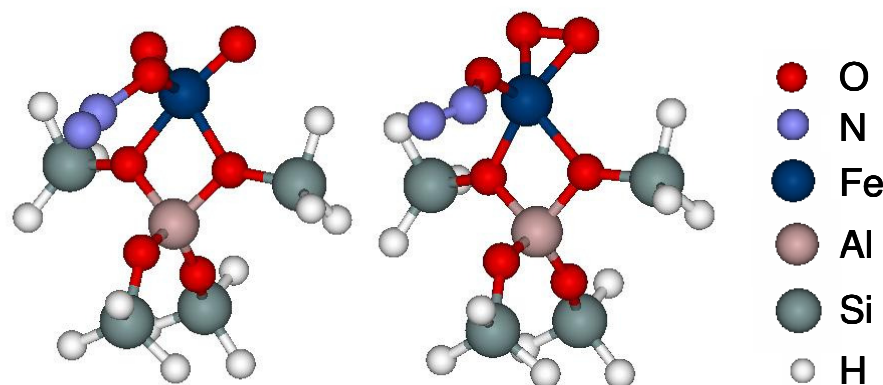


Figure 5.11 Transition state structures for N_2O decomposition on $\text{Z}[\text{OFeO}]^+$. On the left $M_S = 4$, on the right $M_S = 6$. On the sextet PES a superoxide species is formed before N_2O decomposition; on the quartet PES after N_2O decomposition.

$E^\ddagger(M_S = 4) = 24.0$ kcal/mol or $E^\ddagger(M_S = 6) = 20.1$ kcal/mol. The imaginary frequency associated with the transition-state mode is $732i$ cm^{-1} ($M_S = 4$) and $717i$ cm^{-1} ($M_S = 6$). Figure 5.12 illustrates the transition state structures on both PESs. Taking into account the enthalpy of reaction, $\Delta H_R(M_S = 4) = -16.8$ kcal/mol or $\Delta H_R(M_S = 6) = -12.0$ kcal/mol and transition-state energy, it can be concluded that the reverse reaction is slow and that decomposition is again essentially irreversible. It is important to note that the activation barrier with respect to the gas phase for N_2O decomposition on $\text{Z}[\text{FeO}_2]^+$ and on $\text{Z}[\text{OFeO}]^+$, 17.3 kcal/mol or 12 kcal/mol (both $M_S = 6$), is lower than the activation barrier for N_2O decomposition on $\text{Z}[\text{FeO}]^+$, 24.0 or 24.3 kcal/mol (both $M_S = 6$). This relationship is in opposition to conclusions drawn from experimental studies (Kiwi-Minsker, 2003; Wood et al., 2004; Bulushev et al., 2004) and calculations reported by Ryder et al. (2002). Nevertheless, it will be shown in chapter 6 that this result does not contradict experimental data.

$\text{Z}[\text{O}_2\text{FeO}]^+$ consists of a superoxide O_2^- anion and a O^- or O^{2-} anion on top of a Fe^{2+} or Fe^{3+} cation. The O-O bond length of the superoxide O_2^- anion is 1.29 Å ($M_S = 4$) or 1.31 Å ($M_S = 6$). The Fe-O bond distance of the superoxide anion to the iron cation is 1.89 Å and 2.20 Å on the quartet PES and 1.91 Å and 2.06 Å on the sextet PES. Based on the O-O bond distance and the associated vibrational frequency, 1227 cm^{-1} ($M_S = 4$)

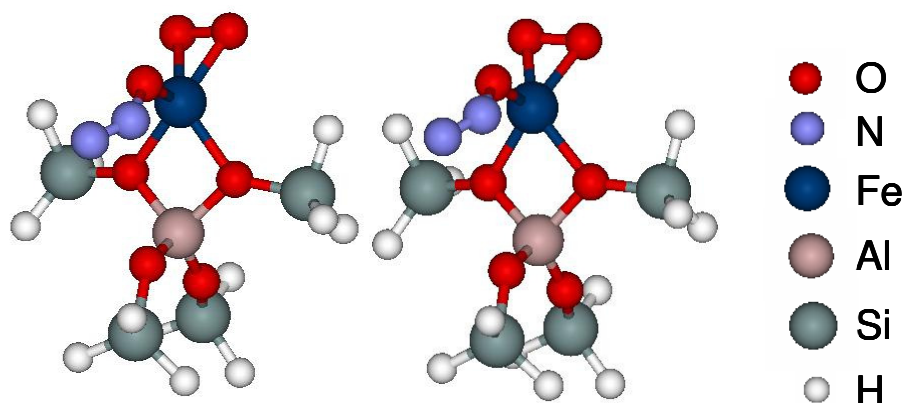


Figure 5.12 Transition state structures for N_2O decomposition on $\text{Z}[\text{FeO}_2]^+$. On the left $M_S = 4$, on the right $M_S = 6$.

or 1191 cm^{-1} ($M_S = 6$), the diatomic oxygen can be best described as a superoxide anion. The third O-anion bonded to the iron cation has a Fe-O distance of $1.63\text{ \AA}$ ($M_S = 4$) or $1.62\text{ \AA}$ ($M_S = 6$) and a vibrational mode associated with Fe-O stretches of 913 cm^{-1} ($M_S = 4$) or 923 cm^{-1} ($M_S = 6$). It is interesting to note that for $\text{Z}[\text{O}_2\text{FeO}]^+$ the quartet PES is again preferred to the sextet PES by 1.5 kcal/mol .

Oxygen can desorb from $\text{Z}[\text{O}_2\text{FeO}]^+$. As mentioned above, the ground state of the oxygen molecule is a triplet $^3\Sigma_g^-$ state with two unpaired electrons so that O_2 desorption is accompanied by a spin change of the zeolite cluster. If the cluster representations of both reactant and product states lie on the sextet PES, the spin-change barrier is calculated to be 8.0 kcal/mol (sextet/octet PES) for the desorption reaction. By contrast, if the reactant state is on the sextet PES and the product state is on the quartet PES no spin change occurs and the transition state for the O_2 desorption can be determined. In this case, the activation barrier is $E^\ddagger = 6.9\text{ kcal/mol}$. The imaginary frequency associated with the transition state mode is $83i\text{ cm}^{-1}$ ($M_S = 6$). Finally, for the case where the reactant and product states are on the quartet PES the calculated spin-surface crossing barrier (quartet/sextet PES) is 21.6 kcal/mol . It is important to note that the enthalpy of O_2 desorption is very small: $\Delta H_R(M_S = 4) = 4.2\text{ kcal/mol}$, $\Delta H_R(M_S = 6) = -0.6\text{ kcal/mol}$, $\Delta H_R(M_S = 6/4) = 3.0\text{ kcal/mol}$. Therefore, O_2 desorption from $\text{Z}[\text{O}_2\text{FeO}]^+$ from the more reactive sextet PES should be very fast. The low enthalpy of desorption

is consistent with the absence of O₂ inhibition on the rate of N₂O decomposition on Fe-ZSM-5 (Fu et al. 1981; Leglise et al., 1984; Panov et al., 1990; Kapteijn et al., 1997). The adsorption process is entropically very unfavorable, so that a significant enthalpy of adsorption is required to poison Z[FeO]⁺ sites by O₂. The fast O₂ desorption process on the other hand is a contradiction to experimental results from Wood et al. (2004) and Bulushev et al. (2004) who claim that the desorption process is the rate-limiting step in the N₂O decomposition cycle.

5.4.3 Catalytic cycle on Z[FeO₂]⁺

A third possible starting structure for the catalytic cycle on iron oxo sites is Z[FeO₂]⁺. Since the N₂O decomposition on Z[FeO₂]⁺ to produce Z[O₂FeO]⁺ was examined in the preceding section, this reaction will not be discussed further here. N₂O adsorbs on Z[O₂FeO]⁺ through the N-end with an enthalpy of adsorption of $\Delta H_{\text{ads}}(M_S = 4) = 0.7$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = 1.4$ kcal/mol. N₂O adsorbs somewhat more strongly through its O-end, $\Delta H_{\text{ads}}(M_S = 4) = -0.2$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = 0.3$ kcal/mol. However, hardly any N₂O would be expected to adsorb on Z[O₂FeO]⁺ sites under reaction conditions. No reaction pathway was found for N₂O decomposition on Z[O₂FeO]⁺ on the quartet PES but only on the sextet PES. The transition state for the decomposition of Z[O₂FeO]⁺(ON₂) to form Z[O₂FeO₂]⁺ on the sextet PES is characterized by a bending of the N₂O molecule from 180° in the adsorbed state to 137.0° ($M_S = 6$) in the transition state and an increase in the N'-O'' bond length from 1.20 Å to 1.35 Å. In addition, the oxygen atom of N₂O forms a bond with the single O-atom attached to Fe. The length of this O-O bond is 1.58 Å. The activation barrier for N₂O decomposition is $E^\ddagger(M_S = 6) = 41.1$ kcal/mol and the imaginary frequency associated with the transition-state mode is 728i cm⁻¹. The enthalpy of reaction for this process is $\Delta H_R(M_S = 6) = -25.5$ kcal/mol. The surface oxygen atoms in Z[O₂FeO₂]⁺ sites are grouped into two adsorbed superoxide anions. The surface O-atoms are 2.02 to 2.05 Å apart from the Fe³⁺ cation. The O-O bond length of the superoxide ions is 1.31 to 1.32 Å. The vibrational modes associated with O-O stretches are 1170 cm⁻¹ and 1206 cm⁻¹.

Oxygen can desorb from $Z[O_2FeO_2]^+$. When the reactant and product states lie on the sextet PES, the spin-change barrier is calculated to be 5.8 kcal/mol (sextet/octet PES) and the enthalpy of desorption is $\Delta H_R(M_S = 6) = -0.2$ kcal/mol. For the case where the reactant is on the sextet PES and the product is on the quartet PES there is no spin change and a transition state for the O_2 desorption can be found. The activation barrier for this reaction is $E^\ddagger = 11.4$ kcal/mol and the enthalpy change for desorption is $\Delta H_R(M_S = 6) = 1.5$ kcal/mol. The imaginary frequency associated with the transition state mode is $68i\text{ cm}^{-1}$ ($M_S = 6$). To conclude, owing to the high activation barrier of $E^\ddagger(M_S = 6) = 41.1$ kcal/mol for the second N_2O decomposition reaction and the very fast O_2 desorption possibility on $Z[O_2FeO]^+$ sites, $Z[FeO_2]^+$ sites are unlikely to be the starting structure for the catalytic cycle for N_2O decomposition on Fe-ZSM-5.

5.4.4 H_2O adsorption on $Z[FeO]^+$

Since $Z[FeO]^+$ sites are expected to be essential for the decomposition of N_2O over Fe-ZSM-5, it is important to understand how such species might interact with water vapor, and whether such interaction could lead to deactivation of these sites. The interaction of water with $Z[FeO]^+$ proceeds via a two step mechanism. First water adsorbs on $Z[FeO]^+$ sites and then the adsorbed water dissociates to form a stable iron dihydroxo species, $Z[Fe(OH)_2]^+$. As illustrated in Figure 5.13 for the quartet PES and in Figure 5.14 for the sextet PES, H_2O adsorption on $Z[FeO]^+$ is barrierless, and occurs with an enthalpy of adsorption of $\Delta H_{ads}(M_S = 4) = -8.8$ kcal/mol or $\Delta H_{ads}(M_S = 6) = -15.6$ kcal/mol. The Fe-O bond distance of the adsorbed water molecule is $2.25\text{ \AA}$ ($M_S = 4$) or $2.15\text{ \AA}$ ($M_S = 6$). The transition state for the dissociation of adsorbed H_2O is characterized by a decrease in the Fe-O (from that for H_2O) bond length to $1.98\text{ \AA}$ ($M_S = 4$) or $2.04\text{ \AA}$ ($M_S = 6$) and an increase in one of the H-O bond lengths from $0.97\text{ \AA}$ ($M_S = 4/6$) to $1.18\text{ \AA}$ ($M_S = 4$) or $1.20\text{ \AA}$ ($M_S = 6$). The H-O distance to the second oxygen atom in the transition state structure is $1.28\text{ \AA}$ ($M_S = 4$) or $1.29\text{ \AA}$ ($M_S = 6$). Thus, in the transition state the transferred H-atom lies midway between the two surface O-atoms. Figure 5.15 illustrates the transition state structures on both PES. The activation barrier for this reaction is $E^\ddagger(M_S = 4) = 1.9$ kcal/mol or $E^\ddagger(M_S = 6) = 9.2$

kcal/mol and the imaginary frequency associated with the transition-state mode is $1421i$ cm^{-1} ($M_S = 4$) or $1528i$ cm^{-1} ($M_S = 6$). Since the enthalpy of reaction is $\Delta H_R(M_S = 4) = -23.5$ kcal/mol or $\Delta H_R(M_S = 6) = -27.1$ kcal/mol, the rate of the forward reaction is predicted to be fast and the rate of the reverse reaction to be slow. Further comparison of the electronic energy of a $Z[\text{Fe}(\text{OH})_2]^+$ site on the quartet and sextet PES shows that the dihydroxo iron species is more stable by 14.9 kcal/mol on the sextet PES than on the quartet PES.

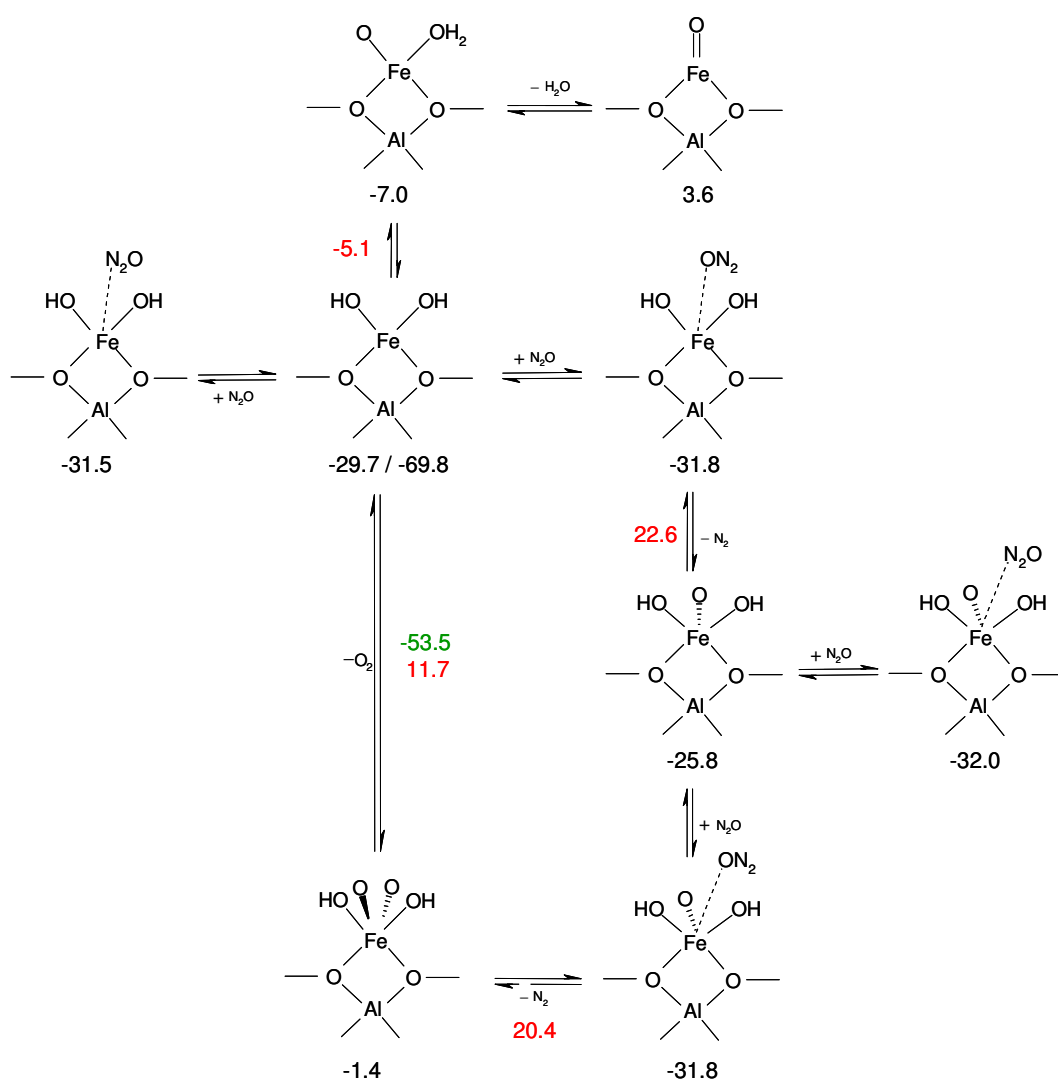


Figure 5.13: Reaction network of the N_2O dissociation on mononuclear iron hydroxo species. All energies are zero-point corrected, in kcal/mol and with reference to $Z[\text{FeO}]^+$ ($M_S = 6$) with the appropriate amounts of N_2O , O_2 , N_2 , H_2O . Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PES ($M_S = 4$ and $M_S = 6$) are in green. Structures in black are on the PES with $M_S = 4$.

Mononuclear iron dihydroxo species exist almost exclusively on the sextet PES. The Fe-OH bond distances in $Z[\text{Fe}(\text{OH})_2]^+$ are 1.77 Å ($M_S = 4$) or 1.80 Å ($M_S = 6$). The calculated vibrational modes associated with O-H stretches are 3829 cm^{-1} and 3836 cm^{-1} on the quartet PES and 3886 cm^{-1} and 3891 cm^{-1} on the sextet PES. Consistent with this analysis, EXAFS studies by Choi et al. (2003) confirm that $Z[\text{Fe}(\text{OH})_2]^+$ is a majority species in Fe-ZSM-5 after pretreatment in He at 573 K.

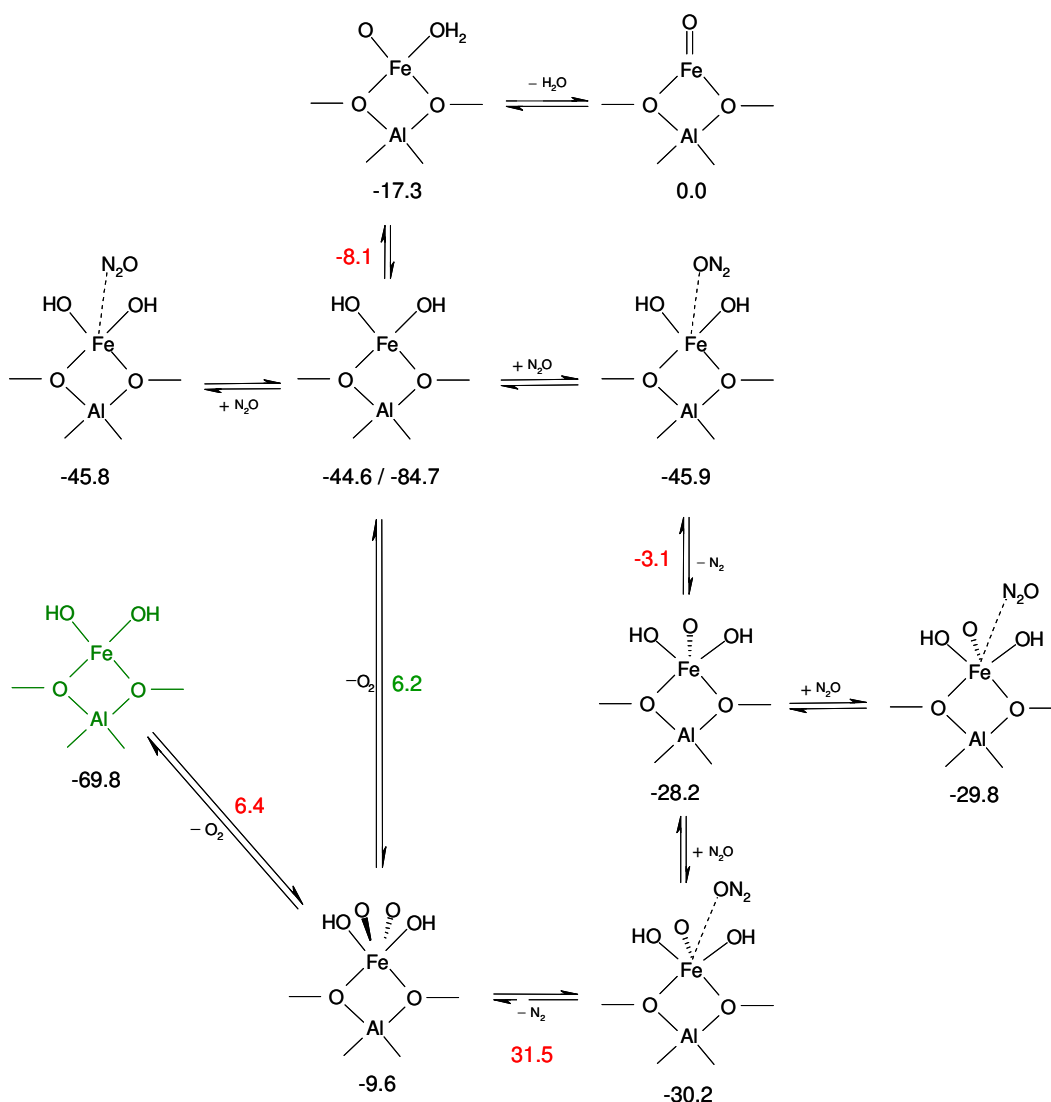


Figure 5.14: Reaction network of the N_2O dissociation on mononuclear iron hydroxo species. All energies are zero-point corrected, in kcal/mol and with reference to $Z[\text{FeO}]^+$ ($M_S = 6$) with the appropriate amounts of N_2O , O_2 , N_2 , H_2O . Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PES ($M_S = 6$ and $M_S = 8$) are in green. Structures in black are on the PES with $M_S = 6$. Structures in green are on the PES with $M_S = 4$.

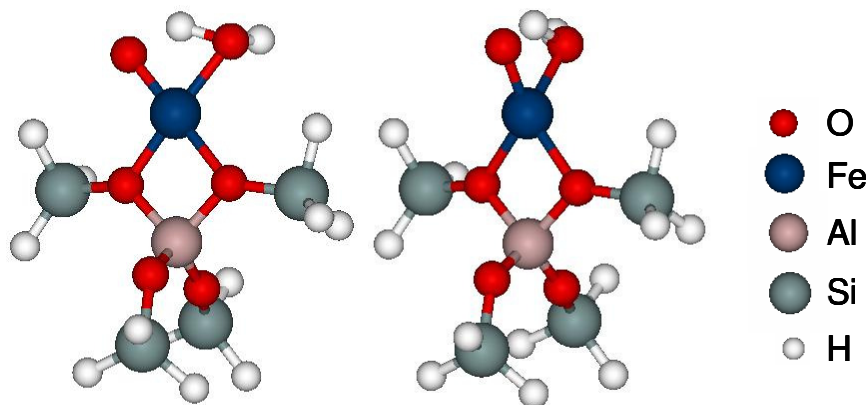


Figure 5.15: Transition state structures for formation of $Z[Fe(OH)_2]^+$. On the left $M_S = 4$, on the right $M_S = 6$.

5.4.5 Catalytic cycle on $Z[Fe(OH)_2]^+$

To assess whether $Z[Fe(OH)_2]^+$ species might be involved in N_2O decomposition on Fe-ZSM-5, an analysis of the energetics for this process was carried out. As illustrated in Figure 5.13 and 5.14, N_2O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{ads}(M_S = 4) = -0.2$ kcal/mol or $\Delta H_{ads}(M_S = 6) = 0.4$ kcal/mol. An equally weak adsorption was calculated for N_2O adsorbing through the O-end, $\Delta H_{ads}(M_S = 4) = -0.5$ kcal/mol or $\Delta H_{ads}(M_S = 6) = 0.2$ kcal/mol. Thus, hardly any N_2O adsorption is expected on $Z[Fe(OH)_2]^+$. Dissociative adsorption of N_2O is possible, but the activation barrier for this process is large. The activation barrier is $E^\ddagger(M_S = 4) = 54.4$ kcal/mol or $E^\ddagger(M_S = 6) = 42.8$ kcal/mol and the imaginary frequency associated with the transition-state mode is $583i$ cm^{-1} ($M_S = 4$) or $676i$ cm^{-1} ($M_S = 6$). The major difference between the transition state and the adsorbed state is the bending of the N-N'-O'' bond angle from 180° in the adsorbed state to 161.9° ($M_S = 4$) or 154.8° ($M_S = 6$) in the transition state. In addition, the N'-O'' bond length increases from 1.20 Å to 1.74 Å ($M_S = 4$) or 1.61 Å ($M_S = 6$). The reaction is endothermic, with an enthalpy of reaction of $\Delta H_R(M_S = 4) = 5.75$ kcal/mol or $\Delta H_R(M_S = 6) = 16.7$ kcal/mol. In the product state the adsorbed O-atom is located 1.71 Å ($M_S = 4/6$) from the Fe atom.

In principle, $Z[\text{OFe}(\text{OH})_2]^+$ species could act as a catalytically active center for N_2O decomposition. N_2O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{\text{ads}}(M_S = 4) = -5.5$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = -0.2$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{\text{ads}}(M_S = 4) = -5.4$ kcal/mol or $\Delta H_{\text{ads}}(M_S = 6) = -0.5$ kcal/mol. The transition state for N_2O dissociation from $Z[\text{OFe}(\text{OH})_2]^+(\text{ON}_2)$ is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 165.8° ($M_S = 4$) or 160.5° ($M_S = 6$) in the transition state and a lengthening of the N'-O'' bond from 1.20 Å to 1.70 Å ($M_S = 4$) or 1.85 Å ($M_S = 6$). The activation barrier for N_2O decomposition is $E^\ddagger(M_S = 4) = 52.2$ kcal/mol or $E^\ddagger(M_S = 6) = 61.7$ kcal/mol and the imaginary frequency associated with the transition state mode is $768i$ cm^{-1} ($M_S = 4$) or $484i$ cm^{-1} ($M_S = 6$). Here too N_2O decomposition is endothermic, with an enthalpy of reaction of $\Delta H_R(M_S = 4) = 30.4$ kcal/mol or $\Delta H_R(M_S = 6) = 19.4$ kcal/mol. Thus, hardly any N_2O is expected to decompose on $Z[\text{OFe}(\text{OH})_2]^+$.

In $Z[\text{O}_2\text{Fe}(\text{OH})_2]^+$, iron takes on an approximately octahedral coordination. The Fe-O distances of the two surface oxygen species are 1.68 Å to 1.71 Å ($M_S = 4$) or 1.79 Å to 1.93 Å ($M_S = 6$). The OH-groups are 1.78 Å to 2.06 Å ($M_S = 4$) or 1.68 Å to 1.74 Å ($M_S = 6$) from the Fe center away. Oxygen can desorb from $Z[\text{O}_2\text{Fe}(\text{OH})_2]^+$. If both the reactant and product states lie on the sextet PES, the spin-change barrier for desorption is calculated to be 15.8 kcal/mol (sextet/octet PES) and the enthalpy of desorption is calculated to be $\Delta H_R(M_S = 6) = -74.3$ kcal/mol. For the case where the reactant is on the sextet PES and the product is on the quartet PES, there is no spin change, and a transition state for the O_2 desorption can be found. The activation barrier in this case is $E^\ddagger = 16.0$ kcal/mol and the enthalpy of desorption is $\Delta H_R(M_S = 6) = -60.2$ kcal/mol. The imaginary frequency associated with the transition state mode (formation of a surface O_2 molecule) is $1076i$ cm^{-1} ($M_S = 6$). When both reactant and product states are on the quartet PES, there is first a transition state for the O_2 formation and then at a significantly lower energy a spin change. The activation barrier for this reaction is therefore determined by the transition state which is $E^\ddagger = 13.1$ kcal/mol, and the enthalpy of desorption that is $\Delta H_R(M_S = 6) = -68.8$ kcal/mol. The imaginary frequency associated with the transition-state mode is $763i$ cm^{-1} ($M_S = 6$).

In summary, throughout the catalytic cycle for N_2O decomposition on $\text{Z}[\text{Fe}(\text{OH})_2]^+$ the sextet PES is significantly lower in energy than the quartet PES. However, $\text{Z}[\text{Fe}(\text{OH})_2]^+$ species are not candidate sites for the N_2O decomposition on Fe-ZSM-5. Both elementary steps involving N_2O dissociation are strongly endothermic and possess significant activation barriers.

5.5 Comparison with experimental observation

The analysis presented in the preceding sections suggests that $\text{Z}[\text{FeO}]^+$ species could serve as the catalytically active center for N_2O decomposition, as previously proposed by Ryder et al. (2002) and Wood et al. (2004). The adsorption of water by these species results in the formation of $\text{Z}[\text{Fe}(\text{OH})_2]^+$, which is projected to exhibit very little activity for N_2O decomposition. Consequently, the dehydration of Fe-ZSM-5 is predicted to be an essential step for its activation. This conclusion is supported by the work from Kiwi-Minsker et al. (2003), who showed that an increasing fraction of the Fe in Fe-ZSM-5 becomes active for N_2O decomposition as the temperature and time of catalyst pretreatment in He is raised. These authors also demonstrated that exposure to water vapor of Fe-ZSM-5 originally pretreated at elevated temperature leads to a loss in the fraction of the Fe sites active for N_2O decomposition.

Since the loss of water via dehydration is projected to be a slow process, given the high activation barrier for desorption and the large heat of adsorption for water, it is likely that in most studies of N_2O decomposition over Fe-ZSM-5 reported in the literature the catalyst is only partially dehydrated. Likewise, it is conceivable that the gases used in experimental studies are not totally free of water vapor and that this too could affect the catalyst activity and the apparent rate coefficient. To determine what effect water vapor might have on the apparent activation energy and preexponential factor for N_2O decomposition, a microkinetic analysis using all 63 elementary reactions listed in Table 5.1 was carried out. The temperature of the reactor was then varied and the logarithm of the apparent first order rate coefficient (obtained under steady state conditions) was

plotted versus inverse absolute temperature, to determine the apparent activation energy and preexponential factor. Separate calculations confirmed that the rate of N_2O decomposition is first order in N_2O and zero order in O_2 concentration, $r_{\text{N}_2\text{O}} = -k_{\text{app}} P_{\text{N}_2\text{O}}$, consistent with experimental observation (Panov et al., 1990; Kapteijn et al., 1997; Fu et al., 1981; Leglise et al., 1984). As noted in Table 5.3, the presence of water concentrations below 100 ppb has a profound effect on the apparent rate. For example, in the absence of any water vapor, the apparent activation energy is predicted to be 25.5 kcal/mol and the preexponential factor is predicted to be $4.0 \times 10^3 \text{ mol}_{\text{N}_2\text{O}}/(\text{s} \cdot \text{mol}_{\text{Fe}} \cdot \text{Pa}_{\text{N}_2\text{O}})$, whereas in the presence of 100 ppb, the activation energy increases to 54.8 kcal/mol and the preexponential factor increases by nine orders of magnitude to $6.8 \times 10^{12} \text{ mol}_{\text{N}_2\text{O}}/(\text{s} \cdot \text{mol}_{\text{Fe}} \cdot \text{Pa}_{\text{N}_2\text{O}})$. Since the water content in the gases used for experimental studies is not reported, it is not possible to make a direct comparison between the apparent activation energy predicted using the rate parameters given in Table 5.1 and those determined from experiments. It is possible to ask, though, what concentration of water vapor would be required to match an experimentally measured value of the apparent activation energy. Comparison was made with the data of Wood et al. (2004), who used a sample of Fe-ZSM-5 for which it had been established by EXAFS that Fe was present as isolated Fe cations. If the water vapor content is assumed to be 23 ppb, then we obtain the same apparent activation energy as that reported by Wood et al. (2004), 44.2 kcal/mol. The apparent preexponential factor measured by these authors is $9.9 \times 10^8 \text{ mol}_{\text{N}_2\text{O}}/(\text{s} \cdot \text{mol}_{\text{Fe}} \cdot \text{Pa}_{\text{N}_2\text{O}})$, whereas that predicted is $3.9 \times 10^9 \text{ mol}_{\text{N}_2\text{O}}/(\text{s} \cdot \text{mol}_{\text{Fe}} \cdot \text{Pa}_{\text{N}_2\text{O}})$. This agreement is quite unanticipated and provides support to our reaction pathway analysis and estimation of rate parameters.

As a further test of the mechanism and kinetics determined in this study, the activation energies and preexponential factors reported by Zhu et al. (2002) for a number of different samples of Fe-ZSM-5 are compared. Figure 5.16 shows that all of the pairs of activation energies and preexponential factors measured by these authors fall along the line predicted on the basis of variations in the concentration of water vapor present in the reactor under steady-state conditions. Also shown for completeness is the data point noted earlier from the work of Wood et al. (2004). The remarkable agreement between

TABLE 5.3: Experimental and computed steady state rate parameters for the overall reaction rate constant of the nitrous oxide decomposition in Fe-ZSM-5[§]

Activation Energies and Preexponential Factors Calculated for the Stoichiometric Decomposition of N ₂ O to N ₂ and O ₂			
Water content (ppb)	Activation energy (kcal/mol)	Preexponential Factor (mol N ₂ O/s·mol Fe·Pa N ₂ O)	Reference
unknown	44.2	9.9×10^8	Wood et al. (2004)
unknown	32.5	4.4×10^5	Zhu et al. (2002) ^a
unknown	36.1	4.4×10^6	Zhu et al. (2002) ^b
unknown	44.4	4.7×10^9	Zhu et al. (2002) ^{a,c}
unknown	50.9	2.4×10^{11}	Zhu et al. (2002) ^{b,c}
unknown	46.6	3.5×10^{10}	Zhu et al. (2002) ^{a,d}
unknown	49.0	1.3×10^{11}	Zhu et al. (2002) ^{b,d}
0	25.5	4.0×10^3	This work
1	28.4	3.7×10^4	This work
23	44.2	3.9×10^9	This work
100	54.8	6.8×10^{12}	This work

(a) Si/Al = 20 (b) Si/Al = 30 (c) High-temperature pretreatment (d) Steam pretreatment

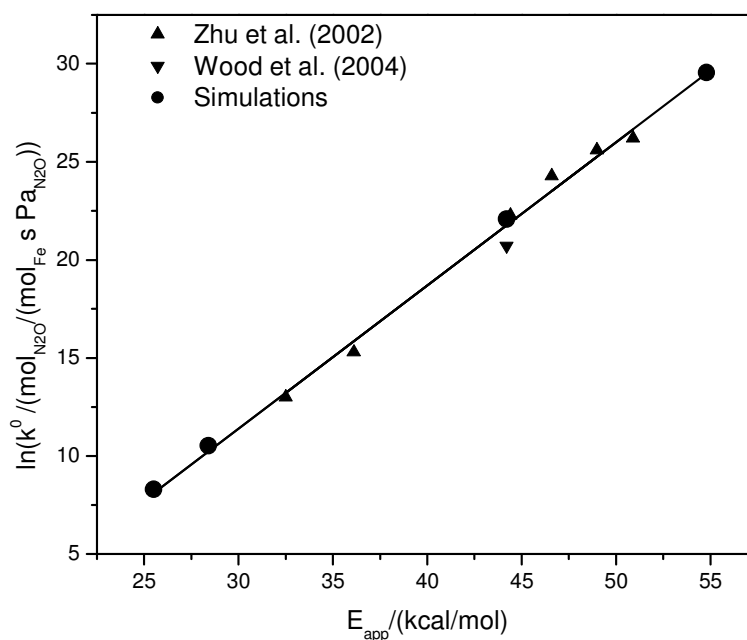
[§] Computed data are calculated with different amounts of water in reactant stream over the temperature range from 600 to 700 K.

Figure 5.16: Plot of logarithm of experimental and computed apparent preexponential factor versus apparent activation barrier.

theory and experiment seen in this figure suggests that the correlation between preexponential factor and activation energy is due primarily to the water vapor content in the reactor. The apparent “compensation relation” (Bond et al., 2000) observed in Figure 5.16 is what would be expected if all catalysts, irrespective of water content in the feed or catalyst, achieve an equivalent rate at some temperature, i.e., all Arrhenius plots cross at a single point. From the slope of the line in Figure 5.16, this temperature is deduced to be 690 K. This means that at 690 K the rate of N_2O decomposition would be expected to be independent of the water content of the reactants because at this temperature only a small fraction of the $\text{Z}[\text{FeO}]^+$ sites will be hydrated, and hence inactive for N_2O decomposition. Below this temperature the water vapor concentration has a significant effect on the apparent rate constant and, consequently, on the apparent preexponential factor and activation barrier obtained experimentally.

The analysis of N_2O decomposition presented here indicates that the rate of molecular oxygen desorption is rapid due to the low activation energy associated with this process, $E^\ddagger (M_S = 6/4) = 6.9 \text{ kcal/mol}$ and $E^\ddagger (M_S = 6) = 8.0 \text{ kcal/mol}$. Although this finding is consistent with the experimental observation that N_2O decomposition is not inhibited by the adsorption of O_2 , the calculated values of $E^\ddagger$ differ from those previously reported on the basis of calculations and determined from temperature-programmed desorption (TPD) studies. Thus, calculations by Ryder et al. (2002) based on DFT report a value of $E^\ddagger = 51.9 \text{ kcal/mol}$ and TPD studies by Wood et al. (2004) and Bulushev et al. (2004) give a value of $E^\ddagger = 45.7 \text{ kcal/mol}$. The high value of $E^\ddagger$ by Ryder et al. (2002) is a consequence of failing to account for the change in spin states occurring during the desorption of O_2 from $\text{Z}[\text{O}_2\text{FeO}]^+$, as was done in the present study. As will be discussed in the next chapter, the values of $E^\ddagger$ determined from TPD experiments are attributable to oxygen desorption from $\text{Z}[\text{FeO}_2]^+$, rather than from $\text{Z}[\text{O}_2\text{FeO}]^+$. In support of this idea, it is noted that in Table 5.1g and h, the value $E^\ddagger$ for the desorption of O_2 from $\text{Z}[\text{Fe}(\text{O})_2]^+$ is calculated to be 50.9 kcal/mol for $M_S = 4$ and 54.2 kcal/mol for $M_S = 6$.

5.6 Conclusions

The reaction mechanism of the nitrous oxide decomposition was investigated on hydrated and dehydrated mononuclear iron sites in Fe-ZSM-5 using density functional theory. The most probable catalytic cycle starts on a $Z[FeO]^+$ site. The first N_2O decomposition results in $Z[FeO_2]^+$ and $Z[OFeO]^+$ sites. These are potential structures for the α -oxygen sites in Fe-ZSM-5 and present, therefore, alternative α -oxygen sites to the $Z[FeO]^+$ site proposed by Yoshizawa et al. (2003). $Z[FeO_2]^+$ sites are much more dominant than $Z[OFeO]^+$ sites. As suggested by experiment, water adsorbs strongly on $Z[FeO]^+$ sites and deactivates these sites. Macroscopic reactor simulations demonstrate that water concentrations in the range of 1 to 100 ppb have a significant influence on the surface composition and apparent rate coefficients. This is especially relevant in the temperature range from 600 to 700 K where most kinetic studies are performed. Apparent activation barriers determined over this temperature range vary from 28.4 kcal/mol (1 ppb H_2O) to 54.8 kcal/mol (100 ppb H_2O). The catalyst surface changes dramatically with temperature if traces of water are present. At 600 K the surface is covered with $Z[Fe(OH)_2]^+$ sites and hardly any active $Z[FeO]^+$ or $Z[FeO_2]^+$ sites are present. At 700 K water desorbs from $Z[Fe(OH)_2]^+$ sites, and $Z[FeO]^+$ sites and $Z[FeO_2]^+$ sites then form the majority surface species. It was possible to match the experimental activation barrier from Wood et al. (2004) of 44.2 kcal/mol with a water content of 23 ppb in the He stream. The preexponential factor is in this case $3.9 \times 10^9 \text{ mol}_{N_2O}/(\text{s} \cdot \text{mol}_{Fe} \cdot \text{Pa}_{N_2O})$. The calculated preexponential factor is approximately a factor four larger than the experimental one. This level of agreement is remarkable, considering all of the approximations existent in the theoretical methods used to calculate the rate parameters for each elementary reaction. Finally, it can be concluded that the spread in the values of the rate parameters reported by different research groups is likely a reflection of the influence of water impurities.

6 Kinetic modeling of nitrous oxide decomposition on Fe-ZSM-5

In chapter 5, a reaction mechanism for the decomposition of N_2O on Fe-ZSM-5 has been proposed based on a detailed density functional theory analysis of the energetics for alternative pathways. This work suggested that isolated Fe cations bound to a single oxygen atom (viz., $\text{Z}[\text{FeO}]^+$) are the active sites for N_2O decomposition. It was also shown that the presence of water vapor in the feed stream to the catalyst can deactivate these sites but this process was demonstrated to be reversible at temperatures above about 690 K.

Goals of this chapter are to demonstrate that mononuclear iron sites represent the main active site in Fe-ZSM-5 and to show that the mechanism and rate parameters reported in the last section can be used to provide insights into the effects of water vapor on experimental observations, particularly those obtained from temperature-programmed reaction (TPR), transient response, and temperature-programmed desorption (TPD) experiments using Fe-ZSM-5. The model of N_2O decomposition kinetics is also used to address the issue of whether O_2 desorption is rate-limiting, as has been suggested by several authors (Mul et al., 2001; Pérez-Ramírez et al., 2002c; Kiwi-Minsker et al., 2003; Wood et al., 2004).

In section 6.1, the kinetics of the N_2O decomposition is analyzed and expressions for the apparent reaction rate constant of the N_2O decomposition and the most abundant surface species are given. The effects of water vapor on the distribution of Fe species and the rate of N_2O decomposition is studied in section 6.2. Next, the decomposition of N_2O is simulated under unsteady-state conditions. Simulated temperature-programmed reaction experiments are presented in section 6.3. Pulsed N_2O decomposition experiments are simulated in section 6.4. These simulations closely reproduce experimental results. The dynamics of water desorption from deactivated Fe sites is

found to be slow. Thus at 773 K, dehydration of a fully hydrated sample of Fe-ZSM-5 can take up to 10 h. Finally, section 6.5 shows that temperature-programmed desorption of O₂ from Fe-ZSM-5 following N₂O decomposition arises from the reaction $Z[FeO_2]^+ \rightleftharpoons Z[Fe]^+ + O_2$, but this process is not a part of the mechanism for N₂O decomposition under steady state conditions.

6.1 Mechanism and kinetics of N₂O decomposition over Fe-ZSM-5

A comprehensive analysis of alternative pathways for the decomposition of N₂O on isolated Fe sites in Fe-ZSM-5 leads to the conclusion that the preferred reaction mechanism is that shown in Figure 6.1. As shown in appendix B, the rate of N₂O decomposition can be written as

$$r_{N_2O} = k_{app} P_{N_2O} \quad (6.1)$$

The apparent rate coefficient appearing in Eqn. (6.1) can be expressed as

$$k_{app} = \frac{2(k_4 + k_{11})K_3}{\left(1 + K_1K_2P_{H_2O} + \frac{(k_4 + k_{11})K_3}{k_6K_5 + k_{13}K_{12}K_{14}}\right)} \quad (6.2)$$

Similarly, it is possible to express the fraction of the most abundant isolated Fe sites that are present as $Z[FeO]^+$, $Z[FeO_2]^+$, and $Z[Fe(OH)_2]^+$ in the following manner:

$$\Theta_{FeO} = \frac{1}{\left(1 + K_1K_2P_{H_2O} + \frac{(k_4 + k_{11})K_3}{k_6K_5 + k_{13}K_{12}K_{14}}\right)} \quad (6.3)$$

$$\Theta_{FeO_2} = \frac{(k_4 + k_{11})K_3}{k_6K_5 + k_{13}K_{12}K_{14}} \Theta_{FeO} \quad (6.4)$$

$$\Theta_{Fe(OH)_2} = K_1K_2 \Theta_{FeO} P_{H_2O} \quad (6.5)$$

The rate coefficients and equilibrium constants appearing in Eqns. (6.1-6.5) are given in Table 6.1.

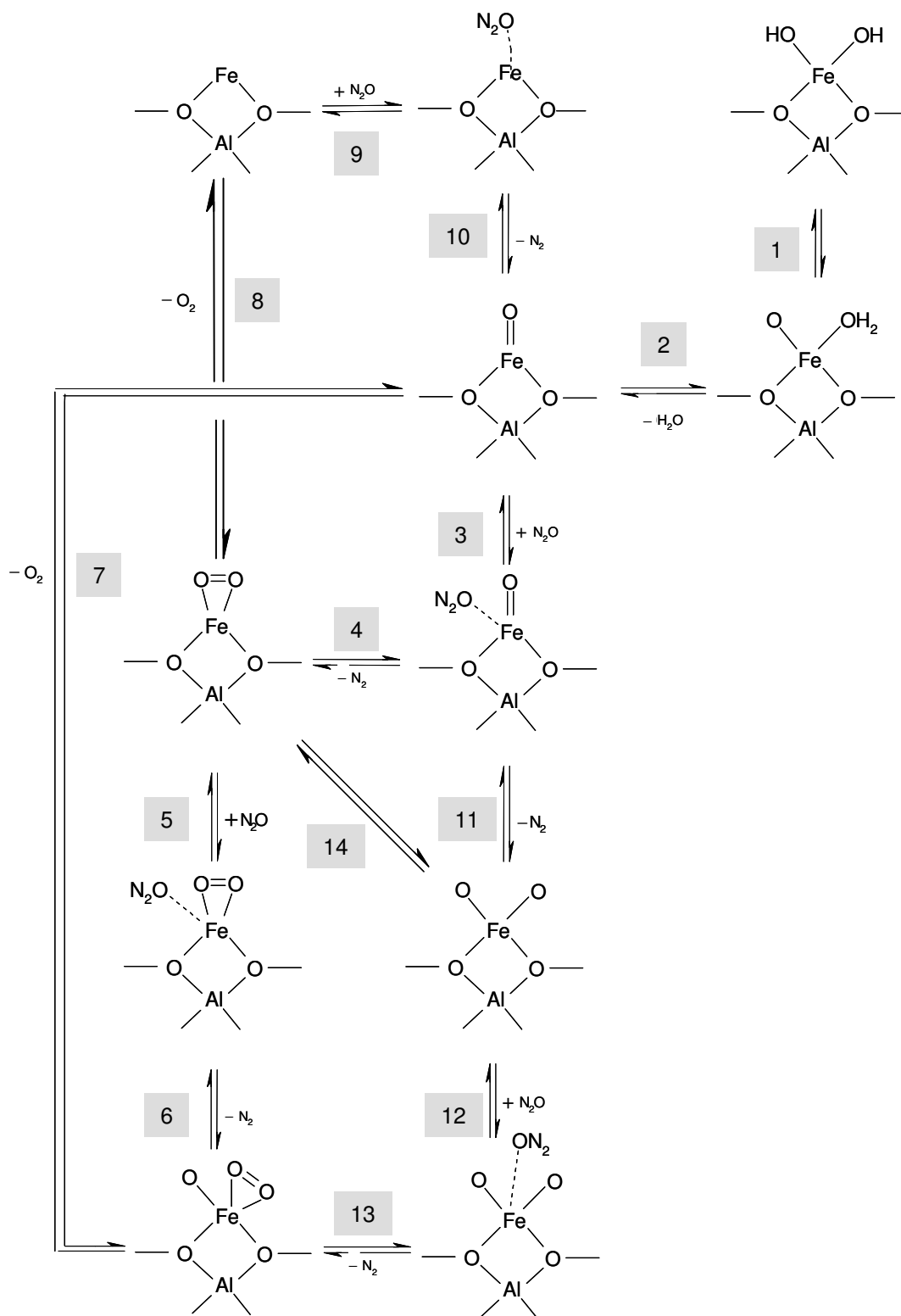


Figure 6.1: Reaction network of the N₂O dissociation on mononuclear iron oxo species and poisoning of single iron sites with water molecules.

TABLE 6.1: Computed reaction enthalpy, activation barriers, preexponential factors for equilibrium constants and preexponential factors for forward reaction

Reaction	Reaction No. used in Table 5.1	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
				600	700	800
1. $Z[FeO]^+(OH_2) \{M=6\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=6\}$	63	$\Delta H_1 = -27.1$ $E_1^\ddagger = 9.2$	$K_{1,}^0, -$ A_1, s^{-1}	2.43E-01 2.28E+12	2.43E-01 2.18E+12	2.44E-01 2.13E+12
2. $Z[FeO]^+ \{M=6\} + H_2O (g) \leftrightarrow$ $Z[FeO]^+(OH_2) \{M=6\}$	61	$\Delta H_2 = -15.6$ $E_2^\ddagger = 0.0$	$K_{2,}^0, bar^{-1}$ $A_2, s^{-1} bar^{-1}$	5.32E-07 1.58E+06	4.76E-07 2.03E+06	4.53E-07 2.57E+06
3. $Z[FeO]^+ \{M=6\} + N_2O (g) \leftrightarrow$ $Z[FeO]^+(ON_2) \{M=6\}$	23	$\Delta H_3 = -4.8$ $E_3^\ddagger = 0.0$	$K_{3,}^0, bar^{-1}$ $A_3, s^{-1} bar^{-1}$	1.70E-06 5.75E+06	1.67E-06 7.95E+06	1.69E-06 1.06E+07
4. $Z[FeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[FeO_2]^+ \{M=6\} + N_2 (g)$	36	$\Delta H_4 = -20.0$ $E_4^\ddagger = 30.4$	$K_{4,}^0, bar$ A_4, s^{-1}	9.12E+05 5.40E+13	9.30E+05 6.22E+13	9.26E+05 6.98E+13
5. $Z[FeO_2]^+ \{M=6\} + N_2O (g) \leftrightarrow$ $Z[FeO_2]^+(ON_2) \{M=6\}$	24	$\Delta H_5 = -1.2$ $E_5^\ddagger = 0.0$	$K_{5,}^0, bar^{-1}$ $A_5, s^{-1} bar^{-1}$	6.31E-07 2.19E+06	6.19E-07 3.01E+06	6.27E-07 3.99E+06
6. $Z[FeO_2]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=6\} + N_2 (g)$	38	$\Delta H_6 = -12.0$ $E_6^\ddagger = 20.1$	$K_{6,}^0, bar$ A_6, s^{-1}	1.62E+01 5.91E+09	3.74E+01 1.56E+10	6.52E+01 3.12E+10
7. $Z[O_2FeO]^+ \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + O_2 (g)$	53	$\Delta H_7 = -0.6$ $E_7^\ddagger = 8.0$	$K_{7,}^0, bar$ A_7, s^{-1}	8.21E+07 1.25E+13	8.33E+07 1.46E+13	8.21E+07 1.67E+13
8. $Z[FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[Fe]^+ \{M=6\} + O_2 (g)$	51	$\Delta H_8 = 52.1$ $E_8^\ddagger = 54.2$	$K_{8,}^0, bar$ A_8, s^{-1}	6.50E+06 1.25E+13	6.66E+06 1.46E+13	6.59E+06 1.67E+13
9. $Z[Fe]^+ \{M=6\} + N_2O (g) \leftrightarrow$ $Z[Fe]^+(ON_2) \{M=6\}$	22	$\Delta H_9 = 1.9$ $E_9^\ddagger = 0.03$	$K_{9,}^0, bar^{-1}$ $A_9, s^{-1} bar^{-1}$	1.04E-03 2.69E+09	1.02E-03 3.86E+09	1.03E-03 5.30E+09
10. $Z[Fe]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + N_2 (g)$	29	$\Delta H_{10} = -67.9$ $E_{10}^\ddagger = 2.8$	$K_{10,}^0, bar$ $A_{10,} s^{-1}$	5.02E+03 6.28E+09	5.11E+03 6.36E+09	5.09E+03 6.43E+09
11. $Z[FeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[OFeO]^+ \{M=6\} + N_2 (g)$	37	$\Delta H_{11} = -11.8$ $E_{11}^\ddagger = 30.7$	$K_{11,}^0, bar$ $A_{11,} s^{-1}$	3.35E+05 1.58E+14	3.38E+05 1.84E+14	3.34E+05 2.09E+14
12. $Z[OFeO]^+ \{M=6\} + N_2O (g) \leftrightarrow$ $Z[OFeO]^+(ON_2) \{M=6\}$	25	$\Delta H_{12} = -3.0$ $E_{12}^\ddagger = 0.0$	$K_{12,}^0, bar^{-1}$ $A_{12,} s^{-1} bar^{-1}$	4.31E-07 1.51E+06	4.22E-07 2.07E+06	4.27E-07 2.74E+06
13. $Z[OFeO]^+(ON_2) \{M=6\} \leftrightarrow$ $Z[O_2FeO]^+ \{M=6\} + N_2 (g)$	39	$\Delta H_{13} = -18.3$ $E_{13}^\ddagger = 16.5$	$K_{13,}^0, bar$ $A_{13,} s^{-1}$	3.08E+06 2.35E+14	3.13E+06 2.81E+14	3.11E+06 3.25E+14
14. $Z[FeO_2]^+ \{M=6\} \leftrightarrow$ $Z[OFeO]^+ \{M=6\}$	59	$\Delta H_{14} = 8.1$ $E_{14}^\ddagger = 22.5$	$K_{14,}^0, -$ $A_{14,} s^{-1}$	3.37E-01 7.68E+12	3.38E-01 8.11E+12	3.39E-01 8.46E+12

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

6.2 Effects of water vapor on the distribution of Fe species and the rate of N₂O decomposition

As noted in chapter 5, small amounts of water vapor can strongly affect the apparent first-order rate coefficient for N₂O decomposition and the fractional distribution of Fe among the species $Z[FeO]^+$, $Z[FeO_2]^+$, and $Z[Fe(OH)_2]^+$. For example, at 700 K the apparent rate constant decreases by a factor of 2.7 if the steady state water pressure is 10^{-6} bar (compared to a water free catalytic system), whereas at 600 K the apparent rate constant decreases by a factor of 360. Figure 6.2 shows the effects of water on the distribution of $Z[FeO]^+$, $Z[FeO_2]^+$, and $Z[Fe(OH)_2]^+$ at 700 K and 600 K. At 700 K, traces of water in the range of 10^{-9} to 10^{-6} bar have very little effect on the fraction of catalytically active sites ($Z[FeO]^+$ and $Z[FeO_2]^+$), whereas at 600 K the fraction of active sites decreases significantly if the water pressure is larger than 10^{-8} bar.

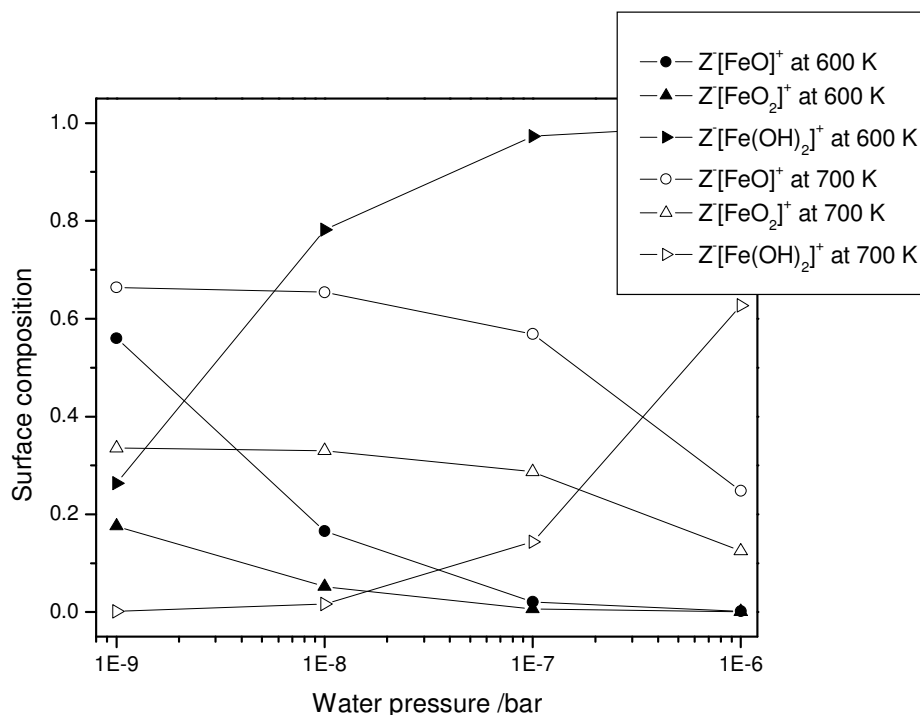


Figure 6.2: Surface composition of single iron species under reaction condition at a temperature of 600 and 700 K. $Z[FeO]^+$ is the active site for N₂O decomposition on Fe-ZSM-5. $Z[FeO_2]^+$ is the one time oxidized active site (possible α -O site), $Z[Fe(OH)_2]^+$ is an inactive single iron site in Fe-ZSM-5.

Experimental measurements of the apparent activation energy and preexponential factor for N_2O decomposition are most often made over the temperature range of 500-700 K, and in this temperature interval low concentrations of water vapor in the feed stream can have a very strong effect on the apparent rate parameters. As shown in Figure 6.3, the reported values of the apparent preexponential factor correlate with the apparent activation energy over a wide range of values. Virtually all of this variation can be attributed to the effects of small amounts of water vapor in the feed. The solid line in Figure 6.3 shows the correlation between the apparent preexponential factor and the apparent activation energy predicted on the basis of the mechanism presented in Figure 6.1 and the values of the rate and equilibrium parameters listed in Table 6.1. A temperature interval of 600-700 K was used for these calculations.

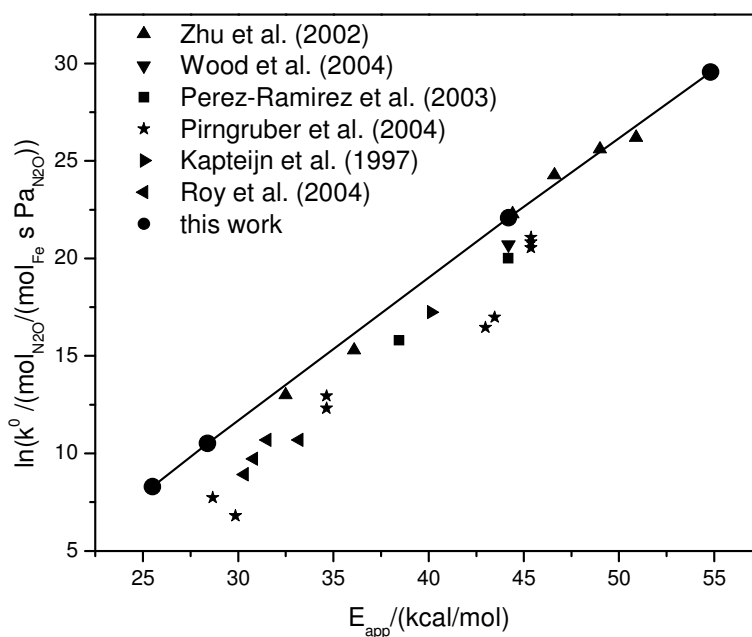


Figure 6.3: Plot of logarithm of experimental and computed apparent preexponential factor versus apparent activation barrier.

The lowest preexponential factor and activation energy are calculated for a zero partial pressure of water, and the highest values are calculated for an assumed water vapor partial pressure of 10^{-7} bar. It is evident that the differences in the concentration of water vapor in the feed can readily account for the wide variation in the apparent rate

parameters determined from experimental data. The absence of full agreement between the theoretical line and some of the data may be due to following two reasons. One is that not all of the iron in the zeolite may be in the form of isolated Fe sites. If the fraction of iron present as isolated sites is less than unity, this would lead to a systematic underestimation of the preexponential factor. The other factor contributing to the absence of full agreement is the temperature interval over which the apparent activation energy was determined. As discussed below, if the temperature interval is large and centered around lower temperatures, the calculated apparent activation energy will be large. These factors might explain why the data of Pirngruber et al. (2004) and Roy et al. (2004) lie below the theoretical line and the rest of the experimental data.

6.3 Simulation of temperature-programmed reaction experiments

A simulation of the temperature-programmed reaction experiment reported by Wood et al. (2004) was performed to further validate the mechanism presented in Figure 6.1 and the kinetics of N_2O decomposition represented by Eqn. (6.1). This work was chosen because the investigators had carried out their studies with a carefully prepared sample of Fe-ZSM-5 ($\text{Si}/\text{Al} = 84$ and $\text{Fe}/\text{Al} = 0.38$), which was shown by EXAFS to contain primarily isolated Fe cations (Choi et al., 2004). Before initiating a TPR experiment, Wood et al. (2004) pretreated 100 mg of catalyst (6.79×10^{-6} mol Fe) at 773 K in 3.0 % N_2O and then cooled the catalyst to 298 K. The catalyst was then exposed to a flow of 15,000 ppm N_2O in He (total flow rate = $60 \text{ cm}^3/\text{min}$; reactor volume = 0.112 cm^3) while the temperature was increased at 5 K/min from 298 K to 773 K. The amount of iron and the N_2O feed flow rate used in the simulation were the same as those used in the experimental work. Since it is not known what fraction of the Fe in the sample used by Wood et al. (2004) was present as isolated sites and what was the feed concentration of water vapor, these parameters were varied to get the best fit between the experimentally observed and simulated N_2 partial pressures. To achieve this fit, the function $F(P_{\text{H}_2\text{O}}, f) = \sum (P_{\text{N}_2}^{\text{exp}} - P_{\text{N}_2}^{\text{sim}})^2$ was minimized.

For the simulations, it was assumed that the iron in the catalyst occurs in two forms, inactive iron clusters and single iron sites, that are active for N_2O decomposition or are poisoned by water molecules. The fraction of iron present as isolated sites is defined as f . The reactor used by Wood et al. (2004) was modeled as a CSTR, since the catalyst bed is shallow and, hence, considerable backmixing is expected. It was also assumed that the surface composition reaches steady-state at each temperature and that the rate of reaction is not diffusionally limited. The latter assumption was supported by estimates of the Thiele modulus, which remains less than 0.2 for temperatures up to 773 K. Under these conditions, the partial pressure of O_2 , N_2 and N_2O can be calculated at every temperature T as:

$$P_{N_2O} = P_{N_2O}^0 \cdot \exp\left(-\frac{fN_{Fe}RT}{V}k_{app}\tau\right) \quad (6.5)$$

$$P_{N_2} = 2 \cdot P_{O_2} = P_{N_2O}^0 - P_{N_2O} \quad (6.6)$$

where V is the reactor volume, τ is the residence time, R is the gas constant, fN_{Fe} is the total amount of single iron atoms in the catalyst and k_{app} is the apparent rate coefficient given by Eqn. (6.1). An optimization algorithm for unconstrained minimizations of a sum of squares was used to determine the fraction of single iron sites and the partial pressure of water in the feed (NAG, 1999). Figure 6.4a illustrates the close agreement between the experimental and simulated TPR profiles. The best fit was obtained with $f = 0.544$ and a partial pressure of water in the feed stream of 406×10^{-9} bar.

Eqn. (6.1) leads to the conclusion that an Arrhenius plot of the apparent first-order rate coefficient for N_2O decomposition will not be linear and will depend on the partial pressure of water vapor in the feed. This expectation is confirmed by Figure 6.4b. The experimental data of Wood et al. (2004) also fail to plot as a straight line. Although the agreement between simulation and experiment is excellent at high temperatures, at temperatures below 670 K the experimental value of the apparent rate coefficient exceeds that determined from the simulation.

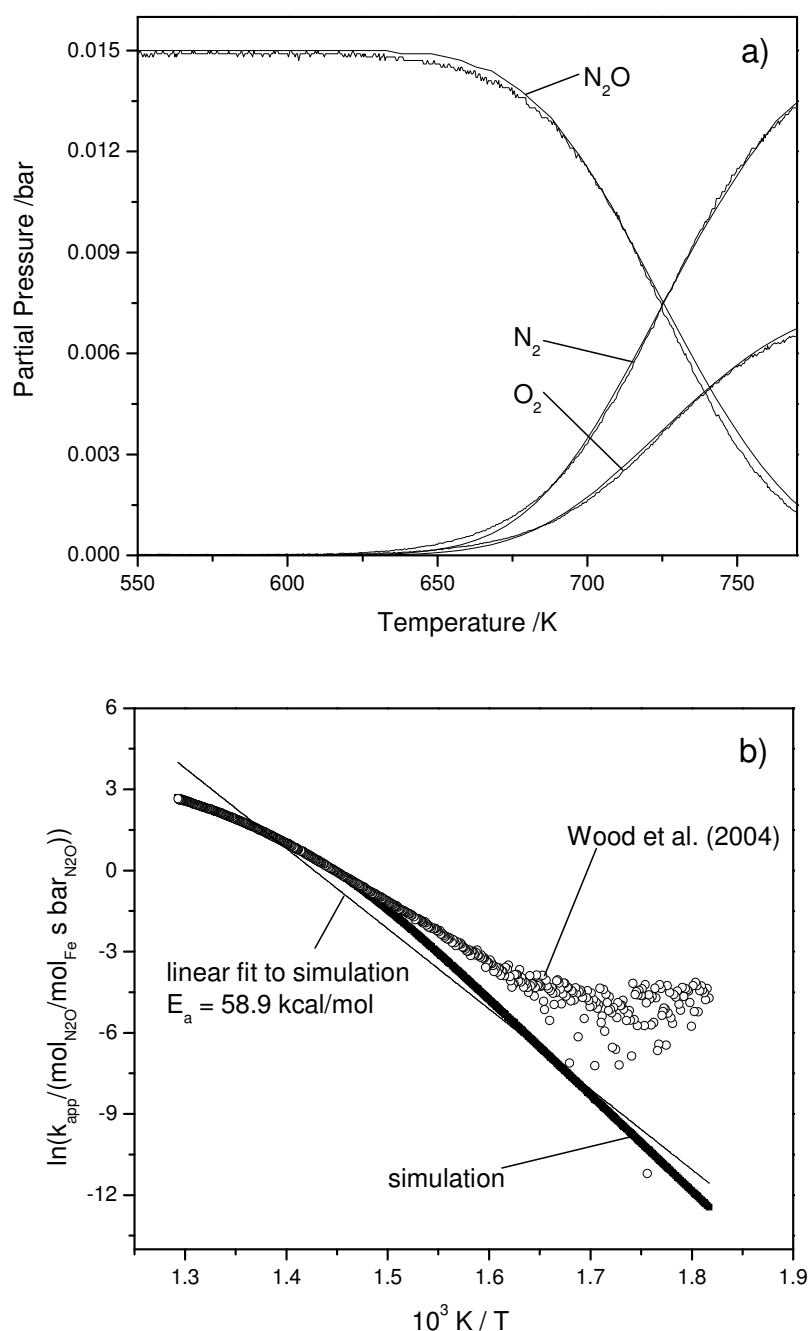


Figure 6.4a: Experimental and simulated temperature programmed decomposition profile observed during the passage of 15,000 ppm N_2O in He over Fe-ZSM-5. The simulated TPR profile was obtained with an optimized single iron fraction of 0.544 (95 % confidence interval: 0.541 – 0.546) and a water pressure of 406×10^{-9} bar (95 % confidence interval: $396 - 416 \times 10^{-9}$ bar). Figure 6.4b: Arrhenius plots for simulated and experimental N_2O decomposition, obtained in a TPR experiment.

A possible cause for this discrepancy might be that the catalyst surface is not in steady state. Because of the catalyst pretreatment more active iron sites appear to be available in the experiments than would be present in the simulation, which assumes that the distribution of adsorbed species reaches a steady-state instantaneously. However, whatever the cause of the discrepancy, it is evident that the value of the calculated apparent activation energy is highly dependent on the temperature range used for the calculation and the water vapor concentration present in the feed (see Figure 6.2).

A corollary to the preceding conclusion is that the water vapor content in the feed required to achieve a match between the experimentally observed and calculated apparent activation energies will be strongly dependent on the temperature range over which the activation energy is determined in the experimental study. For example, in chapter 5 it is reported that the apparent activation barrier determined by Wood et al. (2004) over the temperature range of 600 to 700 K, 44.2 kcal/mol, could be reproduced if the partial pressure of water in the feed were assumed to be 23×10^{-9} bar. However, this result appears to contradict the finding of this chapter, which shows that a feed partial pressure of water vapor of 406×10^{-9} bar is required to achieve agreement between the simulated TPR spectrum and the experimentally observed spectrum reported by Wood et al. (2004) (see Figure 6.4a) over the temperature range of 550 K to 773 K. This difference in partial pressures of water vapor in the feed is directly associated with the temperature range over which agreement between theory and experiment is sought and to the choice of objective function chosen to fit the simulation to the experimental observation. In chapter 5, the objective function was $F(P_{H_2O}, f) = \sum (1 - P_{N_2}^{sim} / P_{N_2}^{exp})^2$, instead of $F(P_{H_2O}, f) = \sum (P_{N_2}^{exp} - P_{N_2}^{sim})^2$, which is used here. The use of the former objective function favors the low temperature data, for which the assumption of a steady-state distribution of adsorbed species may not be valid.

Another significant issue is the rate at which a fully hydrated sample of Fe-ZSM-5 undergoes dehydration. A sense of the time required to dehydrate the catalyst can be obtained with the rate parameters listed in Table 6.1. For this simulation, it is assumed that the Fe-ZSM-5 catalyst is identical to that used in the studies of Wood et al. (2004)

and, as discussed above, that $f = 0.544$ and the partial pressure of water vapor in the incoming gas stream is 406×10^{-9} bar. Figure 6.5 shows that at 773 K it takes about 10 hours for an initially hydrated catalyst to achieve a steady-state surface composition. This observation could explain why high-temperature catalyst pretreatment for an extended period of time is found to be important for achieving a high activity for N_2O decomposition (Kiwi-Minsker et al., 2003). Yet another important point arising from this analysis is that when measurements of N_2O decomposition over Fe-ZSM-5 are carried out by temperature-programmed reaction, the Fe sites will not reach a steady-state distribution with respect to the partial pressure of water vapor in the feed. It is recommended, therefore, that measurements of the rate of N_2O decomposition be made at fixed temperatures that have been maintained for a time sufficient for the catalyst to achieve a steady state with respect to the partial pressure of water in the feed.

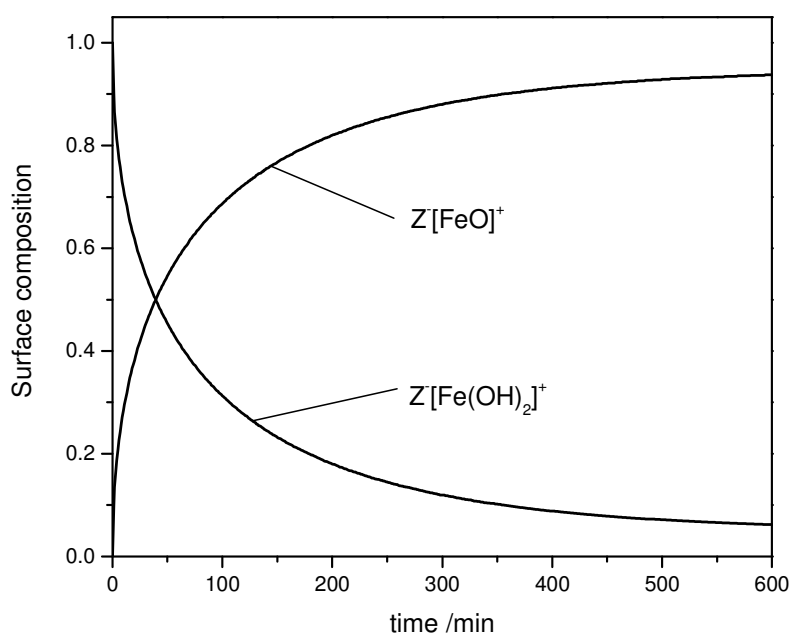


Figure 6.5: Simulation of variation of main single iron sites with time during temperature pretreatment of a wet Fe-ZSM-5 catalyst in He. The pretreatment temperature is 773 K and the water pressure in the incoming gas stream is $P_{\text{H}_2\text{O}} = 406 \times 10^{-9}$ bar.

6.4 Simulation of transient-response experiments

Wood et al. (2004) performed transient-response experiments to investigate the initial stages of the N_2O decomposition. After catalyst pretreatment at 773 K in 3.0 % N_2O , the sample was purged in He and then cooled to the temperature of the experiment. During the experiment, 15,000 ppm N_2O in He ($60 \text{ cm}^3/\text{min}$) was flowed through the reactor for 10 min. Then pure He was flowed through the reactor for 10 min after which the feed was switched back to a flow of 15,000 ppm N_2O in He. Transient-response experiments were performed at temperatures of 509 K, 520 K, 530 K, 540 K and 588 K.

Since the catalyst surface in these experiments is initially not at steady state with respect to the gas phase, the experiments were simulated with the full reaction mechanism illustrated in Figure 6.1 and the rate parameters given in Table 6.1. To fit the N_2 partial pressure observed by Wood et al. (2004) during the first exposure of the catalyst to N_2O , the initial distribution of single iron sites among $\text{Z}[\text{FeO}]^+$, $\text{Z}[\text{FeO}_2]^+$ and $\text{Z}[\text{Fe}(\text{OH})_2]^+$ was optimized with a sequential quadratic programming (SQP) method (NAG, 1999). To improve the fit between experimental and simulated N_2 partial pressure, small adjustments were made in the rate parameters. In particular, the activation barrier for N_2O decomposition on $\text{Z}[\text{FeO}]^+$ sites (reaction 4 and 11 in Table 6.1) was reduced by 6 kcal/mol (without a change the equilibrium constant) and the activation barrier for N_2O decomposition on $\text{Z}[\text{OFeO}]^+$ sites (reactions 13) was reduced by less than 1 kcal/mol. These small adjustments in the rate parameters had to be made because transient-response experiments are very sensitive to small variations in the rate parameters and the presence of species that show a low activity. Although the first of these adjustments might suggest that the mechanism presented in Figure 6.1 is wrong, the author does not believe this to be the case. It is recalled that all activation energies were obtained at the B3LYP/TZVP level of theory with the use of a constrained 5T cluster to represent the Fe site and an associated portion of the zeolite framework, and that the preexponential factors were determined from transition-state theory in the harmonic approximation. While the B3LYP functional is known to underestimate

barrier heights by 4-5 kcal/mol (Zhao et al., 2005), use of the harmonic approximation can lead to an overestimation of the preexponential factor by an order of magnitude. As a result the adjustment in the activation barriers for reactions 4 and 11 still lies within the limits of the accuracy of the rate parameters and experimental data.

Figure 6.6a illustrates both the experimental and the simulated N_2 formation during the first exposure of the catalyst to N_2O at a temperature of 509, 520, 530 and 540 K. In agreement with the experimental observation no O_2 formation was observed during the whole experiment and no N_2 formation occurred during re-exposure of the catalyst to N_2O . The initial burst of N_2 production is simulated at all temperatures with about 18 % of the single iron sites or 0.098 (0.18×0.544) of all of the Fe in the zeolite residing initially in the form of $Z[FeO]^+$. This later figure is very close to that reported by Wood et al. (2004), 0.10. Figure 6.6b shows the evolution of the principal species involving single Fe sites during the experiment carried out at 540 K. The fraction of Fe sites in the form of $Z[Fe(OH)_2]^+$ stays constant during the exposure to N_2O , whereas the fraction of Fe sites present as $Z[FeO]^+$ decreases and the fraction of Fe sites present as $Z[FeO_2]^+$ increases.

Figure 6.7a illustrates the experimental and simulated N_2 and O_2 formation occurring during the transient-response experiment performed for a temperature of 588 K. For this simulation the activation barrier for the N_2O decomposition on $Z[FeO]^+$ was reduced by 5.5 kcal/mol, and the barrier for water desorption was reduced by 5.3 kcal/mol. In agreement with experimental observation, a burst of N_2 is observed in the simulations whenever the catalyst is exposed to N_2O . After that, stoichiometric amounts of N_2 and O_2 are formed. The rates of N_2 and O_2 formation do not increase as rapidly with time as the experimentally observed rates, and the activity of the re-exposed catalyst is higher for the simulations than that seen experimentally. Nevertheless, the characteristic shape of the curve is in good agreement with the experiments, considering all of the approximations inherent in the simulations. Figure 6.7b illustrates the evolution of the principal species involving single Fe sites during the experiment carried out at 588 K.

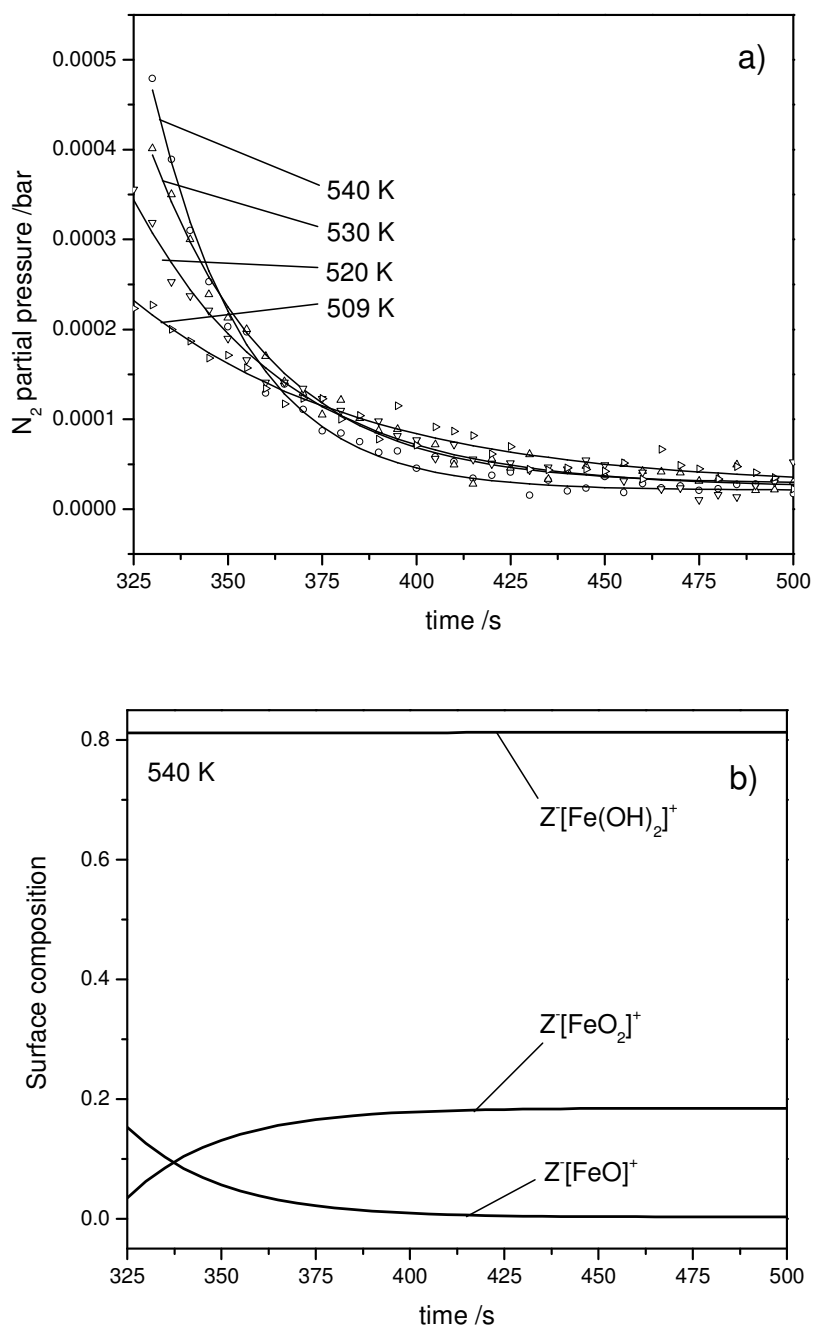


Figure 6.6a: N_2 formation during transient-response decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5 at various temperatures. The weight of catalyst used was 100 mg and the gas flow rate was $60 \text{ cm}^3/\text{min}$. Open symbols are experimental data (Wood et al., 2004). Solid lines are simulated data with an optimized initial surface composition. The activation barrier for the N_2O decomposition on $Z[FeO]^+$ sites is reduced by 6 kcal/mol. The activation barrier for N_2O decomposition on $Z[OFeO]^+$ sites is varied by less than 1 kcal/mol. Figure 6.6b: Distribution of the principal iron-containing species during transient-response decomposition of N_2O upon exposure of the Fe-ZSM-5 to 15,000 ppm N_2O in He at 540 K.

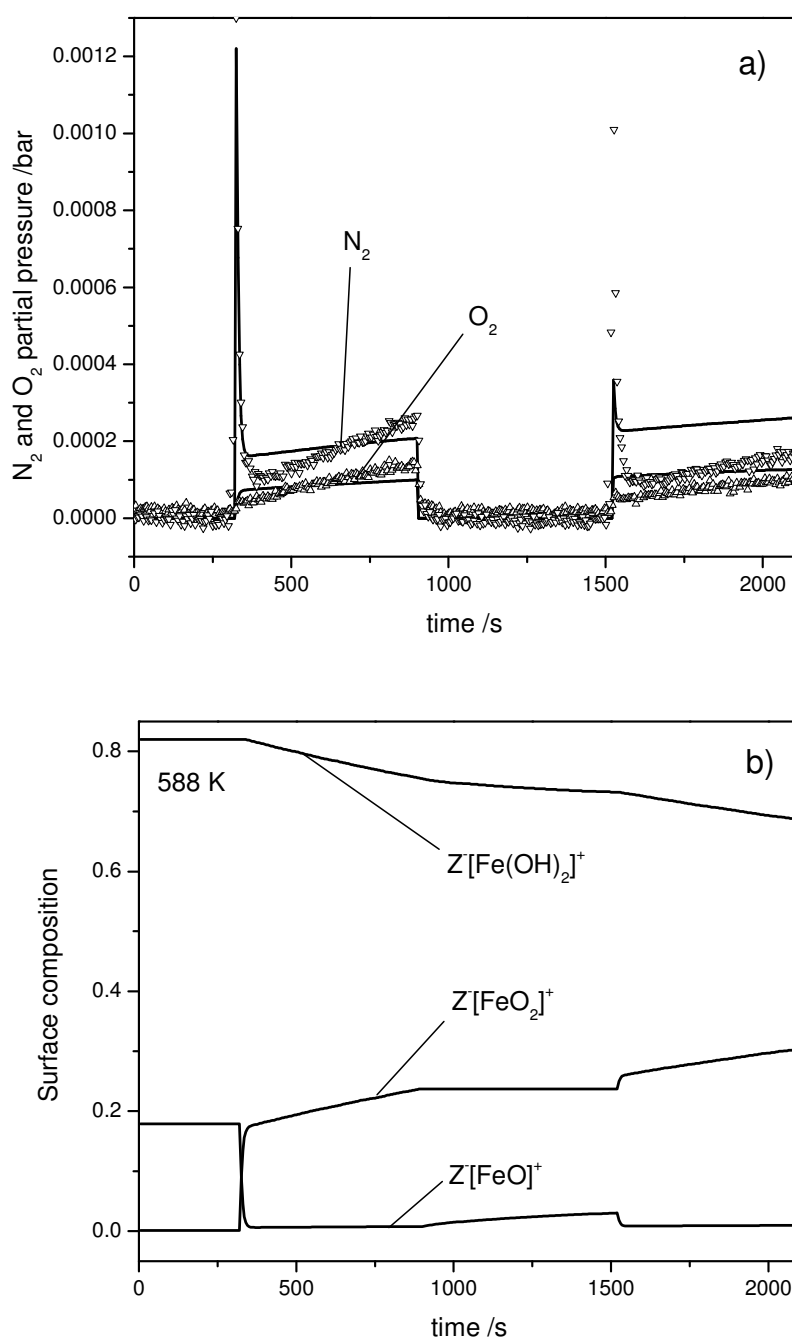


Figure 6.7a: N_2 and O_2 formation during transient-response decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5 at a temperature of 588 K. The weight of catalyst used was 100 mg and the gas flow rate was $60 \text{ cm}^3/\text{min}$. Open symbols are experimental data (Wood et al., 2004). Solid lines are simulated data with an optimized initial surface composition. The activation barrier for the N_2O decomposition on $Z[FeO]^+$ sites is reduced by 5.5 kcal/mol; the water desorption barrier is reduced by 5.3 kcal/mol. Figure 6.7b: Distribution of the principal iron-containing species during transient-response decomposition of N_2O upon exposure of the Fe-ZSM-5 to 15,000 ppm N_2O in He at 588 K.

The fraction of Fe sites present as $Z[FeO]^+$ decreases sharply during N_2O exposure of the catalyst, causing the fraction of Fe sites present as $Z[FeO_2]^+$ to increase. Water slowly desorbs from $Z[Fe(OH)_2]^+$, resulting in a further increase in the fraction of Fe sites present as $Z[FeO_2]^+$ if N_2O is present and an increase in $Z[FeO]^+$ if N_2O is not present in the gas phase. At no time during the experiment is the surface composition at steady state.

In this context it is also important to note that the activation barrier for the elementary step of the first N_2O decomposition on $Z[FeO]^+$ ($E^\ddagger = 30.4$ kcal/mol) is 10 kcal/mol higher than the activation barrier of the second N_2O decomposition on $Z[FeO_2]^+$ ($E^\ddagger = 20.1$ kcal/mol). On the other hand, the product of the equilibrium constant for N_2O adsorption and the rate constant for N_2O dissociation, $K_{ads} \cdot k_{reac}$, is 100 times larger for the first N_2O decomposition on $Z[FeO]^+$ (reaction 3 and 4) than for the second N_2O decomposition on $Z[FeO_2]^+$ (reaction 5 and 6) for temperatures below 600K.

6.5 Oxygen adsorption and desorption from Fe-ZSM-5

The role of oxygen desorption during N_2O decomposition on Fe-ZSM-5 has been the subject of controversy in the literature. The absence of an inverse dependence on O_2 partial pressure for the rate of N_2O decomposition has led a number of authors (Panov et al., 1990; Chang, et al., 1995; Kapteijn et al., 1997; Zhu et al., 2002) to conclude that O_2 desorption is rapid and irreversible, and consequently not rate limiting. The results of this work support this conclusion. The absence of a dependence on O_2 partial pressure in the rate expression for N_2O decomposition seen in Eqn. (6.1) is a consequence of the small heat of adsorption for O_2 (0.6 kcal/mol) and the small activation barrier for O_2 desorption (8 kcal/mol). Isotope exchange experiments reported by Nobukawa et al. (2002) also support the conclusion that O_2 desorption is facile. Nevertheless, several authors (El-Malki et al., 2000; Mul et al., 2001; Pérez-Ramírez et al., 2002c; Kiwi-Minsker et al., 2003; Pirngruber, 2003; Wood et al., 2004) have suggested that O_2 desorption is an energetically demanding step and could be rate limiting. This

conclusion was based on NO-assisted N_2O decomposition experiments by Mul et al. (2001) and Pérez-Ramírez et al. (2002c) and on the observation of a high-temperature O_2 desorption peak during temperature-programmed desorption carried out after a sample of Fe-ZSM-5 had been used for N_2O decomposition in the absence of added NO (El-Malki et al., 2000; Kiwi-Minsker et al., 2003; Wood et al., 2004). Figure 6.8 shows an example of such an experiment taken from the work of Wood et al. (2004). Since the activation barrier estimated for the irreversible O_2 desorption was calculated to be 45.7 kcal/mol, which is close to the apparent activation barrier for N_2O decomposition, 44.2 kcal/mole, the authors concluded that the desorption of O_2 could be rate limiting. The theoretical analysis of N_2O decomposition presented in the last chapter suggests that the O_2 peak observed by Wood et al. (2004) is not likely to arise from the process leading to O_2 formation during steady-state decomposition of N_2O , but, more likely, is due to O_2 release from a species such as $\text{Z}[\text{FeO}_2]^+$ or some other Fe-containing species.

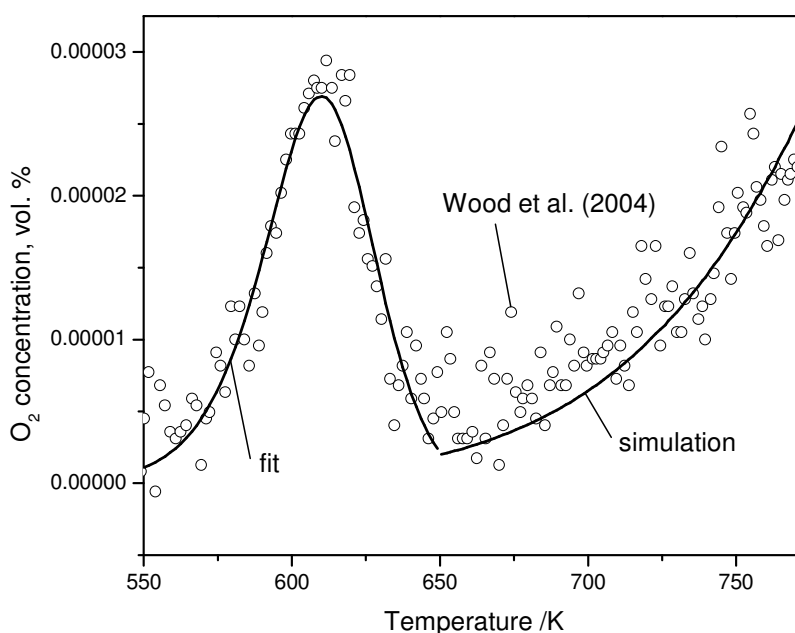


Figure 6.8: TPD of O_2 in He from 528 K to 773 K following decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5 at 528 K. The weight of catalyst used was 100 mg and the gas flow rate was $60 \text{ cm}^3/\text{min}$. The dots correspond to the experimental data, the solid line starting at the beginning of the second TPD peak corresponds to a simulation of O_2 desorption, $\text{Z}[\text{FeO}_2]^+ \rightleftharpoons \text{Z}[\text{Fe}]^+ + \text{O}_2$, with a by 7 kcal/mol reduced desorption barrier.

The amount of O_2 desorbed in the first peak seen in Figure 6.8 corresponds to about 1.3 % of the Fe sites estimated to be present as isolated Fe in the sample of Fe-ZSM-5 used by Wood et al. (2004) ($0.013 O_2/Fe_{total}$). This amount is significantly smaller than the total amount of oxygen deposited in the transient responds experiments, estimated to be about $0.1 O/Fe_{total}$, leading one to suspect that the first O_2 desorption peak seen in Figure 6.8 results from some minority Fe species. To further support this conclusion, it is noted that simulation of O_2 desorption from $Z[FeO_2]^+$ using the rate parameters given in Table 6.1 and Table 5.1 (species in the quartet and sextet state were considered) places the peak position at ~ 900 K, rather than 675 K. Since a number of authors have observed a second O_2 TPD peak at a temperature of 900 K (El-Malki et al., 2000; Nobukawa et al., 2002 and 2005; Kiwi-Minsker et al., 2003; Wood, 2004b), an effort was made to simulate the second desorption peak seen in Figure 6.8. As discussed earlier, the concentration of water vapor in the feed and the fraction of single iron sites in the catalyst were derived from a fit of the simulation of the TPR experiment shown in Figure 6.4a. Figure 6.8 shows very good agreement between simulation and experiment for an optimized distribution of isolated Fe sites of 20.1 % $Z[FeO]^+$, 49.5 % $Z[FeO_2]^+$, and 30.4 % $Z[Fe(OH)_2]^+$, and an activation barrier for O_2 desorption (reaction 8) that is reduced by 7 kcal/mol relative to the value given in Table 6.1 (54.2 kcal/mol). Since Wood et al. (2004) terminated their TPD experiment at 773 K, it was not possible to assess whether the simulation of O_2 desorption from $Z[FeO_2]^+$ would describe the full peak. A TPD experiment similar to that of Wood et al. (2004) has been reported by Kiwi-Minsker et al. (2003), but in this instance the experiment was carried out to 1100 K. As seen in Figure 6.9, the simulation of O_2 desorption from $Z[FeO_2]^+$ is in very good agreement with the experimentally observed peak temperature and width reported by Kiwi-Minsker et al. (2003). What is also remarkable is that the peak intensity and area of the simulated and observed peaks agree, as well.

The findings of Pirngruber and Roy (2004) can also be reconciled with the results of the present study. These authors found a statistical isotope distribution of the O_2 produced during N_2O decomposition by using a feed of 5,000 ppm N_2O in He and repeated pulses of 1 % $^{18}O_2$ into the N_2O flow; from this they argued that N_2O decomposition could not occur via a Rideal-Eley mechanism. The mechanism presented in Figure 6.1 suggests

that isotopic scrambling of O_2 could readily be explained by the interaction of O_2 with $Z[FeO]^+$. Rapid exchange of O atoms in $Z[FeO]^+(O_2)$, formed by this interaction, would lead to a statistical isotope distribution without the need to invoke the concept of a slow O_2 desorption process. In this context it is worth noting that if O_2 desorption were rate limiting, the catalyst surface would be saturated with oxygen atoms and a N_2O decomposition would be zero order in N_2O partial pressure, in contrast to all experimental findings, which show that the rate of N_2O decomposition is first order in N_2O .

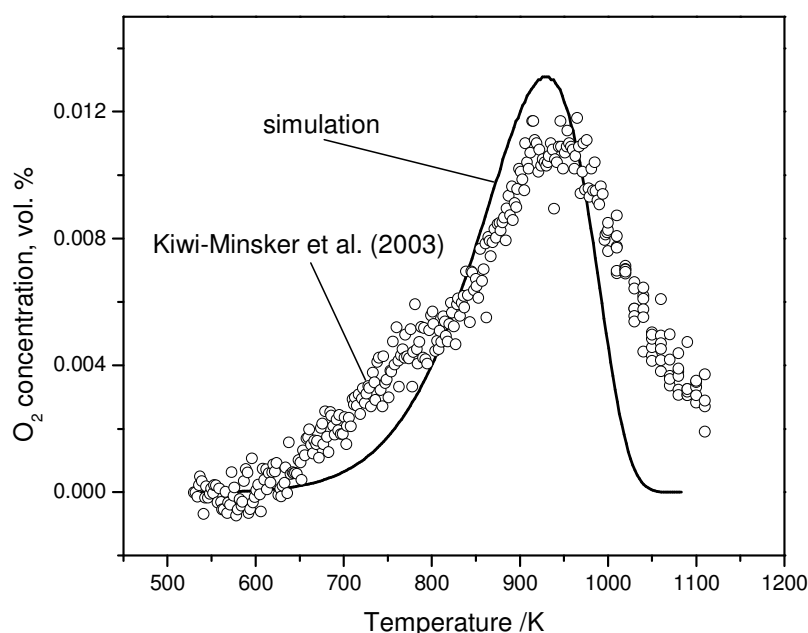


Figure 6.9: TPD of oxygen after its deposition from N_2O (523 K) on an iron ZSM-5 catalyst and after irreversible adsorption of water vapor at 523 K. The simulation is the continuation of the TPD simulation illustrated in Figure 6.8. No fit parameter was used to match the experimental data of Kiwi-Minsker et al. (2003).

6.6 Conclusions

Several transient-response experiments for the decomposition of N_2O over Fe-ZSM-5 have been simulated from first principles and compared with experimental results. It is shown that the reaction mechanism shown in Figure 6.1, together with the rate

coefficients listed in Table 6.1, provides a satisfactory basis for simulating all of the experimental work reported in the literature. The overall rate of N_2O decomposition is found to be first order in N_2O partial pressure and zero order in O_2 partial pressure. The presence of H_2O in the feed gas inhibits the rate of N_2O decomposition by deactivating the active sites required for this process. Site deactivation occurs via the process $\text{Z}[\text{FeO}]^+ + \text{H}_2\text{O} \rightleftharpoons \text{Z}[\text{Fe}(\text{OH})_2]^+$, which is reversible, and consequently, the influence of water vapor is strongly temperature dependent. Because of the high activation barrier for H_2O desorption, dehydration of a hydrated sample of Fe-ZSM-5 can take as much as 10 h at 773 K. The presence of low concentrations of water vapor in the feed stream (ppb to ppm levels) affects the measured values for the apparent activation energy and preexponential factor, and this explains the large spread in values reported in the literature, as well as the appearance of an apparent compensation effect. Finally, it is shown that the desorption of O_2 observed at ~ 900 K in TPD experiments conducted after the use of Fe-ZSM-5 for N_2O decomposition is due to the process $\text{Z}[\text{FeO}_2]^+ \rightleftharpoons \text{Z}[\text{Fe}]^+ + \text{O}_2$; however, this process is not kinetically relevant during steady-state decomposition.

7 Comprehensive DFT study of NO-assisted N₂O decomposition over Fe-ZSM-5

In chapter 5 and 6 the N₂O decomposition was studied on mononuclear iron sites in Fe-ZSM-5. A reaction mechanism was proposed that is able to explain various transient and steady state experiments. Low concentrations of water in the system have a significant effect on the speciation of Fe in Fe-ZSM-5 and allow reproducing experimental data. On single iron sites, the rate limiting step in the reaction mechanism is under steady state conditions the N₂O decomposition reaction, explaining the first order N₂O dependency of the nitrous oxide decomposition rate. A rate limiting O₂ desorption process as proposed by Mul et al. (2001), Pérez-Ramírez et al. (2002c, 2003c and 2004), Wood et al. (2004), and Bulushev et al. (2004), inevitably results in a zero order nitrous oxide decomposition rate and therefore contradicts all experimental findings of the N₂O decomposition at elevated temperatures.

One reason why these authors concluded that O₂ desorption should be rate limiting, results from N₂O decomposition experiments in the presence of a reducing agent by Mul et al. (2001) and Pérez-Ramírez et al. (2002, 2002c, 2003, 2004). A reducing agent like, e.g., nitric oxide, significantly increases the N₂O decomposition rate by removing an oxygen atom from the active site. The increase in the reaction rate is especially pronounced at low temperatures (< 700 K). The presence of nitric oxide shifts the activity of iron zeolite catalysts for N₂O decomposition by 75 to 100 K to lower temperatures (Pérez-Ramírez et al. (2002c), Pérez-Ramírez and Kapteijn (2003)). If the oxygen desorption process would be the slowest step in the catalytic cycle, the presence of a reducing agent could explain the observed enhanced N₂O decomposition rate.

In this chapter, the NO-assisted N₂O decomposition over iron zeolites is studied on a molecular level using density functional theory. The aim of this section is to give a novel explanation of the NO-assisted N₂O decomposition consistent with quantum

chemical calculations and various experimental findings. Experimental data are explained with a fast oxygen desorption rate and a slow N₂O decomposition rate on single iron sites. Section 7.1 summarizes the key experimental observations of NO-assisted nitrous oxide decomposition. The computational methodology used in this work is outlined in section 7.2. Essentially, the same procedure was used as in chapter 5. A discussion of the computational results of this study can be found in section 7.3. This section closes with a presentation of several pathways for the formation of nitric oxide from nitrous oxide on single iron sites. This part of this work was motivated by experimental observations from Sang and Lund (2000, 2001) and Kiwi-Minsker et al. (2005) who suggested that nitric oxide might be formed on the catalyst surface from N₂O in the absence of NO in the feed stream and that the produced nitric oxide might influence the catalytic behavior. Finally, section 7.4 compares the computational results with some experimental findings. A more in depth comparison between computational results and experimental data, including reactor simulations, will be published in a subsequent paper.

7.1 Experimental evidence of NO-assisted nitrous oxide decomposition

The positive effect of NO on N₂O decomposition was first reported by Kapteijn et al. (1996). It was proposed that nitric oxide in the gas phase scavenged adsorbed oxygen, deposited by N₂O during the oxidation of active sites, leading to the formation of NO₂, and regeneration of active sites. If the oxygen desorption process or the second N₂O decomposition on one time oxidized active iron sites is rate limiting, the NO addition leads to an overall increase of the N₂O decomposition rate.

Mul et al. (2001) and Pérez-Ramírez et al. (2002c) observed for a N₂O and NO feed that the formation of NO₂ increases as a function of reaction temperature, reaches a maximum at 650 to 675 K, then decreases, and finally disappears at a temperature of 775 K. At low temperatures NO₂ is produced beyond the thermodynamic equilibrium

of NO and O₂ ($2 \text{ NO} + \text{O}_2 \rightleftharpoons 2 \text{ NO}_2$). The concentration of NO and NO₂ together is constant over the whole temperature range investigated.

Kögel et al. (2001), Mul et al. (2001), Pérez-Ramírez et al. (2002c), Boutarbouch et al. (2004), and Sang et al. (2005) reported that the addition of nitric oxide leads to a catalytic increase in the N₂O decomposition rate that cannot be solely explained by the removal of surface oxygen atoms and the formation of NO₂. If scavenging of adsorbed oxygen atoms, deposited by N₂O would be the only promotion route induced by the addition of nitric oxide, a progressive increase in N₂O conversion upon increasing the inlet NO partial pressure would have been expected. Instead, these authors reported that a relatively small amount of nitric oxide is sufficient to induce a dramatic change in the N₂O decomposition activity. No significant increase in the N₂O decomposition rate was observed by Pérez-Ramírez et al. (2002c) for NO/N₂O feed ratios higher than 0.25, confirming the catalytic nature of nitric oxide on the N₂O decomposition. Since Pérez-Ramírez et al. (2002c) also observed no nitric oxide inhibition at a molar NO/N₂O feed ratio of 10, they suggested that nitric oxide adsorption and oxygen deposition by N₂O occurs at different sites in Fe-ZSM-5. As a result, these authors proposed that two neighboring Fe sites need to be present to account for the NO-assisted N₂O decomposition activity. The apparent need for oligonuclear iron clusters in the NO-assisted N₂O decomposition is also confirmed by NO-assisted N₂O decomposition experiments in the presence of a reducing agent like carbon monoxide (Boutarbouch et al. (2004) and Pérez-Ramírez et al. (2003c)). Carbon monoxide increases the N₂O decomposition rate on single iron sites. In the presence of nitric oxide and carbon monoxide, NO selectively inhibits the N₂O reduction by CO in the low temperature range. Boutarbouch et al. (2004) explained this behavior by nitric oxide selectively inhibiting the reduction of N₂O on isolated iron sites. Nitric oxide adsorbs strongly on mononuclear iron sites, particularly at low temperatures, and blocks CO and N₂O activation. The NO-assisted N₂O decomposition would then proceed on oligonuclear iron clusters that are assumed to be inert to CO oxidation by N₂O.

Consequently, Pérez-Ramírez et al. (2002c, 2003c, 2004) explained the catalytic effect of nitric oxide on the N₂O decomposition by nitric oxide accommodating oxygen from N₂O. The formed adsorbed NO₂ could react with a second oxygen atom from a neighboring site, thus accelerating the recombination of oxygen from N₂O and its subsequent desorption. If the rate-determining process in N₂O decomposition would be the migration of oxygen atoms to recombine to molecular oxygen, this process would indeed be increased by nitric oxide.

Recently, Sang et al. (2005) observed a nitric oxide promotional effect for isolated Fe cations. This observation necessitates a mechanistic explanation that does not involve extra sites adjacent to the catalytically active site, i.e. di-iron or oligonuclear iron sites as proposed by Mul et al. (2001) and Pérez-Ramírez et al. (2002c). Sang et al. (2005) observed a first order N₂O decomposition rate in the presence and absence of nitric oxide and confirmed the experimental finding from Pérez-Ramírez et al. (2002c) that the catalytic effect of nitric oxide declines with increasing temperature. Sang et al. (2005) reports, due to the presence of nitric oxide, a reduction of the apparent activation barrier of the N₂O decomposition of 7 kcal/mol. Pérez-Ramírez et al. (2002c) reports a similar reduction of 11 – 13 kcal/mol.

A number of authors suggested that the formation of nitric oxide from nitrous oxide might play a significant role in N₂O decomposition at low temperatures even in the absence of nitric oxide in the feed stream. Spectroscopic results from Chen et al. (1998), Grubert et al. (2000), El-Malki et al. (2000b) and O₂ exchange experiments performed by Leglise et al. (1984) suggest the presence of adsorbed NO, nitrite, and nitrate species in Fe-ZSM-5. El-Malki et al. (2000b), Bulushev et al. (2004), and Kiwi-Minsker et al. (2005) even observed a nitric oxide peak in a temperature-programmed desorption experiment at about 613 K.

Recently, Kiwi-Minsker et al. (2005) observed a zero order N₂O decomposition in nitrous oxide partial pressure in the temperature range from 553 K to 593 K. These authors assign the zero order N₂O decomposition rate to nitric oxide accelerating the

oxygen recombination and desorption rate. It has to be noted that a zero order N_2O decomposition is, unlike a first order N_2O decomposition, consistent with a slow oxygen desorption step.

Bulushev et al. (2004) reports, in the absence of nitric oxide in the feed and in the temperature range between 573 K and 653 K, a slowly increasing N_2O decomposition with time. If pulses of nitric oxide are introduced in the reactor the steady state nitrous oxide concentration value is reached instantaneously, suggesting a significant role of nitric oxide in attaining the steady state composition. Figure 7.1 illustrates the experimental data from Bulushev et al. (2004) at a temperature of 603 K.

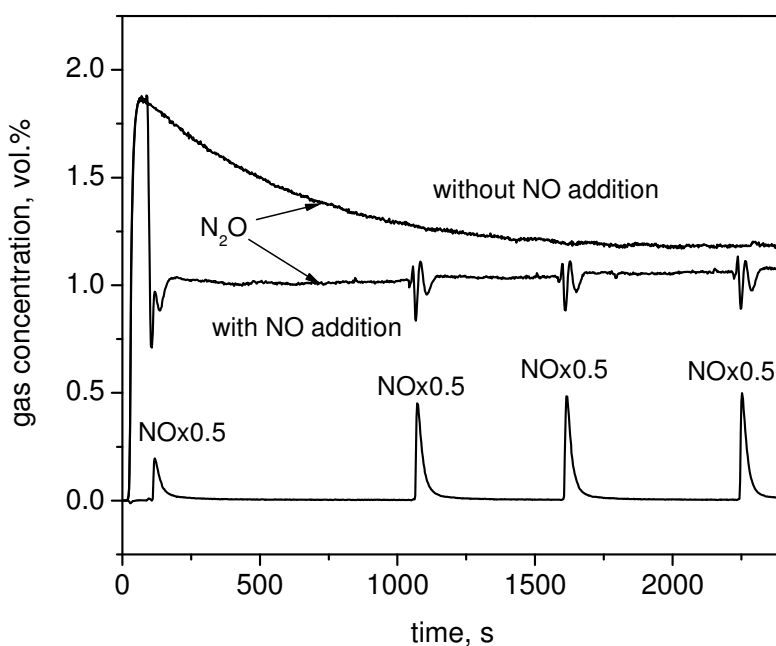


Figure 7.1: Effect of NO pulse introduction (10 vol.% in Ar) on the N_2O response curve during interaction of the mixture of 2 vol.% N_2O / 2 vol.% Ar in He with HZSM-5_{200Fe} at 603 K. Data from: Bulushev et al. (2004).

One problem in proving the formation of nitric oxide from nitrous oxide on iron zeolite catalysts results from nitric oxide impurities in the nitrous oxide feed stream. Sang and Lund (2000, 2001), Bulushev et al. (2004), and Kiwi-Minsker et al. (2004, 2005), report

a NO_x content in the nitrous oxide feed of 2 ppm. Pérez-Ramírez et al. (2002c, 2003c) used nitrous oxide with 150 ppm impurities. In general, authors who hardly observed any spectroscopic evidence of nitric oxide, nitrite, and nitrate species used purified N₂O gases (Wood et al., 2002 and 2004). Kiwi-Minsker et al. (2005) assigned a proportional increase in the nitric oxide concentration with increasing N₂O partial pressure under transient conditions to the formation of nitric oxide; but an increasing nitrous oxide concentration, inevitably results in an increasing amount of nitric oxide impurities, opening up the possibility of nitric oxide impurities to be responsible for this observation.

To summarize, a reaction mechanism of the NO-assisted N₂O decomposition has to give a reaction rate that is first order in N₂O concentration at elevated temperatures. It has to be able to reproduce the catalytic effect of nitric oxide on the N₂O decomposition at low temperatures. The NO₂ formation should increase with temperature, reach a maximum and decrease again until the NO₂ concentration completely disappears. No nitric oxide inhibition on the N₂O decomposition rate should be observed and the concentration of the sum of NO and NO₂ should be constant over the whole temperature range. Ultimately, the reaction network should in principle be able to explain the blocking of carbon monoxide by nitric oxide at low temperatures and should elucidate the role of nitric oxide in attaining instantaneously the steady state nitrous oxide concentration.

Finally, it is noted that the NO-assisted N₂O decomposition is not a special feature of Fe-ZSM-5 catalysts, but is a general phenomenon occurring over many Fe-containing zeolitic and nonzeolitic catalysts (Pérez-Ramírez et al., 2002c).

7.2 Computational methodology

This work is an extension of the N₂O decomposition over Fe-ZSM-5 project described in chapter 5 and 6. As a result, the same cluster model used to describe the catalytically

active site and portion of the zeolite framework as in chapter 5 was employed in this study. The catalytically active center and portion of the zeolite framework are represented by a 23 to 27 atom cluster. As shown in Figure 7.2, the portion of the cluster describing the zeolite contains an Al-atom in T12 position of the framework surrounded by shells of O- and Si-atoms. The terminal Si-atoms are fixed in their crystallographic positions as reported by Olson et al. (1981). Dangling bonds are terminated by H-atoms located 1.48 Å from each terminal Si-atom oriented in the direction of the next O-atom in the zeolite matrix. This corresponds to the Si-H distance in SiH₄. In appendix A.2, it is demonstrated that charge transfer hardly occurs over the zeolite matrix so that the constrained T5 cluster model used in this work gives reliable results for electronic energy differences. To study the influence of nitric oxide on the active iron site, the anionic cluster is charge-compensated by a metal-hydroxo, -nitrite, -nitrate species, [FeOH]⁺, [FeONO]⁺, [FeO₂N]⁺, [FeO₂NO]⁺, placed between two of the four O-atoms surrounding the Al-atom. Figure 7.2 illustrates the bonding and atomic distances in these mononuclear iron species.

Quantum chemical calculations of the geometry and energies of potential energy minima were performed for spin surfaces with spin multiplicity $M_S = 2$ to 8, using non-local, gradient-corrected density-functional theory (DFT). Calculations on different spin surfaces revealed that the energy difference between different spin surfaces is usually significant so that only energies of PES minima for the ground state are reported. Transition-state structures were determined only for the spin PES on that both, reactant and product states, have the lowest electronic energy. Results from chapter 5 demonstrate that spin-accelerated reactions, as depicted in Figure 3.1, are not expected for the N₂O decomposition on single iron sites in Fe-ZSM-5, suggesting that the reaction pathway has to be determined on one PES only. Likewise, minimum energy structures on the seam of two PESs are only determined for the two lowest spin PESs if the reactant and product state have their electronic ground state on different spin PESs. Spin contamination was negligible for ground state minimum structures. Some spin contamination was observed for transition states and minimum structures on a seam of two PESs. In all cases it was still possible to distinguish clearly between states of different spin multiplicities.

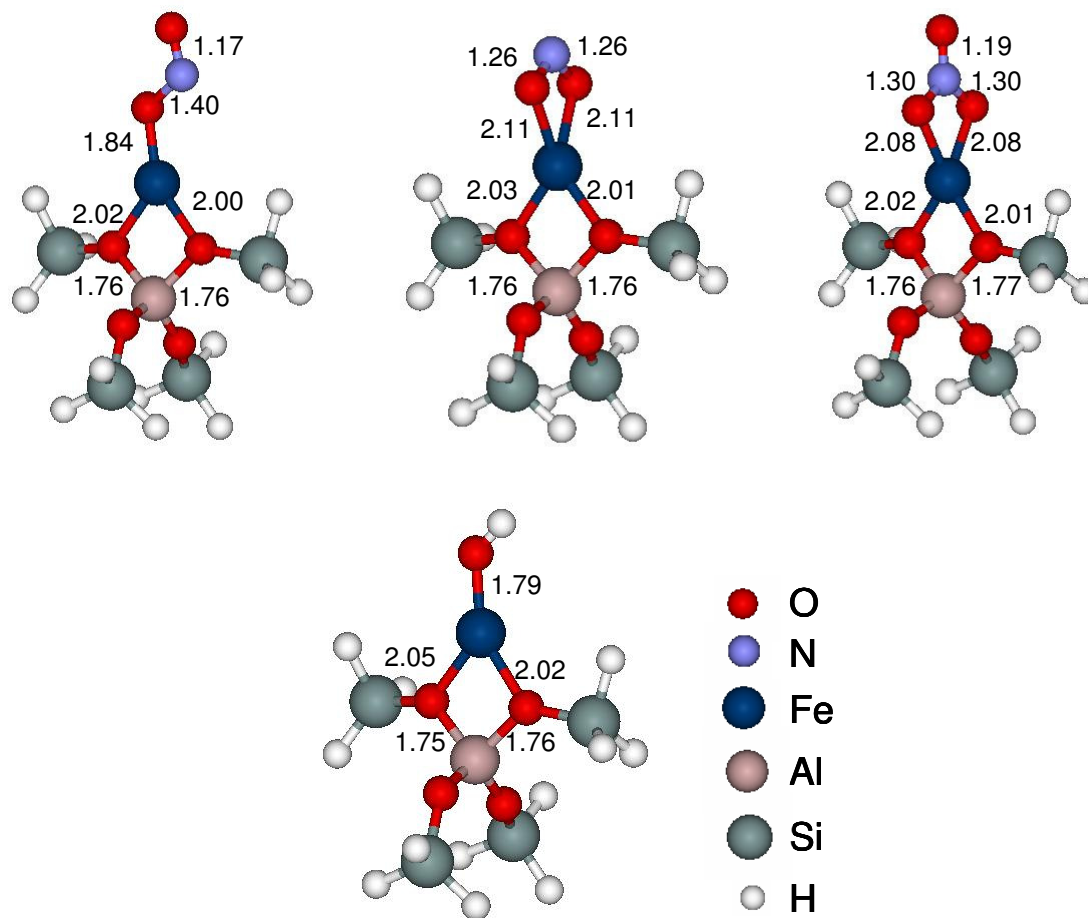


Figure 7.2: Iron-nitrite, -nitrate, -hydroxo zeolite cluster. Structures are potential energy minima on the potential energy surface with spin multiplicity $M_S = 5$. Atomic distances are indicated in angstroms.

To represent the effects of exchange and correlation, Becke's 3-parameter exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) were used with a very fine numerical grid size (m5) (see section 3.2.3). To speed up the calculation of PES minima, all structures were pre-optimized with the pure density functional RI-BP (Becke's 1988 generalized gradient exchange functional together with Perdew's 1986 correlation functional) using the resolution of identity approach for computing the electronic coulomb interaction (Eichkorn et al., 1995 and 1997). Basis sets at the triple-zeta level with polarization functions were used for all atoms, including iron (TZVP). In appendix A.1, it is demonstrated that for the TZVP basis set, relative electronic energies are converged with respect to the basis set size. No corrections were made for the basis set superposition error (BSSE). All calculations and reported values

were carried out using the TURBOMOLE V5.7 suite of programs (Ahlrichs et al., 1989 and 1995).

Minimizations of the constraint cluster model were performed in Cartesian coordinates with an energy convergence criterion of at least 10^{-7} Ha and a gradient norm convergence criterion of 10^{-4} Ha/bohr. At the end of all minimizations or saddle point searches a frequency calculation was done to confirm that for minima all frequencies are positive and for saddle points exactly one frequency is imaginary.

In order to accelerate the search for transition states a combination of interpolation and local methods described in section 4 was used. The growing string method was used in mass-weighted coordinates with a maximum of 13 to 16 nodes. After the two separate ends join, the growing string method was terminated and an approximate saddle point was obtained. To refine the position of the saddle point the modified dimer method was employed. A convergence criterion of the gradient norm of 5×10^{-4} Ha/bohr was used for transition states, and, as described above, first-order saddle points were identified with a frequency calculation. Owing to the use of mass-weighted coordinates in the growing string method an approximation to the minimum energy path (MEP) was obtained, which could be used to determine that reactant and product states are linked by the transition structure found.

Minimum potential energy structures on the seam of two potential energy surfaces were determined with a multiplier penalty function algorithm described in section 4.4. Converged minimum energy crossing point structures had a maximum energy difference on both PESs of less than 10^{-6} Ha.

Overall equilibrium constants and reaction rate constants were computed using standard statistical mechanics and absolute rate theory. To calculate rates of spin surface crossing, e.g., desorption rates of oxygen, the framework of absolute rate theory was used under the assumption that the partition functions of the hypothetical transition state

(minimum on the seam of two PESs) and the minimum on the PES with lower spin multiplicity (adsorbed state) are identical except for the electronic energy (Eq. (3.57)). This procedure completely neglects a low spin surface crossing probability (see section 3.3). To estimate if very low spin surface crossing probabilities could result in very different reaction rate constants, thermally averaged spin transition probabilities are calculated with the Landau-Zener formula (Eq. (3.35)) with a spin-orbit coupling energy H_{I2} of 395 and 825 J/mol, as calculated by Danovich and Shaik (1997) for the oxidative activation of H₂ by FeO⁺. More details about the calculation of rate parameters can be found in section 3.4.4. Altogether, the same computational methodology was applied as in chapter 5.

7.3 Computational results and discussion

There are a number of different possibilities how nitric oxide might influence the N₂O decomposition on single iron sites. In section 7.3.1, the interaction of nitric oxide with the most abundant active single iron sites that are present in the absence of nitric oxide, Z[FeO]⁺, Z[FeO₂]⁺, and Z[OFeO]⁺, is studied. Stable Fe-nitrite and Fe-nitrate species are formed. The catalytic cycle of the N₂O decomposition on Z[FeONO]⁺, Z[FeO₂N]⁺, and Z[FeO₂NO]⁺ centers is investigated in section 7.3.2, 7.3.3 and 7.3.4, respectively. The possible activation of poisoned Z[Fe(OH)₂]⁺ sites by nitric oxide is examined in section 7.3.5. The catalytic decomposition on formed Z[FeOH]⁺ sites and the subsequent formation of Z[FeO]⁺ centers is investigated in section 7.3.6. Finally, the formation of nitric oxide from nitrous oxide on single iron sites is studied in section 7.3.7.

All quantum chemical calculations are summarized in Table 7.1(a)-(n). Thermally averaged Landau-Zener transition probabilities are summarized for a spin-orbit coupling energy of 395 J/mol and 825 J/mol for several temperatures in Table 7.2. All spin

TABLE 7.1a: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
1. $Z[FeO]^+ \{M=6\} + NO(g) \leftrightarrow Z[FeONO]^+ \{M=5\}$	$\Delta H_1 = -32.9$ $E_1^\ddagger = 1.1$ $E_{-1}^\ddagger = 34.3$	K_1, bar^{-1} $A_1, \text{s}^{-1} \text{bar}^{-1}$ $k_1, \text{s}^{-1} \text{bar}^{-1}$ A_{-1}, s^{-1} k_{-1}, s^{-1}	1.54E+04 1.43E+05 5.93E+04 1.25E+13 3.85E+00	2.87E+02 1.68E+05 7.91E+04 1.46E+13 2.76E+02	1.49E+01 1.98E+05 1.02E+05 1.67E+13 6.90E+03
2. $Z[FeONO]^+ \{M=5\} \leftrightarrow Z[Fe]^+ \{M=4\} + NO_2(g)$	$\Delta H_2 = 66.0$ $E_2^\ddagger = 67.9$ $E_{-2}^\ddagger = 0.0$	K_2, bar A_2, s^{-1} k_2, s^{-1} $A_{-2}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-2}, \text{s}^{-1} \text{bar}^{-1}$	5.56E-18 1.25E+13 2.25E-12 4.05E+05 4.05E+05	1.56E-14 1.46E+13 9.01E-09 5.76E+05 5.76E+05	5.81E-12 1.67E+13 4.61E-06 7.93E+05 7.93E+05
3. $Z[FeO]^+ \{M=6\} + NO(g) \leftrightarrow Z[FeO_2N]^+ \{M=5\}$	$\Delta H_3 = -37.8$ $E_3^\ddagger = 1.4$ $E_{-3}^\ddagger = 39.3$	K_3, bar^{-1} $A_3, \text{s}^{-1} \text{bar}^{-1}$ $k_3, \text{s}^{-1} \text{bar}^{-1}$ A_{-3}, s^{-1} k_{-3}, s^{-1}	3.07E+05 6.19E+04 1.85E+04 1.25E+13 6.04E-02	3.18E+03 7.00E+04 2.49E+04 1.46E+13 7.81E+00	1.06E+02 7.98E+04 3.23E+04 1.67E+13 3.05E+02
4. $Z[FeO_2N]^+ \{M=5\} \leftrightarrow Z[Fe]^+ \{M=4\} + NO_2(g)$	$\Delta H_4 = 70.9$ $E_4^\ddagger = 72.5$ $E_{-4}^\ddagger = 0.0$	K_4, bar A_4, s^{-1} k_4, s^{-1} $A_{-4}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-4}, \text{s}^{-1} \text{bar}^{-1}$	2.78E-19 1.25E+13 4.88E-14 1.75E+05 1.75E+05	1.41E-15 1.46E+13 3.37E-10 2.39E+05 2.39E+05	8.16E-13 1.67E+13 2.60E-07 3.19E+05 3.19E+05
5. $Z[FeO]^+ \{M=6\} + NO(g) \leftrightarrow Z[OFeNO]^+ \{M=5\}$	$\Delta H_5 = -13.6$ $E_5^\ddagger = 0.2$ $E_{-5}^\ddagger = 14.9$	K_5, bar^{-1} $A_5, \text{s}^{-1} \text{bar}^{-1}$ $k_5, \text{s}^{-1} \text{bar}^{-1}$ A_{-5}, s^{-1} k_{-5}, s^{-1}	1.05E-02 5.75E+05 4.98E+05 1.25E+13 4.72E+07	1.99E-03 7.38E+05 6.51E+05 1.46E+13 3.28E+08	5.84E-04 9.29E+05 8.34E+05 1.67E+13 1.43E+09
6. $Z[FeO_2]^+ \{M=6\} + NO(g) \leftrightarrow Z[FeOONO]^+ \{M=5\}$	$\Delta H_6 = -9.0$ $E_6^\ddagger = 6.3$ $E_{-6}^\ddagger = 15.5$	K_6, bar^{-1} $A_6, \text{s}^{-1} \text{bar}^{-1}$ $k_6, \text{s}^{-1} \text{bar}^{-1}$ A_{-6}, s^{-1} k_{-6}, s^{-1}	3.90E-05 2.25E+05 1.13E+03 1.25E+13 2.89E+07	1.28E-05 2.59E+05 2.77E+03 1.46E+13 2.15E+08	5.71E-06 3.00E+05 5.65E+03 1.67E+13 9.89E+08
7. $Z[FeOONO]^+ \{M=5\} \leftrightarrow Z[FeO]^+ \{M=6\} + NO_2(g)$	$\Delta H_7 = 1.0$ $E_7^\ddagger = 2.5$ $E_{-7}^\ddagger = 0.0$	K_7, bar A_7, s^{-1} k_7, s^{-1} $A_{-7}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-7}, \text{s}^{-1} \text{bar}^{-1}$	1.14E+07 1.25E+13 1.50E+12 1.32E+05 1.32E+05	1.32E+07 1.46E+13 2.37E+12 1.80E+05 1.80E+05	1.42E+07 1.67E+13 3.40E+12 2.40E+05 2.40E+05

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1b: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
8. $Z[OFeO]^+ \{M=6\} + NO(g) \leftrightarrow Z[OFeONO]^+ \{M=5\}$	$\Delta H_8 = -30.5$	K_8, bar^{-1}	6.27E+03	1.57E+02	1.01E+01
	$E_8^\ddagger = 3.7$	$A_8, \text{s}^{-1} \text{bar}^{-1}$	4.05E+05	4.84E+05	5.75E+05
		$k_8, \text{s}^{-1} \text{bar}^{-1}$	1.86E+04	3.45E+04	5.70E+04
	$E_{-8}^\ddagger = 34.6$	A_{-8}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-8}, s^{-1}	2.97E+00	2.20E+02	5.67E+03
9. $Z[OFeONO]^+ \{M=5\} \leftrightarrow Z[FeO]^+ \{M=6\} + NO_2(g)$	$\Delta H_9 = 14.4$	K_9, bar	1.88E+02	1.09E+03	3.89E+03
	$E_9^\ddagger = 16.0$	A_9, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_9, s^{-1}	1.84E+07	1.46E+08	7.04E+08
	$E_{-9}^\ddagger = 0.0$	$A_{-9}, \text{s}^{-1} \text{bar}^{-1}$	9.78E+04	1.35E+05	1.81E+05
		$k_{-9}, \text{s}^{-1} \text{bar}^{-1}$	9.78E+04	1.35E+05	1.81E+05
10. $Z[OFeO]^+ \{M=6\} + NO(g) \leftrightarrow Z[OFeO_2N]^+ \{M=5\}$	$\Delta H_{10} = -34.0$	K_{10}, bar^{-1}	3.60E+03	5.96E+01	2.80E+00
	$E_{10}^\ddagger = 4.6$	$A_{10}, \text{s}^{-1} \text{bar}^{-1}$	2.61E+04	2.82E+04	3.10E+04
		$k_{10}, \text{s}^{-1} \text{bar}^{-1}$	5.48E+02	1.03E+03	1.71E+03
	$E_{-10} = 38.2$	A_{-10}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-10}, s^{-1}	1.52E-01	1.73E+01	6.11E+02
11. $Z[OFeO_2N]^+ \{M=5\} \leftrightarrow Z[FeO]^+ \{M=6\} + NO_2(g)$	$\Delta H_{11} = 17.9$	K_{11}, bar	3.27E+02	2.85E+03	1.40E+04
	$E_{11}^\ddagger = 19.2$	A_{11}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{11}, s^{-1}	1.27E+06	1.48E+07	9.51E+07
	$E_{-11}^\ddagger = 0.6$	$A_{-11}, \text{s}^{-1} \text{bar}^{-1}$	6.31E+03	7.86E+03	9.77E+03
		$k_{-11}, \text{s}^{-1} \text{bar}^{-1}$	3.89E+03	5.19E+03	6.80E+03
12. $Z[OFeO]^+ \{M=6\} + NO(g) \leftrightarrow Z[FeO_2NO]^+ \{M=5\}$	$\Delta H_{12} = -58.3$	K_{12}, bar^{-1}	1.89E+12	1.70E+09	8.95E+06
	$E_{12}^\ddagger = 5.8$	$A_{12}, \text{s}^{-1} \text{bar}^{-1}$	2.87E+04	2.93E+04	3.07E+04
		$k_{12}, \text{s}^{-1} \text{bar}^{-1}$	2.18E+02	4.47E+02	7.90E+02
	$E_{-12}^\ddagger = 63.2$	A_{-12}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-12}, s^{-1}	1.15E-10	2.63E-07	8.83E-05
13. $Z[FeO_2NO]^+ \{M=5\} \leftrightarrow Z[FeO]^+ \{M=6\} + NO_2(g)$	$\Delta H_{13} = 42.2$	K_{13}, bar	6.23E-07	9.99E-05	4.37E-03
	$E_{13}^\ddagger = 44.2$	A_{13}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{13}, s^{-1}	9.67E-04	2.26E-01	1.37E+01
	$E_{-13}^\ddagger = 1.8$	$A_{-13}, \text{s}^{-1} \text{bar}^{-1}$	6.94E+03	8.16E+03	9.66E+03
		$k_{-13}, \text{s}^{-1} \text{bar}^{-1}$	1.55E+03	2.26E+03	3.14E+03
14. $Z[FeONO]^+ \{M=5\} + N_2O(g) \leftrightarrow Z[FeONO]^+(N_2O) \{M=5\}$	$\Delta H_{14} = -3.1$	K_{14}, bar^{-1}	4.87E-05	3.28E-05	2.50E-05
	$E_{14}^\ddagger = 0.0$	$A_{14}, \text{s}^{-1} \text{bar}^{-1}$	1.17E+07	1.61E+07	2.15E+07
		$k_{14}, \text{s}^{-1} \text{bar}^{-1}$	1.17E+07	1.61E+07	2.15E+07
	$E_{-14}^\ddagger = 4.7$	A_{-14}, s^{-1}	1.25E+13	1.46E+13	1.67E+13
		k_{-14}, s^{-1}	2.39E+11	4.91E+11	8.58E+11

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1c: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T,K		
			600	700	800
15. $Z[FeONO]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeONO]^+(ON_2) \{M=5\}$	$\Delta H_{15} = -1.5$ $E_{15}^\ddagger = 0.0$ $E_{-15}^\ddagger = 3.3$	K_{15}, bar^{-1} $A_{15}, \text{s}^{-1} \text{bar}^{-1}$ $k_{15}, \text{s}^{-1} \text{bar}^{-1}$ A_{-15}, s^{-1} k_{-15}, s^{-1}	5.00E-05 3.99E+07 3.99E+07 1.25E+13 7.98E+11	4.09E-05 5.64E+07 5.64E+07 1.46E+13 1.38E+12	3.61E-05 7.65E+07 7.65E+07 1.67E+13 2.12E+12
16. $Z[FeONO]^+(ON_2) \{M=5\} \leftrightarrow$ $Z[OFeONO]^+ \{M=5\} + N_2(g)$	$\Delta H_{16} = -12.7$ $E_{16}^\ddagger = 24.8$ $E_{-16}^\ddagger = 36.8$	K_{16}, bar A_{16}, s^{-1} k_{16}, s^{-1} $A_{-16}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-16}, \text{s}^{-1} \text{bar}^{-1}$	5.21E+09 3.39E+13 3.08E+04 1.58E+08 5.91E-06	1.16E+09 3.97E+13 7.07E+05 1.97E+08 6.11E-04	3.66E+08 4.52E+13 7.49E+06 2.40E+08 2.05E-02
17. $Z[OFeONO]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[OFeONO]^+(N_2O) \{M=5\}$	$\Delta H_{17} = -0.5$ $E_{17}^\ddagger = 0.0$ $E_{-17}^\ddagger = 1.8$	K_{17}, bar^{-1} $A_{17}, \text{s}^{-1} \text{bar}^{-1}$ $k_{17}, \text{s}^{-1} \text{bar}^{-1}$ A_{-17}, s^{-1} k_{-17}, s^{-1}	1.84E-06 5.24E+06 5.24E+06 1.25E+13 2.85E+12	1.71E-06 7.03E+06 7.03E+06 1.46E+13 4.10E+12	1.66E-06 9.15E+06 9.15E+06 1.67E+13 5.50E+12
18. $Z[OFeONO]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[OFeONO]^+(ON_2) \{M=5\}$	$\Delta H_{18} = -1.5$ $E_{18}^\ddagger = 0.0$ $E_{-18}^\ddagger = 2.8$	K_{18}, bar^{-1} $A_{18}, \text{s}^{-1} \text{bar}^{-1}$ $k_{18}, \text{s}^{-1} \text{bar}^{-1}$ A_{-18}, s^{-1} k_{-18}, s^{-1}	1.41E-06 1.72E+06 1.72E+06 1.25E+13 1.22E+12	1.16E-06 2.30E+06 2.30E+06 1.46E+13 1.98E+12	1.03E-06 3.00E+06 3.00E+06 1.67E+13 2.91E+12
19. $Z[OFeONO]^+(ON_2) \{M=5\} \leftrightarrow$ $Z[O_2FeONO]^+ \{M=5\} + N_2(g)$	$\Delta H_{19} = -20.7$ $E_{19}^\ddagger = 44.9$ $E_{-19}^\ddagger = 66.2$	K_{19}, bar A_{19}, s^{-1} k_{19}, s^{-1} $A_{-19}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-19}, \text{s}^{-1} \text{bar}^{-1}$	2.79E+15 1.80E+14 7.76E-03 3.64E+06 2.79E-18	2.35E+14 2.16E+14 2.03E+00 4.05E+06 8.64E-15	3.60E+13 2.51E+14 1.33E+02 4.53E+06 3.70E-12
20. $Z[O_2FeONO]^+ \{M=5\} \leftrightarrow$ $Z[O_2FeONO]^+ \{M=7\}$	$\Delta H_{20} = -5.4$ $E_{20}^\ddagger = 7.1$ $E_{-20}^\ddagger = 12.4$	$K_{20}, -$ A_{20}, s^{-1} k_{20}, s^{-1} A_{-20}, s^{-1} k_{-20}, s^{-1}	4.83E+01 1.25E+13 3.31E+10 2.22E+13 6.85E+08	2.52E+01 1.46E+13 9.02E+10 2.64E+13 3.58E+09	1.54E+01 1.67E+13 1.95E+11 3.05E+13 1.26E+10
21. $Z[O_2FeONO]^+ \{M=7\} \leftrightarrow$ $Z[FeONO]^+ \{M=5\} + O_2(g)$	$\Delta H_{21} = 3.3$ $E_{21}^\ddagger = 6.0$ $E_{-21}^\ddagger = 1.5$	K_{21}, bar A_{21}, s^{-1} k_{21}, s^{-1} $A_{-21}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-21}, \text{s}^{-1} \text{bar}^{-1}$	1.35E+05 1.11E+14 7.12E+11 1.92E+07 5.28E+06	2.05E+05 1.22E+14 1.60E+12 2.37E+07 7.82E+06	2.72E+05 1.30E+14 2.94E+12 2.85E+07 1.08E+07

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1d: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
22. $Z[O_2FeONO]^+ \{M=7\} \leftrightarrow$ $Z[FeO_2]^+ \{M=6\} + NO_2(g)$	$\Delta H_{22} = 17.3$ $E_{22}^\ddagger = 19.4$ $E_{-22}^\ddagger = 0.0$	K_{22}, bar A_{22}, s^{-1} k_{22}, s^{-1} $A_{-22}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-22}, \text{s}^{-1} \text{bar}^{-1}$	1.68E+00 1.25E+13 1.07E+06 6.38E+05 6.38E+05	1.37E+01 1.46E+13 1.28E+07 9.29E+05 9.29E+05	6.40E+01 1.67E+13 8.34E+07 1.30E+06 1.30E+06
23. $Z[OFeONO]^+ \{M=5\} + NO(g) \leftrightarrow$ $Z[Fe(ONO)_2]^+ \{M=6\}$	$\Delta H_{23} = -31.7$ $E_{23}^\ddagger = 0.0$ $E_{-23}^\ddagger = 32.9$	K_{23}, bar^{-1} $A_{23}, \text{s}^{-1} \text{bar}^{-1}$ $k_{23}, \text{s}^{-1} \text{bar}^{-1}$ A_{-23}, s^{-1} k_{-23}, s^{-1}	1.31E+06 1.73E+07 1.73E+07 1.25E+13 1.32E+01	2.83E+04 2.24E+07 2.24E+07 1.46E+13 7.90E+02	1.64E+03 2.84E+07 2.84E+07 1.67E+13 1.73E+04
24. $Z[Fe(ONO)_2]^+ \{M=6\} \leftrightarrow$ $Z[FeONO]^+ \{M=5\} + NO_2(g)$	$\Delta H_{24} = 13.2$ $E_{24}^\ddagger = 15.6$ $E_{-24}^\ddagger = 0.0$	K_{24}, bar A_{24}, s^{-1} k_{24}, s^{-1} $A_{-24}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-24}, \text{s}^{-1} \text{bar}^{-1}$	2.20E+00 1.25E+13 2.60E+07 1.18E+07 1.18E+07	1.10E+01 1.46E+13 1.97E+08 1.79E+07 1.79E+07	3.53E+01 1.67E+13 9.13E+08 2.59E+07 2.59E+07
25. $Z[Fe(ONO)_2]^+ \{M=6\} \leftrightarrow$ $Z[ONOFEO_2N]^+ \{M=6\}$	$\Delta H_{25} = -4.7$ $E_{25}^\ddagger = 1.3$ $E_{-25}^\ddagger = 5.3$	$K_{25}, -$ A_{25}, s^{-1} k_{25}, s^{-1} A_{-25}, s^{-1} k_{-25}, s^{-1}	1.39E+00 8.12E+11 2.80E+11 1.65E+13 2.01E+11	7.98E-01 8.05E+11 3.23E+11 1.77E+13 4.05E+11	5.24E-01 7.99E+11 3.60E+11 1.87E+13 6.87E+11
26. $Z[OFeONO]^+ \{M=5\} \leftrightarrow$ $Z[FeO_2NO]^+ \{M=5\}$	$\Delta H_{26} = -27.8$ $E_{26}^\ddagger = 10.0$ $E_{-26}^\ddagger = 36.5$	$K_{26}, -$ A_{26}, s^{-1} k_{26}, s^{-1} A_{-26}, s^{-1} k_{-26}, s^{-1}	3.02E+08 3.51E+12 7.69E+08 4.95E+13 2.55E+00	1.09E+07 3.69E+12 2.69E+09 6.08E+13 2.48E+02	8.89E+05 3.83E+12 6.90E+09 7.19E+13 7.76E+03
27. $Z[FeONO]^+ \{M=5\} \leftrightarrow$ $Z[FeO_2N]^+ \{M=5\}$	$\Delta H_{27} = -4.9$ $E_{27}^\ddagger = 3.0$ $E_{-27}^\ddagger = 7.5$	$K_{27}, -$ A_{27}, s^{-1} k_{27}, s^{-1} A_{-27}, s^{-1} k_{-27}, s^{-1}	2.00E+01 2.84E+13 2.36E+12 6.57E+13 1.18E+11	1.11E+01 2.97E+13 3.52E+12 7.14E+13 3.18E+11	7.12E+00 3.07E+13 4.75E+12 7.62E+13 6.67E+11
28. $Z[FeO_2N]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeO_2N]^+(N_2O) \{M=5\}$	$\Delta H_{28} = -4.2$ $E_{28}^\ddagger = 0.0$ $E_{-28}^\ddagger = 5.7$	K_{28}, bar^{-1} $A_{28}, \text{s}^{-1} \text{bar}^{-1}$ $k_{28}, \text{s}^{-1} \text{bar}^{-1}$ A_{-28}, s^{-1} k_{-28}, s^{-1}	3.19E-05 3.41E+06 3.41E+06 1.25E+13 1.07E+11	1.89E-05 4.66E+06 4.66E+06 1.46E+13 2.47E+11	1.31E-05 6.15E+06 6.15E+06 1.67E+13 4.69E+11

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1e: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
29. $Z[FeO_2N]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeO_2N]^+(ON_2) \{M=5\}$	$\Delta H_{29} = -2.5$ $E_{29}^\ddagger = 0.0$ $E_{29}^\ddagger = 4.2$	K_{29}, bar^{-1} $A_{29}, \text{s}^{-1} \text{bar}^{-1}$ $k_{29}, \text{s}^{-1} \text{bar}^{-1}$ A_{29}, s^{-1} k_{29}, s^{-1}	4.22E-05 1.60E+07 1.60E+07 1.25E+13 3.79E+11	3.06E-05 2.23E+07 2.23E+07 1.46E+13 7.28E+11	2.47E-05 2.99E+07 2.99E+07 1.67E+13 1.21E+12
30. $Z[FeO_2N]^+(ON_2) \{M=5\} \leftrightarrow$ $Z[OFeO_2N]^+ \{M=5\} + N_2(g)$	$\Delta H_{30} = -10.2$ $E_{30}^\ddagger = 25.4$ $E_{30}^\ddagger = 34.6$	K_{30}, bar A_{30}, s^{-1} k_{30}, s^{-1} $A_{30}, \text{s}^{-1} \text{bar}^{-1}$ $k_{30}, \text{s}^{-1} \text{bar}^{-1}$	1.78E+08 1.42E+13 7.73E+03 1.77E+08 4.35E-05	5.30E+07 1.63E+13 1.87E+05 2.27E+08 3.54E-03	2.09E+07 1.83E+13 2.07E+06 2.83E+08 9.88E-02
31. $Z[OFeO_2N]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[OFeO_2N]^+(N_2O) \{M=5\}$	$\Delta H_{31} = 1.6$ $E_{31}^\ddagger = 0.0$ $E_{31}^\ddagger = 0.3$	K_{31}, bar^{-1} $A_{31}, \text{s}^{-1} \text{bar}^{-1}$ $k_{31}, \text{s}^{-1} \text{bar}^{-1}$ A_{31}, s^{-1} k_{31}, s^{-1}	1.74E-04 1.64E+09 1.64E+09 1.25E+13 9.45E+12	2.07E-04 2.37E+09 2.37E+09 1.46E+13 1.15E+13	2.42E-04 3.27E+09 3.27E+09 1.67E+13 1.35E+13
32. $Z[OFeO_2N]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[OFeO_2N]^+(ON_2) \{M=5\}$	$\Delta H_{32} = -2.7$ $E_{32}^\ddagger = 0.0$ $E_{32}^\ddagger = 4.3$	K_{32}, bar^{-1} $A_{32}, \text{s}^{-1} \text{bar}^{-1}$ $k_{32}, \text{s}^{-1} \text{bar}^{-1}$ A_{32}, s^{-1} k_{32}, s^{-1}	1.45E-05 4.90E+06 4.90E+06 1.25E+13 3.38E+11	1.03E-05 6.79E+06 6.79E+06 1.46E+13 6.60E+11	8.17E-06 9.08E+06 9.08E+06 1.67E+13 1.11E+12
33. $Z[OFeO_2N]^+(ON_2) \{M=5\} \leftrightarrow$ $Z[O_2FeO_2N]^+ \{M=5\} + N_2(g)$	$\Delta H_{33} = -16.1$ $E_{33}^\ddagger = 45.2$ $E_{33}^\ddagger = 61.8$	K_{33}, bar A_{33}, s^{-1} k_{33}, s^{-1} $A_{33}, \text{s}^{-1} \text{bar}^{-1}$ $k_{33}, \text{s}^{-1} \text{bar}^{-1}$	3.81E+13 1.59E+14 5.15E-03 4.58E+06 1.35E-16	5.61E+12 1.89E+14 1.39E+00 5.07E+06 2.48E-13	1.31E+12 2.18E+14 9.36E+01 5.65E+06 7.15E-11
34. $Z[O_2FeO_2N]^+ \{M=5\} \leftrightarrow$ $Z[O_2FeO_2N]^+ \{M=7\}$	$\Delta H_{34} = -7.7$ $E_{34}^\ddagger = 0.1$ $E_{34}^\ddagger = 7.8$	$K_{34}, -$ A_{34}, s^{-1} k_{34}, s^{-1} A_{34}, s^{-1} k_{34}, s^{-1}	5.97E+02 1.25E+13 1.11E+13 1.31E+13 1.86E+10	2.37E+02 1.46E+13 1.32E+13 1.53E+13 5.55E+10	1.19E+02 1.67E+13 1.52E+13 1.76E+13 1.28E+11
35. $Z[O_2FeO_2N]^+ \{M=7\} \leftrightarrow$ $Z[FeO_2N]^+ \{M=5\} + O_2(g)$	$\Delta H_{35} = 0.7$ $E_{35}^\ddagger = 3.0$ $E_{35}^\ddagger = 1.2$	K_{35}, bar^{-1} $A_{35}, \text{s}^{-1} \text{bar}^{-1}$ $k_{35}, \text{s}^{-1} \text{bar}^{-1}$ A_{35}, s^{-1} k_{35}, s^{-1}	2.70E+06 1.30E+13 1.08E+12 1.13E+06 4.01E+05	2.99E+06 1.38E+13 1.64E+12 1.33E+06 5.47E+05	3.14E+06 1.44E+13 2.23E+12 1.55E+06 7.11E+05

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1f: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
36. $Z[O_2FeO_2N]^+ \{M=7\} \leftrightarrow$ $Z[FeO_2]^+ \{M=6\} + NO_2(g)$	$\Delta H_{36} = 19.6$ $E_{36}^\ddagger = 21.2$ $E_{36}^\ddagger = 0.0$	K_{36}, bar A_{36}, s^{-1} k_{36}, s^{-1} $A_{36}, s^{-1} \text{ bar}^{-1}$ $k_{36}, s^{-1} \text{ bar}^{-1}$	1.68E+00 1.25E+13 2.34E+05 1.39E+05 1.39E+05	1.81E+01 1.46E+13 3.47E+06 1.92E+05 1.92E+05	1.04E+02 1.67E+13 2.67E+07 2.57E+05 2.57E+05
37. $Z[OFeO_2N]^+ \{M=5\} + NO(g) \leftrightarrow$ $Z[ONFeO_2N]^+ \{M=6\}$	$\Delta H_{37} = -32.9$ $E_{37}^\ddagger = 0.0$ $E_{37}^\ddagger = 34.2$	K_{37}, bar^{-1} $A_{37}, s^{-1} \text{ bar}^{-1}$ $k_{37}, s^{-1} \text{ bar}^{-1}$ A_{37}, s^{-1} k_{37}, s^{-1}	3.19E+06 1.32E+07 1.32E+07 1.25E+13 4.14E+00	5.94E+04 1.74E+07 1.74E+07 1.46E+13 2.93E+02	3.08E+03 2.24E+07 2.24E+07 1.67E+13 7.28E+03
38. $Z[ONFeO_2N]^+ \{M=6\} \leftrightarrow$ $Z[FeO_2N]^+ \{M=5\} + NO_2(g)$	$\Delta H_{38} = 12.9$ $E_{38}^\ddagger = 15.0$ $E_{38}^\ddagger = 0.0$	K_{38}, bar A_{38}, s^{-1} k_{38}, s^{-1} $A_{38}, s^{-1} \text{ bar}^{-1}$ $k_{38}, s^{-1} \text{ bar}^{-1}$	3.15E+01 1.25E+13 4.24E+07 1.35E+06 1.35E+06	1.53E+02 1.46E+13 2.99E+08 1.96E+06 1.96E+06	4.80E+02 1.67E+13 1.32E+09 2.75E+06 2.75E+06
39. $Z[ONFeO_2N]^+ \{M=6\} \leftrightarrow$ $Z[Fe(O_2N)_2]^+ \{M=6\}$	$\Delta H_{39} = -0.6$ $E_{39}^\ddagger = 2.8$ $E_{39}^\ddagger = 2.7$	$K_{39}, -$ A_{39}, s^{-1} k_{39}, s^{-1} A_{39}, s^{-1} k_{39}, s^{-1}	4.14E-02 3.65E+11 3.46E+10 8.13E+12 8.35E+11	3.87E-02 3.56E+11 4.72E+10 8.58E+12 1.22E+12	3.67E-02 3.50E+11 5.97E+10 8.96E+12 1.63E+12
40. $Z[OFeO_2N]^+ \{M=5\} \leftrightarrow$ $Z[OFeONO]^+ \{M=5\}$	$\Delta H_{40} = 3.5$ $E_{40}^\ddagger = 5.6$ $E_{40}^\ddagger = 3.0$	$K_{40}, -$ A_{40}, s^{-1} k_{40}, s^{-1} A_{40}, s^{-1} k_{40}, s^{-1}	1.74E+00 3.73E+13 3.50E+11 2.41E+12 2.01E+11	2.63E+00 4.20E+13 7.68E+11 2.45E+12 2.92E+11	3.59E+00 4.61E+13 1.39E+12 2.49E+12 3.86E+11
41. $Z[FeO_2N]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeO_2NO]^+ \{M=5\} + N_2(g)$	$\Delta H_{41} = -37.1$ $E_{41}^\ddagger = 49.6$ $E_{41}^\ddagger = 86.8$	$K_{41}, -$ A_{41}, s^{-1} k_{41}, s^{-1} A_{41}, s^{-1} k_{41}, s^{-1}	3.94E+12 2.53E+08 2.11E-10 2.25E+09 5.35E-23	4.63E+10 3.44E+08 1.10E-07 3.03E+09 2.37E-18	1.65E+09 4.50E+08 1.24E-05 3.92E+09 7.51E-15
42. $Z[FeO_2NO]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeO_2NO]^+(N_2O)\{M=5\}$	$\Delta H_{42} = -1.8$ $E_{42}^\ddagger = 0.0$ $E_{42}^\ddagger = 3.4$	K_{42}, bar^{-1} $A_{42}, s^{-1} \text{ bar}^{-1}$ $k_{42}, s^{-1} \text{ bar}^{-1}$ A_{42}, s^{-1} k_{42}, s^{-1}	2.61E-05 1.82E+07 1.82E+07 1.25E+13 6.97E+11	2.05E-05 2.52E+07 2.52E+07 1.46E+13 1.23E+12	1.76E-05 3.37E+07 3.37E+07 1.67E+13 1.91E+12

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1g: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
43. $Z[FeO_2NO]^+ \{M=5\} + N_2O(g) \leftrightarrow Z[FeO_2NO]^+(ON_2)\{M=5\}$	$\Delta H_{43} = -1.0$ $E_{43}^\ddagger = 0.0$ $E_{43}^\ddagger = 2.7$	K_{43}, bar^{-1} $A_{43}, \text{s}^{-1} \text{bar}^{-1}$ $k_{43}, \text{s}^{-1} \text{bar}^{-1}$ A_{43}, s^{-1} k_{43}, s^{-1}	9.10E-06 1.14E+07 1.14E+07 1.25E+13 1.26E+12	7.89E-06 1.61E+07 1.61E+07 1.46E+13 2.03E+12	7.28E-06 2.17E+07 2.17E+07 1.67E+13 2.97E+12
44. $Z[FeO_2NO]^+(ON_2)\{M=5\} \leftrightarrow Z[OFeO_2NO]^+ \{M=5\} + N_2(g)$	$\Delta H_{44} = -7.0$ $E_{44}^\ddagger = 25.2$ $E_{44}^\ddagger = 31.2$	K_{44}, bar A_{44}, s^{-1} k_{44}, s^{-1} $A_{44}, \text{s}^{-1} \text{bar}^{-1}$ $k_{44}, \text{s}^{-1} \text{bar}^{-1}$	2.50E+07 3.42E+13 2.27E+04 2.13E+08 9.07E-04	1.10E+07 3.99E+13 5.41E+05 2.75E+08 4.93E-02	5.79E+06 4.52E+13 5.91E+06 3.43E+08 1.02E+00
45. $Z[OFeO_2NO]^+ \{M=5\} + N_2O(g) \leftrightarrow Z[OFeO_2NO]^+(N_2O)\{M=5\}$	$\Delta H_{45} = -2.6$ $E_{45}^\ddagger = 0.0$ $E_{45}^\ddagger = 4.1$	K_{45}, bar^{-1} $A_{45}, \text{s}^{-1} \text{bar}^{-1}$ $k_{45}, \text{s}^{-1} \text{bar}^{-1}$ A_{45}, s^{-1} k_{45}, s^{-1}	8.56E-06 3.45E+06 3.45E+06 1.25E+13 4.03E+11	6.17E-06 4.73E+06 4.73E+06 1.46E+13 7.67E+11	4.95E-06 6.27E+06 6.27E+06 1.67E+13 1.27E+12
46. $Z[OFeO_2NO]^+ \{M=5\} + N_2O(g) \leftrightarrow Z[OFeO_2NO]^+(ON_2)\{M=5\}$	$\Delta H_{46} = -2.9$ $E_{46}^\ddagger = 0.0$ $E_{46}^\ddagger = 4.5$	K_{46}, bar^{-1} $A_{46}, \text{s}^{-1} \text{bar}^{-1}$ $k_{46}, \text{s}^{-1} \text{bar}^{-1}$ A_{46}, s^{-1} k_{46}, s^{-1}	3.87E-06 1.14E+06 1.14E+06 1.25E+13 1.14E+06	2.67E-06 1.57E+06 1.57E+06 1.46E+13 1.57E+06	2.07E-06 2.08E+06 2.08E+06 1.67E+13 2.08E+06
47. $Z[OFeO_2NO]^+(ON_2)\{M=5\} \leftrightarrow Z[O_2FeO_2NO]^+ \{M=5\} + N_2(g)$	$\Delta H_{47} = -19.2$ $E_{47}^\ddagger = 41.1$ $E_{47}^\ddagger = 61.0$	K_{47}, bar A_{47}, s^{-1} k_{47}, s^{-1} $A_{47}, \text{s}^{-1} \text{bar}^{-1}$ $k_{47}, \text{s}^{-1} \text{bar}^{-1}$	6.52E+15 1.02E+13 1.05E-02 2.67E+04 1.61E-18	6.60E+14 1.18E+13 1.67E+00 2.82E+04 2.54E-15	1.16E+14 1.32E+13 7.60E+01 3.02E+04 6.53E-13
48. $Z[O_2FeO_2NO]^+ \{M=5\} \leftrightarrow Z[O_2FeO_2NO]^+ \{M=7\}$	$\Delta H_{48} = -8.7$ $E_{48}^\ddagger = 0.4$ $E_{48}^\ddagger = 8.9$	$K_{48}, -$ A_{48}, s^{-1} k_{48}, s^{-1} A_{48}, s^{-1} k_{48}, s^{-1}	6.26E+02 1.25E+13 9.24E+12 2.63E+13 1.48E+10	2.20E+02 1.46E+13 1.13E+13 3.12E+13 5.11E+10	1.01E+02 1.67E+13 1.33E+13 3.62E+13 1.32E+11
49. $Z[O_2FeO_2NO]^+ \{M=7\} \leftrightarrow Z[FeO_2NO]^+ \{M=5\} + O_2(g)$	$\Delta H_{49} = 0.4$ $E_{49}^\ddagger = 3.0$ $E_{49}^\ddagger = 1.5$	K_{49}, bar A_{49}, s^{-1} k_{49}, s^{-1} $A_{49}, \text{s}^{-1} \text{bar}^{-1}$ $k_{49}, \text{s}^{-1} \text{bar}^{-1}$	1.86E+06 1.91E+13 1.57E+12 3.07E+06 8.45E+05	1.98E+06 2.04E+13 2.40E+12 3.68E+06 1.21E+06	2.01E+06 2.15E+13 3.30E+12 4.32E+06 1.64E+06

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1h: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
50. $Z[O_2FeO_2NO]^+ \{M=7\} \leftrightarrow$ $Z[OFeO_2]^+ \{M=6\} + NO_2(g)$	$\Delta H_{50} = 43.2$ $E_{50}^\ddagger = 44.0$ $E_{50}^\ddagger = 0.0$	K_{50}, bar A_{50}, s^{-1} k_{50}, s^{-1} $A_{50}, s^{-1} \text{ bar}^{-1}$ $k_{50}, s^{-1} \text{ bar}^{-1}$	3.88E-09 1.25E+13 1.16E-03 3.00E+05 3.00E+05	8.05E-07 1.46E+13 2.65E-01 3.29E+05 3.29E+05	4.34E-05 1.67E+13 1.58E+01 3.64E+05 3.64E+05
51. $Z[OFeO_2NO]^+ \{M=5\} \leftrightarrow$ $Z[OFeO]^+ \{M=6\} + NO_2(g)$	$\Delta H_{51} = 33.6$ $E_{51}^\ddagger = 40.8$ $E_{51}^\ddagger = 7.2$	K_{51}, bar A_{51}, s^{-1} k_{51}, s^{-1} $A_{51}, s^{-1} \text{ bar}^{-1}$ $k_{51}, s^{-1} \text{ bar}^{-1}$	1.75E-03 1.25E+13 1.71E-02 4.22E+03 9.76E+00	1.00E-01 1.46E+13 2.65E+00 4.81E+03 2.65E+01	2.02E+00 1.67E+13 1.18E+02 5.55E+03 5.86E+01
52. $Z[OFeO_2NO]^+ \{M=5\} + NO(g) \leftrightarrow$ $Z[ONFeO_2NO]^+ \{M=6\}$	$\Delta H_{52} = -37.0$ $E_{52}^\ddagger = 0.0$ $E_{52}^\ddagger = 38.3$	K_{52}, bar^{-1} $A_{52}, s^{-1} \text{ bar}^{-1}$ $k_{52}, s^{-1} \text{ bar}^{-1}$ A_{52}, s^{-1} k_{52}, s^{-1}	8.49E+07 1.18E+07 1.18E+07 1.25E+13 1.39E-01	9.67E+05 1.55E+07 1.55E+07 1.46E+13 1.60E+01	3.46E+04 1.98E+07 1.98E+07 1.67E+13 5.71E+02
53. $Z[ONFeO_2NO]^+ \{M=6\} \leftrightarrow$ $Z[FeO_2NO]^+ \{M=5\} + NO_2(g)$	$\Delta H_{53} = 12.3$ $E_{53}^\ddagger = 14.5$ $E_{53}^\ddagger = 0.0$	K_{53}, bar A_{53}, s^{-1} k_{53}, s^{-1} $A_{53}, s^{-1} \text{ bar}^{-1}$ $k_{53}, s^{-1} \text{ bar}^{-1}$	3.90E+01 1.25E+13 6.76E+07 1.73E+06 1.73E+06	1.76E+02 1.46E+13 4.46E+08 2.54E+06 2.54E+06	5.23E+02 1.67E+13 1.87E+09 3.57E+06 3.57E+06
54. $Z[ONFeO_2NO]^+ \{M=6\} \leftrightarrow$ $Z[NO_2FeO_2NO]^+ \{M=6\}$	$\Delta H_{54} = -1.3$ $E_{54}^\ddagger = 2.5$ $E_{54}^\ddagger = 3.0$	$K_{54}, -$ A_{54}, s^{-1} k_{54}, s^{-1} A_{54}, s^{-1} k_{54}, s^{-1}	5.53E-02 5.32E+11 6.70E+10 1.52E+13 1.21E+12	4.75E-02 5.20E+11 8.80E+10 1.61E+13 1.85E+12	4.22E-02 5.10E+11 1.08E+11 1.70E+13 2.55E+12
55. $Z[Fe(OH)_2]^+ \{M=6\} + NO(g) \leftrightarrow$ $Z[Fe(OH)_2]^+(ON) \{M=7\}$	$\Delta H_{55} = 1.1$ $E_{55}^\ddagger = 0.0$ $E_{55}^\ddagger = 0.5$	K_{55}, bar^{-1} $A_{55}, s^{-1} \text{ bar}^{-1}$ $k_{55}, s^{-1} \text{ bar}^{-1}$ A_{55}, s^{-1} k_{55}, s^{-1}	3.00E-05 2.46E+08 2.46E+08 1.25E+13 8.18E+12	3.29E-05 3.34E+08 3.34E+08 1.46E+13 1.01E+13	3.62E-05 4.39E+08 4.39E+08 1.67E+13 1.21E+13
56. $Z[Fe(OH)_2]^+ \{M=6\} + NO(g) \leftrightarrow$ $Z[Fe(OH)_2]^+(NO) \{M=7\}$	$\Delta H_{56} = -0.9$ $E_{56}^\ddagger = 0.0$ $E_{56}^\ddagger = 2.1$	K_{56}, bar^{-1} $A_{56}, s^{-1} \text{ bar}^{-1}$ $k_{56}, s^{-1} \text{ bar}^{-1}$ A_{56}, s^{-1} k_{56}, s^{-1}	2.37E-05 5.01E+07 5.01E+07 1.25E+13 2.11E+12	2.05E-05 6.52E+07 6.52E+07 1.46E+13 3.17E+12	1.89E-05 8.28E+07 8.28E+07 1.67E+13 4.39E+12

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1i: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
57. $Z[Fe(OH)_2]^+(NO) \{M=7\} \leftrightarrow$ $Z[Fe(OH)_2]^+(NO) \{M=5\}$	$\Delta H_{57} = -0.01$ $E_{57}^\ddagger = 0.1$ $E_{57}^\ddagger = 0.03$	$K_{57}, -$ A_{57}, s^{-1} k_{57}, s^{-1} A_{57}, s^{-1} k_{57}, s^{-1}	5.20E-01 1.25E+13 1.19E+13 2.35E+13 2.30E+13	5.20E-01 1.46E+13 1.40E+13 2.76E+13 2.70E+13	5.19E-01 1.67E+13 1.61E+13 3.16E+13 3.10E+13
58. $Z[Fe(OH)_2]^+(NO) \{M=5\} \leftrightarrow$ $Z[FeOH]^+(t-HNO_2) \{M=5\}$	$\Delta H_{58} = 6.4$ $E_{58}^\ddagger = 9.7$ $E_{58}^\ddagger = 2.3$	$K_{58}, -$ A_{58}, s^{-1} k_{58}, s^{-1} A_{58}, s^{-1} k_{58}, s^{-1}	2.16E-05 3.72E+12 1.05E+09 3.22E+14 4.84E+13	4.68E-05 3.75E+12 3.40E+09 3.68E+14 7.26E+13	8.29E-05 3.77E+12 8.20E+09 4.09E+14 9.89E+13
59. $Z[Fe(OH)_2]^+(NO) \{M=5\} \leftrightarrow$ $Z[FeOH]^+(c-HNO_2) \{M=5\}$	$\Delta H_{59} = 8.7$ $E_{59}^\ddagger = 11.0$ $E_{59}^\ddagger = 1.3$	$K_{59}, -$ A_{59}, s^{-1} k_{59}, s^{-1} A_{59}, s^{-1} k_{59}, s^{-1}	7.12E-06 1.13E+11 1.09E+07 4.49E+12 1.53E+12	2.04E-05 1.06E+11 3.82E+07 4.72E+12 1.88E+12	4.45E-05 1.00E+11 9.76E+07 4.91E+12 2.19E+12
60. $Z[FeOH]^+(t-HNO_2) \{M=5\} \leftrightarrow$ $Z[FeOH]^+ \{M=5\} + t-HNO_2(g)$	$\Delta H_{60} = 5.9$ $E_{60}^\ddagger = 7.9$ $E_{60}^\ddagger = 0.0$	K_{60}, bar A_{60}, s^{-1} k_{60}, s^{-1} $A_{60}, s^{-1} bar^{-1}$ $k_{60}, s^{-1} bar^{-1}$	4.84E+04 1.25E+13 1.61E+10 3.33E+05 3.33E+05	1.01E+05 1.46E+13 4.87E+10 4.84E+05 4.84E+05	1.68E+05 1.67E+13 1.14E+11 6.76E+05 6.76E+05
61. $Z[FeOH]^+(c-HNO_2) \{M=5\} \leftrightarrow$ $Z[FeOH]^+ \{M=5\} + c-HNO_2(g)$	$\Delta H_{61} = 4.3$ $E_{61}^\ddagger = 6.6$ $E_{61}^\ddagger = 0.0$	K_{61}, bar A_{61}, s^{-1} k_{61}, s^{-1} $A_{61}, s^{-1} bar^{-1}$ $k_{61}, s^{-1} bar^{-1}$	6.45E+04 1.25E+13 5.06E+10 7.85E+05 7.85E+05	1.11E+05 1.46E+13 1.30E+11 1.17E+06 1.17E+06	1.61E+05 1.67E+13 2.68E+11 1.66E+06 1.66E+06
62. $Z[FeOH]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeOH]^+(N_2O) \{M=5\}$	$\Delta H_{62} = 0.7$ $E_{62}^\ddagger = 0.0$ $E_{62}^\ddagger = 0.9$	K_{62}, bar^{-1} $A_{62}, s^{-1} bar^{-1}$ $k_{62}, s^{-1} bar^{-1}$ A_{62}, s^{-1} k_{62}, s^{-1}	1.32E-04 7.57E+08 7.57E+08 1.25E+13 5.74E+12	1.41E-04 1.06E+09 1.06E+09 1.46E+13 7.49E+12	1.53E-04 1.42E+09 1.42E+09 1.67E+13 9.30E+12
63. $Z[FeOH]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeOH]^+(ON_2) \{M=5\}$	$\Delta H_{63} = 0.2$ $E_{63}^\ddagger = 0.0$ $E_{63}^\ddagger = 1.3$	K_{63}, bar^{-1} $A_{63}, s^{-1} bar^{-1}$ $k_{63}, s^{-1} bar^{-1}$ A_{63}, s^{-1} k_{63}, s^{-1}	1.03E-04 4.37E+08 4.37E+08 1.25E+13 4.25E+12	1.04E-04 6.03E+08 6.03E+08 1.46E+13 5.79E+12	1.08E-04 8.00E+08 8.00E+08 1.67E+13 7.42E+12

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1j: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
64. $Z[FeOH]^+(ON_2) \{M=5\} \leftrightarrow$ $Z[OFeOH]^+ \{M=5\} + N_2(g)$	$\Delta H_{64} = -18.1$ $E_{64}^\ddagger = 21.8$ $E_{-64}^\ddagger = 38.8$	K_{64}, bar A_{64}, s^{-1} k_{64}, s^{-1} $A_{-64}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-64}, \text{s}^{-1} \text{bar}^{-1}$	8.11E+09 4.52E+10 5.22E+02 8.52E+06 6.43E-08	9.35E+08 4.98E+10 7.81E+03 1.06E+07 8.35E-06	1.81E+08 5.40E+10 6.01E+04 1.30E+07 3.32E-04
65. $Z[OFeOH]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[OFeOH]^+(N_2O) \{M=5\}$	$\Delta H_{65} = -0.8$ $E_{65}^\ddagger = 0.0$ $E_{-65}^\ddagger = 2.5$	K_{65}, bar^{-1} $A_{65}, \text{s}^{-1} \text{bar}^{-1}$ $k_{65}, \text{s}^{-1} \text{bar}^{-1}$ A_{-65}, s^{-1} k_{-65}, s^{-1}	1.25E-04 1.92E+08 1.92E+08 1.25E+13 1.54E+12	1.11E-04 2.68E+08 2.68E+08 1.46E+13 2.42E+12	1.04E-04 3.60E+08 3.60E+08 1.67E+13 3.46E+12
66. $Z[OFeOH]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[OFeOH]^+(ON_2) \{M=5\}$	$\Delta H_{66} = -1.5$ $E_{66}^\ddagger = 0.0$ $E_{-66}^\ddagger = 3.1$	K_{66}, bar^{-1} $A_{66}, \text{s}^{-1} \text{bar}^{-1}$ $k_{66}, \text{s}^{-1} \text{bar}^{-1}$ A_{-66}, s^{-1} k_{-66}, s^{-1}	5.86E-05 5.59E+07 5.59E+07 1.25E+13 9.54E+11	4.83E-05 7.76E+07 7.76E+07 1.46E+13 1.61E+12	4.29E-05 1.04E+08 1.04E+08 1.67E+13 2.42E+12
67. $Z[OFeOH]^+(ON_2) \{M=5\} \leftrightarrow$ $Z[O_2FeOH]^+ \{M=5\} + N_2(g)$	$\Delta H_{67} = -20.5$ $E_{67}^\ddagger = 46.5$ $E_{-67}^\ddagger = 67.7$	K_{67}, bar A_{67}, s^{-1} k_{67}, s^{-1} $A_{-67}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-67}, \text{s}^{-1} \text{bar}^{-1}$	6.27E+13 5.48E+12 6.10E-05 4.70E+06 9.73E-19	5.42E+12 6.52E+12 1.92E-02 5.09E+06 3.54E-15	8.53E+11 7.54E+12 1.45E+00 5.56E+06 1.71E-12
68. $Z[O_2FeOH]^+ \{M=5\} \leftrightarrow$ $Z[O_2FeOH]^+ \{M=7\}$	$\Delta H_{68} = -4.5$ $E_{68}^\ddagger = 6.0$ $E_{-68}^\ddagger = 10.5$	$K_{68}, -$ A_{68}, s^{-1} k_{68}, s^{-1} A_{-68}, s^{-1} k_{-68}, s^{-1}	6.09E+01 1.25E+13 8.19E+10 8.75E+12 1.34E+09	3.57E+01 1.46E+13 1.96E+11 1.02E+13 5.49E+09	2.39E+01 1.67E+13 3.84E+11 1.16E+13 1.61E+10
69. $Z[O_2FeOH]^+ \{M=7\} \leftrightarrow$ $Z[FeOH]^+ \{M=5\} + O_2(g)$	$\Delta H_{69} = 5.8$ $E_{69}^\ddagger = 7.6$ $E_{-69}^\ddagger = 0.8$	K_{69}, bar A_{69}, s^{-1} k_{69}, s^{-1} $A_{-69}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-69}, \text{s}^{-1} \text{bar}^{-1}$	3.58E+04 7.23E+13 1.22E+11 6.59E+06 3.40E+06	7.30E+04 7.93E+13 3.32E+11 8.03E+06 4.55E+06	1.21E+05 8.50E+13 7.05E+11 9.58E+06 5.82E+06
70. $Z[OFeOH]^+ \{M=5\} + NO(g) \leftrightarrow$ $Z[ONFeOH]^+ \{M=6\}$	$\Delta H_{70} = -31.6$ $E_{70}^\ddagger = 0.0$ $E_{-70}^\ddagger = 32.9$	K_{70}, bar^{-1} $A_{70}, \text{s}^{-1} \text{bar}^{-1}$ $k_{70}, \text{s}^{-1} \text{bar}^{-1}$ A_{-70}, s^{-1} k_{-70}, s^{-1}	2.09E+05 2.60E+06 2.60E+06 1.25E+13 1.24E+01	4.56E+03 3.42E+06 3.42E+06 1.46E+13 7.51E+02	2.66E+02 4.42E+06 4.42E+06 1.67E+13 1.66E+04

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1k: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
71. $Z[ONFeOH]^+ \{M=6\} \leftrightarrow$ $Z[FeOH]^+ \{M=5\} + NO_2(g)$	$\Delta H_{71} = 16.8$ $E_{71}^\ddagger = 18.6$ $E_{71}^\ddagger = 0.0$	K_{71}, bar A_{71}, s^{-1} k_{71}, s^{-1} $A_{71}, s^{-1} \text{bar}^{-1}$ $k_{71}, s^{-1} \text{bar}^{-1}$	4.32E+00 1.25E+13 2.08E+06 4.81E+05 4.81E+05	3.32E+01 1.46E+13 2.25E+07 6.80E+05 6.80E+05	1.47E+02 1.67E+13 1.37E+08 9.32E+05 9.32E+05
72. $Z[OFeOH]^+ \{M=5\} + NO(g) \leftrightarrow$ $Z[FeO]^+(t-HNO_2) \{M=6\}$	$\Delta H_{72} = -0.2$ $E_{72}^\ddagger = 0.0$ $E_{72}^\ddagger = 1.4$	K_{72}, bar^{-1} $A_{72}, s^{-1} \text{bar}^{-1}$ $k_{72}, s^{-1} \text{bar}^{-1}$ A_{72}, s^{-1} k_{72}, s^{-1}	1.14E-06 4.28E+06 4.28E+06 1.25E+13 3.74E+12	1.07E-06 5.56E+06 5.56E+06 1.46E+13 5.19E+12	1.05E-06 7.07E+06 7.07E+06 1.67E+13 6.75E+12
73. $Z[FeO]^+(t-HNO_2) \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + t-HNO_2(g)$	$\Delta H_{73} = 11.2$ $E_{73}^\ddagger = 13.5$ $E_{73}^\ddagger = 0.0$	K_{73}, bar A_{73}, s^{-1} k_{73}, s^{-1} $A_{73}, s^{-1} \text{bar}^{-1}$ $k_{73}, s^{-1} \text{bar}^{-1}$	3.08E+02 1.25E+13 1.55E+08 5.01E+05 5.01E+05	1.21E+03 1.46E+13 9.06E+08 7.48E+05 7.48E+05	3.25E+03 1.67E+13 3.47E+09 1.07E+06 1.07E+06
74. $Z[OFeOH]^+ \{M=5\} + t-HNO_2(g) \leftrightarrow$ $Z[OFeOH]^+(t-HNO_2) \{M=5\}$	$\Delta H_{74} = -8.8$ $E_{74}^\ddagger = 0.0$ $E_{74}^\ddagger = 9.5$	K_{74}, bar^{-1} $A_{74}, s^{-1} \text{bar}^{-1}$ $k_{74}, s^{-1} \text{bar}^{-1}$ A_{74}, s^{-1} k_{74}, s^{-1}	7.84E-06 3.33E+04 3.33E+04 1.25E+13 4.25E+09	2.68E-06 4.16E+04 4.16E+04 1.46E+13 1.55E+10	1.23E-06 5.15E+04 5.15E+04 1.67E+13 4.18E+10
75. $Z[OFeOH]^+(t-HNO_2) \{M=5\} \leftrightarrow$ $Z[OFeOH_2]^+(NO_2) \{M=5\}$	$\Delta H_{75} = -1.4$ $E_{75}^\ddagger = 1.9$ $E_{75}^\ddagger = 3.9$	$K_{75}, -$ A_{75}, s^{-1} k_{75}, s^{-1} A_{75}, s^{-1} k_{75}, s^{-1}	7.07E+00 2.06E+12 4.02E+11 1.52E+12 5.68E+10	5.99E+00 2.14E+12 5.27E+11 1.47E+12 8.81E+10	5.30E+00 2.22E+12 6.51E+11 1.44E+12 1.23E+11
76. $Z[OFeOH_2]^+(NO_2) \{M=5\} \leftrightarrow$ $Z[OFeOH_2]^+(NO_2) \{M=7\}$	$\Delta H_{76} = 7.3$ $E_{76}^\ddagger = 6.8$ $E_{76}^\ddagger = 0.8$	$K_{76}, -$ A_{76}, s^{-1} k_{76}, s^{-1} A_{76}, s^{-1} k_{76}, s^{-1}	6.63E+00 1.25E+13 4.22E+10 1.29E+10 6.37E+09	1.59E+01 1.46E+13 1.11E+11 1.28E+10 7.00E+09	3.06E+01 1.67E+13 2.33E+11 1.30E+10 7.63E+09
77. $Z[OFeOH_2]^+(NO_2) \{M=7\} \leftrightarrow$ $Z[FeO]^+(OH_2) \{M=6\} + NO_2(g)$	$\Delta H_{77} = 3.7$ $E_{77}^\ddagger = 5.2$ $E_{77}^\ddagger = 0.0$	K_{77}, bar A_{77}, s^{-1} k_{77}, s^{-1} $A_{77}, s^{-1} \text{bar}^{-1}$ $k_{77}, s^{-1} \text{bar}^{-1}$	1.04E+05 1.25E+13 1.64E+11 1.58E+06 1.58E+06	1.66E+05 1.46E+13 3.56E+11 2.14E+06 2.14E+06	2.30E+05 1.67E+13 6.47E+11 2.82E+06 2.82E+06

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.11: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
78. $Z[FeO]^+(OH_2) \{M=6\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + H_2O (g)$	$\Delta H_{78} = 16.3$ $E_{78}^\ddagger = 17.3$ $E_{78}^\ddagger = 0.0$	K_{78}, bar A_{78}, s^{-1} k_{78}, s^{-1} $A_{78}, s^{-1} \text{ bar}^{-1}$ $k_{78}, s^{-1} \text{ bar}^{-1}$	1.01E+00 1.25E+13 6.13E+06 6.04E+06 6.04E+06	7.35E+00 1.46E+13 5.70E+07 7.75E+06 7.75E+06	3.14E+01 1.67E+13 3.09E+08 9.82E+06 9.82E+06
79. $Z[FeO]^+(OH_2) \{M=6\} \leftrightarrow$ $Z[Fe(OH)_2]^+ \{M=6\}$	$\Delta H_{79} = -27.1$ $E_{79}^\ddagger = 9.2$ $E_{79}^\ddagger = 36.4$	$K_{79}, -$ A_{79}, s^{-1} k_{79}, s^{-1} A_{79}, s^{-1} k_{79}, s^{-1}	1.83E+09 2.28E+12 1.03E+09 1.08E+13 5.63E-01	7.10E+07 2.18E+12 2.97E+09 1.02E+13 4.18E+01	6.26E+06 2.13E+12 6.60E+09 9.69E+12 1.05E+03
80. $Z[OFeO]^+ \{M=6\} + N_2O (g) \leftrightarrow$ $Z[FeO]^+(c-(NO)_2) \{M=6\}$	$\Delta H_{80} = 24.4$ $E_{80}^\ddagger = 28.2$ $E_{80}^\ddagger = 4.5$	K_{80}, bar^{-1} $A_{80}, s^{-1} \text{ bar}^{-1}$ $k_{80}, s^{-1} \text{ bar}^{-1}$ A_{80}, s^{-1} k_{80}, s^{-1}	2.43E-16 2.55E+06 1.39E-04 2.45E+13 5.72E+11	4.46E-15 3.08E+06 4.91E-03 2.76E+13 1.10E+12	4.07E-14 3.65E+06 7.33E-02 3.01E+13 1.80E+12
81. $Z[FeO]^+(c-(NO)_2) \{M=6\} \leftrightarrow$ $Z[FeO]^+(ON) \{M=5\} + NO (g)$	$\Delta H_{81} = -6.1$ $E_{81}^\ddagger = 9.2$ $E_{81}^\ddagger = 16.6$	K_{81}, bar A_{81}, s^{-1} k_{81}, s^{-1} $A_{81}, s^{-1} \text{ bar}^{-1}$ $k_{81}, s^{-1} \text{ bar}^{-1}$	3.40E+12 4.78E+13 2.18E+10 7.02E+03 6.40E-03	1.70E+12 5.62E+13 7.69E+10 6.82E+03 4.54E-02	9.85E+11 6.40E+13 2.00E+11 6.87E+03 2.03E-01
82. $Z[FeO]^+(ON) \{M=5\} \leftrightarrow$ $Z[FeO]^+ \{M=6\} + NO (g)$	$\Delta H_{82} = 3.3$ $E_{82}^\ddagger = 4.8$ $E_{82}^\ddagger = 0.0$	K_{82}, bar A_{82}, s^{-1} k_{82}, s^{-1} $A_{82}, s^{-1} \text{ bar}^{-1}$ $k_{82}, s^{-1} \text{ bar}^{-1}$	2.60E+04 1.25E+13 2.28E+11 8.78E+06 8.78E+06	4.01E+04 1.46E+13 4.72E+11 1.17E+07 1.17E+07	5.41E+04 1.67E+13 8.28E+11 1.53E+07 1.53E+07
83. $Z[ONFeO]^+ \{M=5\} + N_2O (g) \leftrightarrow$ $Z[FeONO]^+(c-(NO)_2) \{M=5\}$	$\Delta H_{83} = 22.2$ $E_{83}^\ddagger = 23.8$ $E_{83}^\ddagger = 3.2$	K_{83}, bar^{-1} $A_{83}, s^{-1} \text{ bar}^{-1}$ $k_{83}, s^{-1} \text{ bar}^{-1}$ A_{83}, s^{-1} k_{83}, s^{-1}	5.95E-14 4.06E+07 8.37E-02 2.07E+13 1.41E+12	8.33E-13 5.31E+07 1.91E+00 2.29E+13 2.29E+12	6.22E-12 6.71E+07 2.05E+01 2.48E+13 3.30E+12
84. $Z[FeONO]^+(c-(NO)_2) \{M=5\} \leftrightarrow$ $Z[FeONO]^+(ON) \{M=4\} + NO (g)$	$\Delta H_{84} = -3.0$ $E_{84}^\ddagger = 6.1$ $E_{84}^\ddagger = 9.7$	K_{84}, bar A_{84}, s^{-1} k_{84}, s^{-1} $A_{84}, s^{-1} \text{ bar}^{-1}$ $k_{84}, s^{-1} \text{ bar}^{-1}$	1.02E+10 2.59E+13 1.51E+11 4.92E+04 1.48E+01	7.42E+09 2.94E+13 3.59E+11 5.05E+04 4.83E+01	5.69E+09 3.25E+13 6.89E+11 5.31E+04 1.21E+02

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1m: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
85. $Z[FeONO]^+(ON) \{M=4\} \leftrightarrow$ $Z[FeONO]^+ \{M=5\} + NO(g)$	$\Delta H_{85} = 0.04$ $E_{85}^\ddagger = 1.7$ $E_{85}^\ddagger = 0.0$	K_{85}, bar A_{85}, s^{-1} k_{85}, s^{-1} $A_{85}, \text{s}^{-1} \text{bar}^{-1}$ $k_{85}, \text{s}^{-1} \text{bar}^{-1}$	8.65E+04 1.25E+13 3.12E+12 3.61E+07 3.61E+07	9.01E+04 1.46E+13 4.44E+12 4.93E+07 4.93E+07	9.05E+04 1.67E+13 5.89E+12 6.51E+07 6.51E+07
86. $Z[OFeO_2N]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeO_2N]^+(c-(NO)_2) \{M=5\}$	$\Delta H_{86} = 21.2$ $E_{86}^\ddagger = 21.8$ $E_{86}^\ddagger = 2.3$	K_{86}, bar^{-1} $A_{86}, \text{s}^{-1} \text{bar}^{-1}$ $k_{86}, \text{s}^{-1} \text{bar}^{-1}$ A_{86}, s^{-1} k_{86}, s^{-1}	1.58E-13 4.88E+07 5.64E-01 2.47E+13 3.58E+12	1.95E-12 6.48E+07 1.02E+01 2.73E+13 5.22E+12	1.33E-11 8.29E+07 9.24E+01 2.95E+13 6.93E+12
87. $Z[FeO_2N]^+(c-(NO)_2) \{M=5\} \leftrightarrow$ $Z[FeO_2N]^+(ON) \{M=4\} + NO(g)$	$\Delta H_{87} = -4.2$ $E_{87}^\ddagger = 7.9$ $E_{87}^\ddagger = 12.9$	K_{87}, bar A_{87}, s^{-1} k_{87}, s^{-1} $A_{87}, \text{s}^{-1} \text{bar}^{-1}$ $k_{87}, \text{s}^{-1} \text{bar}^{-1}$	1.07E+11 2.19E+13 2.96E+10 1.40E+04 2.77E-01	6.68E+10 2.51E+13 8.73E+10 1.40E+04 1.31E+00	4.58E+10 2.80E+13 1.98E+11 1.45E+04 4.31E+00
88. $Z[FeO_2N]^+(ON) \{M=4\} \leftrightarrow$ $Z[FeO_2N]^+ \{M=5\} + NO(g)$	$\Delta H_{88} = 0.8$ $E_{88}^\ddagger = 2.3$ $E_{88}^\ddagger = 0.0$	K_{88}, bar A_{88}, s^{-1} k_{88}, s^{-1} $A_{88}, \text{s}^{-1} \text{bar}^{-1}$ $k_{88}, \text{s}^{-1} \text{bar}^{-1}$	1.09E+05 1.25E+13 1.76E+12 1.62E+07 1.62E+07	1.25E+05 1.46E+13 2.72E+12 2.18E+07 2.18E+07	1.34E+05 1.67E+13 3.84E+12 2.86E+07 2.86E+07
89. $Z[OFeO_2NO]^+ \{M=5\} + N_2O(g) \leftrightarrow$ $Z[FeO_2NO]^+(c-(NO)_2) \{M=5\}$	$\Delta H_{89} = 17.2$ $E_{89}^\ddagger = 18.0$ $E_{89}^\ddagger = 2.4$	K_{89}, bar^{-1} $A_{89}, \text{s}^{-1} \text{bar}^{-1}$ $k_{89}, \text{s}^{-1} \text{bar}^{-1}$ A_{89}, s^{-1} k_{89}, s^{-1}	4.73E-12 4.92E+07 1.41E+01 2.29E+13 2.97E+12	3.65E-11 6.55E+07 1.61E+02 2.55E+13 4.42E+12	1.74E-10 8.40E+07 1.04E+03 2.76E+13 5.96E+12
90. $Z[FeO_2NO]^+(c-(NO)_2) \{M=5\} \leftrightarrow$ $Z[FeO_2NO]^+(ON) \{M=4\} + NO(g)$	$\Delta H_{90} = -5.0$ $E_{90}^\ddagger = 7.4$ $E_{90}^\ddagger = 13.2$	K_{90}, bar A_{90}, s^{-1} k_{90}, s^{-1} $A_{90}, \text{s}^{-1} \text{bar}^{-1}$ $k_{90}, \text{s}^{-1} \text{bar}^{-1}$	1.24E+11 1.60E+13 3.26E+10 1.65E+04 2.62E-01	7.08E+10 1.80E+13 8.92E+10 1.63E+04 1.26E+00	4.54E+10 1.99E+13 1.91E+11 1.67E+04 4.20E+00
91. $Z[FeO_2NO]^+(ON) \{M=4\} \leftrightarrow$ $Z[FeO_2NO]^+ \{M=5\} + NO(g)$	$\Delta H_{91} = 0.8$ $E_{91}^\ddagger = 2.4$ $E_{91}^\ddagger = 0.0$	K_{91}, bar A_{91}, s^{-1} k_{91}, s^{-1} $A_{91}, \text{s}^{-1} \text{bar}^{-1}$ $k_{91}, \text{s}^{-1} \text{bar}^{-1}$	1.03E+05 1.25E+13 1.61E+12 1.57E+07 1.57E+07	1.18E+05 1.46E+13 2.52E+12 2.14E+07 2.14E+07	1.27E+05 1.67E+13 3.58E+12 2.82E+07 2.82E+07

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

TABLE 7.1n: Computed rate parameters for elementary steps in NO-assisted nitrous oxide dissociation over Fe-ZSM-5

Reaction	$E^\ddagger, \Delta H^{(a)}$ kcal/mol	Constant	T, K		
			600	700	800
92. $Z[OFeOH]^+ \{M=5\} + N_2O(g) \leftrightarrow Z[FeOH]^+(c-(NO)_2) \{M=5\}$	$\Delta H_{92} = 22.2$ $E_{92}^\ddagger = 24.6$ $E_{92}^\ddagger = 4.3$	K_{92}, bar^{-1} $A_{92}, \text{s}^{-1} \text{bar}^{-1}$ $k_{92}, \text{s}^{-1} \text{bar}^{-1}$ A_{92}, s^{-1} k_{92}, s^{-1}	5.03E-14 1.18E+07 1.33E-02 9.79E+12 2.65E+11	7.00E-13 1.60E+07 3.42E-01 1.08E+13 4.88E+11	5.21E-12 2.08E+07 4.03E+00 1.16E+13 7.74E+11
93. $Z[FeOH]^+(c-(NO)_2) \{M=5\} \leftrightarrow Z[FeOH]^+(ON) \{M=4\} + NO(g)$	$\Delta H_{93} = 0.9$ $E_{93}^\ddagger = 8.5$ $E_{93}^\ddagger = 8.5$	K_{93}, bar A_{93}, s^{-1} k_{93}, s^{-1} $A_{93}, \text{s}^{-1} \text{bar}^{-1}$ $k_{93}, \text{s}^{-1} \text{bar}^{-1}$	3.25E+08 7.34E+12 5.96E+09 2.30E+04 1.84E+01	3.72E+08 8.14E+12 1.83E+10 2.22E+04 4.91E+01	4.03E+08 8.83E+12 4.25E+10 2.22E+04 1.05E+02
94. $Z[FeOH]^+(ON) \{M=4\} \leftrightarrow Z[FeOH]^+ \{M=5\} + NO(g)$	$\Delta H_{94} = -0.1$ $E_{94}^\ddagger = 1.5$ $E_{94}^\ddagger = 0.0$	K_{94}, bar A_{94}, s^{-1} k_{94}, s^{-1} $A_{94}, \text{s}^{-1} \text{bar}^{-1}$ $k_{94}, \text{s}^{-1} \text{bar}^{-1}$	1.01E+06 1.25E+13 3.70E+12 3.67E+06 3.67E+06	1.04E+06 1.46E+13 5.14E+12 4.94E+06 4.94E+06	1.04E+06 1.67E+13 6.69E+12 6.46E+06 6.46E+06

(a) Calculated enthalpy averaged over 600 - 800 K.

‡ Calculated activation energy including zero-point energy correction.

inversion transmission coefficients are larger than 0.05. As a result, not correcting reaction rates for spin inversion probabilities smaller one creates errors smaller than an error in the activation barrier of 4 kcal/mol (at 700 K).

7.3.1 Interaction of nitric oxide with $Z[FeO]^+$, $Z[FeO_2]^+$ and $Z[OFeO]^+$

In the presence of an oxidation agent like nitrous oxide, bare iron sites, $Z[Fe]^+$, are not present in Fe-ZSM-5. Instead, single iron sites are always oxidized (Heyden et al., 2005b and 2005c). Figure 7.3 illustrates the interaction of nitric oxide with $Z[FeO]^+$ sites. Nitric oxide adsorbs on $Z[FeO]^+$ centers from the nitrogen end with an enthalpy of adsorption of $\Delta H_{\text{ads}} = -32.9$ kcal/mol (averaged over 600 to 800 K), forming

Table 7.2: Norm of the gradient difference at the point of spin surface crossing and thermally averaged Landau-Zener transition probabilities at temperatures of 600, 700 and 800 K^a

Reaction ^b	grad(E ₁) - grad(E ₂) (kJ/mol/Å)	P _{LZ} (H ₁₂ = 395 J/mol)			P _{LZ} (H ₁₂ = 825 J/mol)		
		T, K			T, K		
		600	700	800	600	700	800
1. Z[FeO] ⁺ {M=6} + NO (g) ↔ Z[FeONO] ⁺ {M=5}	0.446	0.992	0.990	0.988	1.000	1.000	1.000
3. Z[FeO] ⁺ {M=6} + NO (g) ↔ Z[FeO ₂ N] ⁺ {M=5}	0.446	0.992	0.990	0.988	1.000	1.000	1.000
5. Z[FeO] ⁺ {M=6} + NO (g) ↔ Z[OFeNO] ⁺ {M=5}	0.446	0.992	0.990	0.988	1.000	1.000	1.000
6. Z[FeO ₂] ⁺ {M=6} + NO (g) ↔ Z[FeOONO] ⁺ {M=5}	141	0.070	0.066	0.062	0.205	0.195	0.186
7. Z[FeOONO] ⁺ {M=5} ↔ Z[FeO] ⁺ {M=6} + NO ₂ (g)	1.47	0.906	0.893	0.882	0.998	0.998	0.997
8. Z[OFeO] ⁺ {M=6} + NO (g) ↔ Z[OFeONO] ⁺ {M=5}	514	0.026	0.025	0.024	0.086	0.081	0.077
9. Z[OFeONO] ⁺ {M=5} ↔ Z[FeO] ⁺ {M=6} + NO ₂ (g)	1.47	0.906	0.893	0.882	0.998	0.998	0.997
10. Z[OFeO] ⁺ {M=6} + NO (g) ↔ Z[OFeO ₂ N] ⁺ {M=5}	514	0.026	0.025	0.024	0.086	0.081	0.077
11. Z[OFeO ₂ N] ⁺ {M=5} ↔ Z[FeO] ⁺ {M=6} + NO ₂ (g)	1.47	0.906	0.893	0.882	0.998	0.998	0.997
12. Z[OFeO] ⁺ {M=6} + NO (g) ↔ Z[FeO ₂ NO] ⁺ {M=5}	514	0.026	0.025	0.024	0.086	0.081	0.077
13. Z[FeO ₂ NO] ⁺ {M=5} ↔ Z[FeO] ⁺ {M=6} + NO ₂ (g)	1.47	0.906	0.893	0.882	0.998	0.998	0.997
20. Z[O ₂ FeONO] ⁺ {M=5} ↔ Z[O ₂ FeONO] ⁺ {M=7}	454	0.034	0.032	0.030	0.108	0.102	0.097
34. Z[O ₂ FeO ₂ N] ⁺ {M=5} ↔ Z[O ₂ FeO ₂ N] ⁺ {M=7}	164	0.072	0.068	0.064	0.211	0.201	0.192
48. Z[O ₂ FeO ₂ NO] ⁺ {M=5} ↔ Z[O ₂ FeO ₂ NO] ⁺ {M=7}	185	0.065	0.061	0.058	0.192	0.182	0.174
51. Z[OFeO ₂ NO] ⁺ {M=5} ↔ Z[OFeO] ⁺ {M=6} + NO ₂ (g)	1.05	0.953	0.945	0.937	1.000	1.000	0.999
57. Z[Fe(OH) ₂] ⁺ (NO) {M=7} ↔ Z[Fe(OH) ₂] ⁺ (NO) {M=5}	1.87	0.671	0.742	0.725	0.981	0.977	0.973
68. Z[O ₂ FeOH] ⁺ {M=5} ↔ Z[O ₂ FeOH] ⁺ {M=7}	129	0.082	0.078	0.074	0.237	0.225	0.215
76. Z[OFeOH ₂] ⁺ (NO ₂) {M=5} ↔ Z[OFeOH ₂] ⁺ (NO ₂) {M=7}	10.1	0.399	0.382	0.367	0.771	0.752	0.736
82. Z[FeO] ⁺ (ON) {M=5} ↔ Z[FeO] ⁺ {M=6} + NO (g)	0.446	0.992	0.990	0.988	1.000	1.000	1.000
85. Z[FeONO] ⁺ (ON) {M=4} ↔ Z[FeONO] ⁺ {M=5} + NO (g)	11.7	0.400	0.383	0.368	0.772	0.753	0.737
88. Z[FeO ₂ N] ⁺ (ON) {M=4} ↔ Z[FeO ₂ N] ⁺ {M=5} + NO (g)	5.92	0.567	0.546	0.529	0.907	0.894	0.883
91. Z[FeO ₂ NO] ⁺ (ON) {M=4} ↔ Z[FeO ₂ NO] ⁺ {M=5} + NO (g)	12.4	0.381	0.364	0.350	0.751	0.732	0.715
94. Z[FeOH] ⁺ (ON) {M=4} ↔ Z[FeOH] ⁺ {M=5} + NO (g)	2.14	0.815	0.797	0.782	0.991	0.988	0.985

(a) Landau-Zener probabilities are calculated for a spin-orbit coupling energy of H₁₂ = 395 and 825 J/mol

(b) Reaction numbers are the same as in Table 7.1

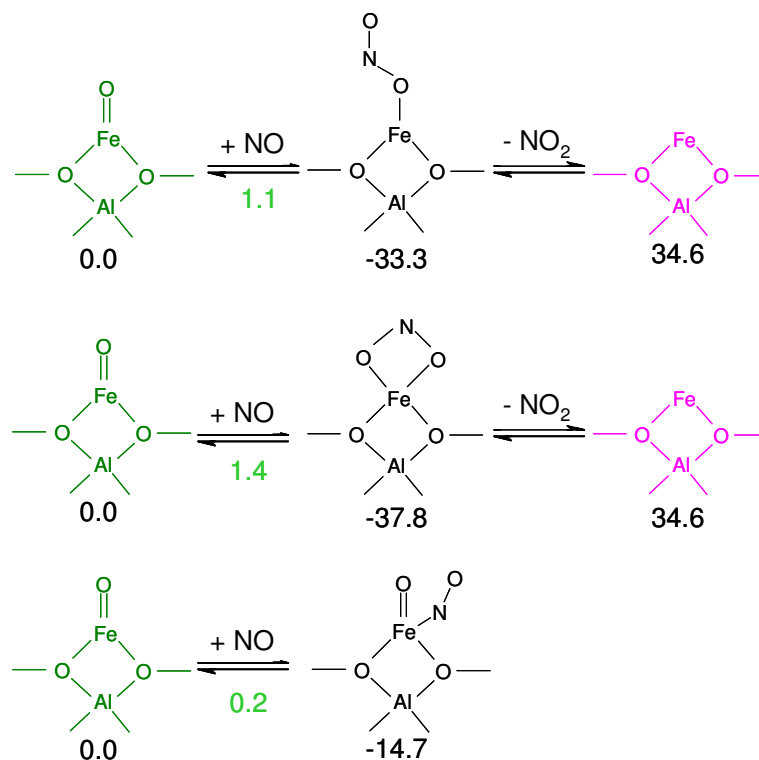


Figure 7.3: Interaction of nitric oxide with Z[FeO]⁺ {M_S = 6} sites. All energies are zero-point corrected, in kcal/mol and with reference to Z[FeO]⁺ {M_S = 6}. Energies of potential energy minima are in black. Energies of minima on the seam of two PESs are in green. Structures in green are on the PES with M_S = 6. Black structures are on the PES with M_S = 5. Structures in magenta are on the PES with M_S = 4.

Z[FeONO]⁺ species. During the adsorption process spin pairing occurs. The ground state of Z[FeO]⁺ is on the sextet PES, whereas the ground state of Z[FeONO]⁺ is on the quintet PES. The adsorption process involves surmounting a negligible spin-change barrier of about 1.1 kcal/mol. The bonding of Z[FeONO]⁺ is illustrated in Figure 7.2, the Fe-O bond increases during the adsorption process from 1.66 Å to 1.84 Å. The O-N'-O'' bond angle is calculated to be 112.9° in the adsorbed state on the PES with spin multiplicity M_S = 5. The characteristic vibrational frequency of adsorbed nitric oxide is calculated to be 1701 cm⁻¹. In principle, nitrogen dioxide can desorb from Z[FeONO]⁺, the enthalpy of desorption for this barrierless process is ΔH_{des} = 66.0 kcal/mol, making this process unlikely to occur, except at very high temperatures and confirming the absence of bare iron sites in the presence of an oxidation agent.

A second potential energy minimum was found for adsorbed nitric oxide, $Z[FeO_2N]^+$, illustrated in Figure 7.2 and 7.3. The enthalpy of adsorption was calculated to be $\Delta H_{ads} = -37.8$ kcal/mol. The adsorption process involves surmounting a spin change barrier of 1.4 kcal/mol. The reason a different spin change barrier was calculated for the formation of $Z[FeONO]^+$ and $Z[FeO_2N]^+$ originates from the calculation of spin change barriers, where it is assumed that the zero-point energy of the adsorbed state and transition state is equivalent. The Fe-O bond length in $Z[FeO_2N]^+$ is found to be 2.11 Å. The O-N'-O'' bond angle is calculated to be 111.3° in the adsorbed state. The characteristic vibrational frequency of adsorbed nitric oxide is 1238 cm⁻¹ and 1330 cm⁻¹. In principle, nitrogen dioxide can desorb from $Z[FeO_2N]^+$, the enthalpy of desorption for this process is $\Delta H_{des} = 70.9$ kcal/mol, making NO₂ desorption very unlikely to occur.

Nitric oxide might also directly adsorb from the nitrogen end on the iron atom in $Z[FeO]^+$, see Figure 7.3. The enthalpy of adsorption is calculated to be $\Delta H_{ads} = -13.6$ kcal/mol, a number significantly lower than for the formation of $Z[FeONO]^+$ and $Z[FeO_2N]^+$ sites. The adsorption process involves surmounting a negligible spin change barrier of 0.2 kcal/mol. The N'-O' bond length is 1.15 Å and therefore essentially unchanged from gaseous nitric oxide. The characteristic harmonic vibrational frequency of adsorbed nitric oxide is calculated to be 1895 cm⁻¹ and is therefore in good agreement with experimental IR bands at 1884 cm⁻¹ and 1874 cm⁻¹ observed by Mul et al. (2001). Owing to the low adsorption enthalpy of just 13.6 kcal/mol, a $Z[OFeNO]^+$ species (or similar ones) is unlikely to play any role in the N₂O decomposition at reaction temperatures above 500 K. In the following, from the N-end weakly adsorbed nitric oxide species on Fe-atoms are not discussed anymore. No other, more stable, potential energy minimum with a nitrogen atom in direct contact with the iron atom could be found in this study.

Figure 7.4 illustrates the interaction of nitric oxide with $Z[FeO_2]^+$ and $Z[OFeO]^+$ sites. Macroscopic simulations reveal that $Z[FeO_2]^+$ and $Z[OFeO]^+$ appear always in equilibrium amounts. Whereas, $Z[FeO_2]^+$ is the more abundant species, $Z[OFeO]^+$ is

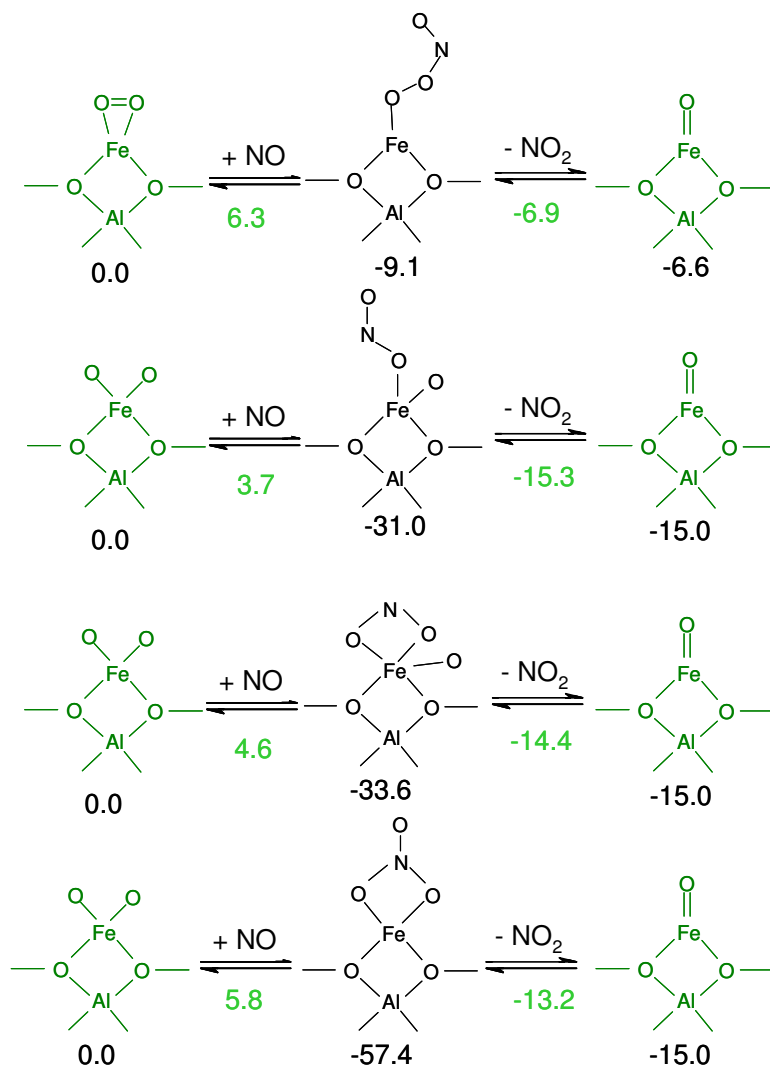


Figure 7.4: Interaction of nitric oxide with $Z[FeO_2]^+$ ($M_S = 6$) and $Z[OFeO]^+$ ($M_S = 6$) sites. All energies are zero-point corrected, in kcal/mol and with reference to $Z[FeO_2]^+$ or $Z[OFeO]^+$. Energies of potential energy minima are in black. Energies of minima on the seam of two PESs are in green. Structures in green are on the PES with $M_S = 6$. Black structures are on the PES with $M_S = 5$.

the more active center. Nitric oxide adsorbs from the N-end with an enthalpy of adsorption of $\Delta H_{ads} = -9.0$ kcal/mol on $Z[FeO_2]^+$ centers forming $Z[FeOONO]^+$ sites. The spin change barrier for adsorption is 6.3 kcal/mol, resulting in a fast adsorption and desorption process. Nitrogen dioxide readily desorbs from $Z[FeOONO]^+$. The spin change barrier from the quintet PES, back to the sextet PES of the active site cluster is below the zero-point corrected energy of $Z[FeO]^+$ and NO_2 . The enthalpy of desorption averaged over 600 K to 800 K is calculated to be only $\Delta H_{des} = 1.0$ kcal/mol. As a result,

in the presence of nitric oxide and at a low temperature, $Z[FeO_2]^+$ sites are rapidly reduced to $Z[FeO]^+$ species.

Sang et al. (2005) calculated for the overall reaction, $Z[FeO_2]^+ + NO \rightleftharpoons Z[FeO]^+ + NO_2$, an electronic energy difference of about -1.5 kcal/mol; a number in reasonable agreement with the zero-point corrected energy difference of -6.6 kcal/mol, calculated in this work, considering that Sang et al. (2005) used an active site cluster in T1 position (T12 position was used in this work) with a different level of theory, B3LYP/LACVP** (basis set of double zeta quality; in the present work a triple zeta basis set was used).

Nitric oxide can also adsorb on $Z[OFeO]^+$ sites forming, $Z[OFeONO]^+$ or $Z[OFeO_2N]^+$ sites. The spin change barrier for adsorption is 3.7 kcal/mol or 4.6 kcal/mol, respectively, leading to a fast adsorption process with an enthalpy of adsorption of $\Delta H_{ads} = -30.5$ kcal/mol and $\Delta H_{ads} = -34.0$ kcal/mol, respectively. The characteristic harmonic vibrational frequency of adsorbed nitric oxide on $Z[OFeO]^+$ sites is calculated to be 1797 cm^{-1} in $Z[OFeONO]^+$ and 1256 cm^{-1} and 1308 cm^{-1} in $Z[OFeO_2N]^+$. Nitrogen dioxide can desorb from $Z[OFeONO]^+$ and $Z[OFeO_2N]^+$ sites. The desorption barrier is 16.0 kcal/mol from $Z[OFeONO]^+$ sites and 19.2 kcal/mol from $Z[OFeO_2N]^+$ sites, suggesting that NO_2 desorption should be fast at reaction temperatures. The enthalpy of desorption is $\Delta H_{des} = 14.4$ kcal/mol from $Z[OFeONO]^+$ sites and $\Delta H_{des} = 17.9$ kcal/mol from $Z[OFeO_2N]^+$ centers. Consequently, $Z[OFeO]^+$ sites are in the presence of nitric oxide rapidly reduced to $Z[FeO]^+$ species.

Finally, nitric oxide can also adsorb on $Z[OFeO]^+$ sites forming stable iron-nitrate species, $Z[FeO_2NO]^+$. The spin change barrier for adsorption is 5.8 kcal/mol, resulting in a fast adsorption process with an enthalpy of adsorption of $\Delta H_{ads} = -58.3$ kcal/mol. The desorption barrier is 63.2 kcal/mol, making the desorption process of nitric oxide from iron-nitrate species unlikely to occur. The bonding of $Z[FeO_2NO]^+$ is illustrated in Figure 7.2, the Fe-O bond increases during the adsorption process from $1.68\text{ \AA}$ in

$Z[OFeO]^+$ to 2.08 Å in the iron-nitrate species. The characteristic harmonic vibrational frequency of adsorbed nitric oxide in $Z[FeO_2NO]^+$ is calculated to be 1641 cm⁻¹. Mul et al. (2001) and Pérez-Ramírez et al. (2003c) observed a sharp IR band at 1635 cm⁻¹ and 1632 cm⁻¹, respectively, suggesting that iron-nitrate species are present in Fe-ZSM-5. Nitrogen dioxide can desorb from $Z[FeO_2NO]^+$ sites. The desorption barrier is 44.2 kcal/mol. The enthalpy of desorption is $\Delta H_{des} = 42.2$ kcal/mol. The spin change barrier for NO₂ adsorption on $Z[FeO]^+$ sites is 1.8 kcal/mol, resulting in a fast NO₂ adsorption process.

To conclude, if $Z[FeO]^+$, $Z[FeO_2]^+$, and $Z[OFeO]^+$ sites are exposed to nitric oxide, three new stable species, $Z[FeONO]^+$, $Z[FeO_2N]^+$, and $Z[FeO_2NO]^+$ are formed. NO₂ desorption does not occur readily from these sites.

7.3.2 Catalytic cycle on $Z[FeONO]^+$

In this section, the nitrous oxide decomposition is studied on $Z[FeONO]^+$ sites. Figure 7.5 illustrates the catalytic cycle of the N₂O decomposition on $Z[FeONO]^+$. N₂O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{ads} = -3.1$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{ads} = -1.5$ kcal/mol. Hardly any N₂O can be expected to adsorb on $Z[FeONO]^+$ sites under reaction conditions. The transition state for the reaction of $Z[FeONO]^+(ON_2)$ to form $Z[OFeONO]^+$ and N₂ is characterized by a bending of the N₂O molecule from 180° in the adsorbed state to 138° in the transition state, whereas the length of the N'-O'' bond of the N₂O molecule increases from 1.20 Å to 1.44 Å. The activation barrier for the decomposition is $E^\ddagger = 24.8$ kcal/mol. The imaginary frequency associated with the transition state mode is 726i cm⁻¹. Figure 7.6 illustrates the transition state structure on the quintet PES. Because of an enthalpy of reaction of $\Delta H_R = -12.7$ kcal/mol, the reverse reaction has a significant barrier and should not occur readily. It is noted that Kiwi-Minsker et al. (2005) found experimentally for the first N₂O decomposition on Fe-ZSM-5 a similar activation barrier of 27.7 kcal/mol.

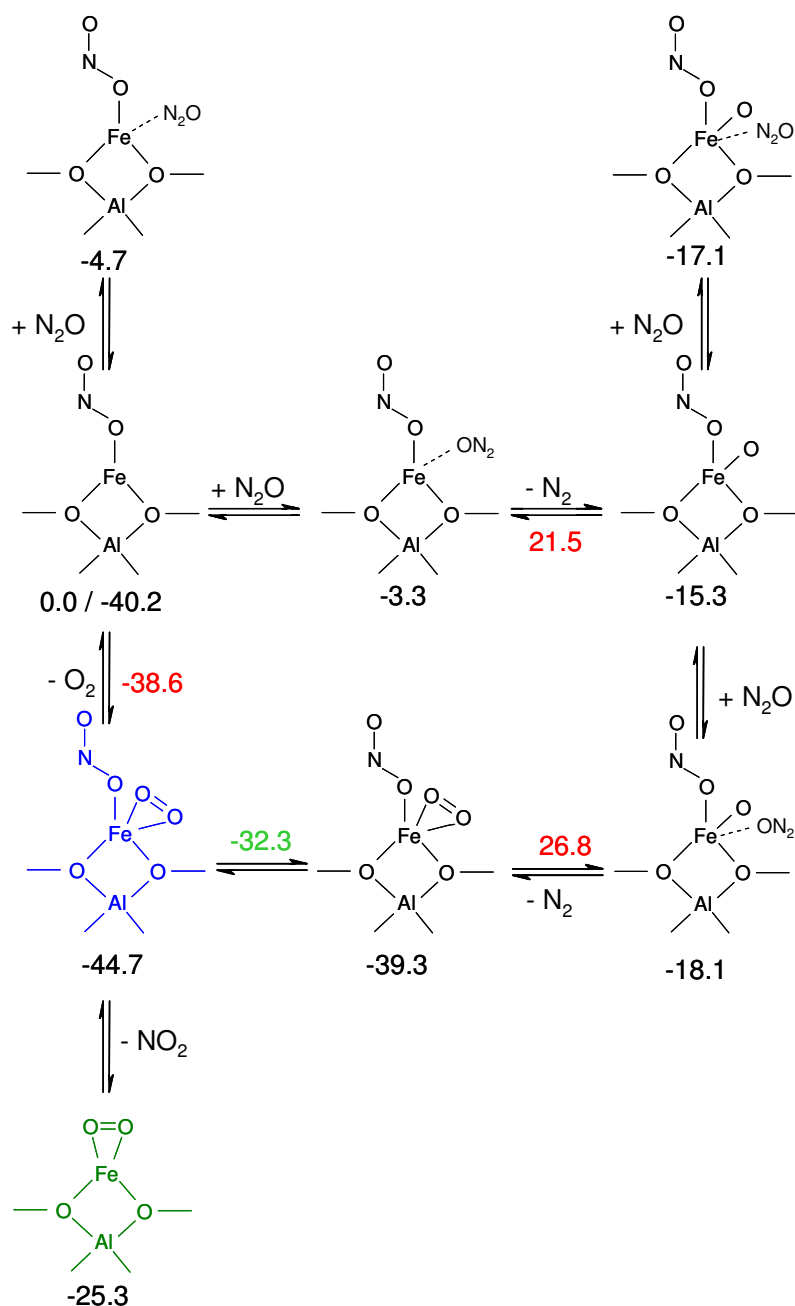


Figure 7.5: Catalytic cycle of the N_2O dissociation on mononuclear $\text{Z}[\text{FeONO}]^+$ ($M_S = 5$) sites. All energies are zero-point corrected, in kcal/mol and with reference to $\text{Z}[\text{FeONO}]^+$ with the appropriate amounts of N_2O , N_2 , and O_2 . Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with $M_S = 5$. Green structures are on the PES with $M_S = 6$. Structures in blue are on the PES with $M_S = 7$.

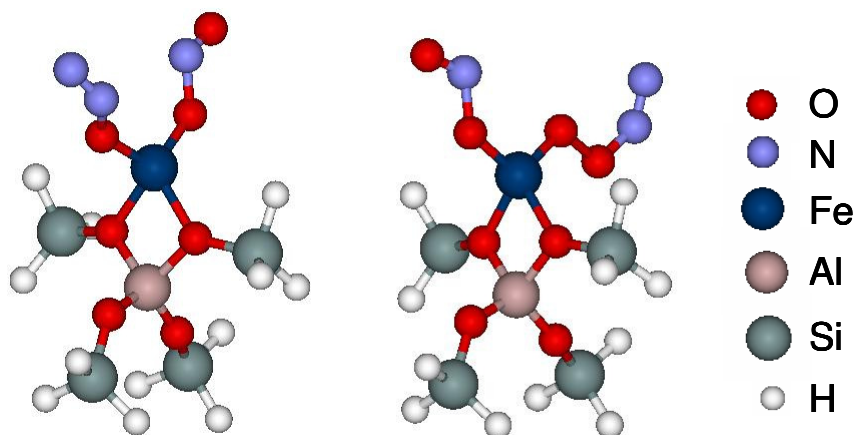


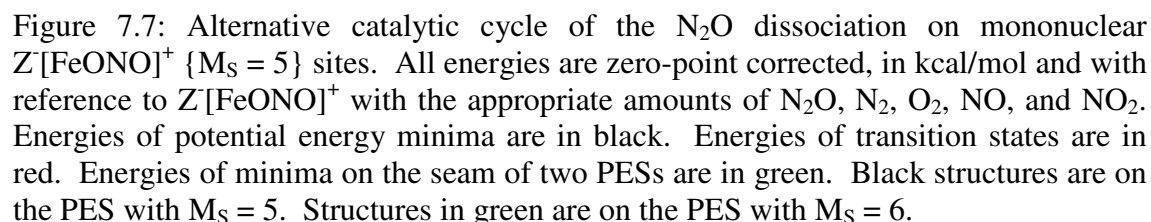
Figure 7.6: Transition state structures for N₂O decomposition on Z[FeONO]⁺ and Z[OFeONO]⁺.

Z[OFeONO]⁺ sites are possible active sites for the N₂O dissociation. N₂O adsorbs on Z[OFeONO]⁺ centers through the N-end with an enthalpy of adsorption of $\Delta H_{\text{ads}} = -0.5$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{\text{ads}} = -1.5$ kcal/mol. Again, hardly any N₂O can be expected to adsorb on Z[OFeONO]⁺ sites under reaction conditions. The transition state for the reaction of Z[OFeONO]⁺(N₂O) to form Z[O₂FeONO]⁺ and N₂ is characterized by a bending of the N₂O molecule from 180° in the adsorbed state to 136.3° in the transition state, whereas the length of the N'-O'' bond of the N₂O molecule increases from 1.20 Å to 1.35 Å. The O-atom from N₂O forms a bond with the lone oxygen atom from Z[OFeONO]⁺. The Fe-O bond increases along the reaction coordinate from 1.61 Å to 1.81 Å in the transition state. The O-O bond is 1.57 Å long. The activation barrier for the decomposition is $E^\ddagger = 44.9$ kcal/mol. The imaginary frequency associated with the transition state mode is 730i cm⁻¹. Figure 7.6 illustrates the transition state structure on the quintet PES. Because of an enthalpy of reaction of $\Delta H_{\text{R}} = -20.7$ kcal/mol, the reverse reaction has an even higher barrier and should not occur. Z[O₂FeONO]⁺ species are more stable on the septet PES than on the quintet PES. A spin change barrier of about 7.1 kcal/mol was found for the spin inversion process. The enthalpy of reaction is $\Delta H_{\text{R}} = -5.4$ kcal/mol, suggesting that Z[O₂FeONO]⁺ species on the quintet and septet PES are in equilibrium. Z[O₂FeONO]⁺ (M_S = 7) species consists of a superoxide O₂⁻ anion and a nitrite-group on top of a Fe²⁺ or Fe³⁺ cation. The Fe-O bond distance of the superoxide anion to the iron cation is 2.06 Å. The O-O bond distance is 1.30 Å and the O-O vibrational

frequency is 1211 cm^{-1} , confirming the superoxide nature of the two adsorbed O-atoms (see Che and Trench, 1983).

Nitrogen dioxide or oxygen can desorb from $Z[\text{O}_2\text{FeONO}]^+(\text{M}_S = 7)$ sites. The O_2 desorption barrier is 6.0 kcal/mol and the enthalpy of desorption is $\Delta H_{\text{des}} = 3.3$ kcal/mol, suggesting a fast O_2 desorption process and confirm that oxygen cannot inhibit the N_2O decomposition on $Z[\text{FeONO}]^+$ sites. The imaginary frequency associated with the transition state mode is $120i\text{ cm}^{-1}$. In principle NO_2 can also desorb from $Z[\text{O}_2\text{FeONO}]^+(\text{M}_S = 7)$ sites forming $Z[\text{FeO}_2]^+$ species. The enthalpy of desorption is $\Delta H_{\text{des}} = 17.3$ kcal/mol. As a result, the oxygen desorption process should be dominant and the catalytic cycle on $Z[\text{FeONO}]^+$ is closed.

The highest barrier in the catalytic cycle is the second N_2O decomposition on $Z[\text{OFeONO}]^+$ sites, with an activation barrier of over 42 kcal/mol with respect to the gas phase, making this catalytic cycle unlikely to occur except at elevated temperatures. Figure 7.7 illustrates alternative pathways that describe how the catalytic cycle can be closed in the presence of nitric oxide. As described in section 7.3.1, NO_2 can desorb from $Z[\text{OFeONO}]^+$ sites and nitric oxide can subsequently adsorb on $Z[\text{FeO}]^+$ sites forming $Z[\text{FeONO}]^+$ species. Alternatively, nitric oxide can adsorb on $Z[\text{OFeONO}]^+$ sites forming $Z[\text{Fe}(\text{ONO})_2]^+$ species. The enthalpy of adsorption is $\Delta H_{\text{ads}} = -31.7$ kcal/mol. $Z[\text{Fe}(\text{ONO})_2]^+$ species are in equilibrium with $Z[\text{ONOFeO}_2\text{N}]^+$ sites. The activation barrier is 1.3 kcal/mol and the imaginary frequency associated with the transition state mode is $52i\text{ cm}^{-1}$. The enthalpy of reaction is $\Delta H_{\text{R}} = -4.7$ kcal/mol. Similar amounts of $Z[\text{ONOFeO}_2\text{N}]^+$ and $Z[\text{Fe}(\text{ONO})_2]^+$ should be present under reaction conditions. At reaction temperatures above 550 K, NO_2 can desorb readily from $Z[\text{Fe}(\text{ONO})_2]^+$ species closing the catalytic cycle on $Z[\text{FeONO}]^+$. The enthalpy of desorption is $\Delta H_{\text{des}} = 13.2$ kcal/mol. In these alternative catalytic cycles, one N_2O molecule dissociates, one NO is consumed and one NO_2 is formed. The highest barrier along this catalytic cycle is the first N_2O decomposition with a barrier of 21.5 kcal/mol, with respect to the gas phase.



$Z[FeONO]^+$ and $Z[OFeONO]^+$ sites can also rearrange to form $Z[FeO_2N]^+$ and $Z[FeO_2NO]^+$ species, respectively. The activation barrier for the formation of $Z[FeO_2N]^+$ from $Z[FeONO]^+$ is only $E^\ddagger = 3.0$ kcal/mol. The imaginary frequency associated with the transition state mode is $117i$ cm^{-1} . Because of an enthalpy of reaction of $\Delta H_R = -4.9$ kcal/mol, both species should be present in equilibrium amounts. $Z[FeO_2N]^+$ should be more abundant. The activation barrier for the formation of $Z[FeO_2NO]^+$ from $Z[OFeONO]^+$ is $E^\ddagger = 10.0$ kcal/mol. The imaginary frequency associated with the transition state mode is $174i$ cm^{-1} . Because of an enthalpy of

reaction of $\Delta H_R = -27.8$ kcal/mol, the reverse reaction should hardly occur and Fe-nitrate species should accumulate. Altogether, the rearrangement reactions for forming the more stable $Z[FeO_2N]^+$ and $Z[FeO_2NO]^+$ species suggest that the catalytic cycle on $Z[FeONO]^+$ sites should not be dominant.

7.3.3 Catalytic cycle on $Z[FeO_2N]^+$

Figure 7.8 illustrates the catalytic cycle of the N_2O decomposition on $Z[FeO_2N]^+$ sites. N_2O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{ads} = -4.2$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{ads} = -2.5$ kcal/mol. Hardly any N_2O can be expected to adsorb on $Z[FeO_2N]^+$ sites under reaction conditions. The transition state for the reaction of $Z[FeO_2N]^+(ON_2)$ to form $Z[OFeO_2N]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 140° in the transition state, whereas the length of the $N'-O''$ bond of the N_2O molecule increases from $1.20 \text{ \AA}$ to $1.47 \text{ \AA}$. The activation barrier for the decomposition is $E^\ddagger = 25.4$ kcal/mol. The imaginary frequency associated with the transition state mode is $765i \text{ cm}^{-1}$. Figure 7.9 illustrates the transition state structure on the quintet PES. Because of an enthalpy of reaction of $\Delta H_R = -10.2$ kcal/mol, the reverse reaction has a significant barrier and should not occur readily.

N_2O adsorbs on $Z[OFeO_2N]^+$ centers through the N-end with an enthalpy of adsorption of $\Delta H_{ads} = 1.6$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{ads} = -2.7$ kcal/mol. Again, hardly any N_2O can be expected to adsorb on $Z[OFeO_2N]^+$ sites under reaction conditions. The transition state for the reaction of $Z[OFeO_2N]^+(ON_2)$ to form $Z[O_2FeO_2N]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 136° in the transition state, whereas the length of the $N'-O''$ bond of the N_2O molecule increases from $1.20 \text{ \AA}$ to $1.36 \text{ \AA}$. The O-atom from N_2O forms a bond with the lone oxygen atom from $Z[OFeO_2N]^+$. The Fe-O bond increases along the reaction coordinate from $1.62 \text{ \AA}$ to $1.80 \text{ \AA}$ in the

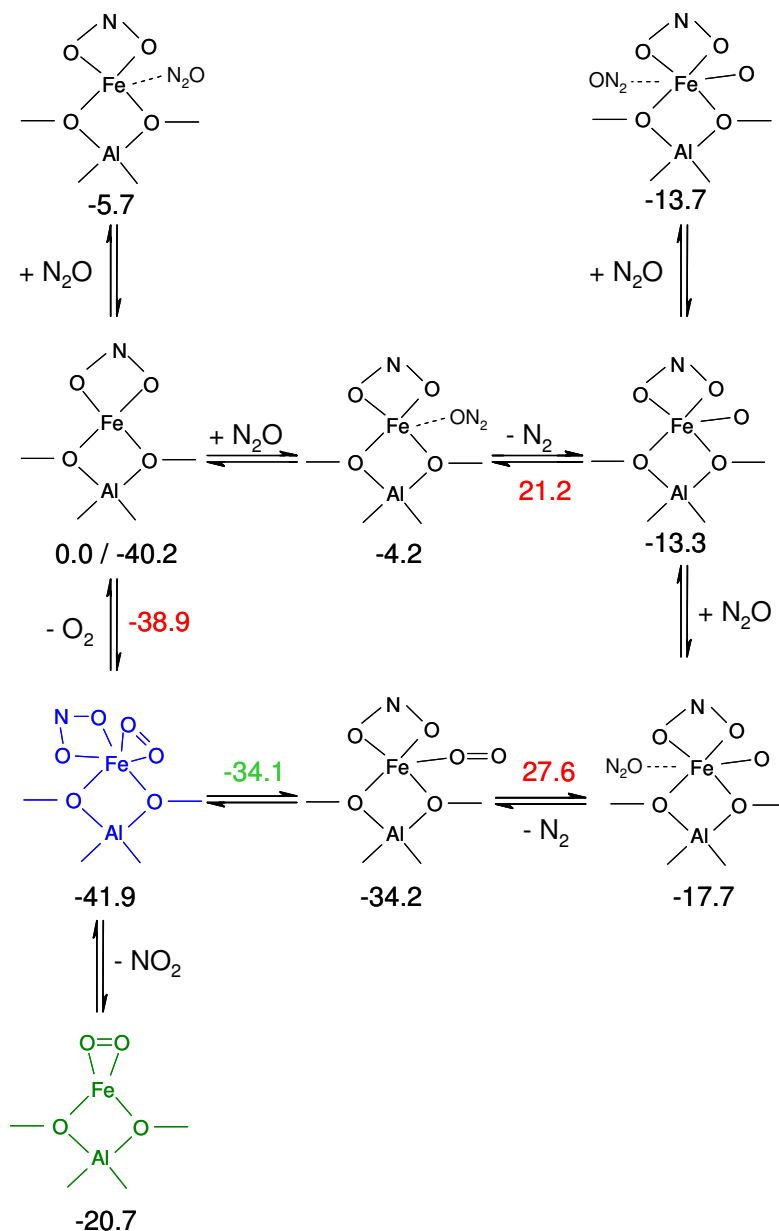


Figure 7.8: Catalytic cycle of the N₂O dissociation on mononuclear Z[FeO₂N]⁺ {M_S = 5} sites. All energies are zero-point corrected, in kcal/mol and with reference to Z[FeO₂N]⁺ with the appropriate amounts of N₂O, N₂, and O₂. Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with M_S = 5. Green structures are on the PES with M_S = 6. Structures in blue are on the PES with M_S = 7.

transition state. The O-O bond is 1.56 Å long. The activation barrier for the decomposition is $E^\ddagger = 45.2$ kcal/mol. The imaginary frequency associated with the transition state mode is 730i cm⁻¹. Figure 7.9 illustrates the transition state structure on

the quintet PES. Because of an enthalpy of reaction of $\Delta H_R = -16.1$ kcal/mol, the reverse reaction has an even higher barrier and should not occur. $Z[O_2FeO_2N]^+$ species are more stable on the septet PES than on the quintet PES. A negligible spin change barrier of about 0.1 kcal/mol was found for the spin inversion process. The enthalpy of reaction is $\Delta H_R = -7.7$ kcal/mol, suggesting that $Z[O_2FeO_2N]^+$ species on the quintet and septet PES are in equilibrium. $Z[O_2FeO_2N]^+$ ($M_S = 7$) species consists of a superoxide O_2^- anion and a nitrite-group on top of a Fe^{2+} or Fe^{3+} cation. The Fe-O bond distance of the superoxide anion to the iron cation is 2.07 Å. The O-O bond distance is 1.30 Å and the O-O vibrational frequency is 1228 cm^{-1} .

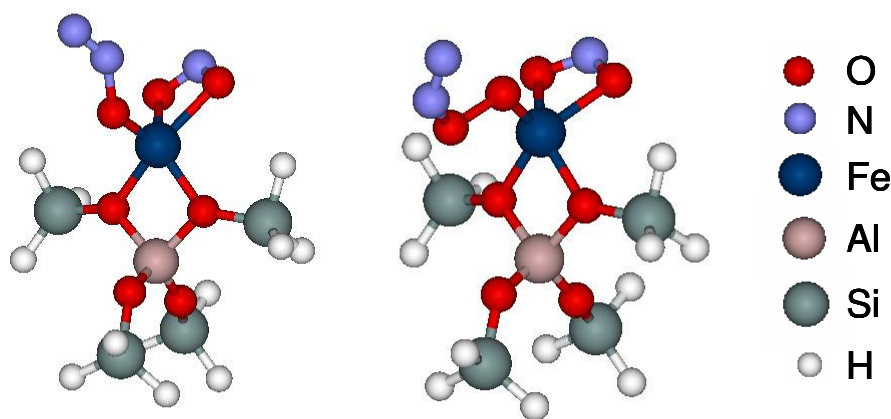


Figure 7.9: Transition state structures for N_2O decomposition on $Z[FeO_2N]^+$ and $Z[OFeO_2N]^+$.

Nitrogen dioxide or oxygen can desorb from $Z[O_2FeO_2NO]^+(M_S = 7)$. The O_2 desorption barrier is $E^\ddagger = 3.0$ kcal/mol and the enthalpy of desorption is $\Delta H_{des} = 0.7$ kcal/mol, suggesting a fast O_2 desorption process and confirm that oxygen cannot inhibit the N_2O decomposition on $Z[FeO_2N]^+$ sites. The imaginary frequency associated with the transition state mode is $93i$ cm^{-1} . NO_2 can also desorb from $Z[O_2FeO_2N]^+(M_S = 7)$ sites forming $Z[FeO_2]^+$ species. The enthalpy of desorption is $\Delta H_{des} = 19.6$ kcal/mol. As a result, the oxygen desorption process should be dominant and the catalytic cycle on $Z[FeO_2N]^+$ is closed.

As in the catalytic cycle on $Z[\text{FeONO}]^+$ species, the highest barrier in the catalytic cycle on $Z[\text{FeO}_2\text{N}]^+$ is the second N₂O decomposition on $Z[\text{OFeONO}]^+$ sites, with an activation barrier of over 40 kcal/mol with respect to the gas phase, making this catalytic cycle unlikely to occur except at elevated temperatures. Figure 7.10 illustrates alternative pathways that describe how the catalytic cycle can be closed in the presence of nitric oxide. As described in section 7.3.1, NO₂ can desorb from $Z[\text{OFeO}_2\text{N}]^+$ sites and nitric oxide can subsequently adsorb on $Z[\text{FeO}]^+$ sites forming $Z[\text{FeO}_2\text{N}]^+$ species.

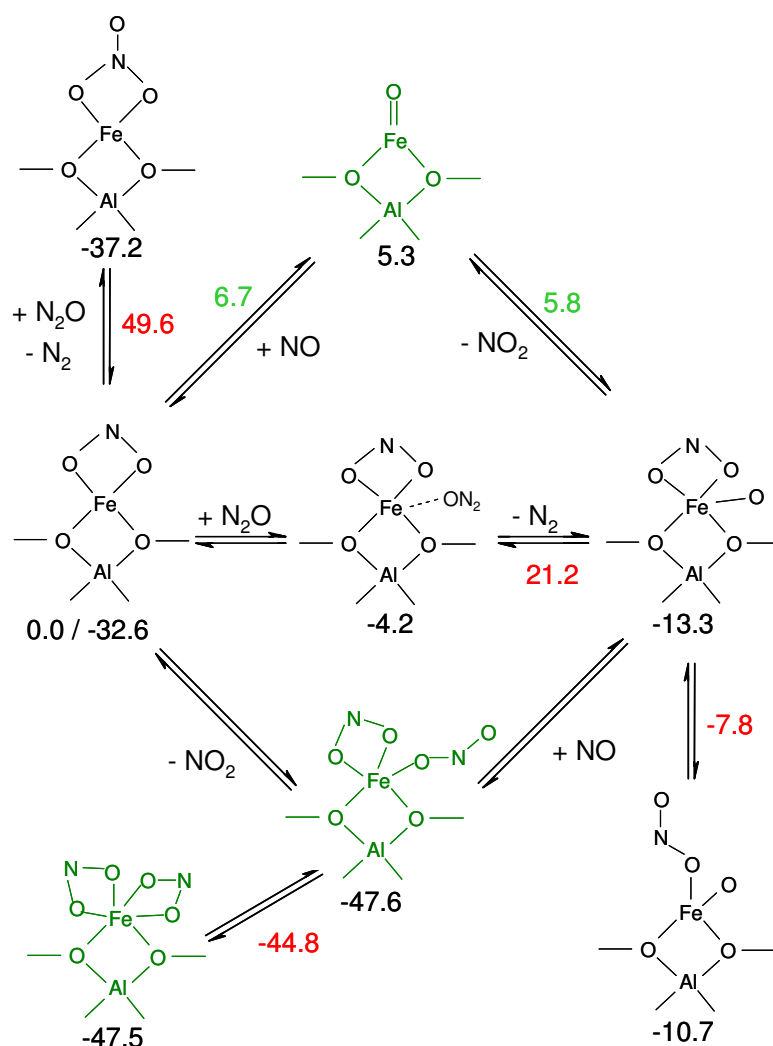


Figure 7.10: Alternative catalytic cycle of the N₂O dissociation on mononuclear $Z[\text{FeO}_2\text{N}]^+$ ($M_S = 5$) sites. All energies are zero-point corrected, in kcal/mol and with reference to $Z[\text{FeO}_2\text{N}]^+$ with the appropriate amounts of N₂O, N₂, O₂, NO, and NO₂. Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with $M_S = 5$. Structures in green are on the PES with $M_S = 6$.

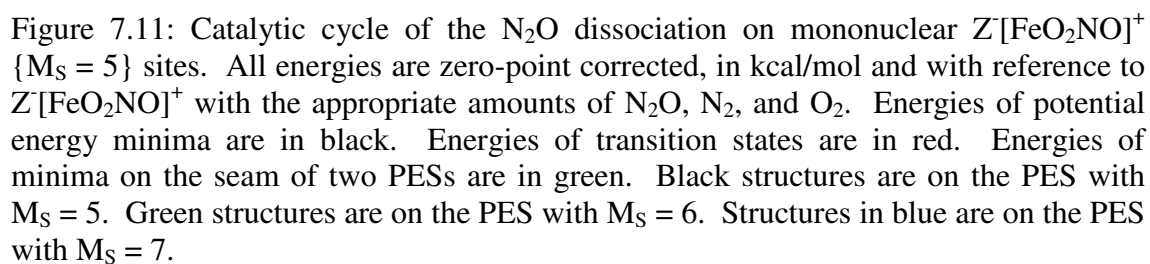
Alternatively, nitric oxide can adsorb on $Z[OFeO_2N]^+$ sites forming $Z[ONFeO_2N]^+$ species. The enthalpy of adsorption is $\Delta H_{ads} = -32.9$ kcal/mol. $Z[ONFeO_2N]^+$ species are in equilibrium with $Z[Fe(O_2N)_2]^+$ sites. The activation barrier is 2.8 kcal/mol, the enthalpy of reaction is $\Delta H_R = -0.6$ kcal/mol and the imaginary frequency associated with the transition state mode is $107i$ cm⁻¹. At reaction temperatures above 550 K, NO₂ can desorb from $Z[ONFeO_2N]^+$ species closing the catalytic cycle on $Z[FeO_2N]^+$. The enthalpy of desorption is $\Delta H_{des} = 12.9$ kcal/mol.

Figure 7.10 also illustrates that $Z[OFeO_2N]^+$ centers are in equilibrium with $Z[OFeONO]^+$ sites. The activation barrier for the rearrangement reaction from $Z[OFeO_2N]^+$ to $Z[OFeONO]^+$ is $E^\ddagger = 5.6$ kcal/mol. The enthalpy of reaction is $\Delta H_R = 3.5$ kcal/mol and the imaginary frequency associated with the transition state mode is $118i$ cm⁻¹.

Finally, it was tested if N₂O can decompose on the nitrogen atom of $Z[FeO_2N]^+$ centers to form iron-nitrate species. The activation barrier for this reaction is $E^\ddagger = 49.6$ kcal/mol so that despite an enthalpy of reaction of $\Delta H_R = -37.1$ kcal/mol, this reaction is not occurring. The imaginary frequency associated with the transition state mode is $813i$ cm⁻¹.

7.3.4 Catalytic cycle on $Z[FeO_2NO]^+$

As shown in section 7.3.1, Fe-nitrate species can be formed in the presence of nitric oxide on $Z[OFeO]^+$ sites and from $Z[OFeONO]^+$ species. Figure 7.11 illustrates the catalytic cycle of the N₂O decomposition on $Z[FeO_2NO]^+$ sites. N₂O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{ads} = -1.8$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{ads} = -1.0$ kcal/mol. Hardly any N₂O can be expected to adsorb on $Z[FeO_2NO]^+$ sites under reaction conditions. The transition state



for the reaction of $Z[FeO_2NO]^+(ON_2)$ to form $Z[OFeO_2NO]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 143.4° in the transition state, whereas the length of the $N'-O''$ bond of the N_2O molecule increases from $1.20 \text{ \AA}$ to $1.49 \text{ \AA}$. The activation barrier for the decomposition is $E^\ddagger = 25.2 \text{ kcal/mol}$ and the enthalpy of reaction is $\Delta H_R = -7.0 \text{ kcal/mol}$. The imaginary frequency associated with the transition state mode is $767i \text{ cm}^{-1}$. Figure 7.12 illustrates the transition state structure on the quintet PES.

N_2O adsorbs on $Z[OFeO_2NO]^+$ centers through the N-end with an enthalpy of adsorption of $\Delta H_{ads} = -2.6 \text{ kcal/mol}$ and through the O-end with an enthalpy of adsorption of $\Delta H_{ads} = -2.9 \text{ kcal/mol}$. Hardly any N_2O can be expected to adsorb on $Z[OFeO_2NO]^+$ sites under reaction conditions. The transition state for the reaction of $Z[OFeO_2NO]^+(ON_2)$ to form $Z[O_2FeO_2NO]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 158.6° in the transition state, whereas the length of the $N'-O''$ bond of the N_2O molecule increases from $1.20 \text{ \AA}$ to $1.64 \text{ \AA}$. The activation barrier for the decomposition is $E^\ddagger = 41.1 \text{ kcal/mol}$. The imaginary frequency associated with the transition state mode is $752i \text{ cm}^{-1}$. Figure 7.12 illustrates the transition state structure on the quintet PES. Because of an enthalpy of reaction of $\Delta H_R = -19.2 \text{ kcal/mol}$, the reverse reaction has a significant barrier and

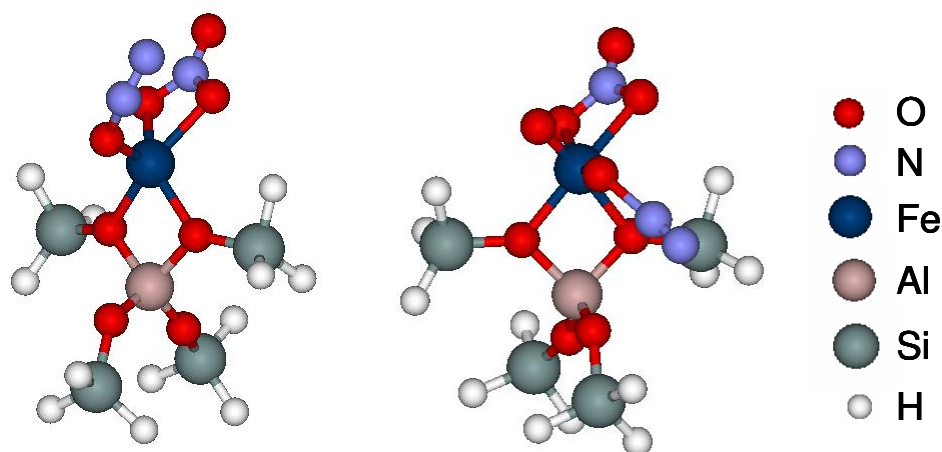


Figure 7.12: Transition state structures for N_2O decomposition on $Z[FeO_2NO]^+$ and $Z[OFeO_2NO]^+$.

should not occur readily. $Z[O_2FeO_2NO]^+$ species are more stable on the septet PES than on the quintet PES. A negligible spin change barrier of about 0.4 kcal/mol was found for the spin inversion process. The enthalpy of reaction is $\Delta H_R = -8.7$ kcal/mol, suggesting that $Z[O_2FeO_2NO]^+$ species on the quintet and septet PES are in equilibrium. $Z[O_2FeO_2NO]^+$ ($M_S = 7$) species consists of a superoxide O_2^- anion and a nitrate-group on top of a Fe^{2+} or Fe^{3+} cation. The Fe-O bond distance of the superoxide anion to the iron cation is 2.07 Å. The O-O bond distance is 1.29 Å and the O-O vibrational frequency is 1231 cm^{-1} . Oxygen can desorb from $Z[O_2FeO_2NO]^+(M_S = 7)$ sites, closing the catalytic cycle. The O_2 desorption barrier is $E^\ddagger = 3.0$ kcal/mol and the enthalpy of desorption is $\Delta H_{des} = 0.4$ kcal/mol, suggesting a rapid O_2 desorption process. The imaginary frequency associated with the transition state mode is 85i cm^{-1} . NO_2 can in principle also desorb from $Z[O_2FeO_2NO]^+(M_S = 7)$ sites forming $Z[OFeO_2]^+$ species. The enthalpy of desorption is $\Delta H_{des} = 43.2$ kcal/mol so that NO_2 desorption will hardly occur.

Altogether, the highest barrier in the catalytic cycle on $Z[FeO_2NO]^+$ is the second N_2O decomposition on $Z[OFeO_2NO]^+$ sites with an activation barrier of over 36 kcal/mol with respect to the gas phase. Even though this barrier is 4-6 kcal/mol lower than the highest barrier in the catalytic cycle on Fe-nitrite sites, this process should only occur at elevated temperatures. Figure 7.13 illustrates further pathways that describe how the catalytic cycle can be closed in the presence of nitric oxide. NO_2 can desorb from $Z[OFeO_2NO]^+$ sites forming $Z[OFeO]^+$ species. An approximate spin change barrier of $E^\ddagger = 40.8$ kcal/mol and an enthalpy of desorption of $\Delta H_{des} = 33.6$ kcal/mol was calculated for this process. As described in section 7.3.1, nitric oxide can then adsorb on $Z[OFeO]^+$ sites and form $Z[FeO_2NO]^+$ species to close the catalytic cycle. An even faster pathway for closing the catalytic cycle on $Z[OFeO_2NO]^+$ species, involves first a nitric oxide adsorption forming $Z[ONOFEO_2NO]^+$ species and then a NO_2 desorption. The enthalpy of NO_2 adsorption is $\Delta H_{ads} = -37.0$ kcal/mol. $Z[ONOFEO_2NO]^+$ species are in equilibrium with $Z[NO_2FeO_2NO]^+$ sites. The activation barrier is 2.5 kcal/mol, the enthalpy of reaction is $\Delta H_R = -1.3$ kcal/mol and the imaginary frequency associated

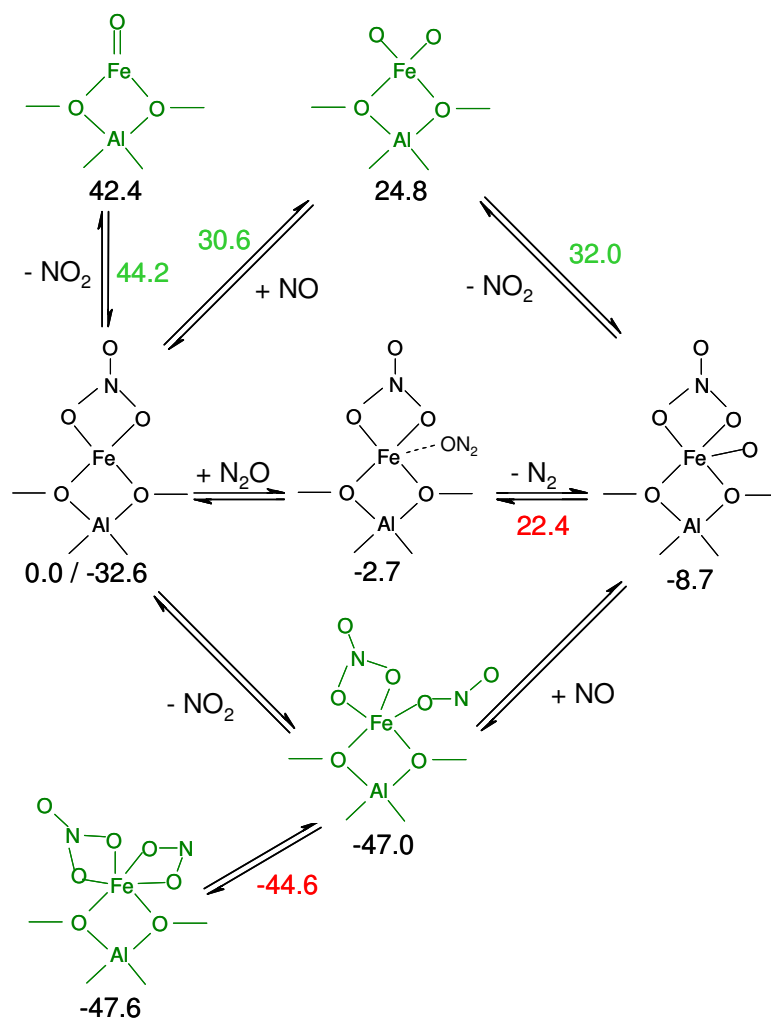


Figure 7.13: Alternative catalytic cycle of the N₂O dissociation on mononuclear Z[FeO₂NO]⁺ { $M_S = 5$ } sites. All energies are zero-point corrected, in kcal/mol and with reference to Z[FeO₂NO]⁺ with the appropriate amounts of N₂O, N₂, O₂, NO, and NO₂. Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with $M_S = 5$. Structures in green are on the PES with $M_S = 6$.

with the transition state mode is $95i\text{ cm}^{-1}$. NO₂ desorption from Z[ONOF₂O₂NO]⁺ species is rapid. The desorption barrier is 14.5 kcal/mol and the enthalpy of desorption is $\Delta H_{\text{des}} = 12.3\text{ kcal/mol}$ at reaction conditions.

To concluded, in the presence of nitric oxide iron-nitrite and –nitrate species can be formed. The first N₂O dissociation barrier with respect to the gas phase is on these sites 21.5, 21.2, and 22.4 kcal/mol, respectively. The first N₂O dissociation barrier on

$Z[FeO]^+$ sites that are present in the absence of nitric oxide is only marginally larger, 24 to 24.3 kcal/mol. The second N₂O dissociation barrier on Fe-nitrite /-nitrate species is with respect to the gas phase greater than 36 kcal/mol. On Fe-nitrite /-nitrate species no O₂⁻ superoxide species can be formed on the Fe-atom before the third oxygen atom is loaded on the iron atom and the barrier for the second N₂O dissociation is therefore significantly larger than on $Z[FeO_2]^+$ / $Z[OFeO]^+$ sites. Altogether, the reported catalytical increase in the N₂O decomposition rate at low temperatures can hardly result from Fe-nitrite /-nitrate species as speculated by Sang and Lund (2000, 2001).

7.3.5 Activation of poisoned $Z[Fe(OH)_2]^+$ sites

In chapter 5 and 6 it was shown that at low temperatures small water impurities in the feed stream poison active iron sites. Hardly any active $Z[FeO]^+$ species is present at 600 K. Almost all single iron sites are $Z[Fe(OH)_2]^+$ species. One mechanism that could explain a significant increase in the N₂O decomposition rate at low temperatures involves an activation of poisoned $Z[Fe(OH)_2]^+$ sites. Figure 7.14 illustrates a mechanism by which nitric oxide converts $Z[Fe(OH)_2]^+$ species in $Z[FeOH]^+$ sites and small amounts of HNO₂. Recently, Nobukawa et al. (2004) proposed $Z[FeOH]^+$ sites to be active for N₂O decomposition in iron zeolites. Nitric oxide can adsorb on the septet spin PES on $Z[Fe(OH)_2]^+$ sites. The enthalpy of adsorption is $\Delta H_{ads} = -0.9$ kcal/mol from the N-end and $\Delta H_{ads} = 1.1$ kcal/mol from the O-end. There is a negligible spin change barrier of 0.1 kcal/mol from $Z[Fe(OH)_2]^+(NO)$ {M_S = 7} to $Z[Fe(OH)_2]^+(NO)$ {M_S = 5} sites. The spin change process involves an enthalpy change of only $\Delta H_R = -0.01$ kcal/mol. Once adsorbed on the quintet PES, nitric oxide interacts with one hydroxo-group to form adsorbed *cis*- or *trans*-HNO₂. The transition state is characterized by a N-O distance of the N-atom from nitric oxide and one O-atom from one hydroxo-group on the Fe-atom of 1.87 Å for the formation of t-HNO₂ and 1.75 Å for the formation of c-HNO₂. The Fe-OH bond length increases in the transition state from 1.80 Å to 1.97 Å (t-HNO₂) or 2.05 Å (c-HNO₂). The activation barrier is $E^\ddagger = 9.7$ kcal/mol (t-HNO₂) or $E^\ddagger = 11.0$ kcal/mol (c-HNO₂). The imaginary frequency associated with the transition state mode is 196i cm⁻¹ (t-HNO₂) or 101i cm⁻¹ (c-HNO₂).

The enthalpy of reaction is $\Delta H_R(t\text{-HNO}_2) = 6.4$ kcal/mol or $\Delta H_R(c\text{-HNO}_2) = 8.7$ kcal/mol, respectively. HNO_2 desorbs readily to form mono-hydroxo-Fe sites. The enthalpy of desorption is $\Delta H_R(t\text{-HNO}_2) = 5.9$ kcal/mol or $\Delta H_R(c\text{-HNO}_2) = 4.3$ kcal/mol.

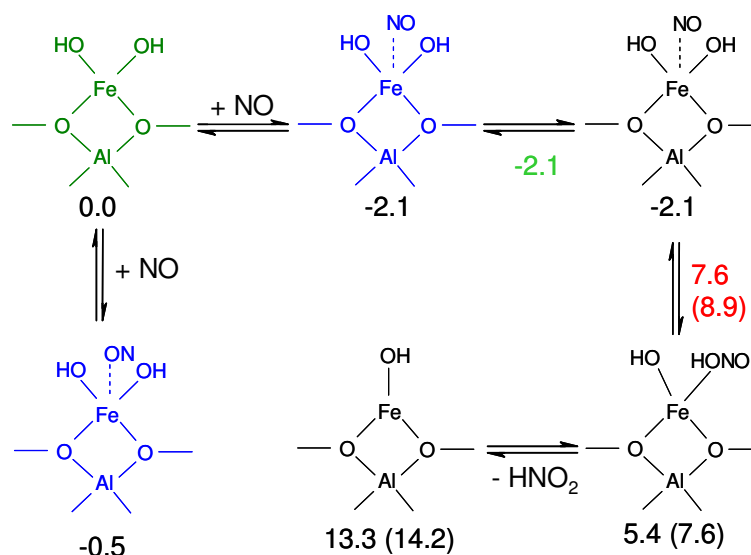


Figure 7.14: Activation of poisoned $Z[\text{Fe}(\text{OH})_2]^+ \{M_S = 6\}$ sites. All energies are zero-point corrected, in kcal/mol and with reference to $Z[\text{Fe}(\text{OH})_2]^+$ with the appropriate amounts of NO, t-HNO₂, and c-HNO₂. Numbers in brackets correspond to c-HNO₂. Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with $M_S = 5$. Green structures are on the PES with $M_S = 6$. Structures in blue are on the PES with $M_S = 7$.

7.3.6 Catalytic cycle on $Z[\text{FeOH}]^+$

Figure 7.15 illustrates the catalytic cycle of the N_2O decomposition on $Z[\text{FeOH}]^+$ sites. N_2O adsorbs through the N-end with an enthalpy of adsorption of $\Delta H_{\text{ads}} = 0.7$ kcal/mol and through the O-end with an enthalpy of adsorption of $\Delta H_{\text{ads}} = 0.2$ kcal/mol. N_2O is essentially not adsorbing on $Z[\text{FeOH}]^+$ sites under reaction conditions. The transition state for the reaction of $Z[\text{FeOH}]^+(\text{ON}_2)$ to form $Z[\text{OFeOH}]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 137.4° in the

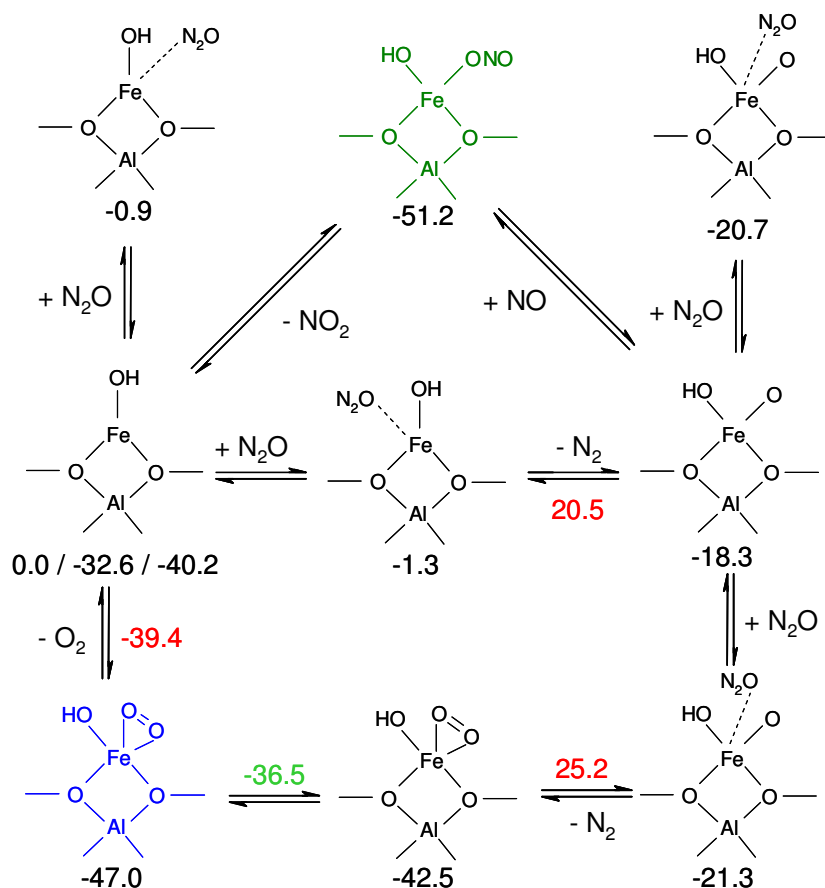


Figure 7.15: Catalytic cycle of the N₂O dissociation on mononuclear Z[FeOH]⁺ {M_S = 5} sites. All energies are zero-point corrected, in kcal/mol and with reference to Z[FeOH]⁺ with the appropriate amounts of N₂O, N₂, O₂, NO, and NO₂. Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with M_S = 5. Structures in green are on the PES with M_S = 6. Structures in blue are on the PES with M_S = 7.

transition state, whereas the length of the N'-O'' bond of the N₂O molecule increases from 1.20 Å to 1.38 Å. The activation barrier for the decomposition is E[‡] = 21.8 kcal/mol. The imaginary frequency associated with the transition state mode is 473i cm⁻¹. Figure 7.16 shows the transition state structure on the quintet PES. Because of an enthalpy of reaction of ΔH_R = -18.1 kcal/mol, the reverse reaction has a significant barrier and should not occur readily. N₂O adsorbs on Z[OFeOH]⁺ centers through the N-end with an enthalpy of adsorption of ΔH_{ads} = -0.8 kcal/mol and through the O-end with an enthalpy of adsorption of ΔH_{ads} = -1.5 kcal/mol. Again, hardly any N₂O can be expected to adsorb on Z[OFeOH]⁺ sites under reaction conditions. The transition state

for the reaction of $Z[\text{OFeOH}]^+(\text{ON}_2)$ to form $Z[\text{O}_2\text{FeOH}]^+$ and N_2 is characterized by a bending of the N_2O molecule from 180° in the adsorbed state to 136.8° in the transition state, whereas the length of the $\text{N}'\text{-O}''$ bond of the N_2O molecule increases from $1.20 \text{ \AA}$ to $1.34 \text{ \AA}$. The O-atom from N_2O forms a bond with the lone oxygen atom from $Z[\text{OFeOH}]^+$. The Fe-O bond increases along the reaction coordinate from $1.62 \text{ \AA}$ to $1.83 \text{ \AA}$ in the transition state. The O-O bond is $1.59 \text{ \AA}$ long. The activation barrier for the decomposition is $E^\ddagger = 46.5 \text{ kcal/mol}$. The imaginary frequency associated with the transition state mode is $710i \text{ cm}^{-1}$. Figure 7.16 illustrates the transition state structure on the quintet PES. Because of an enthalpy of reaction of $\Delta H_R = -20.5 \text{ kcal/mol}$, the reverse reaction has an even higher barrier and should not occur. $Z[\text{O}_2\text{FeOH}]^+$ species are more stable on the septet PES than on the quintet PES. A negligible spin change barrier of about $E^\ddagger = 6.0 \text{ kcal/mol}$ was found for the spin inversion process. The enthalpy of reaction is $\Delta H_R = -4.5 \text{ kcal/mol}$, suggesting that $Z[\text{O}_2\text{FeOH}]^+$ species on the quintet and septet PES are in equilibrium. Oxygen can desorb from $Z[\text{O}_2\text{FeOH}]^+(\text{M}_S = 7)$. The O_2 desorption barrier is $E^\ddagger = 7.6 \text{ kcal/mol}$ and the enthalpy of desorption is $\Delta H_{\text{des}} = 5.8 \text{ kcal/mol}$. The imaginary frequency associated with the transition state mode is $58i \text{ cm}^{-1}$. As in all catalytic cycles on single iron sites the O_2 desorption process is fast and there is no oxygen inhibit.

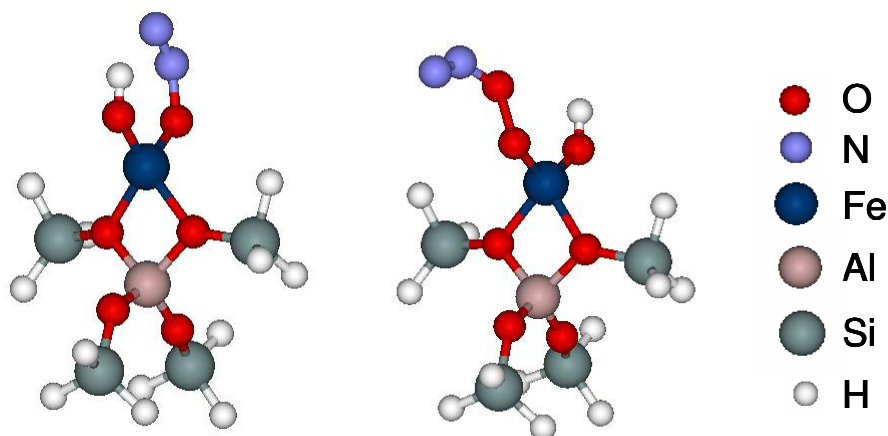


Figure 7.16: Transition state structures for N_2O decomposition on $Z[\text{FeOH}]^+$ and $Z[\text{OFeOH}]^+$.

As in the catalytic cycles on Fe-nitrite /-nitrate species, the highest barrier in the catalytic cycle on $Z[FeOH]^+$ is the second N₂O decomposition on $Z[OFeOH]^+$ sites, with an activation barrier of over 43 kcal/mol with respect to the gas phase, making this catalytic cycle unlikely to occur except at elevated temperatures. Nitric oxide can adsorb on $Z[OFeOH]^+$ sites forming $Z[ONFeOH]^+$ species and NO₂ can desorb from $Z[ONFeOH]^+$ sites to bypass the second N₂O dissociation on $Z[OFeOH]^+$ sites. The enthalpy of nitric oxide adsorption is $\Delta H_{ads} = -31.6$ kcal/mol. The enthalpy of NO₂ desorption is $\Delta H_{des} = 16.8$ kcal/mol, suggesting a fast reaction mechanism in the presence of nitric oxide.

Nitric oxide might also interact with the hydroxo-group on $Z[OFeOH]^+$ sites instead of the lone oxygen atom in $Z[OFeOH]^+$ to form adsorbed HNO₂ and $Z[FeO]^+$. Figure 7.17 illustrates this reaction pathway. Nitric oxide adsorbs barrierless from the N-end on the oxygen atom of the hydroxo-group on the Fe-atom forming $Z[FeO]^+(t-HNO_2)$ sites. The enthalpy of adsorption is $\Delta H_{ads} = -0.2$ kcal/mol. $t-HNO_2$ can then desorb from $Z[FeO]^+(t-HNO_2)$ sites to form active $Z[FeO]^+$ centers. The enthalpy of desorption is $\Delta H_{des} = 11.2$ kcal/mol. Alternatively, locally formed HNO₂ can adsorb on $Z[OFeOH]^+$ sites to form $Z[OFeOH]^+(t-HNO_2)$ species. The enthalpy of adsorption is $\Delta H_{ads} = -8.8$ kcal/mol. The adsorbed HNO₂ can then transfer a hydrogen atom to the hydroxo-group to form a $Z[OFeOH_2]^+(NO_2)\{M_S = 5\}$ species. The activation barrier for the hydrogen transfer is $E^\ddagger = 1.9$ kcal/mol. The imaginary frequency associated with the transition state mode is $927i\text{ cm}^{-1}$. The enthalpy of reaction is $\Delta H_R = -1.4$ kcal/mol. For NO₂ to desorb from this species, the cluster has to change the spin surface first. The spin change barrier from the quintet PES to the septet PES is 6.8 kcal/mol. The enthalpy of reaction of this process is $\Delta H_R = 7.3$ kcal/mol. The subsequent NO₂ desorption involves an enthalpy change of $\Delta H_{des} = 3.7$ kcal/mol. Finally, water can desorb from $Z[FeO]^+(OH_2)$ centers to form $Z[FeO]^+$ sites or a hydrogen atom is transferred to form poisoned $Z[Fe(OH)_2]^+$ sites as described in chapter 5.

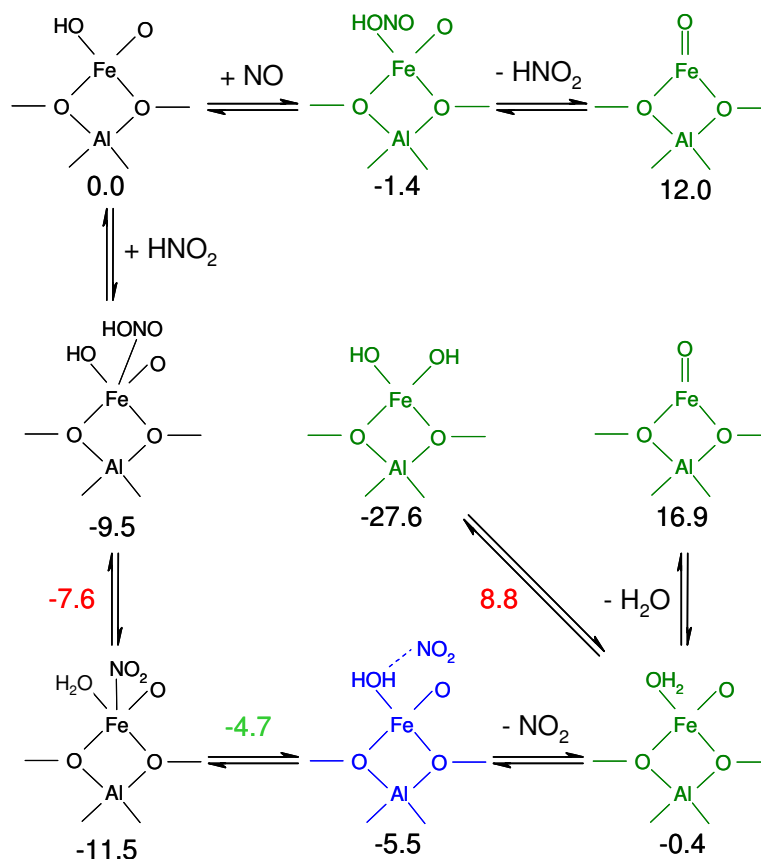


Figure 7.17: Two pathways from $Z[\text{OFeOH}]^+$ sites to active $Z[\text{FeO}]^+$ ($M_S = 6$) sites. All energies are zero-point corrected, in kcal/mol and with reference to $Z[\text{OFeOH}]^+$ with the appropriate amounts of H_2O , $t\text{-HNO}_2$, NO , and NO_2 . Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with $M_S = 5$. Structures in green are on the PES with $M_S = 6$. Structures in blue are on the PES with $M_S = 7$.

To conclude, in the absence of nitric oxide and at temperatures below 650 K, the majority of active iron sites is in the form of $Z[\text{Fe}(\text{OH})_2]^+$ species. The zero-point corrected energy barrier for water to desorb and to form active $Z[\text{FeO}]^+$ sites is about 44.5 kcal/mol. Owing to the entropy gain in splitting off a water molecule this process is occurring at high temperatures but essentially absent at low temperatures. If nitric oxide is added to a Fe-ZSM-5 catalyst system the zero-point corrected energy barrier for the formation of active $Z[\text{FeOH}]^+$ sites is about 13.3 kcal/mol and therefore significantly lower than for the water desorption process. As a result, if nitric oxide is added to a Fe-ZSM-5 catalyst at low temperatures, as done by Bulushev et al. (2004) (see Figure 7.1), the catalyst is activated immediately. Active $Z[\text{FeOH}]^+$ sites are

formed much faster than active $Z[FeO]^+$ species. The barrier for N₂O decomposition on $Z[FeOH]^+$ species is with respect to the gas phase 20.5 kcal/mol, about 3.5 kcal/mol lower than for the N₂O decomposition on $Z[FeO]^+$ sites. At elevated temperatures, on the other hand, the water desorption process should be dominant for activating $Z[Fe(OH)_2]^+$ sites. No net gas species is formed in the production process of $Z[FeOH]^+$ species so that at high temperatures the entropy gain in splitting off an adsorbed water molecule should outweigh the higher energy barrier for the reaction, $Z[Fe(OH)_2]^+ \rightleftharpoons Z[FeO]^+ + H_2O$.

7.3.7 Formation of nitric oxide on single iron sites

El-Malki et al. (2000b), Bulushev et al. (2004), and Kiwi-Minsker et al. (2005) suggested that nitric oxide might be formed from nitrous oxide, and that the produced nitric oxide might play a significant role in N₂O decomposition at low temperatures in the absence of nitric oxide in the feed. Figure 7.18 illustrates reaction pathways for the formation of nitric oxide on single iron sites oxidized once, $Z[OFeO]^+$, $Z[ONOFEO]^+$, $Z[OFeO_2N]^+$, $Z[OFeO_2NO]^+$, $Z[OFeOH]^+$. Formation of nitric oxide on once oxidized iron sites was suggested by Kiwi-Minsker et al. (2005). In the following, the formation of nitric oxide from nitrous oxide is exemplified for the interaction of nitrous oxide with $Z[OFeO]^+$ sites. Similar reaction pathways and transition state structures were found for the nitric oxide formation on $Z[ONOFEO]^+$, $Z[OFeO_2N]^+$, $Z[OFeO_2NO]^+$, and $Z[OFeOH]^+$ sites. Nitrous oxide interacts from the N-end with the oxygen atom deposited on the mononuclear iron site and can form an adsorbed nitric oxide dimer. The transition state for the reaction, $Z[OFeO]^+ + N_2O \rightleftharpoons Z[FeO]^+(c-(NO)_2)$, is characterized by a bending of the N₂O molecule from 180° to 152.8° in the transition state, whereas the length of the N-N' bond of the N₂O molecule increases from 1.12 Å to 1.17 Å. The N-O (oxygen bond to the iron atom) bond length is 1.67 Å in the transition state. The activation barrier for the nitric oxide dimer is $E^\ddagger = 28.2$ kcal/mol and the enthalpy of reaction is $\Delta H_R = 24.4$ kcal/mol (for the NO formation on $Z[ONOFEO]^+$, $Z[OFeO_2N]^+$, $Z[OFeO_2NO]^+$, $Z[OFeOH]^+$ sites the activation barrier

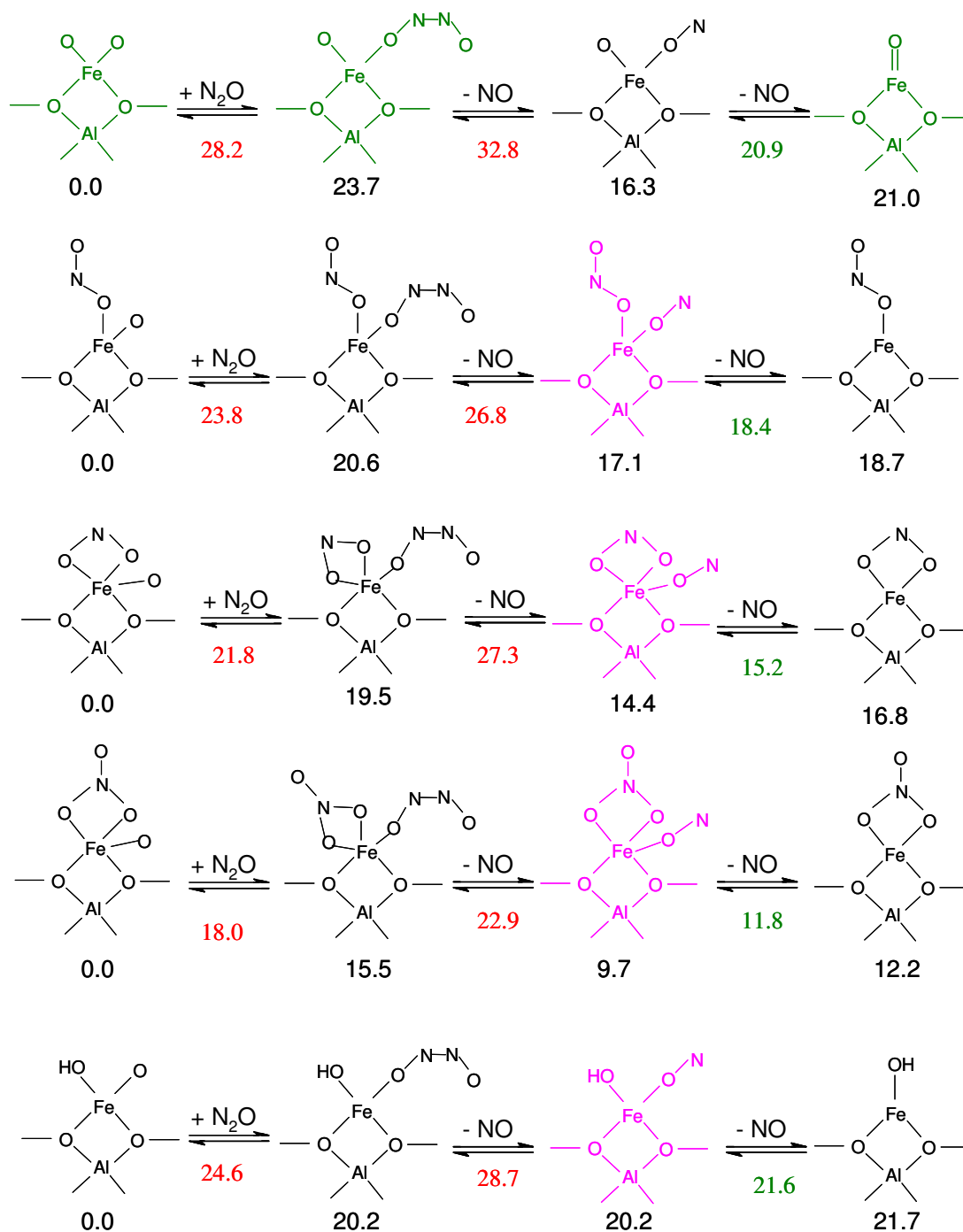


Figure 7.18: Possible pathways for the formation of nitric oxide. All energies are zero-point corrected, in kcal/mol and with reference to $Z[OFeO]^+$, $Z[OFeONO]^+$, $Z[OFeO_2N]^+$, $Z[OFeO_2NO]^+$ or $Z[OFeOH]^+$ with the appropriate amounts of N_2O and NO . Energies of potential energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Structures in magenta are on the PES with $M_S = 4$. Black structures are on the PES with $M_S = 5$. Green structures are on the PES with $M_S = 6$.

and enthalpy of reaction is found to be slightly smaller; see Table 7.1). The imaginary frequency associated with the transition state mode is $614i\text{ cm}^{-1}$. Gonzalez et al. (2001) found a very similar activation barrier of 27.7 kcal/mol for the reaction, $\text{O}(^3\text{P}) + \text{N}_2\text{O} \rightleftharpoons 2\text{NO}$. The geometry of the transition state structure is also quite similar with an O-N distance of 1.66 Å, a N-N' distance of 1.17 Å, and a N₂O bending of 157.3° in the transition state. Nitric oxide can desorb from $\text{Z}[\text{FeO}]^+(\text{c}(\text{NO})_2)$ sites. The transition state for the reaction of $\text{Z}[\text{FeO}]^+(\text{c}(\text{NO})_2)$ to form $\text{Z}[\text{FeO}]^+(\text{ON})$ and NO is characterized by an increase in the N-N' bond length from 1.23 Å in the adsorbed state to 1.44 Å in the transition state. The activation barrier for the dissociation is $E^\ddagger = 9.2\text{ kcal/mol}$. The imaginary frequency associated with the transition state mode is $677i\text{ cm}^{-1}$. The enthalpy of reaction is $\Delta H_{\text{R}} = -6.1\text{ kcal/mol}$. At reaction conditions the dissociation of the NO-dimer is fast. Nitric oxide rapidly desorbs from $\text{Z}[\text{FeO}]^+(\text{ON})$ sites. The spin change barrier for desorption is $E^\ddagger = 4.8\text{ kcal/mol}$ and the enthalpy of desorption is $\Delta H_{\text{des}} = 3.3\text{ kcal/mol}$. If, under reaction conditions, a significant fraction of surface sites is present in the form of $\text{Z}[\text{OFeO}]^+$, $\text{Z}[\text{ONFeO}]^+$, $\text{Z}[\text{OFeO}_2\text{N}]^+$, $\text{Z}[\text{OFeO}_2\text{NO}]^+$, and $\text{Z}[\text{OFeOH}]^+$ sites, nitric oxide can be formed from nitrous oxide. The energetically most demanding step is the formation of an adsorbed nitric oxide dimer; once formed, nitric oxide production occurs readily.

7.4 Comparison with experimental observation

In this section, the importance of different reaction pathways for the NO-assisted N₂O decomposition is studied for various gas concentrations and temperatures. It is investigated whether the reaction network determined from first principles in section 7.3 and 5.4 is able to explain experimental observations of the NO-assisted N₂O decomposition, i.e., the catalytic effect of nitric oxide on the N₂O decomposition rate at low temperatures. Macroscopic apparent reaction rates and surface compositions have been determined under steady state conditions. All elementary rate processes studied in this work have been considered. At a fixed gas composition and temperature the steady state material balance of the main surface species can be written as a set of linear

equations. These equations were preconditioned and solved with interval methods developed by Rump (1980 and 1983). A closed solution could be given in all cases presented in this chapter. In chapter 6, it was shown that experimental data could be reproduced with a reaction network based on single iron sites and a water partial pressure in the feed of 10^{-7} to 10^{-6} bar. As a result, all simulations presented in this chapter have been done with a water partial pressure of 10^{-7} and 10^{-6} bar. This allows evaluating the sensitivity of the results with varying water partial pressure.

Fu et al. (1981), Panov et al. (1990), Kapteijn et al. (1997), and Wood et al. (2004) report a first order N_2O decomposition rate in the absence of nitric oxide. Sang et al. (2005) observed a first order N_2O decomposition rate in the presence and absence of nitric oxide. Figure 7.19 illustrates the logarithm of the N_2O decomposition rate versus the logarithm of the N_2O partial pressure at a temperature of 650 K and a nitric oxide concentration of 0.1 ppb NO (no nitric oxide added) and 100 ppm NO. The N_2O

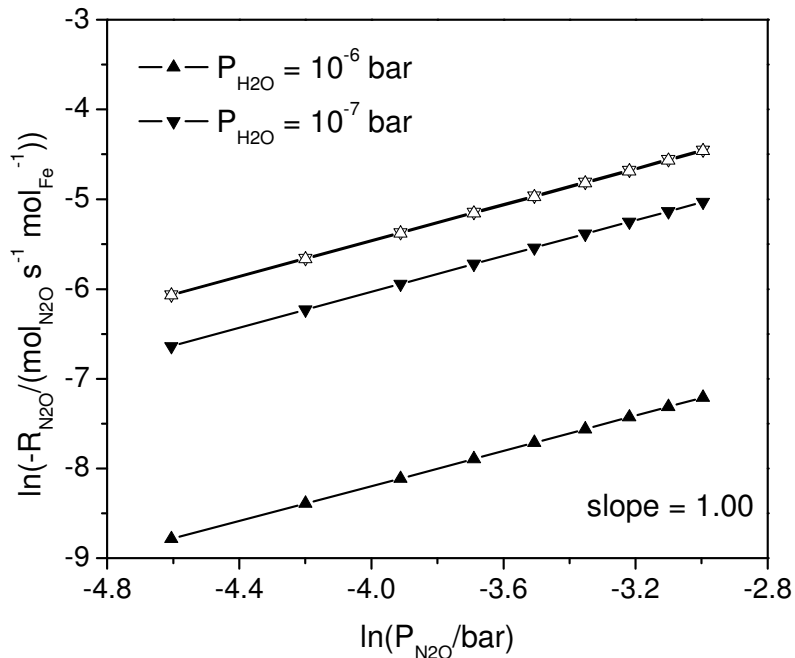


Figure 7.19: Determination of the order of the steady state N_2O decomposition over Fe-ZSM-5 at 650 K. The N_2O decomposition rate was determined at a gas composition of 0.1 ppb NO (solid symbols), 100 ppm NO (open symbols), 1 ppm H_2O , 0.1 ppm H_2O , and varying amounts of N_2O in He (10,000 – 50,000 ppm N_2O). The simulation was performed with all reaction rate parameters from Table 7.1 and Table 6.1.

decomposition rate is found to be first order in nitrous oxide partial pressure in the presence and absence of nitric oxide and independent of the water concentration in the feed, confirming experimental observations. Figure 7.19 also illustrates that in the absence of nitric oxide the water concentration has a significant effect on the N₂O decomposition rate at 650 K (also shown in chapter 6). In the presence of 100 ppm NO the influence of water impurities on the N₂O decomposition rate seems to have disappeared. Figure 7.20 illustrates an Arrhenius plot of the N₂O decomposition rate in

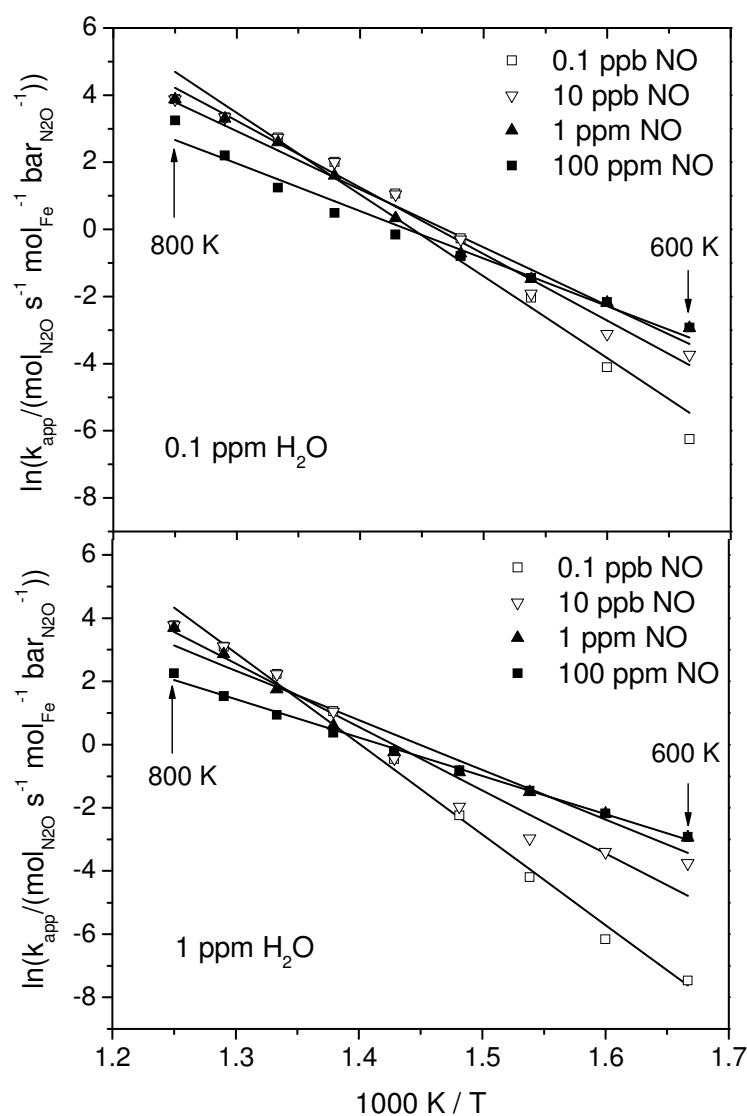


Figure 7.20: Arrhenius plot of the first order steady state N₂O decomposition over Fe-ZSM-5 in the presence of nitric oxide. The N₂O decomposition rate was determined at a gas composition of varying amounts of NO, 0.1 ppm / 1 ppm H₂O, and 15,000 ppm N₂O in He. The simulation was performed with all reaction rate parameters from Table 7.1 and Table 6.1.

the presence of varying amounts of nitric oxide. The addition of NO significantly increases the apparent reaction rate constant for the N_2O decomposition at low temperatures, whereas the promotional effect of nitric oxide vanishes at high temperatures. The influence of nitric oxide on the apparent rate constant is more pronounced for a larger water concentration in the feed stream. At a H_2O partial pressure of 10^{-7} bar, the presence of nitric oxide increases the N_2O decomposition rate at a temperature of 600 K by a factor 27. At a H_2O partial pressure of 10^{-6} bar, the N_2O decomposition rate is increased by a factor 93. It is interesting to note that the absolute value of the apparent reaction rate constant becomes, for significant nitric oxide concentrations, essentially independent of the water concentration in the feed. For nitric oxide concentrations larger 1 ppm NO, no promotional effect of nitric oxide on the N_2O decomposition rate can be observed. At the same time no nitric oxide inhibition could be observed at low temperatures for a nitric oxide concentration of 0.1 bar (not shown). Table 7.3 summarizes experimental and calculated apparent rate constants, activation barriers, and preexponential factors for various nitric oxide concentrations. Simulations of N_2O decomposition reproduce experimental apparent rate constants for the N_2O dissociation in the presence and absence of nitric oxide from Sang et al. (2005). To sum up, it can be concluded that the reaction mechanism determined from first-principles

TABLE 7.3: Experimental and computed apparent steady state rate parameters for the nitrous oxide decomposition over Fe-ZSM-5 in the presence of nitric oxide[§]

H_2O content (ppb)	NO content (ppb)	E_{app} (kcal/mol)	Preexponential factor ($\text{mol}_{\text{N}_2\text{O}}/\text{s} \cdot \text{mol}_{\text{Fe}} \cdot \text{bar}_{\text{N}_2\text{O}}$)	Apparent rate constant ($\text{mol}_{\text{N}_2\text{O}}/\text{s} \cdot \text{mol}_{\text{Fe}} \cdot \text{bar}_{\text{N}_2\text{O}}$) at 650 K	Rate increase due to NO at 600 K	Reference
unknown	0 (unknown)	46.3	5.2×10^{13}	0.014	--	(a)
unknown	6.7×10^6	39.4	4.5×10^{12}	0.250	28	(a)
100	0.1	48.3	1.8×10^{15}	0.097	--	(b)
100	10	39.3	3.9×10^{12}	0.224	12	(b)
100	1000	34.3	1.1×10^{11}	0.302	27	(b)
100	100000	28.1	6.8×10^8	0.243	27	(b)
1000	0.1	57.0	2.9×10^{17}	0.019	--	(b)
1000	10	39.8	2.6×10^{12}	0.109	41	(b)
1000	1000	31.2	7.9×10^9	0.244	92	(b)
1000	100000	24.1	2.9×10^7	0.233	93	(b)

[§] Computed data are calculated with different amounts of water and nitric oxide in reactant stream over the temperature range from 600 to 800 K.

(a) Sang et al. (2005) (b) this work

and presented in section 7.3 and 5.4 is able to describe the experimentally observed catalytic effect of nitric oxide on the N₂O decomposition rate at low temperatures. No nitric oxide inhibition is observed at low temperatures.

Mul et al. (2001) reports for the NO-assisted N₂O decomposition a maximum in the outlet NO₂ partial pressure versus temperature. Simultaneously, the nitric oxide partial pressure shows a minimum, so that the concentration of the sum of NO and NO₂ stays constant over temperature. To investigate if such a behavior is also observed for the reaction network developed in this work, the reaction rate of NO₂ formation and NO depletion versus temperature is shown in Figure 7.21. For a gas composition of 1 ppm NO, 0.1 ppm H₂O, and 15,000 ppm N₂O in He, the NO₂ formation rate displays a significant maximum and the NO depletion rate a minimum at a temperature of about 720 K. The sum of both reaction rates is zero, leading to a constant sum of NO and

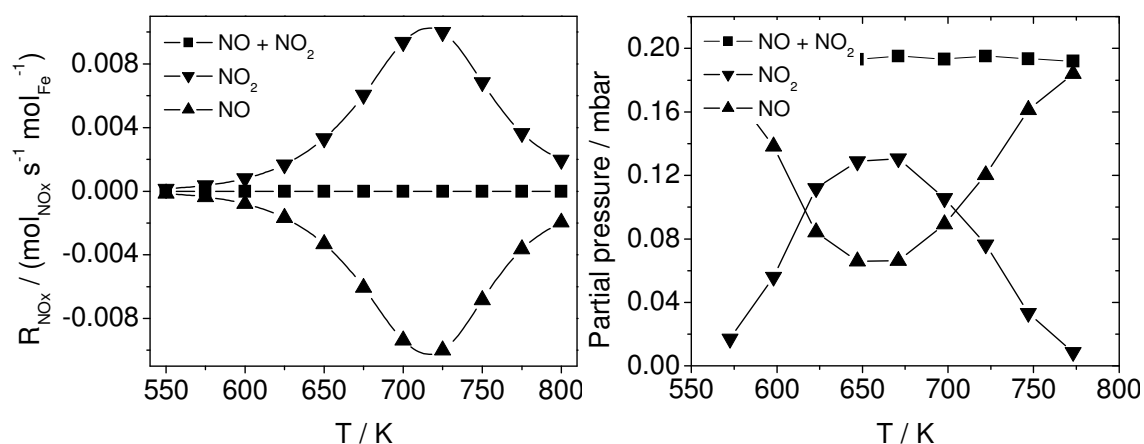


Figure 7.21: Left: Steady state turnover frequency of single iron sites in Fe-ZSM-5 for the formation of NO and NO₂ versus temperature. The turnover frequencies are determined at a gas composition of 1 ppm NO, 0.1 ppm H₂O, and 15,000 ppm N₂O in He. The simulation was performed with all reaction rate parameters from Table 7.1 and Table 6.1. Right: Partial pressure of NO, NO₂, and sum of NO and NO₂ versus temperature during catalytic decomposition of N₂O in 15,000 ppm N₂O and 2,000 ppm NO (space velocity 60000 h⁻¹). Data from Mul et al. (2001).

NO₂ concentration as reported by Mul et al. (2001). The maximum in the NO₂ formation rate occurs at a slightly higher temperature (about 50 K) than the one observed by Mul et al. (2001). The reason for this discrepancy might originate from inaccuracies in the theoretical rate parameters, or more likely from different gas concentrations present in the experiment and simulation, e.g., the NO₂ partial pressure was set to zero in the simulations so that the reaction, $2 \text{NO}_2 \rightleftharpoons 2 \text{NO} + \text{O}_2$, (occurring at high temperatures) is not included in the reaction network studied in this work. Nevertheless, the qualitative agreement is very good, considering that no fit parameter was used and all reaction rates were determined from first principles.

To understand why small nitric oxide concentrations result in a strong promotional effect on the nitrous oxide decomposition rate at low temperatures the variation of the surface composition with temperature and nitric oxide concentration was analyzed. Figures 7.22 and 7.23 illustrate the steady state surface fraction of the most abundant surface sites, $\text{Z}[\text{Fe}(\text{OH})_2]^+$, $\text{Z}[\text{FeO}_2]^+$, $\text{Z}[\text{FeO}]^+$, $\text{Z}[\text{FeOH}]^+$, $\text{Z}[\text{OFeOH}]^+$, and Fe-nitrite /-nitrate in Fe-ZSM-5 versus temperature for a gas composition of 0.1 ppm H₂O, 15,000 ppm N₂O, and varying amounts of nitric oxide in He. If no nitric oxide is added to the nitrous oxide feed, single iron sites in Fe-ZSM-5 are poisoned with H₂O at low temperatures, whereas $\text{Z}[\text{FeO}]^+$ and $\text{Z}[\text{FeO}_2]^+$ sites are present at high temperatures. Water desorbs with increasing temperature. Nearly 50 % of the single iron sites are present in the form of $\text{Z}[\text{FeO}_2]^+$ species at high temperatures. Active Fe-nitrite /-nitrate and $\text{Z}[\text{FeOH}]^+$ species are not present in the absence of nitric oxide. $\text{Z}[\text{OFeOH}]^+$ sites are found in small amounts (< 2.5 %) at low temperatures. N₂O cannot dissociate on $\text{Z}[\text{OFeOH}]^+$ sites (barrier > 43 kcal/mol). In addition, the NO-concentration is too low for $\text{Z}[\text{ONFeOH}]^+$ site formation so that $\text{Z}[\text{OFeOH}]^+$ sites accumulate at a low level. As $\text{Z}[\text{Fe}(\text{OH})_2]^+$ sites, $\text{Z}[\text{OFeOH}]^+$ sites are not active for N₂O decomposition. To conclude, in the absence of nitric oxide in the feed, the N₂O decomposition rate changes significantly with H₂O concentration in the low temperature range due to the large enthalpy of water adsorption on $\text{Z}[\text{FeO}]^+$ sites. By increasing the nitric oxide

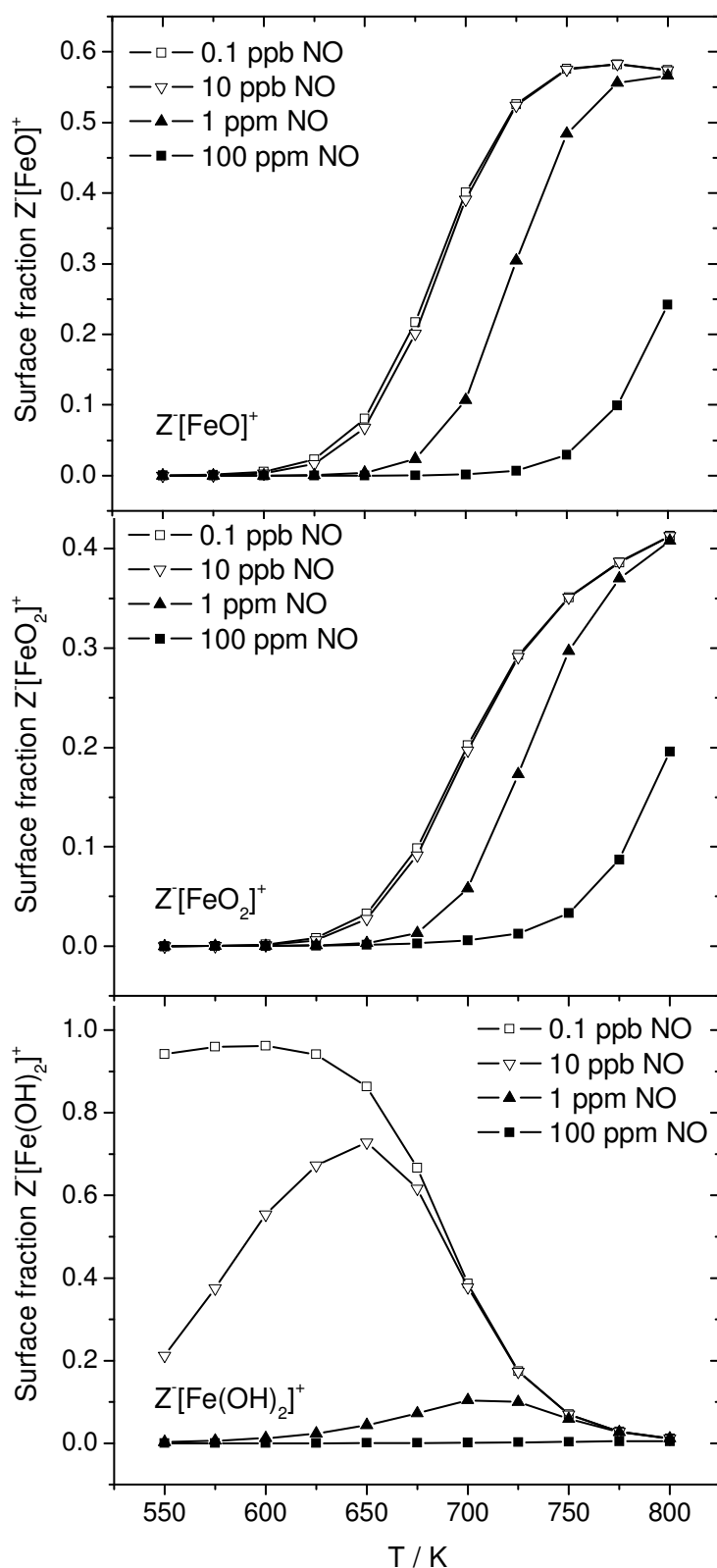


Figure 7.22: Steady state surface fraction of $Z[Fe(OH)_2]^+$, $Z[FeO_2]^+$, $Z[FeO]^+$ in Fe-ZSM-5 versus temperature. The surface composition was determined at a gas composition with varying amounts of NO, 0.1 ppm H₂O, and 15,000 ppm N₂O in He.

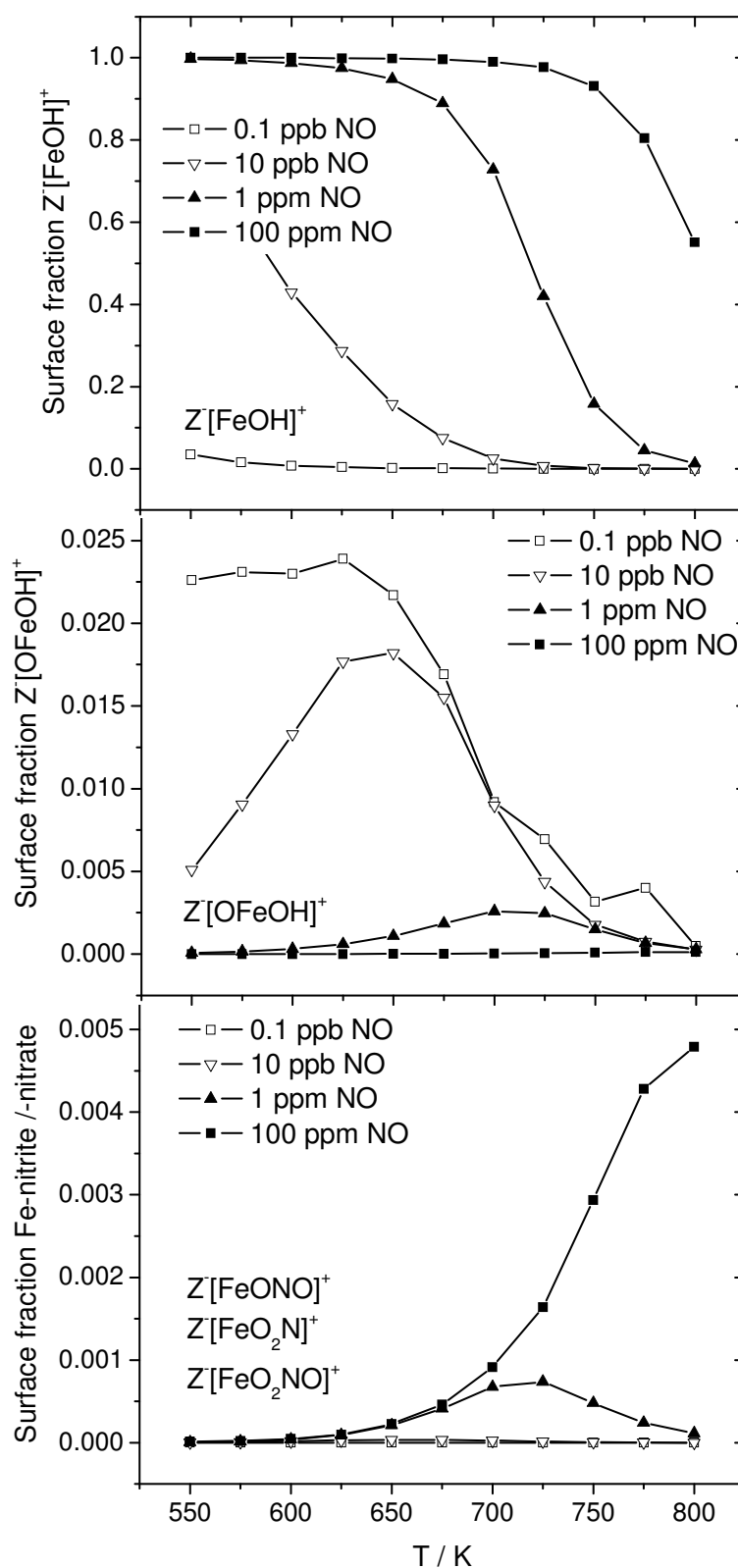


Figure 7.23: Steady state surface fraction of $Z[\text{FeOH}]^+$, $Z[\text{OFeOH}]^+$, and sum of $Z[\text{FeONO}]^+$, $Z[\text{FeO}_2\text{N}]^+$, $Z[\text{FeO}_2\text{NO}]^+$ in Fe-ZSM-5 versus temperature. The surface composition was determined at a gas composition with varying amounts of NO, 0.1 ppm H_2O , and 15,000 ppm N_2O in He.

concentration the surface composition changes significantly at low temperatures. As illustrated in Figure 7.14, nitric oxide activates poisoned $Z[\text{Fe}(\text{OH})_2]^+$ sites by forming $Z[\text{FeOH}]^+$ species. In the presence of small amounts of nitric oxide (about 1 ppm NO), $Z[\text{Fe}(\text{OH})_2]^+$ sites are displaced by $Z[\text{FeOH}]^+$ sites; poisoned $Z[\text{Fe}(\text{OH})_2]^+$ sites are only found in a small temperature window. Likewise, $Z[\text{OFeOH}]^+$ sites had completely disappeared. In the presence of nitric oxide, the highest barrier for the N₂O decomposition on $Z[\text{FeOH}]^+$ sites is the first N₂O dissociation and not the nitric oxide adsorption on $Z[\text{OFeOH}]^+$ sites anymore. Consequently, $Z[\text{OFeOH}]^+$ sites are rapidly converted to $Z[\text{FeOH}]^+$ sites. The fraction of active $Z[\text{FeO}]^+$ and $Z[\text{FeO}_2]^+$ sites versus temperature is shifted to higher temperatures. At low temperatures, $Z[\text{FeOH}]^+$ sites displace $Z[\text{FeO}]^+$ and $Z[\text{FeO}_2]^+$ sites. The enthalpy of $Z[\text{FeO}]^+$ formation from $Z[\text{Fe}(\text{OH})_2]^+$ sites is about 32 kcal/mol higher than the enthalpy of $Z[\text{FeOH}]^+$ formation. But, the formation of $Z[\text{FeO}]^+$ sites involves the production of a net gas species (H₂O) so that at elevated temperatures, the entropy gain in splitting off an adsorbed water molecule outweighs the higher energy barrier. $Z[\text{FeO}]^+$ and $Z[\text{FeO}_2]^+$ sites displace $Z[\text{FeOH}]^+$ species. Figure 7.23 illustrates that Fe-nitrite /-nitrate species play no significant role in the NO-assisted N₂O decomposition. At low temperatures, where the formation of Fe-nitrite /-nitrate species is favorable with respect to $Z[\text{FeO}]^+$ sites, the formation of $Z[\text{FeOH}]^+$ species is even more favorable. At high temperatures nitric oxide desorbs from Fe-nitrite /-nitrate species and $Z[\text{FeO}]^+$ sites are formed. Just at a significant nitric oxide partial pressure (> 0.1 bar) there exists a temperature window where Fe-nitrite /-nitrate species are present to a significant amount and contribute to the nitrous oxide dissociation.

Figures 7.24 and 7.25 illustrate the share of the main active single iron species in N₂O decomposition over Fe-ZSM-5 versus temperature. In the absence of nitric oxide or at elevated temperatures, $Z[\text{FeO}]^+$ and $Z[\text{FeO}_2]^+$ / $Z[\text{OFeO}]^+$ sites contribute each 50 % to the N₂O decomposition rate. $Z[\text{FeO}_2]^+$ sites hardly contribute to N₂O dissociation. $Z[\text{OFeO}]^+$ sites, that are in equilibrium with $Z[\text{FeO}_2]^+$ sites, are the active once oxidized single iron site. Nitrogen and oxygen are formed in stoichiometric amounts. With increasing nitric oxide partial pressure the share of these sites versus temperature is shifted to higher temperatures. $Z[\text{FeOH}]^+$ sites are the main contributor to the nitrous

oxide dissociation at low temperatures in the presence of nitric oxide. It is important to note that even at a nitric oxide partial pressure of 10^{-10} bar NO, where $Z[\text{FeOH}]^+$ sites constitute only about 1-3 % of the single iron sites, $Z[\text{FeOH}]^+$ sites are the only source of nitrous oxide decomposition activity. $Z[\text{FeO}]^+$ and $Z[\text{FeO}_2]^+$ sites are present at an even smaller amount. Fe-nitrite /-nitrate species, though slightly more active than $Z[\text{FeO}]^+$ and $Z[\text{FeO}_2]^+$ sites, are hardly present and their share in the N_2O decomposition rate is negligible.

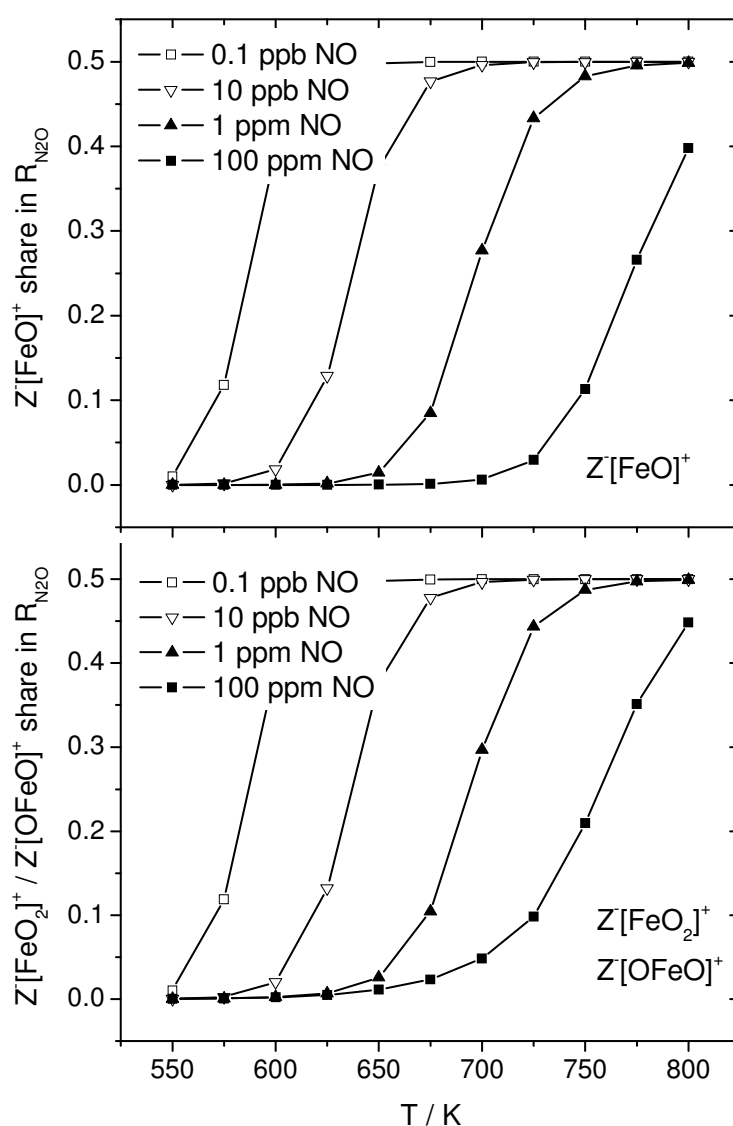


Figure 7.24: Steady state share of $Z[\text{FeO}]^+$, $Z[\text{FeO}_2]^+$, $Z[\text{OFeO}]^+$ in N_2O conversion over Fe-ZSM-5 versus temperature. The N_2O dissociation rate was determined at a gas composition with varying amounts of NO, 0.1 ppm H_2O , and 15,000 ppm N_2O in He.

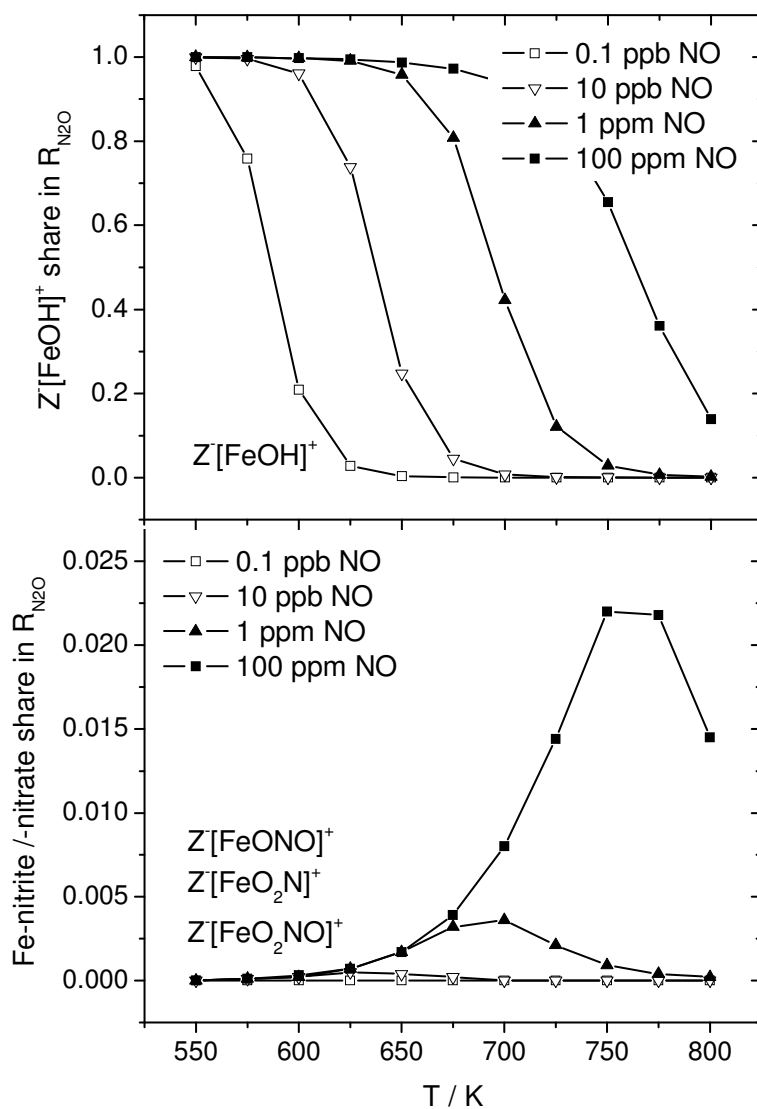


Figure 7.25: Steady state share of $Z[FeOH]^+$ and sum of $Z[FeONO]^+$, $Z[FeO_2N]^+$, $Z[FeO_2NO]^+$ in N₂O conversion over Fe-ZSM-5 versus temperature. The N₂O dissociation rate was determined at a gas composition with varying amounts of NO, 0.1 ppm H₂O, and 15,000 ppm N₂O in He.

To conclude, the catalytic effect of nitric oxide on the N₂O decomposition rate at low temperatures results from the activation of $Z[Fe(OH)_2]^+$ sites by formation of $Z[FeOH]^+$ species. The promotional effect of nitric oxide vanishes at high temperatures since the surface composition becomes independent of nitric oxide partial pressure and because $Z[FeO]^+$ and $Z[OFeO]^+$ sites are responsible for N₂O decomposition. Contrary to the N₂O dissociation on $Z[OFeOH]^+$ sites, the second N₂O dissociation reaction on $Z[OFeO]^+$ sites is rapid (even more rapid than on $Z[FeO]^+$

sites) so that the nitric oxide concentration has no influence on the N_2O dissociation rate. Nitric oxide can also not block single iron sites for the N_2O dissociation at high nitric oxide partial pressures; the enthalpy of nitric oxide adsorption is too small. A higher nitric oxide concentration results only in a complete coverage of $\text{Z}[\text{FeOH}]^+$ sites at higher temperatures. No influence can be observed in the low temperature range.

The experimentally observed maximum in the nitrogen dioxide rate versus temperature results from a change in the active single iron site responsible for N_2O dissociation with increasing temperature. At low temperatures the catalytic N_2O dissociation cycle occurs on $\text{Z}[\text{FeOH}]^+$ sites and involves adsorption of nitric oxide on $\text{Z}[\text{OFeOH}]^+$ species and subsequent NO_2 desorption. With increasing temperature the rate of N_2O decomposition on $\text{Z}[\text{FeOH}]^+$ sites increases. As a result, the rate of NO_2 production and NO depletion increases. A further increase in temperature shifts the active single iron site to $\text{Z}[\text{FeO}]^+$ and $\text{Z}[\text{FeO}_2]^+$ species. The catalytic cycle of the N_2O dissociation on $\text{Z}[\text{FeO}]^+$ sites does not involve nitric oxide so that the NO_2 production rate decreases with temperature again.

In this context, it is also possible to speculate why Pérez-Ramírez et al. (2003c) and Boutarouch et al. (2004) report an inhibitory effect of nitric oxide on the N_2O reduction by CO and hydrocarbons in the low temperature range. Hydrocarbon and CO interaction with N_2O over Fe-ZSM-5 is known to take place preferably on single iron sites at a temperature where $\text{Z}[\text{FeO}]^+$ sites are hardly present (but $\text{Z}[\text{Fe}(\text{OH})_2]^+$ sites). As a result, hydrocarbons should be able to activate $\text{Z}[\text{Fe}(\text{OH})_2]^+$ sites for N_2O dissociation. If this activation is absent on $\text{Z}[\text{FeOH}]^+$ sites, e.g., because water cannot be formed during the catalytic cycle, nitric oxide inhibits the N_2O reduction with hydrocarbons and carbon monoxide.

Kiwi-Minsker et al. (2005) studied the N_2O decomposition in the absence of nitric oxide in the feed at a temperature below 600 K. The NO_x concentration in the nitrous oxide feed is reported to be smaller 2 ppm. They observed a zero-order N_2O decomposition rate and report the formation of small amounts of nitric oxide on the catalyst surface.

Figure 7.26 illustrates the logarithm of the N₂O decomposition rate versus the logarithm of the N₂O partial pressure under the assumption that the ratio of nitrous oxide and nitric oxide partial pressure is 10^7 (corresponds to 0.1 ppm NO impurities in the N₂O feed). The N₂O decomposition rate is found to be first order in N₂O partial pressure. Figure 7.27 illustrates the surface composition of the most abundant surface species at a temperature of 593 K versus nitrous oxide partial pressure. The surface composition is independent of the nitrous oxide partial pressure, and there are significantly more Z[FeOH]⁺ sites than Z[OFeOH]⁺ sites present, suggesting that the slowest step in the catalytic cycle is the N₂O dissociation. As a result, the decomposition rate is first order in N₂O partial pressure.

Figure 7.28 illustrates the logarithm of the N₂O decomposition rate versus the logarithm of the N₂O partial pressure if, for an unknown reason, the nitric oxide partial pressure is independent of nitrous oxide concentration (the nitric oxide partial pressure is set to 10^{-9}

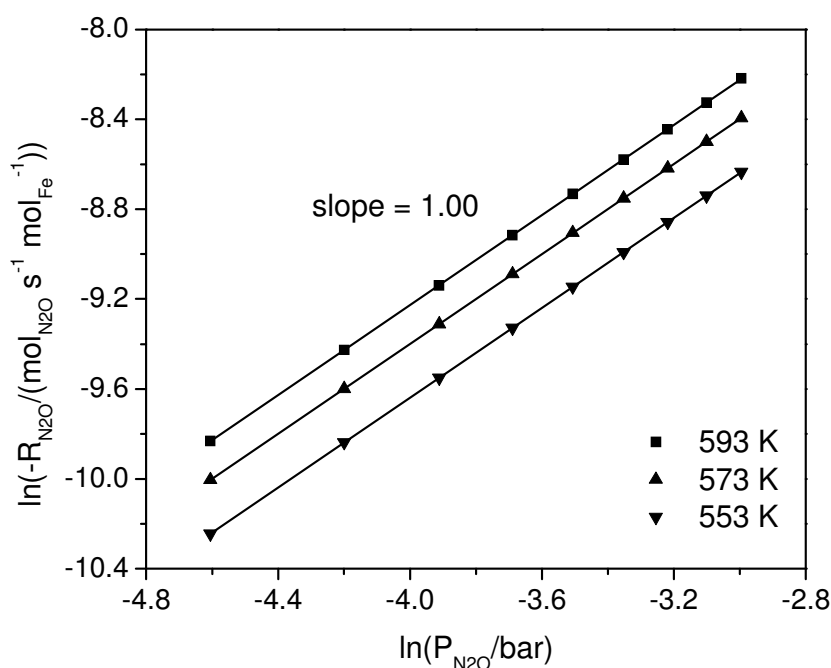


Figure 7.26: Determination of the order of the steady state N₂O decomposition over Fe-ZSM-5 at low temperatures. The N₂O decomposition rate was determined at a gas composition of 1 ppm H₂O and varying amounts of N₂O and NO in He ($P_{\text{N}_2\text{O}} = 10,000 - 50,000$ ppm; $P_{\text{N}_2\text{O}}/P_{\text{NO}} = 10^7$). The simulation was performed with all reaction rate parameters from Table 7.1 and Table 6.1.

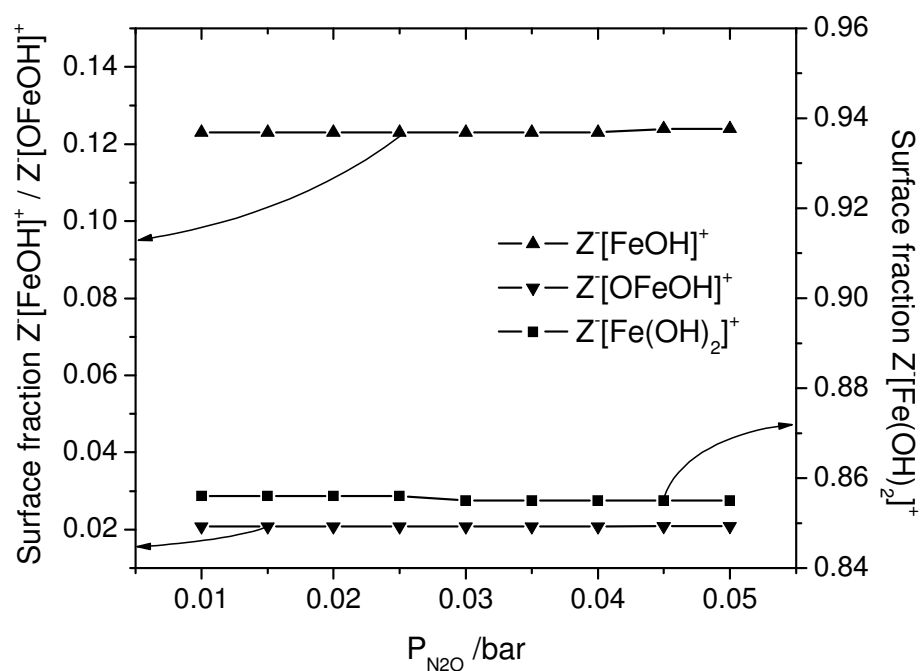


Figure 7.27: Surface composition of the most abundant surface species in Fe-ZSM-5 at a temperature of 593 K. The steady state surface composition was determined at a gas composition of 1 ppm H₂O and varying amounts of N₂O and NO in He ($P_{\text{N}_2\text{O}}/P_{\text{NO}} = 10^7$).

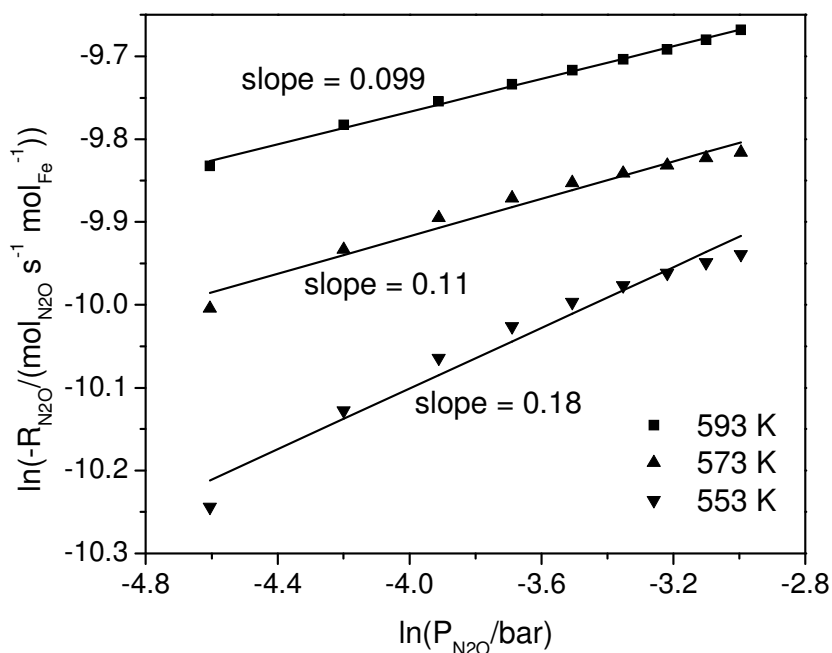


Figure 7.28: Determination of the order of the steady state N₂O decomposition over Fe-ZSM-5 at low temperatures. The N₂O decomposition rate was determined at a gas composition of 1 ppb NO, 1 ppm H₂O, and varying amounts of N₂O in He.

bar). The order of the N₂O dissociation rate is found to be about 0.1, a value close to the zero order N₂O decomposition rate reported by Kiwi-Minsker et al. (2005). The reason for the low order of the N₂O decomposition rate is a change of the surface composition with N₂O partial pressure. Figure 7.29 illustrates the surface composition of the main surface species at a temperature of 593 K versus N₂O partial pressure. The fraction of Z[FeOH]⁺ sites active for N₂O dissociation decreases with N₂O partial pressure, reducing the apparent order of the N₂O decomposition rate. As a result, no active iron site other than mononuclear Fe species are necessary to understand the unique zero order N₂O decomposition rate observed by Kiwi-Minsker et al. (2005) at low temperatures.

Finally, it was tested if nitric oxide can be produced by nitrous oxide to significant amounts at low temperatures, as suggested by Grubert et al. (2000), El-Malki et al. (2000b), and Kiwi-Minsker et al. (2005). Figure 7.30 illustrates the nitric oxide formation rate on single iron sites in Fe-ZSM-5 at a temperature below 600 K and a gas

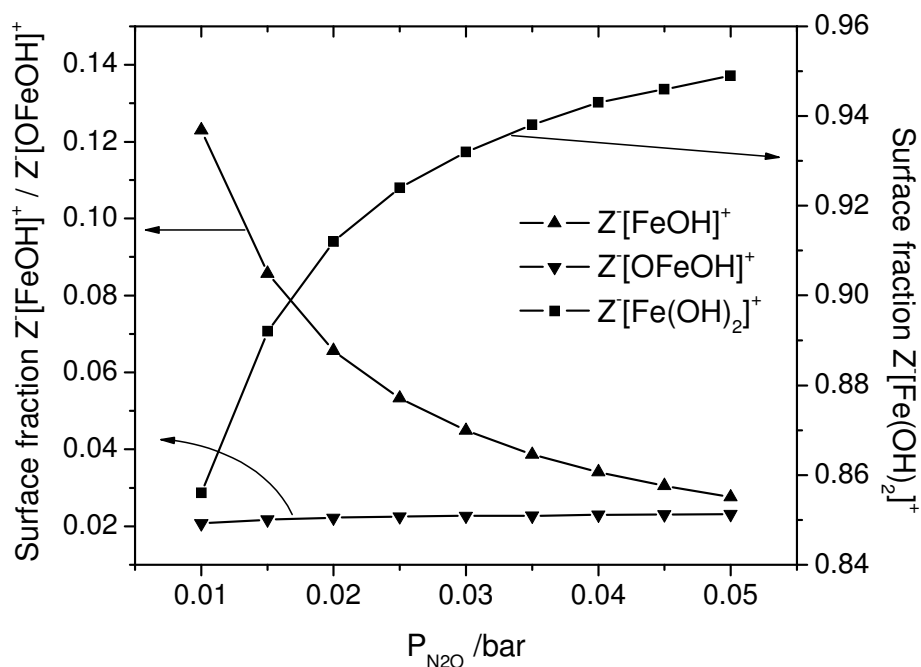


Figure 7.29: Surface composition of the most abundant surface species in Fe-ZSM-5 at a temperature of 593 K. The steady state surface composition was determined at a gas composition of 1 ppb NO, 1 ppm H₂O, and varying amounts of N₂O in He.

composition of 0.1 ppb NO, 1 ppm H₂O, and varying amounts of N₂O in He. Except at a nitrous oxide partial pressure larger 0.5 bar, nitric oxide is consumed, suggesting that at these conditions the nitric oxide concentration is below 0.1 ppb. As a result, formed nitric oxide has only any significance on the N₂O decomposition rate at a high N₂O partial pressure or a very low temperature. It was illustrated in Figure 7.25 though, that, despite the presence of only small amounts of Z[FeOH]⁺ sites, the share of Z[FeOH]⁺ sites on the N₂O decomposition rate is significant at low temperatures. Consequently, at low temperatures the production of nitric oxide or small amounts of nitric oxide impurities in the nitrous oxide feed might be important for the nitrous oxide decomposition rate. A more elaborate investigation of the production of nitric oxide by nitrous oxide, including reactor simulations, will be published in a subsequent paper.

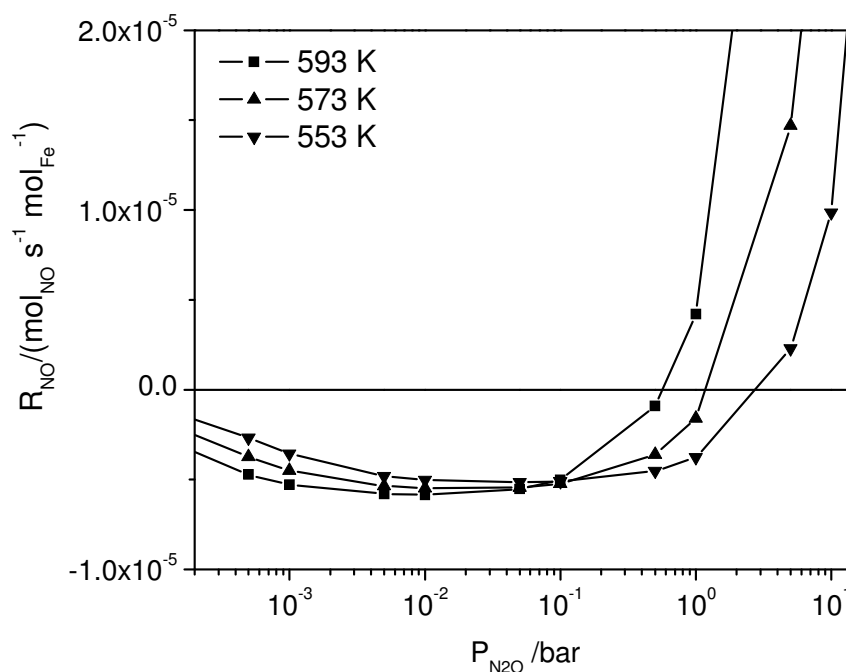


Figure 7.30: Steady state turnover frequency of single iron sites in Fe-ZSM-5 for the formation of nitric oxide at low temperatures. The NO formation rate was determined at a gas composition of 0.1 ppb NO, 1 ppm H₂O, and varying amounts of N₂O in He. The simulation was performed with all reaction rate parameters from Table 7.1 and Table 6.1.

7.5 Conclusions

The reaction mechanism of the NO-assisted N₂O decomposition was investigated on Fe-nitrite, Fe-nitrate, and Z[FeOH]⁺ sites in Fe-ZSM-5 using density functional theory. On these sites the first N₂O dissociation barrier with respect to the gas phase is calculated to be 20.5 to 22.4 kcal/mol. The second N₂O dissociation barrier is with respect to the gas phase greater than 36 kcal/mol. As a result, the catalytic cycle of the N₂O dissociation on Fe-nitrite /-nitrate and Z[FeOH]⁺ sites requires a reducing agent. Nitric oxide can activate poisoned Z[Fe(OH)₂]⁺ sites by forming Z[FeOH]⁺ species. Active Z[FeOH]⁺ sites are formed much faster and to a larger amount than active Z[FeO]⁺ species at low temperatures, explaining the promotional effect of nitric oxide on the N₂O decomposition rate. Nitric oxide increases the N₂O decomposition rate at a temperature of 600 K by a factor of up to 93. Fe-nitrite and Fe-nitrate species play no significant role in the N₂O decomposition on Fe-ZSM-5 under reaction conditions. At elevated temperatures, water desorbs from Z[Fe(OH)₂]⁺ sites, Z[FeO]⁺ and Z[FeO₂]⁺ species are formed and Z[FeOH]⁺ sites are displaced. A reducing agent has no effect on the N₂O decomposition rate on Z[FeO]⁺ sites. The experimentally observed maximum in the nitrogen dioxide rate versus temperature originates from a change in active single iron site responsible for N₂O dissociation with increasing temperature. At low temperatures the catalytic N₂O dissociation cycle occurs on Z[FeOH]⁺ sites and involves adsorption of nitric oxide and desorption of nitrogen dioxide. With increasing temperature the active single iron site responsible for N₂O dissociation shifts to Z[FeO]⁺ and Z[FeO₂]⁺ species. The catalytic cycle of the N₂O dissociation on Z[FeO]⁺ sites does not involve NO₂ production, resulting in a decrease of NO₂ partial pressure with temperature. Consistent with experimental observations, the reaction mechanism proposed, predicts a N₂O decomposition rate that is first order in N₂O partial pressure in the presence and absence of nitric oxide.

To conclude, it is shown that the reaction mechanism, illustrated in Figures 6.1 and 7.15, together with rate parameters calculated from first principles on single iron sites is able to consistently describe the experimentally observed catalytic behavior in N₂O and

NO-assisted N_2O decomposition over a wide temperature range. Neighboring iron sites as suggested by Pérez-Ramírez (2002c) and Kiwi-Minsker et al. (2005) are not necessary to explain experimental observations.

8 Summary

In this thesis, the nitrous oxide decomposition over iron zeolite catalysts was investigated on a molecular level using density functional theory. The results of this study have implications on the development of iron zeolite catalysts for nitrous oxide decomposition in industrial tail gas streams and therefore, have an effect on efforts to address global warming. During the process of this study, highly efficient algorithms for finding transition states on potential energy surfaces determined from quantum chemical calculations were developed. These algorithms significantly accelerate the calculation of chemical reaction rates and thus, represent a step in the direction of predicting catalyst activity and selectivity from first principles.

Calculating reaction rates from first principles usually requires the determination of the reactant minimum energy configuration and the highest energy configuration along the reaction path. For reactions on one spin potential energy surface, the highest energy configuration connecting reactant and product states is a first order saddle point. For reactions on two spin potential energy surfaces, a minimum energy crossing point is often the highest energy state along the reaction coordinate. While locating potential energy minima can routinely be done, finding transition states on potential energy surfaces determined from quantum chemical calculations can be extremely difficult, and continues to be one of the major challenges in chemical kinetics for large systems.

Three different types of algorithms for finding transition states in chemical reactions, the growing string method, the improved dimer method, and a multiplier penalty function algorithm, have been developed and programmed in this thesis that require only the evaluation of the system energy and force. These algorithms eliminate the need for the often very time consuming second derivative matrix calculations of the potential energy. As a result, these methods are especially suitable for high dimensional systems as well as quantum chemical program systems that have no efficient

parallelized routine for calculating the second derivative matrix of the potential energy but possess efficient parallelized routines for computing the system energy and gradient, such as the TURBOMOLE program system.

Locating first order saddle points on potential energy surfaces determined from quantum chemical calculations usually involves a two step procedure. First, an interpolation algorithm is applied to determine an approximate intrinsic reaction coordinate connecting reactant and product states and hence, provides a reasonable approximation to the first order saddle point. A version of the growing string method has been developed in this work. In the growing string method, no initial intrinsic reaction coordinate has to be assumed and only few calculations have to be performed on initial approximate intrinsic reaction coordinates that are far away from the true intrinsic reaction coordinate. After a reasonable estimation of a transition state and intrinsic reaction coordinate has been obtained, a local surface walking algorithm should be used to determine the first order saddle point. An improved dimer method has been developed for this purpose. The improved dimer method is much more robust and requires significantly fewer gradient calculations than the original dimer method when energies and forces are subject to numerical noise. This new algorithm was compared with the partitioned rational function optimization (P-RFO) method for finding first order saddle points after the use of an interpolation method. If the Hessian matrix is calculated in the P-RFO methods every 10th cycle, the improved dimer method is recommended for systems with more than 12 to 15 atoms in lieu of P-RFO methods. If efficient parallelized routines for energy and gradient calculations are available, but not for Hessian calculations, the improved dimer method is recommended for even smaller system sizes.

For calculating minimum energy crossing points on the seam of two potential energy surfaces, a simple constrained optimization algorithm based on Powell's (1969) multiplier penalty function algorithm, was programmed. This method was found to be efficient and reliable.

Additional goals of this thesis were to determine the reaction mechanism of the nitrous oxide decomposition over iron zeolites, identify the rate limiting step and catalytically active sites, and explain apparently contradictory experimental observations. In order to accomplish this, the role of water vapor and nitric oxide on the nitrous oxide decomposition over iron zeolites had to be elucidated.

To identify the active site in iron zeolite catalysts and to study the effects of traces of water vapor on experimental observations of the N_2O decomposition in the absence of nitric oxide, the energetics and kinetics of the nitrous oxide decomposition were analyzed on hydrated and dehydrated mononuclear iron sites in Fe-ZSM-5. In total, 63 elementary reactions were investigated. Isolated iron cations bound to a single oxygen atom (viz., $\text{Z}[\text{FeO}]^+$) have been identified as the active sites for N_2O decomposition under reaction conditions. The presence of H_2O in the feed gas inhibits the rate of N_2O decomposition by deactivating active sites required for this process. Site deactivation occurs via the process $\text{Z}[\text{FeO}]^+ + \text{H}_2\text{O} \rightleftharpoons \text{Z}[\text{Fe}(\text{OH})_2]^+$, which is reversible, and consequently, strongly temperature dependent. The presence of low concentrations of water vapor in the feed stream (ppb to ppm levels) significantly affects the measured values for the apparent activation energy and preexponential factor, explaining the large spread in values reported in the literature, as well as the appearance of an apparent compensation effect.

To demonstrate that single iron sites represent the main active site in iron zeolites and to identify the rate limiting step in the nitrous oxide decomposition, transient and steady state macroscopic reactor simulations have been performed from first principles and compared with experimental data. Taking into account the effects of low concentrations of water vapor, simulations could reproduce temperature-programmed reaction, transient-response, and temperature-programmed desorption (TPD) experiments. The overall rate of N_2O decomposition was found to be first order in N_2O partial pressure and zero order in O_2 partial pressure. The desorption of O_2 observed at ~ 900 K in TPD experiments conducted after the use of Fe-ZSM-5 for N_2O decomposition could be attributed to the process $\text{Z}[\text{FeO}_2]^+ \rightleftharpoons \text{Z}[\text{Fe}]^+ + \text{O}_2$; however, this process is not

kinetically relevant during steady-state decomposition. An O₂-TPD peak at around 610 K, reported by several authors, was the only experimental observation that could not be simulated on single iron sites; instead, it was shown that this O₂-TPD peak should result from a minority iron species. Several authors have suggested that oxygen desorption is rate-limiting. However, this thesis has been shown that N₂O dissociation is the slowest step in the nitrous oxide decomposition on mononuclear iron sites under steady state conditions. A slow oxygen desorption step contradicts the experimental findings of a first order N₂O decomposition rate. A rate limiting N₂O dissociation step is consistent with the observed order of the N₂O decomposition.

Finally, the peculiar behavior of iron zeolites showing an enhanced activity for N₂O decomposition in the presence of nitric oxide at low temperatures was investigated on a molecular level using density functional theory. In total, 92 elementary reactions have been investigated and a novel explanation of the promotional effect of nitric oxide on the nitrous oxide decomposition could be given that is consistent with quantum chemical calculations and experimental findings. Both iron-nitrite and iron-nitrate species have been proposed in the literature as active sites in NO-assisted N₂O decomposition, but were found to play only a negligible role under reaction conditions in this work. Instead, nitric oxide was shown to activate poisoned Z[Fe(OH)₂]⁺ sites by forming active Z[FeOH]⁺ species. Z[FeOH]⁺ sites are formed much faster and to a larger amount than active Z[FeO]⁺ sites at low temperatures, explaining the promotional effect of nitric oxide on the N₂O decomposition rate. The catalytic N₂O dissociation cycle on Z[FeOH]⁺ sites involves adsorption of nitric oxide and desorption of nitrogen dioxide. With increasing temperature, the active single iron site responsible for N₂O dissociation shifts to Z[FeO]⁺ and Z[FeO₂]⁺ species and Z[FeOH]⁺ sites are displaced. A reducing agent like nitric oxide has no effect on the N₂O decomposition rate on Z[FeO]⁺ sites. Consistent with experimental observations, the reaction mechanism determined from first principles predicts a NO-assisted N₂O decomposition rate that is first order in N₂O partial pressure. The presence of neighboring iron sites, as proposed by several authors, appear to be unnecessary in explaining experimental observations.

List of acronyms

AO	atomic orbital
B3LYP	Becke's 3-parameter hybrid functional
B88	Becke's gradient correction to the exchange functional
BB1K	specific hybrid functional
BFGS	Broyden-Fletcher-Goldfarb-Shanno (minimization)
BO	Born-Oppenheimer
BSSE	basis set superposition error
CASSCF-MCQDPT2	multi-reference method
CC	coupled-cluster
CG	conjugate gradient
CGTO	contracted Gaussian type orbital
CI	configuration-interaction
CP	counterpoise method
def-SV(P)	split valence basis set with polarization functions
DFT	density functional theory
ENO	essentially non-oscillatory
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
Fe-ZSM-5	specific zeolite with iron inserted
GGA	generalized gradient approximation
GTO	Gaussian type orbital
GWP	global warming potential
HF	Hartree-Fock
HFC	hydrofluorocarbon
HK	Hohenberg-Kohn
IRC	intrinsic reaction coordinate
KS	Kohn-Sham
LCAO-MO	linear combinations of atomic orbitals – molecular orbitals
LDA	local density approximation

LSDA	local spin density approximation
LYP	correlation functional of Lee, Yang and Parr
m3, m5	specific numerical integration grid
MECP	minimum energy crossing point
MEP	minimum energy path
MM	molecular mechanics
MMO	methane monooxygenase
MWC	mass-weighted coordinates
NEB	Nudged elastic band
NR	Newton-Raphson
NSCR	non-selective catalytic reduction
O3LYP	specific optimized hybrid functional
OPTX	specific optimized exchange functional
OLYP	specific optimized exchange correlation functional
P-RFO	partitioned rational function optimization
PES	potential energy surface
PFC	perfluorocarbon
PW91	Perdew-Wang gradient correction to the correlation functional
QM	quantum mechanics
QZVP	split-valence quadruple zeta basis with polarization functions
RFO	rational function optimization
RI-BP	BP exchange-correlation functional applied together with the resolution of identity approach
SCF	self-consistent mean-field theory
SCR	selective catalytic reduction
SD	steepest descent
SR1	symmetric rang-one updating scheme
STO	Slater type orbital
SV	split valence basis set
T12, T5	site in zeolite or number of tetrahedral atoms in cluster model
TPD	temperature-programmed desorption
TPR	temperature-programmed reaction
TST	transition state theory
TZ	triple zeta basis

TZVP	split-valence triple zeta basis with polarization functions
UKS	unrestricted Kohn-Sham
ZSM-5	specific zeolite

List of symbols

A	preexponential factor
C	curvature
E	energy
F	Helmoltz free energy
F_{HK}	Hohenberg-Kohn functional
f	Fock operator, function, or fraction of single iron sites
f_{KS}	Kohn-Sham operator
G	Gibbs free energy
g	coefficient taking deviations from equilibrium distributions into account or electronic degeneracy
H	Hamiltonian or enthalpy
I	moment of inertia
K	equilibrium constant
k	reaction rate constant
M	mass of nuclei or multiplicity
m	mass of electron
N	number of nuclei
N_{Fe}	number of iron atoms in the system
n	number of electrons or number of moles of gas species
P	probability or pressure
Q	partition function of a system
q	partition function of a single molecule
S	spin or entropy
s	normalized arc length
T	kinetic energy or temperature
t	time
u	velocity
V	potential energy or volume
x	Cartesian coordinate
y	Cartesian coordinate

Z	atomic number
z	Cartesian coordinate

Vectors

$\mathbf{f}$	force
$\mathbf{G}$	search direction
$\mathbf{N}$	unit vector in dimer algorithm
$\mathbf{R}$	nuclei coordinates
$\mathbf{r}$	electron coordinates
$\mathbf{t}$	normalized tangent vector
$\mathbf{u}$	eigenvector
$\mathbf{x}$	Cartesian coordinate vector
Θ	unit vector in dimer algorithm

Matrices

$\mathbf{C}$	square matrix of molecular orbital coefficients
$\mathbf{F}$	Fock matrix
$\mathbf{H}'$	Hamiltonian in adiabatic representation
$\mathbf{H}$	Hamiltonian in diabatic representation or second derivative matrix of potential energy
$\mathbf{M}$	diagonal matrix of atomic masses
$\mathbf{S}$	overlap matrix
ϵ	diagonal matrix of orbital energies

Greek letters

α	spin state
β	spin state
γ	generalized transmission coefficient or shift parameter
Γ	dynamical recrossing coefficient
ϵ	orbital energy
Θ	fraction of a specific single iron site
κ	transmission coefficient for spin inversion or tunneling
λ	eigenvalue of Hessian matrix or Lagrange multiplier
μ	penalty function parameter

v	mass-weighted velocity or vibrational frequency
ρ	electron density or parameterization density
σ	spin of electron, symmetry index, or parameterization variable
τ	residence time
v^{eff}	effective potential
Φ_e	normalized electronic wave function
ϕ	basis function or Kohn-Sham orbital
φ	path or rotation angle
χ	spin orbital
Ψ	wave function

Indices

ads	adsorption
C	correlation
des	desorption
el	electron
equil	equilibrium
high	high spin
low	low spin
nucl	nuclei
rot	rotation
S	spin
SO	spin-orbit
trans	translation
vib	vibration
X	exchange
XC	exchange-correlation

Physical constants

c	speed of light
e	charge of an electron
ϵ_0	vacuum permittivity
h	Planck's constant

$\hbar$	Planck's constant divided by 2π
k_B	Boltzmann's constant
R	gas constant

Literature cited

AEA Technology Environment (1998). *Options to reduce nitrous oxide emissions*. AEAT-4180: Issue 3.

Ahlrichs, R., Bär, M., Häser, M., Horn, H., Kölmel, C. (1989). Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* **162**, 165.

Ahlrichs, R., v. Armin, M. (1995). TURBOMOLE, parallel implementation of SCF, density functional, and chemical shift modules. In: *Methods and Techniques in Computational Chemistry: METECC-95*. Clementi, E., Corongiu, G., Eds.; STEF: Calgari.

Alcami, M, Mo, O., Yanez, M., Cooper, I.L. (2000). The performance of density-functional theory in challenging cases: Halogen oxides. *J. Chem. Phys.* **112**, 6131.

Althorpe, S.C., Clary, D.C. (2003). Quantum scattering calculations on chemical reactions. *Annu. Rev. Phys. Chem.* **54**, 493.

Anderson, J. (1995). Predicting Rare Events in Molecular Dynamics. *Adv. Chem. Phys.* **91**, 381.

Baerlocher, C., Meier, W.M., Olson, D.H. (2001). *Atlas of zeolite framework types*. 5th revised Edition, Elsevier, Amsterdam.

Baker, J. (1986). An algorithm for the location of transition states. *J. Comput. Chem.* **7**, 385.

Baker, J., Chan, F. (1996). The location of transition states: A comparison of Cartesian, Z-matrix, and natural internal coordinates. *J. Comput. Chem.* **17**, 888.

Baker, J., Kessi, A., Delley, B. (1996). The generation and use of delocalized internal coordinates in geometry optimization. *J. Chem. Phys.* **105**, 192.

Baker, J., Pulay, P. (2003). Assessment of the OLYP and O3LYP density functionals for first-row transition metals. *J. Comput. Chem.* **24**, 1184.

Banerjee, A., Adams, N., Simons, J., Shepard, R. (1985). Search for stationary points on surfaces. *J. Phys. Chem.* **89**, 52.

Bates, S.P., van Santen, R.A. (1998). The molecular basis of zeolite catalysis: A review of theoretical simulations. *Adv. Catal.* **42**, 1.

Battiston, A.A., Bitter, J.H., Koningsberger, D.C. (2000). XAFS characterization of the binuclear iron complex in overexchanged Fe/ZSM5 – structure and reactivity. *Catal. Lett.* **66**, 75.

Battiston, A.A., Bitter, J.H., de Groot, F.M.F., Overweg, A.R., Stephan, O., van Bokhoven, J.A., Kooyman, P.J., van der Spek, C., Vankó, G., Koningsberger, D.C. (2003). Evolution of Fe species during the synthesis of over-exchanged Fe/ZSM5 obtained by chemical vapor deposition of FeCl₃. *J. Catal.* **213**, 251.

Battiston, A.A., Bitter, J.H., Heijboer, W.M., de Groot, F.M.F., Koningsberger, D.C. (2003b). Reactivity of Fe-binuclear complexes in over-exchanged Fe/ZSM5, studied by in situ XAFS spectroscopy – Part 1: Heat treatment in He and O₂. *J. Catal.* **215**, 279.

Battiston, A.A., Bitter, J.H., Koningsberger, D.C. (2003c). Reactivity of binuclear Fe complexes in over-exchanged Fe/ZSM5, studied by in situ XAFS spectroscopy – 2. Selective catalytic reduction of NO with isobutene. *J. Catal.* **218**, 163.

Bauschlicher, C.W., Hudgins, D.M., Allamandola, L.J. (1999). The infrared spectra of polycyclic aromatic hydrocarbons containing a five-membered ring: Symmetry breaking and the B3LYP functional. *Theor. Chem. Acc.* **103**, 154.

Bearpark, M.J., Robb, M.A., Schlegel, H.B. (1999). A direct method for the location of the lowest energy point on a potential surface crossing. *Chem. Phys. Lett.* **223**, 269.

Becke, A.D. (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **38**, 3098.

Behler, J. (2004). *Dissociation of oxygen molecules on the Al(111) surface*. Ph.D. thesis. Technische Universität Berlin, Berlin.

Bell, A.T. (2004). Challenges for the application of quantum chemical calculations to problems in catalysis. *Mol. Phys.* **102**, 319.

Bell, S., Crighton, J.S. (1984). Locating transition states. *J. Chem. Phys.* **80**, 2464.

Berlier, G., Spoto, G., Bordiga, S., Ricchiardi, G., Fisicaro, P., Zecchina, A., Rossetti, I., Selli, E., Forni, L., Giamello, E., Lamberti, C. (2002). Evolution of extraframework iron species in Fe silicalite. 1. Effect of Fe content, activation temperature, and interaction with redox agents. *J. Catal.* **208**, 64.

Berlier, G., Zecchina, A., Spoto, G., Ricchiardi, G., Bordiga, S., Lamberti, C. (2003). The role of Al in the structure and reactivity of iron centers in Fe-ZSM-5-based catalysts: a statistically based infrared study. *J. Catal.* **215**, 264.

Berlier, G., Ricchiardi, G., Bordiga, S., Zecchina, A. (2005). Catalytic activity of Fe ions in iron-based crystalline and amorphous systems: role of dispersion, coordinative unsaturation and Al content. *J. Catal.* **229**, 127.

Bickelhaupt, F.M., Baerends, E.J. (2000). Kohn-Sham density functional theory: Predicting and understanding chemistry. *Rev. Comput. Chem.* **15**, 1.

Bofill, J.M. (1994). Updated Hessian matrix and the restricted step method for locating transition structures. *J. Comput. Chem.* **15**, 1.

Bolhuis, P.G., Chandler, D., Dellago, C., Geissler, P.L. (2002). Transition path sampling: Throwing ropes over rough mountain passes, in the dark. *Annu. Rev. Phys. Chem.* **53**, 291.

Bond, G.C., Keane, M.A., Kral, H., Lercher, J.A. (2000). Compensation phenomena in heterogeneous catalysis: General principles and a possible explanation. *Catal. Rev.-Sci. Eng.* **42**, 323.

Born, M., Oppenheimer, R. (1927). Zur Quantentheorie der Molekeln. *Ann. Phys.* **84**, 457.

Boutarbouch, M.N.D., Cortés, J.M.G., El Begrani, M.S., de Lecea, C.S.M., Pérez-Ramírez, J. (2004). Catalytic conversion of N₂O over Fe-ZSM-5 zeolite in the presence of CO and NO. *Appl. Catal. B* **54**, 115.

Boys, S.F., Bernardi, F. (1970). The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol. Phys.* **19**, 553.

Bulushev, D.A., Kiwi-Minsker, L., Renken, A. (2004). Dynamics of N₂O decomposition over HZSM-5 with low Fe content. *J. Catal.* **222**, 389.

Butler, L.J. (1998). Chemical reaction dynamics beyond the Born-Oppenheimer approximation. *Annu. Rev. Phys. Chem.* **49**, 125.

Centi, G., Galli, A., Montanari, B., Perathoner, S., Vaccaria, A. (1997). Catalytic decomposition of N₂O over noble and transition metal containing oxides and zeolites. Role of some variables on reactivity. *Catal. Today* **35**, 113.

Centi, G., Perathoner, S., Vanazza, F. (1999). Catalytic control of non-CO₂ greenhouse gases. *CHEMTECH* **29**, 48.

Centi, G., Perathoner, S., Vanazza, F., Marella, M., Tomaselli, M., Mantegazza, M. (2000). Novel catalysts and catalytic technologies for N₂O removal from industrial emissions containing O₂, H₂O and SO₂. *Adv. Env. Res.* **4**, 325.

Ceperley, D.M., Alder, B.J. (1980). Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.* **45**, 566.

Cerjan, C.J., Miller, W.H. (1981). On finding transition states. *J. Chem. Phys.* **75**, 2800.

Chandler, D. (1987). *Introduction of modern statistical mechanics*, Oxford University Press, New York.

Chang, Y.-F., McCarty, J.G., Zhang, Y.L. (1995). N₂O decomposition over [Fe]-ZSM-5 and Fe-HZSM-5 zeolites. *Catal. Lett.* **34**, 163.

Che, M., Tench, A.J. (1983). Characterization and reactivity of molecular oxygen species on oxide surfaces. *Adv. Catal.* **32**, 1.

Chen, H.-Y., Voskoboinikov, T., Sachtler, W.M.H. (1998). Reduction of NO_x over Fe/ZSM-5 catalysts: Adsorption complexes and their reactivity toward hydrocarbons. *J. Catal.* **180**, 171.

- Chen, H.-Y., El-Malki, El-M., Wang, X., van Santen, R.A., Sachtler, W.M.H. (2000). Identification of active sites and adsorption complexes in Fe/MFI catalysts for NO_x reduction. *J. Mol. Catal. A* **162**, 159.
- Choi, S.H., Wood, B.R., Ryder, J.A., Bell, A.T. (2003). X-ray absorption fine structure characterization of the local structure of Fe in Fe-ZSM-5. *J. Phys. Chem. B* **107**, 11843.
- Choi, S.H., Wood, B.R., Bell, A.T., Janicke, M.T., Ott, K.C. (2004). X-ray absorption fine structure analysis of the local environment of Fe in Fe/Al-MFI. *J. Phys. Chem. B* **108**, 8970.
- Chorkendorff, I., Niemantsverdriet, J.W. (2003). *Concepts of modern catalysis and kinetics*, Wiley-VCH, Weinheim.
- Cohen-Tannoudji, C., Diu, B., Laloë, F. (1977). *Quantum mechanics*, Vol. 1 and 2, John Wiley & Sons, New York.
- Crutzen, P.J. (1971). Ozone production rates in an oxygen-hydrogen-nitrogen oxide atmosphere. *J. Geophys. Res.* **76**, 7311.
- Crutzen, P.J., Howard, C.J. (1978). The effect of the HO₂ + NO reaction rate constant on one-dimensional model calculations of stratospheric ozone perturbations. *Pure Appl. Geophys.* **116**, 487.
- Danovich, D., Shaik, S. (1997). Spin-orbit coupling in the oxidative activation of H-H by FeO⁺. Selection rules and reactivity effects. *J. Am. Chem. Soc.* **119**, 1773.
- Darling, G.R., Holloway, S. (1995). The dissociation of diatomic molecules at surfaces. *Rep. Prog. Phys.* **58**, 1595.
- Dellago, C., Bolhuis, P.G., Geissler, P.L. (2002). Transition path sampling. *Adv. Chem. Phys.* **123**, 1.
- Doménech, A., Pérez-Ramírez, J., Ribera, A., Kapteijn, F., Mul, G., Moulijn, J.A. (2002). Characterization of iron species in ex-framework FeZSM-5 by electrochemical methods. *Catal. Lett.* **78**, 303.

Doménech, A., Pérez-Ramírez, J., Ribera, A., Mul, G., Kapteijn, F., Arends, I.W.C.E. (2002b). Electrochemical characterization of iron sites in ex-framework FeZSM-5. *J. Electroanal. Chem.* **519**, 72.

Dreizler, R.M., Gross, E.K.U. (1990). *Density functional theory*. Springer-Verlag, Berlin.

Drukker, K. (1999). Basics of surface hopping in mixed quantum / classical simulations. *J. Comput. Phys.* **153**, 225.

Dubkov, K.A., Ovanesyan, N.S., Shteinman, A.A., Starokon, E.V., Panov, G.I. (2002). Evolution of iron states and formation of alpha-sites upon activation of FeZSM-5 zeolites. *J. Catal.* **207**, 341.

E, W., Ren, W., Vanden-Eijnden, E. (2002). String method for the study of rare events. *Phys. Rev. B* **66**, 052301.

Eichkorn, K., Treutler, O., Öhm, H., Häser, M., Ahlrichs, R. (1995). Auxiliary basis sets to approximate coulomb potentials. *Chem. Phys. Lett.* **242**, 652.

Eichkorn, K., Weigend, F., Treutler, O., Ahlrichs, R. (1997). Auxiliary basis sets for main row atoms and transition metals and their use to approximate coulomb potentials. *Theor. Chem. Acc.* **97**, 119.

El-Malki, E.M., van Santen, R.A., Sachtler, W.M.H. (2000). Isothermal oscillations during N₂O decomposition over Fe/ZSM-5: Effect of H₂O vapor. *Microporous Mater.* **35-36**, 235.

El-Malki, E.M., van Santen, R.A., Sachtler, W.M.H. (2000b). Active sites in Fe/MFI catalysts for NO_x reduction and oscillating N₂O decomposition. *J. Catal.* **196**, 212.

Elber, R., Karplus, M. (1987). A method for determining reaction paths in large molecules: Application to myoglobin. *Chem. Phys. Lett.* **139**, 375.

Evans, M.G., Polanyi, M. (1935). Some applications of the transition state method to the calculation of reaction velocities, especially in solution. *Trans. Faraday Soc.* **31**, 875.

Eyring, H. (1935). The activated complex in chemical reactions. *J. Chem. Phys.* **3**, 107.

Eyring, H., Stern, A.E. (1939). The application of the theory of absolute reaction rates of proteins. *Chem. Rev.* **24**, 253.

Feng, X., Hall, W.K. (1997). Limitations on the formation of oxygen-bridged divalent cations in FeZSM-5. *Catal. Lett.* **46**, 11.

Ferretti, A.M., Oliva, C., Forni, L., Berlier, G., Zecchina, A., Lamberti, C. (2002). Evolution of extraframework iron species in Fe silicalite. 2. Effect of steaming. *J. Catal.* **208**, 83.

Fischer, S., Karplus, M. (1992). Conjugate peak refinement: an algorithm for finding reaction paths and accurate transition states in systems with many degrees of freedom. *Chem. Phys. Lett.* **194**, 252.

Fletcher, R. (1987). *Practical methods of optimization*. 2nd Edition John Wiley & Sons, New York.

Fock, V. (1930). Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Z. Physik* **61**, 126.

Fu, C.M., Korchak, V.N., Hall, W.K. (1981). Decomposition of nitrous oxide on FeY zeolite. *J. Catal.* **68**, 166.

Gao, Z.-X., Kim, H.-S., Sun, Q., Stair, P.C., Sachtler W.M.H. (2001). UV-Raman characterization of iron peroxo adsorbates on Fe/MFI catalyst with high activity for NO_x reduction. *J. Phys. Chem. B* **105**, 6186.

Geerlings, P., De Proft, F., Langenaeker, W. (2003). Conceptual density functional theory. *Chem. Rev.* **103**, 1793.

Gonzalez, C., Schlegel, H.B. (1991). Improved algorithms for reaction path following: Higher-order implicit algorithms. *J. Chem. Phys.*, **95**, 5853.

Gonzalez, M., Valero, R., Sayos, R. (2001). Ab initio and DFT study of the ground ³A' potential energy surface for the O(³P) + N₂O → 2NO reaction. *Chem. Phys. Lett.* **343**, 119.

Goodman, B.R., Hass, K.C., Schneider, W.F., Adams, J.B. (2000). Statistical analysis of Al distributions and metal ion pairing probabilities in zeolites. *Catal. Lett.* **68**, 85.

Gritsenko, O.V., Baerends, E.J. (1997). Electron correlation effects on the shape of the Kohn-Sham molecular orbitals. *Theor. Chem. Acc.* **96**, 44.

Grubert, G., Hudson, M.J., Joyner, R.W., Stockenhuber, M. (2000). The room temperature, stoichiometric conversion of N₂O to adsorbed NO by Fe-MCM-41 and Fe-ZSM-5. *J. Catal.* **196**, 126.

Hafner, J. (2000). Atomic-scale computational materials science. *Acta Materialia* **48**, 71.

Halgren, T.A., Lipscomb, W.N. (1977). The synchronous-transit method for determining reaction pathways and locating molecular transition states. *Chem. Phys. Lett.* **49**, 225.

Halls, M.D., Velkovski, J., Schlegel, H.B. (2001). Harmonic frequency scaling factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ electric property basis set. *Theor. Chem. Acc.* **105**, 413.

Hammer, B., Norskov, J.K. (2000). Theoretical surface science and catalysis – Calculations and concepts. *Adv. in Catal.* **45**, 71.

Han, O.H., Kim, C.-S., Hong, S.B. (2002). Direct evidence for the nonrandom nature of Al substitution in zeolite ZSM-5: An investigation by ²⁷Al MAS and MQ MAS NMR. *Angew. Chem. Int. Ed.* **41**, 469.

Handy, N.C., Cohen, A.J. (2001). Left-right correlation energy. *Mol. Phys.* **99**, 403.

Hänggi, P., Talkner, P., Borkovec, M. (1990). Reaction-rate theory: fifty years after Kramers. *Rev. Mod. Phys.* **62**, 251.

Hartree, D.R. (1928). The wave mechanics of an atom with a non-Coulomb central field. Part I. Theory and methods. *Proc. Camb. Philos. Soc.* **24**, 89.

Hartree, D.R. (1928). The wave mechanics of an atom with a non-Coulomb central field. Part II. Theory and methods. *Proc. Camb. Philos. Soc.* **24**, 111.

Hehre, W.J., Radom, L., Schleyer, P.v.R., Pople, J.A. (1986). *Ab initio molecular orbital theory*. John Wiley & Sons, New York.

Helgaker, T., Jorgensen, P., Olsen, J. (2002). *Molecular electronic structure theory*. John Wiley & Sons, New York.

Henkelman, G., Jónsson, H. (1999). A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. *J. Chem. Phys.* **111**, 7010.

Henkelman, G., Jónsson, H. (2000). Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **113**, 9978.

Hensen, E.J.M., Zhu, Q., Hendrix, M.M.R.M., Overweg, A.R., Kooyman, P.J., Sychev, M.V., van Santen, R.A. (2004). Effect of high-temperature treatment on Fe/ZSM-5 prepared by chemical vapor deposition of FeCl₃. I. Physicochemical characterization. *J. Catal.* **221**, 560.

Hensen, E.J.M., Zhu, Q., van Santen, R.A. (2003). Extraframework Fe-Al-O species occluded in MFI zeolite as the active species in the oxidation of benzene to phenol with nitrous oxide. *J. Catal.* **220**, 260.

Heyden, A., Keil, F.J. (2003). Analyzing the performance of the dimer method for finding transition states on the high dimensional potential energy surface of the nitrous oxide dissociation on a Fe-ZSM-5 cluster. *AIChE Annual meeting*, paper 566h, San Francisco.

Heyden, A., Bell, A.T., Keil, F.J. (2005). Efficient methods for finding transition states in chemical reactions: Comparison of improved dimer method and partitioned rational function optimization method. *J. Chem. Phys.* accepted.

Heyden, A., Peters, B., Bell, A.T., Keil, F.J. (2005b). Comprehensive DFT study of nitrous oxide decomposition over Fe-ZSM-5. *J. Phys. Chem. B.* **109**, 1857.

Heyden, A., Bell, A.T., Keil, F.J. (2005c). Kinetic modeling of nitrous oxide decomposition on Fe-ZSM-5 based on parameters obtained from first-principles calculations. *J. Catal.* **233**, 26.

Hirst, D.M. (1985). *Potential energy surfaces: Molecular structure and reaction dynamics*, Taylor and Francis, London.

Hohenberg, P., Kohn, W. (1964). Inhomogeneous electron gas. *Phys. Rev.* **136**, B864.

Jasper, A.W., Kendrick, B.K., Mead, C.A., Truhlar, D.G. (2004). Non-Born-Oppenheimer chemistry: Potential surfaces, couplings, and dynamics, In: *Modern trends in chemical reaction dynamics, Part I*, ed. X. Yang and K. Liu, World Scientific, Singapore, 329.

Jensen, F. (1992). Locating minima on seams of intersecting potential energy surfaces. An application to transition structure modeling. *J. Am. Chem. Soc.* **114**, 1596.

Jensen, F. (1999). *Introduction to computational chemistry*. John Wiley & Sons, New York.

Jia, J., Sun, Q., Wen, B., Chen, L.X., Sachtler, W.M.H. (2002). Identification of highly active iron sites in N₂O-activated Fe/MFI. *Catal. Lett.* **82**, 7.

Joyner, R., Stockenhuber, M. (1999). Preparation, characterization, and performance of Fe-ZSM-5 catalysts. *J. Phys. Chem. B* **103**, 5963.

Kachurovskaya, N.A., Zhidomirov, G.M., Hensen, E.J.M., van Santen, R.A. (2003). Cluster model DFT study of the intermediates of benzene to phenol oxidation by N₂O on FeZSM-5 zeolites. *Catal. Lett.* **86**, 25.

Kapteijn, F., Rodriguez-Mirasol, J., Moulijn, J.A. (1996). Heterogeneous catalytic decomposition of nitrous oxide. *Appl. Catal. B* **9**, 25.

Kapteijn, F., Marban, G., Rodriguez-Mirasol, J., Moulijn, J.A. (1997). Kinetic analysis of the decomposition of nitrous oxide over ZSM-5 catalysts. *J. Catal.* **167**, 256.

Keil, F.J. (2004). Molecular modeling in chemical engineering. *J. of the Univ. of Chem. Techn. and Metallurgy* **39**, 245.

Keil, F.J. (2004b). Catalytic reactions and reactors. *Chem. Eng. Sci.* **59**, 5473.

Kestner, N.R., Combariza, J.E. (1999). Basis set superposition errors: theory and practice, In *Reviews in Computational Chemistry*, Vol. 13, Lipkowitz, K.B., Boyd, D.B., Wiley-VCH, New York.

Kiwi-Minsker, L., Bulushev, D.A., Renken, A. (2003). Active sites in HZSM-5 with low Fe content for the formation of surface oxygen by decomposing N₂O: Is every deposited oxygen active? *J. Catal.* **219**, 273.

Kiwi-Minsker, L., Bulushev, D.A., Renken, A. (2004). Transient response method for characterization of active sites in HZSM-5 with low content of iron during N₂O decomposition. *Catal. Today* **91**, 165.

Kiwi-Minsker, L., Bulushev, D.A., Renken, A. (2005). Low temperature decomposition of nitrous oxide over Fe/ZSM-5: Modelling of the dynamic behaviour. *Catal. Today* accepted.

Knowles, P.J.; Schütz, M.; Werner, H.J. (2000). Ab initio methods for electron correlation in molecules, In *Modern method and algorithms of Quantum Chemistry*, Vol. 1, publication series of the John von Neumann Institut for Computing (NIC).

Koch, W., Holthausen, M.C. (2001). *A chemist's guide to density functional theory*, 2nd Edition, Wiley-VCH, Weinheim.

Kögel, M. (2001). *Katalytische Entfernung von N₂O aus Salpetersäureabgasen mit Hilfe zeolithischer Katalysatoren*. Ph.D. thesis, Shaker Verlag, Aachen.

Kögel, M., Abu-Zied, B.M., Schwefer, M., Turek, T. (2001). The effect of NO_x on the catalytic decomposition of nitrous oxide over Fe-MFI zeolites. *Catal. Comm.* **2**, 273.

Kohn, W., Sham, L.J. (1965). Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, A1133.

Kuchеров, A.V., Shelef, M. (2000). Quantitative determination of isolated Fe³⁺ cations in FeHZSM-5 catalysts by ESR. *J. Catal.* **195**, 106.

Laidler, K.J. (1987). *Chemical Kinetics*, 3rd Edition, Harper & Row, New York.

Landau, L. (1932). Zur Theorie der Energieübertragung II, *Physik. Zeits. Sowjetunion* **2**, 46.

Lee, C., Yang, W., Parr, R.G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785.

Leglise, J., Petunchi, J.O., Hall, W.K. (1984). N₂O decomposition over iron-exchanged mordenite. *J. Catal.* **86**, 392.

- Levine, I.N. (2000). *Quantum chemistry*, 5th Edition, Prentice Hall, New York.
- Lewis, D.W., Catlow, C.R.A., Sankar, G., Carr, S.W. (1995). Structure of iron-substituted ZSM-5. *J. Phys. Chem.* **99**, 2377.
- Li, Y., Armor, J.N. (1992). Catalytic decomposition of nitrous oxide on metal exchange zeolites. *Appl. Catal. B* **1**, L21.
- Lobree, L.J., Hwang, I.C., Reimer, J.A., Bell, A.T. (1999). Investigations of the state of Fe in H-ZSM-5. *J. Catal.* **186**, 242.
- Makri, N. (1999). Time-dependent quantum methods for large systems. *Annu. Rev. Phys. Chem.* **50**, 167.
- Malek, R., Mousseau, N. (2000). Dynamics of Lennard-Jones clusters: A characterization of the activation-relaxation technique. *Phys. Rev. E* **62**, 7723.
- Marturano, P., Drozdová, L., Kogelbauer, A., Prins, R. (2000). Fe/ZSM-5 prepared by sublimation of FeCl₃: The structure of the Fe species as determined by IR, Al-27 MAS NMR, and EXAFS spectroscopy. *J. Catal.* **192**, 236.
- Marturano, P., Drozdová, L., Pirngruber, G.D., Kogelbauer, A., Prins, R. (2001). The mechanism of formation of the Fe species in Fe/ZSM-5 prepared by CVD. *Phys. Chem. Chem. Phys.* **3**, 5585.
- Melian-Cabrera, Mentrut, C., Pieterse, J.A.Z., van den Brink, R.W., Mul, G., Kapteijn, F., Moulijn, J.A. (2005). Highly active and stable ion-exchanged Fe-Ferrierite catalyst for N₂O decomposition under nitric acid tail gas conditions. *Catal. Commun.* **6**, 301.
- McQuarrie, D.A. (1973). *Statistical Mechanics*. Harper Collins Publisher, New York.
- Mills, G., Jónsson, H. (1994). Quantum and thermal effects in H₂ dissociative adsorption: Evaluation of free energy barriers in multidimensional quantum systems. *Phys. Rev. Lett.*, **72**, 1124.
- Müller, K., Brown, L.D. (1979). Location of saddle points and minimum energy paths by a constrained simplex optimization procedure. *Theor. Chim. Acta* **53**, 75.

Mul, G., Pérez-Ramírez, J., Kapteijn, F., Moulijn, J.A. (2001). NO-assisted N₂O decomposition over ex-framework FeZSM-5: Mechanistic aspects. *Catal. Lett.* **77**, 7.

Murtagh, B.A., Sargent, R.W.H. (1970). Computational experience with quadratically convergent minimisation methods. *Comput. J.*, **13**, 185.

Nakamura, H. (1997). Theoretical studies of chemical dynamics: Overview of some fundamental mechanisms. *Annu. Rev. Phys. Chem.* **48**, 299.

Nichols, J., Taylor, H., Schmidt, P., Simons, J. (1990). Walking on potential energy surfaces. *J. Chem. Phys.*, **92**, 340.

Nikitin, E.E. (1999). Nonadiabatic transitions: What we learned from old masters and how much we owe them. *Annu. Rev. Phys. Chem.* **50**, 1.

Nobukawa, T., Tanaka, S., Ito, S., Tomishige, K., Kameoka, S., Kunimori, K. (2002). Isotopic study of N₂O decomposition on an ion-exchanged Fe-zeolite catalyst: Mechanism of O₂ formation. *Catal. Lett.* **83**, 5.

Nobukawa, T., Yoshida, M., Kameoka, S., Ito, S., Tomishige, K., Kunimori, K. (2004). Selective catalytic reduction of N₂O with CH₄ and N₂O decomposition over Fe-zeolite catalysts. *Studies in Surface Science and Catalysis* **154**, 2514.

Nobukawa, T., Yoshida, M., Okumura, K., Tomishige, K., Kunimori, K. (2005). Effect of reductants in N₂O reduction over Fe-MFI catalysts. *J. Catal.* **229**, 374.

Kongshaug, G., Hjørnevik, L., Fareid, E., Nirisen, Ø. (1990). *Method for the reduction of nitrogen oxide*. US Patent: 4,973,457. Assignee: Norsk Hydro.

Nováková, J., Lhotka, M., Tvarůžková, Z., Sobalík, Z. (2002). Decomposition of nitrous oxide over Fe-ferrierites. Effect of deposited oxygen on the framework oxygens studied by ¹⁸O isotopic exchange. *Catal. Lett.* **83**, 215.

Nováková, J., Schwarze, M., Tvarůžková, Z., Sobalík, Z. (2004). Decomposition of nitrous oxide over Fe-ferrierites. Effect of high-temperature pretreatment on the formation of deposited oxygen. *Catal. Lett.* **98**, 123.

Nocedal, J., Wright, S.J. (1999). *Numerical Optimization*. Springer-Verlag, New York.

Numerical Algorithms Group Fortran Library, Mark 19 (1999). NAG GmbH, Garching, Routine: E04FYF (fit), E04UNF (SQP).

Oi, J., Obuchi, A., Bamwenda, G.R., Ogata, A., Yagita, H., Kushiya, S., Mizuno, K. (1997). Decomposition of nitrous oxide over supported rhodium catalysts and dependency on feed gas composition. *Appl. Catal. B* **12**, 277.

Okuno, Y., Mashiko, S. (2005). Convenient expression of the rate constant for nonadiabatic transition. *Int. J. Quant. Chem.* **102**, 8.

Olsen, R.A., Kroes, G.J., Henkelman, G., Arnaldsson, A., Jónsson, H. (2004). Comparison of methods for finding saddle points without knowledge of the final states. *J. Chem. Phys.* **121**, 9776.

Olson, D.H., Kokotallo, G.T., Lawton, S.L., Meier, W.M. (1981). Crystal structure and structure-related properties of ZSM-5. *J. Phys. Chem.* **85**, 2238.

Overweg, A.R., Crajé, M.W.J., van der Kraan, A.M., Arends, I.W.C.E., Ribera, A., Sheldon, R.A. (2004). Remarkable N₂ affinity of a steam-activated FeZSM-5 catalyst: A Fe-57 Mössbauer study. *J. Catal.* **223**, 262.

Pabchanda, S., Pantu, P., Tantanak, D., Limtrakul, J. (2004). Structure and energetics of nitrous oxide and methane adsorption on the Fe-ZSM-5 zeolite: Oniom and density functional studies. In: *Studies in surface science and catalysis*, Vol. 154, Editor: van Steen, E., Callanan, L.H., Claeys, M., 1844.

Page, M., McIver, J.W. Jr. (1988). On evaluating the reaction path Hamiltonian. *J. Chem. Phys.* **88**, 922.

Panov, G.I., Sobolev, V.I., Kharitonov, A.S. (1990). The role of iron in N₂O decomposition on ZSM-5 zeolite and reactivity of the surface oxygen formed. *J. Mol. Catal.* **61**, 85.

Panov, G.I., Uriarte, A.K., Rodkin, M.A., Sobolev, V.I. (1998). Generation of active oxygen species on solid surfaces. Opportunity for novel oxidation technologies over zeolites. *Catal. Today* **41**, 365.

Payne, M.C., Teter, M.P., Allan, D.C., Arias, T.A., Joannopoulos, J.D. (1992). Iterative minimization techniques for ab-initio total energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* **64**, 1045.

Parr, R.G., Yang, W. (1989). *Density-Functional theory of atoms and molecules*. Oxford University Press, Oxford.

Perdew, J.P. (1986). Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **33**, 8822.

Perdew, J.P. (1991). Unified Theory of Exchange and Correlation Beyond the Local Density Approximation. In: *Electronic structure of Solids*. Ziesche, P., Eschrig, H., Eds.; Akademie Verlag; Berlin, 11.

Perdew, J.P., Wang, Y. (1992). Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **45**, 13244.

Perdew, J.P., Kurth, S. (2003). Density functionals for non-relativistic coulomb systems in the new century. In *LPN 620*, Fiolhais, C., Nogueira, F., Marques, M., Springer-Verlag Berlin Heidelberg.

Pérez-Ramírez, J., Kapteijn, F., Mul, G., Moulijn, J.A. (2001). Superior performance of ex-framework FeZSM-5 in direct N₂O decomposition in tail-gases from nitric acid plants. *Chem. Commun.*, **8**, 693.

Pérez-Ramírez, J. (2002). *Catalyzed N₂O activation. Promising (new) catalysts for abatement and utilization*. Ph.D. thesis. Technische Universiteit Delft, Delft.

Pérez-Ramírez, J., Mul, G., Kapteijn, F., Moulijn, J.A., Overweg, A.R., Doménech, A., Ribera, A., Arends, I.W.C.E. (2002). Physicochemical characterization of isomorphously substituted FeZSM-5 during activation. *J. Catal.* **207**, 113.

Pérez-Ramírez, J., Kapteijn, F., Mul, G., Moulijn, J.A. (2002b). Highly active SO₂-resistant ex-framework FeMFI catalysts for direct N₂O decomposition. *Appl. Catal. B* **35**, 227.

Pérez-Ramírez, J., Kapteijn, F., Mul, G., Moulijn, J.A. (2002c). NO-assisted N₂O decomposition over Fe-based catalysts: Effects of gas-phase composition and catalyst constitution. *J. Catal.* **208**, 211.

Pérez-Ramírez, J., Kapteijn, F., Mul, G., Xu, X., Moulijn, J.A. (2002d). Ex-framework FeZSM-5 for control of N₂O in tail-gases. *Catal. Today* **76**, 55.

Pérez-Ramírez, J., Kapteijn, F., Groen, J.C., Doménech, A., Mul, G., Moulijn, J.A. (2003). Steam-activated FeMFI zeolites. Evolution of iron species and activity in direct N₂O decomposition. *J. Catal.* **214**, 33.

Pérez-Ramírez, J., Kapteijn, F., Brückner, A. (2003b). Active site structure sensitivity in N₂O conversion over FeMFI zeolites. *J. Catal.* **218**, 234.

Pérez-Ramírez, J., Mul, G., Kapteijn, F., Moulijn, J.A. (2003c). Elucidation of the surprising role of NO in N₂O decomposition over Fe-ZSM-5. *Kinetics and Catalysis* **44**, 639

Pérez-Ramírez, J., Kapteijn, F. (2003). Effect of NO on the catalytic removal of N₂O over Fe-ZSM-5. Friend or foe. *Catal. Comm.* **4**, 333.

Pérez-Ramírez, J., Kumar, M.S., Brückner, A. (2004). Reduction of N₂O with CO over FeMFI zeolites: Influence of the preparation method on the iron species and catalytic behavior. *J. Catal.* **223**, 13.

Pérez-Ramírez, J. (2004). Active iron sites associated with the reaction mechanism of N₂O conversions over steam-activated FeMFI zeolites. *J. Catal.* **227**, 512.

Peters, B. (2004). *Reaction pathways and rates from electronic structure theory*. Ph.D. thesis, University of California, Berkeley.

Peters, B., Heyden, A., Bell, A.T., Chakraborty, A. (2004). A growing string method for determining transition states: Comparison to the nudged elastic band and string methods. *J. Chem. Phys.* **120**, 7877.

Pirngruber, G.D. (2003). The surface chemistry of N₂O decomposition on iron containing zeolites (I). *J. Catal.* **219**, 456.

Pirngruber, G.D., Luechinger, M., Roy, P.K., Cecchetto, A., Smirniotis, P. (2004). N₂O decomposition over iron-containing zeolites prepared by different methods: A comparison of the reaction mechanism. *J. Catal.* **224**, 429.

- Pirngruber, G.D., Roy, P.K. (2004). The mechanism of N_2O decomposition on Fe-ZSM-5: An isotope labeling study. *Catal. Lett.* **93**, 75.
- Platter, D.A. (1999). Interspin crossing and reactivity. *Angew. Chem. Int. Ed.* **38**, 82.
- Polak, E., Ribière, G. (1969). *Note sur la convergence de méthodes de directions conjuguées*. *Revue Française d'Informatique et de Recherche Opérationnelle* **16**, 35.
- Pople, J.A., Nesbet, R.K. (1954). Self-consistent orbitals for radicals. *J. Chem. Phys.* **22**, 571.
- Powell, M.J.D. (1969). A method for nonlinear constraints in minimization problems. In: *Optimization*; Fletcher, R., Ed., Academic Press: London.
- Powell, M.J.D. (1970). *Nonlinear programming*. Academic: New York.
- Preston, R.K., Tully, J.C. (1971). Effects of surface crossing in chemical reactions: the H_3^+ system. *J. Chem. Phys.* **54**, 4297.
- Pulay, P., Fogarasi, G. (1992). Geometry optimization in redundant internal coordinates. *J. Chem. Phys.* **96**, 2856.
- Quapp, W. (2004). Reaction pathways and projection operators: Application to string methods. *J. Comput. Chem.* **25**, 1277.
- Quapp, W. (2005). A growing string method for the reaction pathway defined by a Newton trajectory. *J. Chem. Phys.* **122**, 174106.
- Ren, W. (2002). *Numerical Methods for the Study of Energy Landscapes and Rare Events*. Ph.D. thesis, Department of Mathematics, New York University.
- Ren, W. (2003). Higher order string method for finding minimum energy paths. *Comm. Math. Sci.* **1**, 377.
- Rice, M.J., Chakraborty, A.K., Bell, A.T. (1999). Al next nearest neighbor, ring occupation, and proximity statistics in ZSM-5. *J. Catal.* **186**, 222.

Rice, M.J., Chakraborty, A.K., Bell, A.T. (2000). Site availability and competitive siting of divalent metal cations in ZSM-5. *J. Catal.* **194**, 278.

Rohde, H. (1990). A comparison of the contribution of various gases to the greenhouse effect. *Science* **248**, 1217.

Roothaan, C.C.J. (1951). New Developments in Molecular Orbital Theory. *Rev. Modern Phys.* **23**, 69.

Roy, P.K., Pirngruber, G.D. (2004). The surface chemistry of N₂O decomposition on iron-containing zeolites (II) – The effect of high-temperature pretreatments. *J. Catal.* **227**, 164.

Rump, S.M. (1980). *Kleine Fehlerschranken bei Matrixproblemen*. Ph.D. thesis, Department of Applied Mathematics, Universität Karlsruhe, Karlsruhe.

Rump, S.M. (1983). Solving algebraic problems with high accuracy. In: *A new approach to scientific computation*. Academic Press, New York, 51.

Ryder, J.A., Chakraborty, A.K., Bell, A.T. (2002). Density functional theory study of nitrous oxide decomposition over Fe- and Co-ZSM-5. *J. Phys. Chem. B* **106**, 7059.

Sakurai, J.J. (1994). *Modern quantum mechanics*. Addison-Wesley, New York.

Sang, C., Lund, C.R.F. (2000). Isothermal "light-off" during catalytic N₂O decomposition over Fe/ZSM-5. *Catal. Lett.* **70**, 165.

Sang, C., Lund, C.R.F. (2001). Possible role of nitrite/nitrate redox cycles in N₂O decomposition and light-off over Fe-ZSM-5. *Catal. Lett.* **73**, 73.

Sang, C., Kim, B.H., Lund, C.R.F. (2005). Effect of NO upon N₂O decomposition over Fe/ZSM-5 with low iron loading. *J. Phys. Chem. B* **109**, 2295.

Santiso, E.E., Gubbins, K.E. (2004). Multi-scale molecular modeling of chemical reactivity. *Molec. Simul.* **30**, 699.

Sauer, J. (1989). Molecular models in ab initio studies of solids and surfaces: from ionic crystals and semiconductors to catalysts. *Chem. Rev.* **89**, 199.

Sauer, J. (1994). Structure and reactivity of zeolite catalysts – atomistic modeling using ab-initio techniques. In: *Zeolites and related microporous materials: state of the art 1994 studies in surface science and catalysis* **84**, 2039.

Sauer, J., Ugliengo, P., Garrone, E., Saunders, V.R. (1994). Theoretical study of van-der-Waals complexes at surface sites in comparison with the experiment. *Chem. Rev.* **94**, 2095.

Schäfer, A., Huber, C., Ahlrichs, R. (1994). Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **100**, 5829.

Schipper, P.R.T., Gritsenko, O.V., Baerends, E.J. (1998). One-determinantal pure state versus ensemble Kohn-Sham solutions in the case of strong electron correlation: CH₂ and C₂. *Theor. Chem. Acc.* **99**, 329.

Schlegel, H.B. (2003). Exploring potential energy surfaces for chemical reactions: An overview of some practical methods. *J. Comp. Chem.* **24**, 1514.

Schröder, D., Shaik, S., Schwarz, H. (2000). Two-state reactivity as a new concept in organometallic chemistry. *Acc. Chem. Res.* **33**, 139.

Schumacher, V., Bürger, G., Fetzer, T., Baier, M., Hesse, M. (1998). *Verfahren zur katalytischen Zersetzung von N₂O*. Patent: DE19819882A1. Assignee: BASF.

Schwarz, H. (2004). On the spin-forbiddenness of gas-phase ion-molecule reactions: a fruitful intersection of experimental and computational studies. *Int. J. Mass Spec.* **237**, 75.

Schwefer, M. (2005). *Catalyst for decomposing N₂O, its use and method for the production thereof*. US Patent: 6,890,499B2. Assignee: Uhde GmbH.

Scott, A.P., Radom, L. (1996). Harmonic vibrational frequencies: An evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. *J. Phys. Chem.* **100**, 16502.

Shizgal, B., Karplus, M. (1970). Nonequilibrium contributions to the rate of reaction. I. Perturbation of the velocity distribution function. *J. Chem. Phys.* **52**, 4262.

Shaik, S., Danovich, D., Fiedler, A., Schröder, D., Schwarz, H. (1995). 2-state reactivity in organometallic gas-phase ion chemistry. *Helv. Chim. Acta* **78**, 1393.

Shaik, S., Filatov, M., Schröder, D., Schwarz, H. (1998). Electronic structure makes a difference: Cytochrome P-450 mediated hydroxylations of hydrocarbons as a two-state reactivity paradigm. *Chem. Eur. J.* **4**, 193.

Sierka, M. (2000). *Combining quantum mechanics and interatomic potential functions in quantum chemical studies of extended systems*. Ph.D thesis, Humboldt-Universität, Berlin.

Sierka, M., Sauer, J. (2000). Finding transition structures in extended systems: A strategy based on a combined quantum mechanics-empirical valence bond approach. *J. Chem. Phys.* **112**, 6983.

Simons, J., Jørgensen, P., Taylor, H., Ozment, J. (1983). Walking on potential energy surfaces. *J. Phys. Chem.* **87**, 2745.

Simons, J. (2003). *An Introduction to Computational Chemistry*, Cambridge University Press, Cambridge.

Sitz, G. (2005). Approximate challenges. *Nature* **433**, 470.

Slater, J.C. (1929). The theory of complex spectra. *Phys. Rev.* **34**, 126.

Smit, A.W., Gent, M.M.C., van den Brink, R.W. (2001). *Market potential for reduction of N₂O emission at nitric acid plants*. Jacobs Engineering Nederland, Document 63578-0302.

Springborg, M. (2000). *Methods of electronic-structure calculations*. WILEY-VCH, Weinheim.

Staemmler, V. (2005). The cluster approach for the adsorption of small molecules on oxide surfaces. *Top. Organomet. Chem.* **12**, 219.

Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J. (1994). Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **98**, 11623.

Stern, A.E., Eyring, H. (1935). Nonadiabatic reactions. The decomposition of N_2O . *J. Chem. Phys.* **3**, 778.

Stückelberg, E.C.G. (1932). Theorie der unelastischen Stösse zwischen Atomen. *Helv. Phys. Acta* **5**, 369.

Sun, J.-Q., Ruedenberg, J. (1993). Quadratic steepest descent on potential energy surfaces. II. Reaction path following without analytic Hessians. *J. Chem. Phys.* **99**, 5269.

Szabo, A., Ostlund, N.S. (1996). *Modern quantum mechanics*. Dover Publications.

Taboada, J.B., Overweg, A.R., Kooyman, P.J., Arends, I.W.C.E., Mul, G. (2005). Following the evolution of iron from framework to extra-framework positions in isomorphously substituted [Fe,Al]MFI with ^{57}Fe Mössbauer spectroscopy. *J. Catal.* **231**, 56.

Treutler, O., Ahlrichs, R. (1995). Efficient molecular numerical integration schemes. *J. Chem. Phys.* **102**, 346.

Truhlar, D.G., Hase, W.L., Hynes, J.T. (1983). Current status of transition-state theory. *J. Phys. Chem.* **87**, 2664.

Truhlar, D.G., Garrett, B.C., Klippenstein, S.J. (1996). Current status of transition-state theory. *J. Phys. Chem.* **100**, 12771.

Tully, J.C. (1976). Nonadiabatic processes in molecular collisions. In: *Dynamics of molecular collisions, Part B*, ed. W.H. Miller, New York: Plenum, 217.

Tully, J.C., Preston, R.K. (1971). Trajectory surface hopping approach to nonadiabatic molecular collisions: the reaction of H^+ with D_2 . *J. Chem. Phys.* **55**, 562.

Tully, J.C. (1990). Molecular dynamics with electronic transitions. *J. Chem. Phys.* **93**, 1061.

Van Duijneveldt, F.B., van Duijneveldt-van de Rijdt, J.G.C.M., van Lenthe, J.H. (1994). State of the art in counterpoise theory. *Chem. Rev.* **94**, 1873.

Van Santen, R.A., Kramer, G.J. (1995). Reactivity theory of zeolitic Bronsted acidic sites. *Chem. Rev.* **95**, 637.

Van Santen, R.A., Neurock, M. (1995). Concepts in theoretical heterogeneous catalytic reactivity. *Catal. Rev.-Sci. Eng.* **37**, 557.

Van Santen, R.A. (1997). Theory of heterogeneous catalytic reactivity using the cluster approximation. *Chemisorption and reactivity on supported clusters and thin films*. R.M. Lambert and G. Pachioni (eds.), 371.

Vineyard, G.H. (1957). Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids* **3**, 121.

Vosko, S.J., Wilk, L., Nusair, M. (1980). Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **58**, 1200.

Wąclaw, A., Nowinska, K., Schwieger, W., Zielinska, A. (2004). N₂O decomposition over iron modified zeolites ZSM-5. *Catal. Today* **90**, 21.

Wales, D. J. (1989). Finding saddle points for clusters. *J. Chem. Phys.*, **91**, 7002.

Wert, C., Zener, C. (1949). Interstitial atomic diffusion coefficients. *Phys. Rev.* **76**, 1169.

White, J.D., Chen, J., Matsiev, D., Auerbach, D.J., Wodtke, A.M. (2005). Conversion of large-amplitude vibration to electron excitation at a metal surface. *Nature* **433**, 503.

Whitten, J.L., Yang, H. (1996). Theory of chemisorption and reactions on metal surfaces. *Surf. Sci. Rep.* **24**, 59.

Wilson, E.B., Decius, J.C., Cross, P.C. (1955). *Molecular vibrations: The theory of infrared and Raman vibrational spectra*, McGraw-Hill, New York.

Wong, M.W. (1996). Vibrational frequency prediction using density functional theory. *Chem. Phys. Lett.* **256**, 391.

Wood, B.R., Reimer, J.A., Bell, A.T. (2002). Studies of N₂O adsorption and decomposition on Fe-ZSM-5. *J. Catal.* **209**, 151.

Wood, B.R., Reimer, J.A., Bell, A.T., Janicke, M.T., Ott, K.C. (2004). Nitrous oxide decomposition and surface oxygen formation on Fe-ZSM-5. *J. Catal.* **224**, 148.

Wood, B.R. (2004b), private communication.

Worth, G.A., Cederbaum, L.S. (2004). Beyond Born-Oppenheimer: Molecular dynamics through a conical intersection. *Annu. Rev. Phys. Chem.* **55**, 127.

Wynne-Jones, W.F.K., Eyring, H. (1935). The absolute rate of reactions in condensed phases. *J. Chem. Phys.* **3**, 492.

Yakovlev, A.L., Zhidomirov, G.M., van Santen, R.A. (2001). N₂O decomposition catalyzed by transition metal ions. *Catal. Lett.* **75**, 45.

Yakovlev, A.L., Zhidomirov, G.M., van Santen, R.A. (2001b). DFT calculations on N₂O decomposition by binuclear Fe complexes in Fe/ZSM-5. *J. Phys. Chem. B* **105**, 12297.

Yarkony, D.R. (1995). *Modern electronic structure theory*, Part 1, World Scientific, Singapore.

Yoshizawa, K., Shiota, Y., Yamabe, T. (1999). Intrinsic reaction coordinate analysis of the conversion of methane to methanol by an iron-oxo species: A study of crossing seams of potential energy surfaces. *J. Chem. Phys.* **111**, 538.

Yoshizawa, K., Yumura, T., Shiota, Y., Yamabe, T. (2000). Formation of an iron-oxo species upon decomposition of dinitrogen oxide on a model of Fe-ZSM-5 zeolite. *Bull. Chem. Soc. Jpn.* **73**, 29.

Yoshizawa, K., Shiota, Y., Yumura, T., Yamabe, T. (2000b). Direct methane-methanol and benzene-phenol conversions on Fe-ZSM-5 zeolite: Theoretical predictions on the reaction pathways and energetics. *J. Phys. Chem. B* **104**, 734.

Yoshizawa, K., Shiota, Y., Kamachi, T. (2003). Mechanistic proposals for direct benzene hydroxylation over Fe-ZSM-5 zeolite. *J. Phys. Chem. B*, **107**, 11404.

- Zener, C. (1932). Non-adiabatic crossing of energy levels, *Proc. R. Soc.* **A137**, 696.
- Zener, C. (1933). Dissociation of excited diatomic molecules by external perturbations. *Proc. R. Soc.* **A140**, 660.
- Zhao, Y., Pu, J., Lynch, B.J., Truhlar, D.G. (2004). Test of second-generation and third-generation density functionals for thermochemical kinetics. *Phys. Chem. Chem. Phys.* **6**, 673.
- Zhao, Y., Lynch, B.J., Truhlar, D.G. (2004b). Development and assessment of a new hybrid density functional model for thermochemical kinetics. *J. Phys. Chem. A* **108**, 2715.
- Zhao, Y., González-García, N., Truhlar, D.G. (2005). Benchmark database of barrier heights for heavy atom transfer, nucleophilic substitution, association, and unimolecular reactions and its use to test theoretical methods. *J. Phys. Chem. A* **109**, 2012.
- Zhu, C., Nakamura, H. (1994). Theory of nonadiabatic transition for general two-state curve crossing problems. I. Nonadiabatic tunneling case. *J. Chem. Phys.* **101**, 10630.
- Zhu, C., Nakamura, H. (1995). Theory of nonadiabatic transition for general two-state curve crossing problems. II. Landau-Zener case. *J. Chem. Phys.* **102**, 7448.
- Zhu, Q., Mojet, B.L., Janssen, R.A.J., Hensen, E.J.M., van Grondelle, J., Magusin, P.C.M.M., van Santen, R.A. (2002). N₂O decomposition over Fe/ZSM-5: Effect of high-temperature calcinations and steaming. *Catal. Lett.* **81**, 205.
- Zhu, Q., van Teeffelen, R.M., van Santen, R.A., Hensen, E.J.M. (2004). Effect of high-temperature treatment on Fe/ZSM-5 prepared by chemical vapor deposition of FeCl₃. II. Nitrous oxide decomposition, selective oxidation of benzene to phenol, and selective reduction of nitric oxide by isobutene. *J. Catal.* **221**, 575.
- Zilberberg, I., Gora, R.W., Zhidomirov, G.M., Leszczynski, J. (2002). Bonding in the oxo ferrous iron species: A complete active-space self-consistent-field theory verification of the molecular-oxygen-like pattern. *J. Chem. Phys.* **117**, 7153.
- Zygmunt, S.A., Mueller, R.M., Curtiss, L.A., Iton, L.E. (1998). An assessment of density functional methods for studying molecular adsorption in cluster models of zeolites. *J. Mol. Struct. (Theochem)* **430**, 9.

Appendix

A Convergence tests

One of the main sources of error in a DFT calculation is the approximate exchange-correlation functional. This work relies on studies from Zygmunt et al. (1998), Yoshizawa et al. (1999), Koch and Holthausen (2001), and Zilberberg et al. (2002) who showed that the B3LYP functional produces reliable results for iron oxide systems in agreement with experiment and very accurate multi-reference calculations. However, the numerical accuracy of density-functional calculations depends also on the type of basis set and size of basis set used for the calculations. In section A.1, the influence of different basis sets on the geometry and electronic reaction energy of two characteristic sample reactions of the N₂O decomposition on Fe-ZSM-5 is examined. The reactions studied are the N₂O decomposition on Z[FeO]⁺ sites, $Z[FeO]^+ + N_2O(g) \rightleftharpoons Z[FeO_2]^+ + N_2(g)$, and the dehydration of poisoned Z[Fe(OH)₂]⁺ sites, $Z[Fe(OH)_2]^+ \rightleftharpoons Z[FeO]^+ + H_2O(g)$. It is shown that for the triple split valence basis set with polarization functions, TZVP, the geometry and reaction energy are converged with respect to the basis set size. The error in reaction energy is approximated to be smaller than 1.5 kcal/mol.

In section A.2, the influence of the cluster size on the geometry and electronic reaction energy is investigated. As discussed in section 5.2.3, cluster calculations do not account for the long-range interaction, an interrupted charge transfer, and a missing structure constraint. To examine the influence of the cluster size on geometry and electronic reaction energy four different cluster models have been studied for the N₂O decomposition on Z[FeO]⁺ sites and the dehydration of Z[Fe(OH)₂]⁺ sites. The constraint T5 cluster model used in this work is found to give reliable results. Reaction energies calculated with the constraint T5 cluster model and a constrained T17 cluster model vary by less than 2 kcal/mol.

A.1 Basis set

In this section the reliability of the level of theory (B3LYP/TZVP), used throughout this work, is tested with respect to the basis set size in the quantum chemical calculations. In chapter 6, it was shown that during the decomposition of N_2O over Fe-ZSM-5 the majority of iron is present in the form of $\text{Z}[\text{FeO}]^+$, $\text{Z}[\text{FeO}_2]^+$, and $\text{Z}[\text{Fe}(\text{OH})_2]^+$. To be able to estimate the influence of the basis set on the geometry of these sites, the $\text{Z}[\text{FeO}]^+$, $\text{Z}[\text{FeO}_2]^+$, and $\text{Z}[\text{Fe}(\text{OH})_2]^+$ clusters were optimized with the split valence basis set (SV), the split valence with polarization functions basis set (def-SV(P)), the triple split valence basis set with polarization functions (TZVP), and the quadruple split valence basis set with polarization functions (QZVP). Table A.1, A.2, and A.3 summarize the characteristic bonding of the iron atom in $\text{Z}[\text{FeO}]^+$, $\text{Z}[\text{FeO}_2]^+$, and $\text{Z}[\text{Fe}(\text{OH})_2]^+$. For basis sets larger than the def-SV(P) basis set the atomic distances do not change significantly any more. Polarization functions are necessary to describe the bonding in these single iron sites.

**TABLE A.1: Characteristic atomic distances [Å]
in a constraint T5 $\text{Z}[\text{FeO}]^+$ cluster***

	Al - Fe	Fe - O (cluster)	Fe - O (on top)
SV	2.81	1.98	1.68
def-SV(P)	2.85	2.03	1.65
def-TZVP	2.85	2.03	1.66
def-QZVP	2.83	2.03	1.65

* calculated with DFT-B3LYP

**TABLE A.2: Characteristic atomic distances [Å]
in a constraint T5 $\text{Z}[\text{FeO}_2]^+$ cluster***

	Al - Fe	Fe - O (cluster)	Fe - O (on top)	O=O (on top)
SV	2.80	1.97	1.99	1.42
def-SV(P)	2.85	2.02	1.97	1.34
def-TZVP	2.86	2.03	1.95	1.36
def-QZVP	2.83	2.04	1.94	1.35

* calculated with DFT-B3LYP

TABLE A.3: Characteristic atomic distances [$\text{\AA}$] in a constraint T5 $Z[\text{Fe}(\text{OH})_2]^+$ cluster*

	Al - Fe	Fe - O (cluster)	Fe - OH (on top)
SV	2.80	1.98	1.77
def-SV(P)	2.86	2.03	1.79
def-TZVP	2.86	2.03	1.80
def-QZVP	2.83	2.03	1.80

* calculated with DFT-B3LYP

To calculate apparent reaction rate constants for the N_2O dissociation and to study the effect of different gas species on the speciation of iron in Fe-ZSM-5, reaction energies have to be calculated accurately. Figure A.1 illustrates the influence of the basis set size on the electronic reaction energy for the N_2O decomposition on $Z[\text{FeO}]^+$ sites, $Z[\text{FeO}]^+ + \text{N}_2\text{O}(\text{g}) \rightleftharpoons Z[\text{FeO}_2]^+ + \text{N}_2(\text{g})$. For basis sets larger than the def-SV(P) basis set the electronic reaction energy varies by less than 0.7 kcal/mol, confirming that the reaction energy is converged with respect to the basis set size.

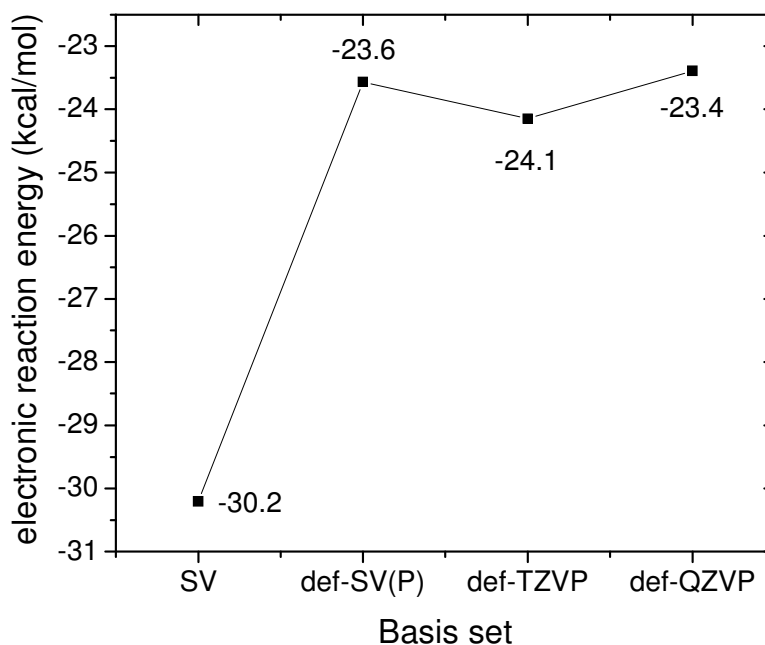


Figure A.1: Electronic reaction energy calculated with DFT-B3LYP and various basis sets for the N_2O decomposition on $Z[\text{FeO}]^+$ sites; $Z[\text{FeO}]^+ + \text{N}_2\text{O}(\text{g}) \rightleftharpoons Z[\text{FeO}_2]^+ + \text{N}_2(\text{g})$.

Figure A.2 illustrates the influence of the basis set size on the electronic reaction energy for the dehydration of $Z[\text{Fe}(\text{OH})_2]^+$ sites, $Z[\text{Fe}(\text{OH})_2]^+ \rightleftharpoons Z[\text{FeO}]^+ + \text{H}_2\text{O}(\text{g})$. The difference in the electronic reaction energy calculated with the double zeta basis set, def-SV(P), and the quadruple zeta basis set, QZVP, is 4 kcal/mol, suggesting that the def-SV(P) basis set is not large enough to accurately determine reaction energies. The difference in the electronic reaction energy calculated with the triple zeta basis set, TZVP, and the quadruple zeta basis set, QZVP, is 1.3 kcal/mol. As a result, the triple split valence basis set with polarization functions, TZVP, is large enough to describe the bonding and electronic reaction energies in iron zeolites.

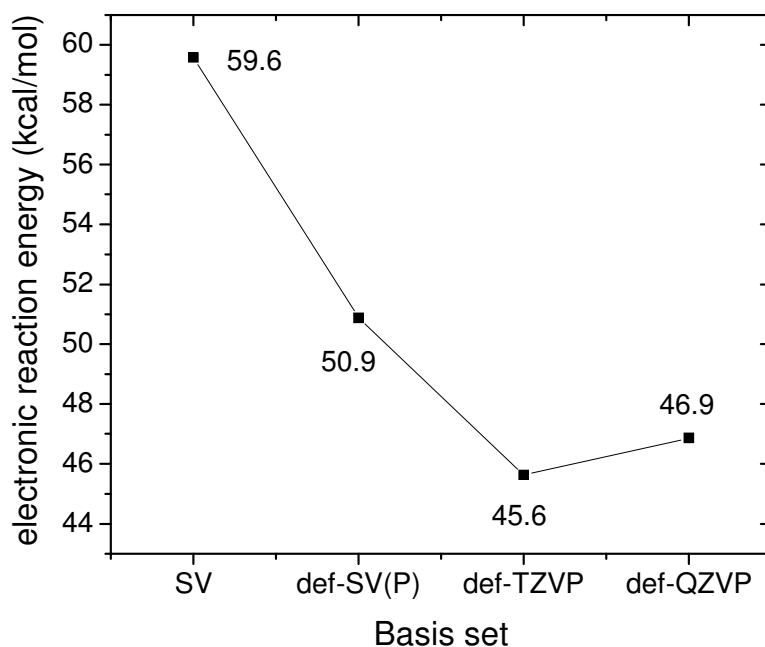


Figure A.2: Electronic reaction energy calculated with DFT-B3LYP and various basis sets for the dehydration of $Z[\text{Fe}(\text{OH})_2]^+$ sites; $Z[\text{Fe}(\text{OH})_2]^+ \rightleftharpoons Z[\text{FeO}]^+ + \text{H}_2\text{O}(\text{g})$.

A.2 Cluster size

To study the influence of cluster size on the geometry and electronic reaction energy four different cluster models have been investigated for the N_2O decomposition on $Z[\text{FeO}]^+$ sites and the dehydration of $Z[\text{Fe}(\text{OH})_2]^+$ sites. Figure A.3 illustrates a T3 cluster model and the T5 cluster model used in this work of a $Z[\text{FeO}]^+$ site. The portion

of the cluster describing the zeolite contains an Al-atom in T12 position surrounded by shells of O- and Si-atoms. The terminal Si-atoms are fixed in their crystallographic position as reported by Olson et al. (1981). Dangling bonds are terminated by H-atoms located 1.48 Å from each terminal Si-atom oriented in the direction of the next oxygen atom in the zeolite matrix. In the T3 cluster model the Al-atom is terminated by OH-groups that are not constraint in their position.

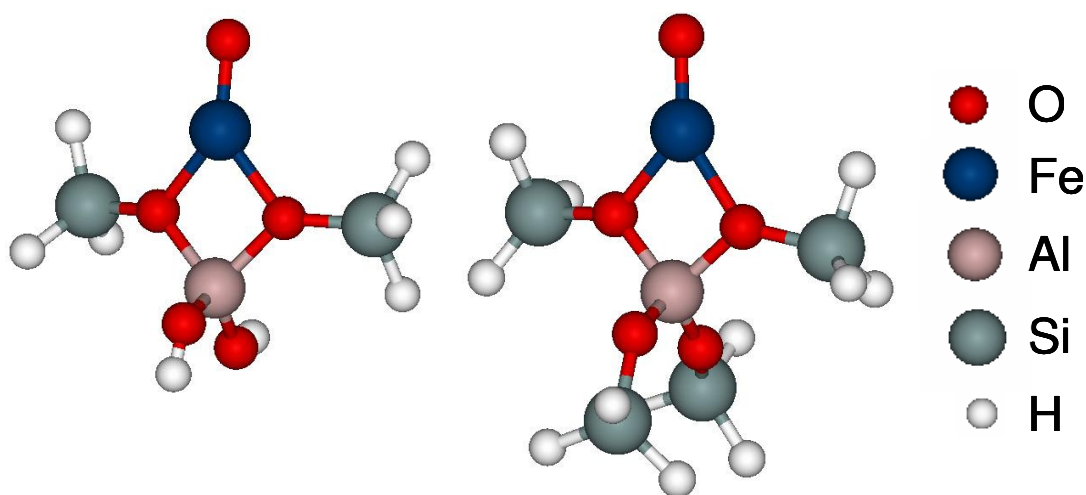


Figure A.3: T3 and T5 active site model ($Z[FeO]^+$) for the N_2O decomposition in Fe-ZSM-5. Si-atoms are fixed in their crystallographic position in ZSM-5. Dangling bonds are terminated by H-atoms and fixed 1.48 Å apart from the Si-atoms in the direction of next O-atom.

Figure A.4 illustrates a T17 cluster model of the active $Z[FeO]^+$ site in Fe-ZSM-5. The terminal Si-atoms are fixed in their crystallographic position as reported by Olson et al. (1981); dangling bonds are again terminated by H-atoms located 1.48 Å from each terminal Si-atom oriented in the direction of the next oxygen atom in the zeolite matrix. In the third cluster model studied in this section, the T17 cluster model was used with all Si-atoms and the outer O-atoms fixed in crystallographic position. As a result, there are as many flexible atoms that have to be optimized in their position as in the T5 cluster site model used throughout this work. In the last active site model studied all

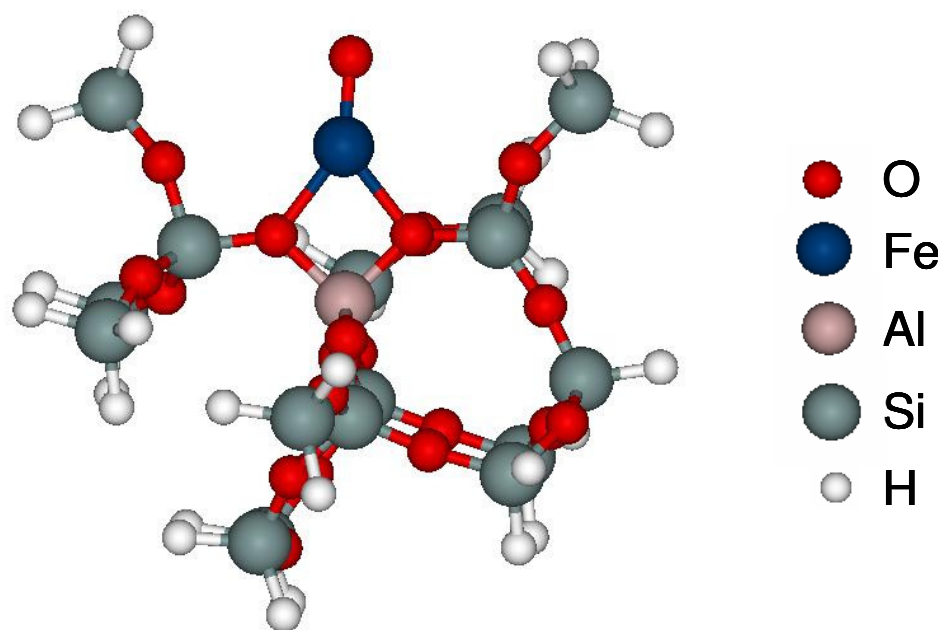


Figure A.4: T17 cluster model ($Z[\text{FeO}]^+$) for the N_2O decomposition in Fe-ZSM-5. Si-atoms are fixed in their crystallographic position in ZSM-5. Dangling bonds are terminated by H-atoms and fixed 1.48 Å apart from the Si-atoms in the direction of next O-atom.

atoms are optimized except the outer Si-atoms that are terminated with H-atoms. As a result, in this cluster model 27 to 30 atoms have to be optimized in their position. All calculations were done at the B3LYP/TZVP level of theory.

Table A.4, A.5, and A.6 summarize the characteristic bonding of iron in $Z[\text{FeO}]^+$, $Z[\text{FeO}_2]^+$, and $Z[\text{Fe}(\text{OH})_2]^+$. The local environment of the iron atom is independent of cluster model. Only the Al-Fe atomic distance varies between cluster models. If there are no constraints on the Si-atoms below the Al-atom, as is the case in the T17 and the T3 cluster model, the Al-Fe atomic distance is about 2.92 Å. In the constraint cluster models T5, and T17 (fixed), where all silica atoms are fixed in their crystallographic position, the Al-Fe atomic distance is 2.85 Å.

TABLE A.4: Influence of cluster size on local Fe bonding [Å] in a $Z[FeO]^+$ cluster*

	Al - Fe	Fe - O (cluster)	Fe - O (on top)
T3	2.92	2.01	1.66
T5	2.85	2.03	1.66
T17 (fixed) [§]	2.85	2.06	1.66
T17	2.92	2.03	1.66

* calculated with B3LYP/TZVP

§ only inner 7 atoms were optimized

TABLE A.5: Influence of cluster size on local Fe bonding [Å] in a $Z[FeO_2]^+$ cluster*

	Al - Fe	Fe - O (cluster)	Fe - O (on top)	O=O (on top)
T3	2.93	2.02	1.95	1.36
T5	2.86	2.03	1.95	1.36
T17 (fixed) [§]	2.84	2.06	1.95	1.35
T17	2.92	2.04	1.95	1.36

* calculated with B3LYP/TZVP

§ only inner 8 atoms were optimized

TABLE A.6: Influence of cluster size on local Fe bonding [Å] in a $Z[Fe(OH)_2]^+$ cluster*

	Al - Fe	Fe - O (cluster)	Fe - OH (on top)
T3	2.93	2.01	1.80
T5	2.86	2.03	1.80
T17 (fixed) [§]	2.84	2.05	1.80
T17	2.92	2.03	1.80

* calculated with B3LYP/TZVP

§ only inner 10 atoms were optimized

To evaluate the influence of the cluster model on electronic reaction energies, the reaction energy is calculated for the N_2O decomposition on $Z[FeO]^+$ sites, $Z[FeO]^+ + N_2O(g) \rightleftharpoons Z[FeO_2]^+ + N_2(g)$, and for the dehydration of poisoned $Z[Fe(OH)_2]^+$ sites, $Z[Fe(OH)_2]^+ \rightleftharpoons Z[FeO]^+ + H_2O(g)$. Figure A.5 and A.6 demonstrate that the size of the cluster model has only a very small effect on reaction energies. For the N_2O decomposition on $Z[FeO]^+$ sites, the reaction energy varies by about 1 kcal/mol between different cluster models. For the dehydration reaction of $Z[Fe(OH)_2]^+$ sites, the difference in the reaction energy is about 2 kcal/mol. Although the bonding in the T17 cluster model is more similar to the T3 cluster model than to the T5 active site

model, the reaction energy calculated on the T17 cluster model is more similar to the T5 cluster model. The T5 cluster model can describe charge delocalization around the iron atom slightly better than the smaller T3 cluster model. Another, more important reason, why the constraint T5 cluster model was used throughout this work and not the smaller T3 cluster model is the appearance of O-H groups in the T3 active site model. These terminal O-H groups can form hydrogen bonds with adsorbed gas molecules and artificially stabilize states along the reaction coordinate. Altogether, charge transfer hardly occurs over the zeolite matrix so that the constrained T5 cluster model used in this work gives reliable results for electronic reaction energies.

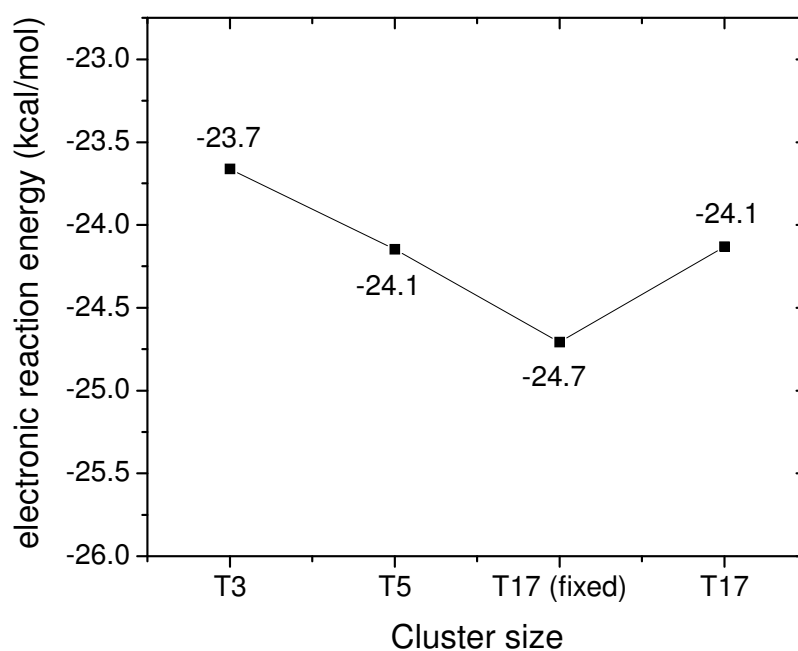


Figure A.5: Influence of cluster size on electronic reaction energy for the N_2O decomposition on $\text{Z}[\text{FeO}]^+$ sites; $\text{Z}[\text{FeO}]^+ + \text{N}_2\text{O}(\text{g}) \rightleftharpoons \text{Z}[\text{FeO}_2]^+ + \text{N}_2(\text{g})$. All energies are calculated at the B3LYP/TZVP level of theory.

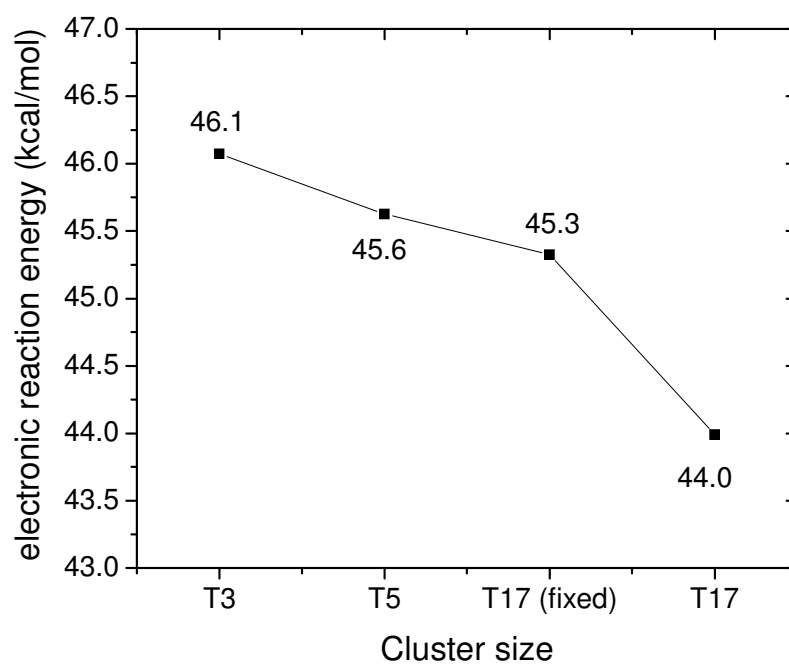


Figure A.6: Influence of cluster size on electronic reaction energy for the dehydration of $Z[\text{Fe}(\text{OH})_2]^+$ sites; $Z[\text{Fe}(\text{OH})_2]^+ \rightleftharpoons Z[\text{FeO}]^+ + \text{H}_2\text{O}(\text{g})$. All energies are calculated at the B3LYP/TZVP level of theory.

B Apparent reaction rate constant for the N₂O decomposition on Fe-ZSM-5

In this section, an analytical solution of the apparent reaction rate constant for the N₂O decomposition is calculated from first principles. It is assumed that the only gas molecules in the system are N₂O, N₂, O₂, and H₂O. The apparent reaction rate constant for N₂O decomposition is calculated using the reaction network illustrated in Figure 5.1. Under steady-state conditions bare iron sites are not present so that the catalytic cycle on Z[Fe]⁺ is not considered. To calculate macroscopic reaction rates from microscopic elementary reaction rate data the mean field approximation is applied, i.e., it is assumed that all species are randomly distributed and that the rate of reaction is proportional to the product of the interacting species (Chorkendorff and Niemantsverdriet, 2003; Keil, 2004b). Figure B.1 illustrates the use of the mean field approximation. Since the reaction temperature is high for the N₂O decomposition and the main active sites are probably single iron sites, the use of this approximation is justified.

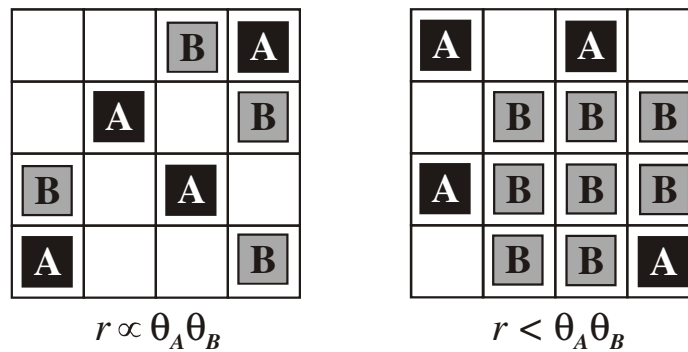


Figure B.1: Checker board model of a surface with two adsorbates. Left: Random distribution of surface sites. Right: Attractive interactions give rise to islands of B. Reaction between A and B is only possible at the perimeter of the islands. Hence, the rate of reaction is not proportional to the coverage of B.

B.1 System of rate equations

In the following, P_i is the pressure of component i in bar, t is the time in seconds, Θ_i is the fraction of single iron sites occupied by species i , N is the number of moles of single iron sites, and n_i is the number of moles of species i in the gas phase. The rate parameters k_i and the equilibrium constants K_i were calculated from first principles and can be obtained from Table 5.1.

B.1.1 Gas species

$$\begin{aligned} \frac{d \frac{n_{N_2O}}{N}}{dt} = & -k_3 \Theta_{FeO} P_{N_2O} + k_{-3} \Theta_{FeO(ON_2)} - k_5 \Theta_{FeO_2} P_{N_2O} + k_{-5} \Theta_{FeO_2(ON_2)} \\ & - k_{12} \Theta_{OFeO} P_{N_2O} + k_{-12} \Theta_{OFeO(ON_2)} \end{aligned} \quad (B.1)$$

$$\begin{aligned} \frac{d \frac{n_{N_2}}{N}}{dt} = & +k_4 \Theta_{FeO(ON_2)} - k_{-4} \Theta_{FeO_2} P_{N_2} + k_{11} \Theta_{FeO(ON_2)} - k_{-11} \Theta_{OFeO} P_{N_2} \\ & + k_6 \Theta_{FeO_2(ON_2)} - k_{-6} \Theta_{O_2FeO} P_{N_2} + k_{13} \Theta_{OFeO(ON_2)} - k_{-13} \Theta_{O_2FeO} P_{N_2} \end{aligned} \quad (B.2)$$

$$\frac{d \frac{n_{O_2}}{N}}{dt} = +k_7 \Theta_{O_2FeO} - k_{-7} \Theta_{FeO} P_{O_2} \quad (B.3)$$

$$\frac{d \frac{n_{H_2O}}{N}}{dt} = -k_2 \Theta_{FeO} P_{H_2O} + k_{-2} \Theta_{FeO(H_2O)} \quad (B.4)$$

B.1.2 Surface species

$$\frac{d \Theta_{Fe(OH)_2}}{dt} = +k_1 \Theta_{FeO(H_2O)} - k_{-1} \Theta_{Fe(OH)_2} \quad (B.5)$$

$$\frac{d\Theta_{FeO(H_2O)}}{dt} = +k_2 \Theta_{FeO} P_{H_2O} - k_{-2} \Theta_{FeO(H_2O)} - k_1 \Theta_{FeO(H_2O)} + k_{-1} \Theta_{Fe(OH)_2} \quad (B.6)$$

$$\begin{aligned} \frac{d\Theta_{FeO(ON_2)}}{dt} = & +k_3 \Theta_{FeO} P_{N_2O} - k_{-3} \Theta_{FeO(ON_2)} - k_4 \Theta_{FeO(ON_2)} + k_{-4} \Theta_{FeO_2} P_{N_2} \\ & - k_{11} \Theta_{FeO(ON_2)} + k_{-11} \Theta_{OFeO} P_{N_2} \end{aligned} \quad (B.7)$$

$$\frac{d\Theta_{FeO_2(ON_2)}}{dt} = +k_5 \Theta_{FeO_2} P_{N_2O} - k_{-5} \Theta_{FeO_2(ON_2)} - k_6 \Theta_{FeO_2(ON_2)} + k_{-6} \Theta_{O_2FeO} P_{N_2} \quad (B.8)$$

$$\frac{d\Theta_{OFeO(ON_2)}}{dt} = +k_{12} \Theta_{OFeO} P_{N_2O} - k_{-12} \Theta_{OFeO(ON_2)} - k_{13} \Theta_{OFeO(ON_2)} + k_{-13} \Theta_{O_2FeO} P_{N_2} \quad (B.9)$$

$$\begin{aligned} \frac{d\Theta_{O_2FeO}}{dt} = & -k_7 \Theta_{O_2FeO} + k_{-7} \Theta_{FeO} P_{O_2} + k_6 \Theta_{FeO_2(ON_2)} - k_{-6} \Theta_{O_2FeO} P_{N_2} \\ & + k_{13} \Theta_{OFeO(ON_2)} - k_{-13} \Theta_{O_2FeO} P_{N_2} \end{aligned} \quad (B.10)$$

$$\begin{aligned} \frac{d\Theta_{OFeO}}{dt} = & +k_{14} \Theta_{FeO_2} - k_{-14} \Theta_{OFeO} - k_{12} \Theta_{OFeO} P_{N_2O} + k_{-12} \Theta_{OFeO(ON_2)} \\ & + k_{11} \Theta_{FeO(ON_2)} - k_{-11} \Theta_{OFeO} P_{N_2} \end{aligned} \quad (B.11)$$

$$\begin{aligned} \frac{d\Theta_{FeO}}{dt} = & +k_7 \Theta_{O_2FeO} - k_{-7} \Theta_{FeO} P_{O_2} - k_2 \Theta_{FeO} P_{H_2O} + k_{-2} \Theta_{FeO(H_2O)} \\ & - k_3 \Theta_{FeO} P_{N_2O} + k_{-3} \Theta_{FeO(ON_2)} \end{aligned} \quad (B.12)$$

$$\begin{aligned} \frac{d\Theta_{FeO_2}}{dt} = & -k_{14} \Theta_{FeO_2} + k_{-14} \Theta_{OFeO} - k_5 \Theta_{FeO_2} P_{N_2O} + k_{-5} \Theta_{FeO_2(ON_2)} \\ & + k_4 \Theta_{FeO(ON_2)} - k_{-4} \Theta_{FeO_2} P_{N_2} \end{aligned} \quad (B.13)$$

B.2 Pseudo-steady state approximation

Next, the pseudo-steady state approximation is applied to all surface species.

$$\frac{d\Theta_{Fe(OH)_2}}{dt} = 0 \Rightarrow \Theta_{Fe(OH)_2} = K_1 \Theta_{FeO(H_2O)} \quad (B.14)$$

$$\frac{d\Theta_{FeO(H_2O)}}{dt} = 0 \Rightarrow \Theta_{FeO(H_2O)} = K_2 \Theta_{FeO} P_{H_2O} \quad (B.15)$$

$$\frac{d\Theta_{FeO(ON_2)}}{dt} = 0 \Rightarrow \Theta_{FeO(ON_2)} = \frac{k_3\Theta_{FeO}P_{N_2O} + k_{-4}\Theta_{FeO_2}P_{N_2} + k_{-11}\Theta_{OFeO}P_{N_2}}{k_{-3} + k_4 + k_{11}} \quad (B.16)$$

since $k_3\Theta_{FeO}P_{N_2O} \gg k_{-4}\Theta_{FeO_2}P_{N_2} + k_{-11}\Theta_{OFeO}P_{N_2}$ Eqn. (B.16) can be rewritten as:

$$\Theta_{FeO(ON_2)} = \frac{K_3\Theta_{FeO}P_{N_2O}}{1 + \frac{k_4 + k_{11}}{k_{-3}}} \approx \left(1 - \frac{k_4 + k_{11}}{k_{-3}}\right) K_3\Theta_{FeO}P_{N_2O}, \quad \frac{k_4 + k_{11}}{k_{-3}} \ll 1 \quad (B.17)$$

$$\frac{d\Theta_{FeO_2(ON_2)}}{dt} = 0 \Rightarrow \Theta_{FeO_2(ON_2)} = \frac{k_5\Theta_{FeO_2}P_{N_2O} + k_{-6}\Theta_{O_2FeO}P_{N_2}}{k_{-5} + k_6} \quad (B.18)$$

since $k_5\Theta_{FeO_2}P_{N_2O} \gg k_{-6}\Theta_{O_2FeO}P_{N_2}$ Eqn. (B.18) can be rewritten as:

$$\Theta_{FeO_2(ON_2)} = \frac{K_5\Theta_{FeO_2}P_{N_2O}}{1 + \frac{k_6}{k_{-5}}} \approx \left(1 - \frac{k_6}{k_{-5}}\right) K_5\Theta_{FeO_2}P_{N_2O}, \quad \frac{k_6}{k_{-5}} \ll 1 \quad (B.19)$$

$$\frac{d\Theta_{OFeO(ON_2)}}{dt} = 0 \Rightarrow \Theta_{OFeO(ON_2)} = \frac{k_{12}\Theta_{OFeO}P_{N_2O} + k_{-13}\Theta_{O_2FeO}P_{N_2}}{k_{-12} + k_{13}} \quad (B.20)$$

since $k_{12}\Theta_{OFeO}P_{N_2O} \gg k_{-13}\Theta_{O_2FeO}P_{N_2}$ Eqn. (B.20) can be rewritten as:

$$\Theta_{OFeO(ON_2)} = \frac{K_{12}\Theta_{OFeO}P_{N_2O}}{1 + \frac{k_{13}}{k_{-12}}} \approx \left(1 - \frac{k_{13}}{k_{-12}}\right) K_{12}\Theta_{OFeO}P_{N_2O}, \quad \frac{k_{13}}{k_{-12}} \ll 1 \quad (B.21)$$

$$\begin{aligned} \frac{d\Theta_{O_2FeO}}{dt} = 0 = & -k_7\Theta_{O_2FeO} + k_{-7}\Theta_{FeO}P_{O_2} + k_6\left(1 - \frac{k_6}{k_{-5}}\right)K_5\Theta_{FeO_2}P_{N_2O} \\ & - k_{-6}\Theta_{O_2FeO}P_{N_2} + k_{13}\left(1 - \frac{k_{13}}{k_{-12}}\right)K_{12}\Theta_{OFeO}P_{N_2O} - k_{-13}\Theta_{O_2FeO}P_{N_2} \end{aligned} \quad (B.22)$$

since $\left(1 - \frac{k_6}{k_{-5}}\right) \approx 1, \left(1 - \frac{k_{13}}{k_{-12}}\right) \approx 1$ Eqn. (B.22) can be rewritten as:

$$\Theta_{O_2FeO} = \frac{k_{-7}\Theta_{FeO}P_{O_2} + k_6K_5\Theta_{FeO_2}P_{N_2O} + k_{13}K_{12}\Theta_{OFeO}P_{N_2O}}{k_7 + k_{-6}P_{N_2} + k_{-13}P_{N_2}} \quad (B.23)$$

since $k_7 \gg k_{-6}P_{N_2} + k_{-13}P_{N_2}$ Eqn. (B.23) can be rewritten as:

$$k_7 \Theta_{O2FeO} = k_{-7} \Theta_{FeO} P_{O2} + k_6 K_5 \Theta_{FeO2} P_{N2O} + k_{13} K_{12} \Theta_{OFeO} P_{N2O} \quad (B.24)$$

$$\begin{aligned} \frac{d\Theta_{OFeO}}{dt} = 0 = & k_{14} \Theta_{FeO2} - k_{-14} \Theta_{OFeO} - k_{12} \Theta_{OFeO} P_{N2O} + k_{-12} \left(1 - \frac{k_{13}}{k_{-12}}\right) K_{12} \Theta_{OFeO} P_{N2O} \\ & + k_{11} \left(1 - \frac{k_4 + k_{11}}{k_{-3}}\right) K_3 \Theta_{FeO} P_{N2O} - k_{-11} \Theta_{OFeO} P_{N2} \end{aligned} \quad (B.25)$$

since $\left(1 - \frac{k_4 + k_{11}}{k_{-3}}\right) \approx 1$ Eqn. (B.25) can be rewritten as:

$$k_{-14} \Theta_{OFeO} + k_{13} K_{12} \Theta_{OFeO} P_{N2O} + k_{-11} \Theta_{OFeO} P_{N2} = k_{14} \Theta_{FeO2} + k_{11} K_3 \Theta_{FeO} P_{N2O} \quad (B.26)$$

since $k_{-14} \Theta_{OFeO} \gg k_{13} K_{12} \Theta_{OFeO} P_{N2O} + k_{-11} \Theta_{OFeO} P_{N2}$ and

$k_{14} \Theta_{FeO2} \gg k_{11} K_3 \Theta_{FeO} P_{N2O}$ Eqn. (B.26) becomes:

$$\Theta_{OFeO} \approx K_{14} \Theta_{FeO2} \quad (B.27)$$

$$\begin{aligned} \frac{d\Theta_{FeO}}{dt} = 0 = & k_7 \Theta_{O2FeO} - k_{-7} \Theta_{FeO} P_{O2} - k_3 \Theta_{FeO} P_{N2O} \\ & + k_{-3} \left(1 - \frac{k_4 + k_{11}}{k_{-3}}\right) K_3 \Theta_{FeO} P_{N2O} \end{aligned} \quad (B.28)$$

$$\Rightarrow k_7 \Theta_{O2FeO} = (k_{-7} P_{O2} + (k_4 + k_{11}) K_3 P_{N2O}) \Theta_{FeO} \quad (B.29)$$

B.3 Determination of main surface sites

If Eqn. (B.24) is equated with Eqn. (B.29) and Eqn. (B.27) is used, Eqn. (B.30) is obtained:

$$\Theta_{FeO2} = \frac{(k_4 + k_{11}) K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} \Theta_{FeO} \quad (B.30)$$

From simulations of the whole system it is known that:

$$\Theta_{Fe(OH)2} + \Theta_{FeO} + \Theta_{FeO2} + \Theta_{OFeO} + \Theta_{O2FeO} \approx 1 \quad (B.31)$$

Inserting all surface species in Eqn. (B.31):

$$1 = \left(1 + K_1 K_2 P_{H_2O} + \frac{(k_4 + k_{11})K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} (1 + K_{14}) + \frac{P_{O_2}}{K_7} + \frac{(k_4 + k_{11})K_3}{k_7} P_{N_2O} \right) \Theta_{FeO} \quad (B.32)$$

since $K_{14} \ll 1$ and $\frac{P_{O_2}}{K_7} + \frac{(k_4 + k_{11})K_3}{k_7} P_{N_2O} \ll 1$ Eqn. (B.32) becomes:

$$1 = \left(1 + K_1 K_2 P_{H_2O} + \frac{(k_4 + k_{11})K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} \right) \Theta_{FeO} \quad (B.33)$$

Consequently, the surface fraction of the main surface species can be calculated as:

$$\Theta_{FeO} = \frac{1}{\left(1 + K_1 K_2 P_{H_2O} + \frac{(k_4 + k_{11})K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} \right)} \quad (B.34)$$

$$\Theta_{FeO_2} = \frac{(k_4 + k_{11})K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} \Theta_{FeO} \quad (B.35)$$

$$\Theta_{OFeO} = K_{14} \Theta_{FeO_2} \quad (B.36)$$

$$\Theta_{O_2FeO} = \frac{1}{k_7} (k_{-7} P_{O_2} + (k_4 + k_{11})K_3 P_{N_2O}) \Theta_{FeO} \quad (B.37)$$

$$\Theta_{Fe(OH)_2} = K_1 K_2 \Theta_{FeO} P_{H_2O} \quad (B.38)$$

B.4 Rate of change of nitrogen, oxygen and nitrous oxide

$$\begin{aligned} \frac{d \frac{n_{N_2}}{N}}{dt} = - \frac{d \frac{n_{N_2O}}{N}}{dt} = & k_3 \Theta_{FeO} P_{N_2O} - k_{-3} \left(1 - \frac{k_4 + k_{11}}{k_{-3}} \right) K_3 P_{N_2O} \Theta_{FeO} \\ & + k_5 \Theta_{FeO_2} P_{N_2O} - k_{-5} \left(1 - \frac{k_6}{k_{-5}} \right) K_5 P_{N_2O} \Theta_{FeO_2} \\ & + k_{12} \Theta_{OFeO} P_{N_2O} - k_{-12} \left(1 - \frac{k_{13}}{k_{-12}} \right) K_{12} P_{N_2O} \Theta_{OFeO} \end{aligned} \quad (B.39)$$

$$\begin{aligned}
\frac{d \frac{n_{N_2}}{N}}{dt} &= -\frac{d \frac{n_{N_2O}}{N}}{dt} = (k_4 + k_{11}) K_3 P_{N_2O} \Theta_{FeO} + k_6 K_5 P_{N_2O} \Theta_{FeO_2} + k_{13} K_{12} P_{N_2O} \Theta_{OFeO} \\
&= \left(\frac{(k_4 + k_{11}) K_3 + k_6 K_5 \frac{(k_4 + k_{11}) K_3}{k_6 K_5 + k_{13} K_{12} K_{14}}}{+ k_{13} K_{12} \frac{(k_4 + k_{11}) K_3 K_{14}}{k_6 K_5 + k_{13} K_{12} K_{14}}} \right) P_{N_2O} \Theta_{FeO} \\
&= 2(k_4 + k_{11}) K_3 P_{N_2O} \Theta_{FeO} \\
&= \frac{2(k_4 + k_{11}) K_3}{\left(1 + K_1 K_2 P_{H_2O} + \frac{(k_4 + k_{11}) K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} \right)} P_{N_2O} \\
&= k_{app} P_{N_2O} = 2 \frac{d \frac{n_{O_2}}{N}}{dt}
\end{aligned} \tag{B.40}$$

Finally, the apparent reaction rate constant for the N_2O decomposition becomes:

$$\begin{aligned}
k_{app} &= \frac{2(k_4 + k_{11}) K_3}{\left(1 + K_1 K_2 P_{H_2O} + \frac{(k_4 + k_{11}) K_3}{k_6 K_5 + k_{13} K_{12} K_{14}} \right)} \\
&= 2 \frac{\sum \text{rate of 1st } N_2O \text{ dissociation}}{1 + \text{amount of water poisoning} + \frac{\sum \text{rate of 1st } N_2O \text{ dissociation}}{\sum \text{rate of 2nd } N_2O \text{ dissociation}}} \\
&\approx 2 \cdot \frac{9.2 \cdot 10^8 \frac{\text{mol}_{N_2O}}{\text{mol}_{Fe} \text{ s bar}_{N_2O}} \exp\left(-\frac{26.9 \text{ kcal/mol}}{RT}\right)}{1 + 5.9 \cdot 10^{-8} \frac{1}{\text{bar}_{H_2O}} \exp\left(\frac{43.6 \text{ kcal/mol}}{RT}\right) P_{H_2O} + 8.4 \exp\left(-\frac{3.9 \text{ kcal/mol}}{RT}\right)}
\end{aligned} \tag{B.41}$$

Lebenslauf

Persönliche Daten

Name	Andreas Heyden
Geburtsdatum	29.05.1975
Geburtsort	Pinneberg

Schul Ausbildung

1981 – 1985	Grundschule in Rellingen
1985 – 1994	Gymnasium in Pinneberg
6 / 1994	Abitur

Wehrdienst

1994 – 1995	Grundwehrdienst in Heide
-------------	--------------------------

Studium

10 / 1995 – 12 / 2000	Verfahrenstechnik an der TU Hamburg-Harburg
08 / 1998 – 05 / 1999	Chemical Engineering an der UC Berkeley
06 / 2000 – 09 / 2000	Chemical Engineering an der University of Edinburgh
12 / 2000	Abschluss: Diplom-Ingenieur

Wissenschaftliche Tätigkeit

01 / 2001 – 12 / 2005	Wissenschaftlicher Mitarbeiter an der TU Hamburg-Harburg, Arbeitsbereich Chemische Reaktionstechnik
08 / 2001 – 12 / 2001, 08 / 2002 – 12 / 2002, 08 / 2003 – 03 / 2004	Forschungsaufenthalt an der UC Berkeley