

Measuring Adsorbate Profiles in Heterogeneous Catalytic Reactors by Iso-Potential Operando DRIFTS applied to CO₂ Methanation on Ni

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Abstract

The operation of industrial heterogeneous reactors is largely based on many years of empirical knowledge gained through trial-and-error approaches, as direct insights into the internal state of the catalyst and the reaction environment under real operating conditions are lacking. This lack of insight prevents a deep understanding of catalyst dynamics, reaction mechanisms, and structure-activity relationships, thereby limiting the systematic optimization of process conditions and the targeted development of reactor and catalyst systems. To address this gap, advanced *operando* spectroscopic techniques have been developed in recent years. These methods enable the real-time observation of catalytic processes under reaction conditions, offering valuable mechanistic insights and providing a promising basis for catalyst and reactor modeling. Despite their potential, *operando* techniques remain almost exclusively an academic field and are subject to significant limitations. Even with the use of custom-designed *operando* spectroscopic reactors or reaction cells, compromises have to be made in favor of the functionality of the "catalytic reactor" and the "spectroscopic cell": Spectroscopic methods frequently lack optical access at relevant process conditions, *operando* setups are often kinetically suboptimal, and limitations in cell design can lead to poor analytical signal quality. Consequently, *operando* measurements may not fully reflect industrially relevant or optimal reaction conditions.

This work introduces the methodology of iso-potential *operando* spectroscopy using DRIFTS to simultaneously measure surface adsorbate profiles as well as concentration and temperature gradients in catalytic reactors under *operando* reaction conditions. For the proof of concept, a laboratory-scale catalytic profile reactor is used, equipped with a capillary sampling technique for spatially resolved measurements of gas composition and temperature. By moving the capillary axially through the catalyst bed, small quantities of the reaction mixture can be sampled locally through a sampling orifice and continuously transferred to a coupled DRIFTS cell. The spectroscopic cell is filled with a very small sample of the same catalyst as in the reactor and is heated to the same temperature, which is measured locally in the reactor. Since the pressure, temperature, and composition of the reaction mixture are the same, the catalyst sample is exposed to the same chemical potential as

locally in the catalytic reactor. In this way, the dynamic change of the catalyst in response to the local chemical potential in the reactor is transferred to the catalyst sample in the spectroscopic cell, which hypothetically assumes the same structure, surface adsorbates, and reactivity. To demonstrate this concept, CO₂ methanation on Ni/ γ -Al₂O₃ catalysts is used as a test system. During measurements, two surface adsorbate species are detected. The first is formate, whose band intensity along the catalyst bed decreases with the CO₂ concentration in the gas phase. This identifies surface formate as a kinetically relevant intermediate, consistent with the associative reaction mechanism – CO₂ adsorbs on alumina as carbonate or bicarbonate and rapidly hydrogenates to formate. The formate reduction is the rate-determining step, while all subsequent hydrogenation steps to CH₄ are again rapid. The second surface adsorbates detected are carbonyl species – formed by dissociative adsorption of CO₂ on nickel –, whose intensity does not change over the length of the catalyst bed specified in the experiment. Within the given experimental environment, it is not possible to distinguish precisely between carbonyl adsorbates as spectator species or reaction intermediates.

This novel measurement method offers a powerful approach for identifying active intermediates and spectator species. By revealing reaction mechanisms under realistic reaction conditions, it facilitates the development of detailed reactor models, thus enabling more precise and sustainable optimization of catalytic processes and the development of catalysts.

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Contents

1	Introduction	1
2	Theoretical Background	5
2.1	Heterogeneous Catalysis	5
2.2	The Way to Operando Catalyst Characterization	8
2.3	Iso-Potential Operando Spectroscopy	12
2.3.1	Chemical Potential	13
2.3.2	Setup of Iso-Potential Coupling	16
2.4	IR Spectroscopy	18
2.4.1	Fundamentals of IR Spectroscopy	18
2.4.2	Diffuse Reflection Spectroscopy	24
2.5	Adsorption on Solid Surfaces	26
2.5.1	Historical Overview	26
2.5.2	Physisorption	27
2.5.3	Chemisorption	29
2.5.4	Vibrational Properties of Adsorbates	31
2.5.5	Adsorption Sites on Catalytic Support Surfaces	34
2.6	CO ₂ Methanation	36
2.6.1	History of Catalytic Methanation	36
2.6.2	Fundamentals	37
2.6.3	Chemical Equilibrium	38
2.6.4	Catalyst	45
2.6.5	Reaction Mechanism	48
3	Material and Methods	51
3.1	Material	51
3.1.1	List of Chemicals	51
3.1.2	Catalyst Synthesis and Characterization Methods	51
3.1.3	Compact Profile Reactor	54

3.1.4	Gas Dosing System	57
3.1.5	Mass Spectrometry	58
3.1.6	FTIR Spectroscopy	61
3.2	Methodology of Iso-Potential Operando DRIFTS	63
3.2.1	Methodical Approach for the Measurement of Adsorbates using DRIFTS	64
3.2.2	Iso-Potential Operando DRIFTS Workflow	67
3.2.3	Extraction of Catalyst Surface Adsorbate Spectra	69
4	Results and Discussion	75
4.1	Experimental Setup	75
4.2	Experimental Conditions and Procedures	78
4.2.1	Catalyst Dilution for DRIFTS Measurements	81
4.2.2	Gas Analysis and Mass Balance	83
4.3	Catalyst Characterization	86
4.3.1	ICP-OES	87
4.3.2	Physisorption Analysis	87
4.3.3	STEM-EDS Mapping	89
4.3.4	Chemisorption Analysis	91
4.3.5	X-ray Diffraction	94
4.3.6	Raman Spectroscopy	94
4.3.7	LIBS	96
4.4	Iso-Potential DRIFTS Profiling	99
4.4.1	Temperature and Gas Composition Profiles in the CPR (X)	99
4.4.2	Conversion Profiles with and without the DRIFTS cell	102
4.4.3	IPO DRIFTS measurements of the Diluent (C, D)	105
4.4.4	IPO DRIFTS measurements of the diluted Catalyst Sample (A, B)	110
4.4.5	Extraction of the Catalyst Surface Adsorbate Spectra	115
4.4.6	Interpretation of evaluated IPO-DRIFTS Measurements	119
5	Summary and Future Perspective	123
A	Appendices	127
A.1	Chemical equilibrium of CO ₂ methanation under experimental reaction con- ditions	127
A.2	Pressure drop in the CPR under experimental reaction conditions	129

A.3 Axial dispersion in the CPR under experimental reaction conditions	131
A.4 External Mass Transfer Limitation in the CPR under experimental reaction conditions	134
A.5 Intraparticle Mass Transfer Limitation in the CPR under experimental reaction conditions	136
Abbreviations	141
Greek letters	143
Latin letters	145
List of Figures	149
List of Tables	157
Bibliography	159

1 Introduction

Catalysis is crucial for today's industry and plays a key role in manufacturing processes of the chemical, petrochemical, biochemical, and polymer industries, as well as in environmental protection [1]. Due to climate change, the latter is gaining in importance for the transition to sustainable energy systems. However, the majority of global primary energy is still obtained from fossil fuels through the transformation of hydrocarbon resources [2]. Therefore, innovative heterogeneous catalytic processes are essential to overcome the transition from fossil energy systems and feedstocks to sustainable, renewable alternatives. The centerpiece of this catalytic technology is the reactor, most commonly a tubular reactor, and the solid catalysts filled into it, which are spatially fixed as a bed and through which a gaseous reactant mixture flows under continuous conditions determined by pressure, temperature, concentration and contact time [3, 4]. Catalysts enhance the rate and optimize the activity and selectivity of chemical reactions by providing regenerating surface sites on which reactants adsorb, react, and desorb, thereby reducing the activation energy barrier of the process. In this cyclic process, the catalytic surface does not behave statically but responds dynamically to the chemical potential of the surrounding reaction mixture across the entire reactor bed [5–7]. Changes in the physical, chemical, and electronic properties of the catalyst can occur, for example, in the bulk and surface structure or the number and type of active sites. This affects the way adsorbates populate the surface and, in turn, affects catalytic performance [8]. To meet the challenge of dynamically operating catalysts in the development and optimization of catalyst materials and reactor operation, detailed knowledge of surface chemistry, including the underlying reaction mechanisms and resulting kinetics along the catalyst bed, is required. However, the acquisition of information on the atomic scale in catalytic reactors is limited. Classical reactor analysis is often based on the trial-and-error principle, in which only the known influent and analyzed effluent components are compared in a large number of experiments under varying process conditions, while the interior of the reactor is treated as a black box due to the lack of access [9]. By neglecting structural gradients and catalyst dynamics, catalytically relevant adsorbates, reaction intermediates, or spectator species can be misinterpreted, leaving gaps in the derivation of the reaction mechanism and the resulting kinetics.

Optical spectroscopic, synchrotron-based or magnetic resonance techniques offer the possibility to analyze the structure and surface chemistry of solid catalysts [10–13]. To observe catalysts in their respective working states, reaction cells have been designed for spectroscopic analysis under reaction conditions that correspond as closely as possible to industrial reaction conditions [14, 15]. Even though these *in situ* spectroscopic cells facilitate the acquisition of high-quality data, only a small part of the broad spectrum of process conditions that prevail in an industrial catalytic reactor can be captured in a sequence of experiments. Temperature, composition, and, to a lesser extent, pressure vary throughout the catalyst bed, contributing to significant spatial gradients within it. To rudimentarily replicate these dynamic changes in *in situ* experiments, screening requires numerous experiments with varying reaction parameters, making the process highly time-consuming [6]. Moreover, these cells are often characterized by bypass flows, dead volumes or temperature and concentration gradients, which compromise the accuracy of activity and selectivity measurements [16–18]. To close the gaps of *in situ* techniques, these have been replaced by so-called *operando* spectroscopic methodologies, which combine the spectroscopic characterization of catalysts with activity and selectivity data for simultaneous quantitative evaluation [18–23]. For this purpose, laboratory reactors have been adapted to spectroscopic reaction cells to simultaneously measure a direct relationship between the catalyst structure and the catalytic performance under *operando* reaction conditions, e.g., by online analysis with mass spectrometry or gas chromatography of the effluent reaction mixture. A relatively new tool in *operando* catalysis research is the spatially resolved measurement method using a capillary-based sampling technique, which provides local information about the entire catalyst bed with sub-millimeter resolution [24–30]. The development of intrareactor diagnostic techniques is the focus of the research group of Horn et al. [31, 32]. Using a minimally invasive sampling capillary that moves axially through the catalyst bed to take samples of the gas mixture for GC or MS measurements, they were able to observe spatially resolved concentration and temperature profiles in a catalytic reactor [33, 34]. Recently, the group succeeded in simultaneously performing XAS [35] or XRD [36, 37] measurements together with concentration and temperature measurements by using a novel *operando* reactor design with an optimized capillary sampling technique. However, spatially resolved measurements along the catalytic fixed bed under *operando* conditions were only possible due to the high penetration power of hard X-rays from synchrotron sources through the reactor. The development and adaptation of *operando* catalytic reactors to other analytical methods remains a challenge. For example, IR or UV/Vis spectroscopy requires optical access to the interior of the catalyst bed. EPR and NMR spectroscopy are not compatible

with metallic components built into a reactor. In the case of electron microscopy, the reactor cells would be too small to provide a realistic reaction environment and accurate kinetic data. Overall, despite all efforts to improve the fundamental understanding of catalysis and to optimize the process control of catalytic reactors, the development and application of *operando* spectroscopic reactors remains an academic discipline and lacks a transfer to industrial applications. Typical industrial reactors are difficult to access, non-transparent, constructed as steel pressure vessels and characterized by strong gradients in temperature, pressure and species concentrations.

The work aims to introduce the application of a novel *operando* technique called Iso-Potential *Operando* Spectroscopy (IPOS), which provides spatially resolved concentration, temperature and spectroscopic profiles along a catalytic fixed-bed under realistic reaction conditions, while separating the functions of the "catalytic reactor" and the "spectroscopic cell" [38]. A catalytic profile reactor is equipped with a capillary sampling technique to continuously transfer an invasive portion of a locally sampled reaction mixture into a coupled spectroscopic cell containing a minimal amount of the same catalyst as in the reactor. To adapt the target temperature in the spectroscopy cell to the locally measured temperature in the reactor, a spatial temperature measurement is installed in the reactor. This type of coupling technique ensures that the catalyst in the spectroscopic cell is exposed to the same chemical potential as locally in the reactor and thus experiences the same chemical changes to the catalyst surface and structure.

To prove the principle of IPOS and highlight its potential, the methodology is demonstrated in this work using Diffuse Reflectance Infrared Fourtier Transform Spectroscopy (DRIFTS) and applied to the hydrogenation of carbon dioxide (CO₂ methanation) over an alumina-supported nickel catalyst (Ni/ γ -Al₂O₃ catalyst) as a test reaction system. In recent decades, CO₂ methanation has emerged as a promising approach in many power-to-gas concepts for chemical energy storage using green hydrogen [39, 40]. However, there is disagreement in the literature about the types of reaction intermediates and the reaction path CO₂ methanation follows [41–46]. DRIFTS is a spectroscopic method widely used to characterize surface chemistry in heterogeneous catalysis. It provides insights into the interfacial chemistry between the gas phase and the catalyst and sheds light on adsorbate-adsorbent interactions to characterize reaction intermediates on the catalyst surface [10, 47]. Spatial concentration and temperature profiles along the catalyst bed are determined with a profile reactor, while Iso-Potential *Operando* DRIFTS (IPO DRIFTS) measurements

provide the corresponding profiles of the surface adsorbates. The correlation of the obtained structure-activity information allows the distinction between reaction intermediates and spectator species that populate the catalyst surface under reaction conditions, thus providing a unique basis for the derivation of a plausible reaction mechanism.

2 Theoretical Background

2.1 Heterogeneous Catalysis

Heterogeneous catalysis is a chemical reaction process that takes place at an interface, typically between the gas phase of a reaction mixture and the surface of porous solid catalyst materials [1]. Catalysts lower the energy barrier that must be overcome for a thermodynamically feasible reaction, thereby enhancing the rate and selectivity of the reaction without changing the overall standard Gibbs free energy [48]. This allows reaction systems to be operated at lower temperatures and pressures that are technically achievable. Today's economy and modern lifestyle are based on the development and investigation of heterogeneous catalytic processes in the chemical, petrochemical, energy, pharmaceutical, and food industries, among others [9]. The driving force behind this has been and remains the need to provide chemical solutions for a developing society. A well-known example of catalytic heterogeneous processes is the Haber-Bosch ammonia synthesis. The first plant went into operation in 1913, but the reaction mechanism and functioning of the catalyst were not elucidated until 100 years later by Ertl [49, 50]. The Ostwald process, discovered at the same time, gained importance through industrial ammonia production, as it could be used for the selective oxidation to nitric acid using Pt–Rh catalysts. Ostwald's law of thermodynamics laid the fundamental principles for the definition of catalysis and contributed to the understanding of chemical equilibrium [50]. Another milestone in catalysis was the Sabatier principle, which created a conceptual framework for the theory of catalysis that became the basis of modern surface chemistry and the theory of the catalytic cycle. Sabatier proposed the idea of an unstable intermediate at an active site of catalyst surface atoms that is formed with at least one of the reactants and contributes to the formation of the product [51, 52]. From this, an overall process for heterogeneous catalytic reactions could be derived, which can be broken down into a sequence of seven steps [9, 53]:

1. Mass transfer (film diffusion) of reactant(s) from the bulk fluid to the external surface of the catalyst particle.
2. Diffusion (pore diffusion) of the reactant(s) from the pore opening through the catalyst pores.

3. Adsorption of the reactant(s) at an active site(s) of the internal catalytic surface.
4. Surface reaction of the reactant(s) to the product(s).
5. Desorption of the adsorbed species from the active site(s) of the catalyst surface.
6. Diffusion (pore diffusion) of the product(s) back to the pore opening on the external surface of the catalyst particle.
7. Mass transfer (film diffusion) of the product(s) from the external surface of the catalyst particle to the bulk fluid.

For a reaction to occur, the participating species must reach specific catalytically active sites or centers dispersed on the catalyst surface. Taylor [54] visualized these as unsaturated atoms at locations on solids that can arise on terraces, edges, kinks, and vacancies with different coordination numbers [1, 53]. The reactants are adsorbed at these active sites and activated by various electron transfer steps. The formation of strong chemical bonds leads to the formation of surface intermediates, which are, however, unstable enough to decompose and yield a product without consuming the catalyst. The final product formation occurs by desorption of the product molecules, which regenerates the free catalyst surface and allows new reactants to be adsorbed [50]. These reaction steps – adsorption, surface reaction and desorption (3. – 5.) – are the principle of catalytic action, which depend exponentially on the temperature and require sufficiently large activation energies compared to the diffusion processes of the other steps [9]. At high reaction temperatures, the activation energy is reached quickly, and the rate of the reaction steps increases relative to the diffusion steps (1. – 2., 6. – 7.). To maximize the reaction rate and product selectivity, it is essential to maximize the accessibility of the reactants to the active catalytic sites. At a diffusion rate much faster than the surface reaction rate, the concentration of potential reactant molecules at the internal catalyst surface within the pore structure is the same as in the bulk fluid, and diffusion does not affect the overall reaction rate. However, the slowest step determines the overall reaction rate of this mechanism. Assuming that the reaction steps are faster than the diffusion steps, the reactants primarily react on the external surface of the catalyst without taking advantage of the internal surface within the pore structures, resulting in low catalyst efficiency [53].

Catalysts are chemically and physically complex materials that are applied in a wide variety of compositions, structures and sizes in industry and can be categorized into three main groups: Bulk catalysts consisting only of an active component, coated catalysts consisting of catalytically active layers deposited on inert structured surfaces, and supported catalysts, in which the active material is deposited as nanoparticles on a support material. In particular, supported catalysts are used in many industrial processes because they offer a

large surface area on which the active components are finely dispersed. This increases the number of accessible and active catalytic sites and enhances the catalytic activity [50, 55]. Support materials are often porous materials and determine the surface chemistry for a given active phase in terms of physical, chemical and catalytic properties, e.g., dispersion, thermal stability, particle size, activity or selectivity [9]. Commonly used supports are ceramic-based oxides (Al_2O_3 , SiO_2), transition metal oxides (TiO_2 , ZrO_2), as well as multi-component oxides ($\text{CeO}_2\text{--ZrO}_2$, $\text{SiO}_2\text{--Al}_2\text{O}_3$ or zeolites). In most cases, the support material is inert and irrelevant to the reaction mechanism. However, supports such as alumina or silica impact the catalytic processes due to the active interaction between the support surface and the active phase. Since the active phases, typically transition metals (Ni, Ru, Fe, Co) and noble metals (Pt, Pd, Rh), tend to agglomerate on the surface of the support material, metal-support interactions stabilize the dispersed nanoparticles, e.g., through electronic transfers [55].

Catalytic gas-solid reactions predominantly take place in tubular fixed-bed reactors filled with the catalyst material, which is fixed in space and through which a gaseous reaction mixture flows [3]. For an optimal catalyst, various requirements must be met, i.e., a limited catalyst size to avoid pressure drops across the catalyst bed, a sufficient catalyst surface to ensure heat transfer for the reaction heat released during exothermic reactions, or an appropriate void volume of the bed to control mass transport. Since the requirements are in some cases contradictory, there is a wide variety of catalysts in different shapes and arrangements in the industry [4]. The most common are randomly packed pellet beds in a tubular reactor in various geometries such as spheres, cylinders, rings or different particle shapes of a certain sieve fraction. Shaped bodies such as monoliths with a defined structure are also used, for example, in automotive exhaust gas catalysis, where they are coated to form a structured catalyst bed [3].

Understanding the catalytic process is fundamental for the development and optimization of industrial catalysts and appropriate fixed-bed reactors, as well as for optimal process control. The mechanism of a catalytic cycle is the basis for deriving reaction kinetics and can be described by the surface chemistry of the catalyst – a sequence of elementary reaction steps including adsorption, surface diffusion, chemical transformations of adsorbed species and desorption [1]. To obtain the pure rate law of a catalytic reaction, kinetic measurements are carried out in small-scale kinetic test reactors in the laboratory, which offer precise but simplified mixing and reaction conditions compared to industrial reactors [3]. Steady-state

fixed-bed tubular reactors with plug flow behavior are typically used as laboratory test reactors for several reasons: The small amount of catalyst required, and the simple handling enables cost-effective and time-saving experiments. The plug flow behavior ensures ideal mixing of the fluid exclusively in the radial direction without axial dispersion and simplifies the mathematical modeling in the kinetic derivations. Catalysts and operating conditions in the tubular reactor can be easily adapted to provide isothermal operation, negligible pressure drop, and insignificant heat and mass transfer limitations [1]. Under these ideal conditions, automated high-throughput screening experiments in parallel fixed-bed reactors or channel reactors were developed to obtain detailed information on a large number of catalysts under a wide range of reaction conditions in a short time [56]. By varying process parameters, e.g., temperature, pressure and the inlet conditions of the gaseous reaction mixture in terms of flow rate and composition, the analytical quantification of the product phase at the outlet allows conclusions to be drawn about the catalyst activity and selectivity. With the aid of the obtained data, kinetics can be established using computational modeling.

2.2 The Way to Operando Catalyst Characterization

The interior of fixed-bed reactors is typically inaccessible for measurement purposes, allowing only the inlet and outlet of the reactor and the specified reaction conditions to be considered for kinetic measurements. Therefore, a kinetic measurement provides a single data point that offers a rough overview of the catalyst activity under given process conditions. Moreover, the chemical composition, temperature, and flow conditions vary considerably along the fixed-bed of industrial catalytic reactors (the pressure to a lesser extent). Consequently, the decision on which reaction conditions to investigate in laboratory test reactors rests with the experimenter. This turns classical kinetic measurements into a trial-and-error method. Consequently, the major drawback of fixed-bed reactors or industrial reactors in general is that they are treated like a black box, while the dynamic behavior of the catalysts under working conditions remains undetected [8]. To shed light on the interior of the reactor and to uncover the surface chemistry and structural changes of the catalyst, the development of new measurement concepts and tailor-made research reactors has attracted considerable attention in recent decades. Of particular note is the comprehensive overview by Morgan et al. [57], which summarizes the development of spatially resolved measurement techniques for characterizing heterogeneously catalyzed reactions. The following provides a brief overview, among other things.

To increase spatial resolution along the catalytic fixed bed during kinetic measurements, novel designs of laboratory reactors with physical probes, such as the "Zapfstellenreaktor", were introduced [3, 58]. Taps are installed at defined intervals along the reactor wall, through which gas samples can be fed to analytical devices for quantitative evaluation or in which thermocouples can be placed. The quantitative analyses of the gas composition and local temperature measurements provide a concentration and temperature profile along the fixed-bed, which, however, is of coarse resolution due to the small number of taps at discrete intervals. Another negative aspect of the tapping points is the gas extraction near the reactor wall, which may have a different composition than within the bed due to bypass flows caused by a higher void fraction near the wall, which is typical for packed beds [3]. A decisive advance was the development of minimally invasive, capillary-based sampling techniques that provide high-resolution concentration and temperature profiles along the axial direction through the catalyst bed. Spatially resolved profile measurements are defined as the analysis of relevant state variables (e.g., concentrations of chemical species, mass flows, gas temperatures, or pressure) as a function of the spatial coordinate within the catalyst bed. The approach was developed independently and in various forms by different groups [3, 57]. To name just a few examples, Partridge et al. [59] developed a tailored capillary-inlet mass spectrometer and demonstrated its application on a NO_x adsorber of automotive catalyst systems to extract emission gases in a minimally invasive manner and obtain temporally resolved concentration profiles. The technique has been further improved to obtain spatially and temporally resolved concentration and temperature profiles within a monolithic channel reactor during the CO oxidation reaction occurring in automotive catalytic converters [27]. Thin thermocouples and fused-silica capillaries connected to the spatially resolved capillary-inlet mass spectrometer (Spaci-MS) were axially inserted into different monolithic channels and moved during the reaction process using a stepper motor. Vogel et al. [26, 28] developed an optically accessible catalytic plate reactor that replicates the conditions within a single monolith channel and allows temperature profiles along the catalyst bed to be obtained using infrared (IR) thermography. At the same time, spatially resolved measurements of the gas composition were performed using a movable sampling capillary above the catalyst plate by analyzing the capillary effluent using MS and GC. The group of Schmidt and Horn et al. [24, 25] developed a customized fixed-bed tubular reactor with a single capillary-based sampling technique for gas samples from the center of the catalyst bed, which was connected to (MS or GC) for quantification. The reactor system was tested using the catalytic partial oxidation of methane and ethane on foam monoliths to obtain concentration and temperature profiles along the catalyst axis with high-resolution

in the sub-millimeter range. The measurements were compared with numerical simulations to investigate the reaction mechanism. At the start of the method development, a quartz capillary was inserted through a centrally drilled channel of the foam, with the open end used for sampling [24]. Additionally, a thermocouple was inserted and tip-aligned with the open end of the capillary to perform spatial temperature monitoring. The capillary holder was connected to a micrometer to enable axial movement of the capillary through the catalyst bed. During development, longer capillaries were used that were closed on one side and had side sampling orifices to avoid invasive disruption of the concentration, flow, and temperature fields at the sampling positions and to improve the movement of the capillary through the catalyst bed [25, 60]. By using capillaries with lengths exceeding the bed dimensions, mechanical problems such as blocking or breakage due to tilt or friction in the passage area of the catalyst bed could be effectively prevented. By integrating a stepper motor with an additional roto-translation stage, automated capillary movements in both axial and rotational directions with a μm -resolution became possible [33, 61–63]. Goguet et al. [29, 30, 64] developed a similar tubular reactor system using a single capillary-based sampling technique coupled with a Spaci-MS. The catalyst bed was moved relative to the sampling ports instead of moving the capillary. A disadvantage of this reactor design is that it relies on hot air blowers as a heating system, which limits the size of the catalyst bed to ensure a uniform reaction temperature across the catalyst bed. Overall, the examples of tailor-made profile reactors presented so far are limited in their application possibilities due to their complex and inflexible design. The working group of Horn has specialized in the development of intrareactor diagnostic techniques and founded the company Reacnostics GmbH, which brought a commercially available Compact Profile Reactor (CPR) to the market [32]. It was designed as a laboratory-scale tubular reactor with an integrated heating and cooling system, as well as a capillary-based sampling technique, enabling flexible and user-friendly integration into a wide variety of reaction systems [35–37, 65, 66]. The CPR enables the measurement of high-resolution, spatially resolved concentration and temperature profiles, forming the basis of this work.

As mentioned above, catalysts are subject to dynamic changes: structure, defect distributions, electronic properties, and active centers continuously adapt to the chemical potential of the surrounding reaction atmosphere, within the framework of complex structure-activity relationships [3]. However, profile reactors for performance analysis only capture one aspect of this complex system, since they generally do not account for the state of the catalyst and its surface chemistry. Initially, catalysis research was based on *ex situ*

characterization approaches, in which the catalysts were analyzed spectroscopically after the reaction or treatment, i.e., postmortem, and "off-site" the reactor [15]. These characterization techniques were limited in terms of their surface sensitivity, particularly regarding material and pressure gaps [18]. Further developments in various spectroscopic methods, such as optical spectroscopy, synchrotron-based technology, magnetic resonance technology, and electron microscopy, have closed these gaps and now enable detailed structural and chemical insights at the atomic scale through the investigation of catalysts in controlled environments [18]. This type of catalyst characterization, in which catalysts are examined "on-site" in a spectroscopic cell during a chemical reaction and changes are observed during their working process, is referred to as *in situ* [10, 11, 13]. Advances in specialized *in situ* reactor cell designs have contributed significantly to a more detailed investigation of structure–activity relationships. In adapted cells, activity and selectivity measurements could be performed under kinetically relevant operating conditions while simultaneously allowing spectroscopic characterization of the catalyst [13, 19, 20]. This type of measurement method is referred to as *operando* catalyst characterization. In recent years, research in the field of operando spectroscopy has increasingly focused on the investigation and characterization of the dynamics of heterogeneous catalytic reaction systems. For this reason, capillary-based sampling techniques are increasingly being integrated into tailored spectroscopic reactors and cells to perform spatially resolved *operando* measurements [7, 22, 67–69].

IR spectroscopy, the most commonly used spectroscopic method in heterogeneous catalysis research [47], is of particular interest for *operando* catalyst characterization [11, 16]. By investigating the surface chemistry and adsorption processes on the catalyst, adsorption centers or catalytically active sites, as well as adsorbate complexes and reaction intermediates, can be characterized [10, 70]. Transient methods already exist that combine *in situ* IR spectroscopy and quantitative *on line* analysis with techniques such as Steady-State Iso-Topic Transient Kinetic Analysis (SSITKA) [71, 72]. Nevertheless, the characterization of surface species and the interpretation of reaction intermediates remain challenging because they are short-lived and constitute only a small fraction compared to the spectroscopic signatures of the reactants and products [73]. DRIFTS is a widely used *operando* measurement method in the field of IR spectroscopy. There are numerous studies in which specially designed DRIFTS cells have been used to investigate catalytic processes under real reaction conditions [17, 71, 74].

2.3 Iso-Potential Operando Spectroscopy

The question arises why *operando* spectroscopy has so far only been used in academic research and is not also applied in industry, e.g., for the optimized process control of reactors or for industrial catalyst research under operating conditions. This can be explained by several challenges that need to be addressed. First of all, despite significant progress and the potential offered by *operando* catalyst characterization on a laboratory scale – for example, through the use of optical (IR, UV/Vis), X-ray-based (XAS, XRD), magnetic resonance-based (EPR, NMR) spectroscopy methods, or electron microscopy – as a basis for kinetic modeling, mathematical models for reactor and catalyst design continue to be based on idealized laboratory conditions that differ from the actual dynamic behavior of catalysts in industrial reactors [8]. The temperature, concentration, and flow gradients encountered during operation of a large-scale fixed-bed reactor vary too widely to be imaged in a series measurements in custom-built *operando* spectroscopy reactors. The experimenter must decide which reaction conditions to set in an *operando* experiment. Therefore, the postulated reaction mechanisms and kinetics are often only simplifications of the actual surface chemistry at the catalyst surface and merely represent the sequence of experimental situations or a snapshot under given process conditions. Even if spatially resolved measurement methods are used in some studies, either the catalyst activity or the catalyst properties are investigated in a spatially resolved manner, so that only one-sided addressing is achieved. Second, *operando* spectroscopic reactors are in many cases neither designed as perfect catalytic reactors nor as spectroscopic cells but represent a compromise between a mixture of both units [16, 18]. They may contain structural faults that can affect the accuracy of kinetic measurements due to undefined mixing patterns, dead volumes or bypass flows, and can influence high-quality recordings due to unheated optical windows where gas species can condense, or built-in components where reactants and products can react [14, 17, 21]. Third, and this is more of a technical than a fundamental challenge, catalytic fixed-bed reactors are not accessible to spectroscopic methods. Large-scale reactors, such as those used in industry up to several hundred cubic meters, are typically pressure vessels and made of steel, which makes them impermeable to electromagnetic radiation. They often contain hazardous chemicals at high temperatures and pressures, which makes optical access through some kind of window technically impossible.

Taking all of this into account, a technology is required that separates the functionalities of the "catalytic reactor" and the "spectroscopic cell" to obtain kinetically and spectroscopically well-defined measurements. The concept of **Iso-Potential Operando Spectroscopy (IPOS)**

combines spatially resolved fluid sampling and temperature measurements in a catalytic reactor with simultaneous operando spectroscopy measurements performed in a separate spectroscopic cell [38]. By using a catalytic reactor equipped with a spatially resolved sampling technique, a small fraction of the reaction mixture can be sampled locally from the interior of the fixed-bed and transferred continuously into a spectroscopic cell containing a small amount of the same catalyst as in the reactor. To ensure consistent measurement conditions, the chemical potential in the cell must be identical to the chemical potential at the local position in the reactor to be investigated. The concept of IPOS is based on the hypothesis that the state of the catalyst analyzed in the cell behaves identically to the catalyst locally in the reactor when exposed to the same chemical potential as in the reactor.

2.3.1 Chemical Potential

In a simple closed system with a constant chemical composition, the change of state can be expressed thermodynamically by Gibbs' fundamental equation [75]:

$$dG = -S dT + V dp \quad (2.1)$$

The term $-S dT$ covers the change in Gibbs free energy (G) as a result of temperature change, with entropy serving as a measure of the heat change in reversible processes. The term $V dp$, on the other hand, describes the influence of a change in pressure, which contributes to the change in free energy via volume work. In most chemical systems, however, a change in composition is to be expected. For example, chemical reactions can occur in a closed system but involve a change in the amount of substance of each species, or in an open system where the composition can vary due to species fluxes through the boundaries of the system [76]. A chemical system is therefore specified by the independent state variables temperature (T), pressure (p), and the composition variables of the various species ($n_1, \dots, n_i$) contained therein [77]. The total differential form of Gibbs free energy can express the change of state of a chemical system [76]:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p,n} dT + \left(\frac{\partial G}{\partial p} \right)_{T,n} dp + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j} dn_i \quad (2.2)$$

The first two partial derivatives can be taken from the Gibbs fundamental equation (Eq. (2.1)) for a closed simple system with constant composition ($dn_i = 0$) and stand for [76]:

$$\left(\frac{\partial G}{\partial T}\right)_{p, n_i} = -S \quad \left(\frac{\partial G}{\partial p}\right)_{T, n_i} = V \quad (2.3)$$

The last factor of Eq. (2.2) is the partial derivative of the Gibbs free energy with respect to the amount of substance (n) of each component i , keeping temperature (T), pressure (p) and the amount of substance of all other components ($n_{j \neq i}$) constant [76]. These partial derivatives were introduced by Gibbs in the 19th century and is known as the chemical potential. It represents one of the most important quantities in thermodynamics for describing chemical reactions and phase equilibria [78]. The chemical potential of component i is defined as:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_j} = \mu_i \quad (2.4)$$

The chemical potential is a partial molar quantity and corresponds to the partial molar Gibbs energy. It describes the change in the Gibbs free energy per mole of a given component i when only its amount of substance varies, while temperature, pressure and amounts of substance of the other components remain constant [77]. The chemical potential thus represents the contribution of this component to the total energy of a multicomponent system, for example, in a gas mixture, and is a measure of the chemical stability or the quantification of the reactivity of the component at a specific spatial location [79].

Combining the expressions of the partial derivatives (cf. eqs. (2.3) and (2.4)), infinitesimal changes in Gibbs energy for an open multicomponent chemical system can be written in the extended differential form:

$$dG = -S dT + V dp + \sum_i (\mu_i dn_i) \quad (2.5)$$

Using the differential form of Gibbs free energy, infinitesimal changes in entropy, volume, and composition can be analyzed at constant temperature, pressure, and chemical potential. In the thermodynamic analysis of chemical reactions, equilibrium is determined by assuming infinitesimal changes of state at constant temperature and constant pressure. These assumptions simplify the mathematical expression and form the basis for the equilibrium state in chemical reaction systems, which is discussed in more detail in Section 2.6.3.

A change in the chemical potential acts as a driving force for a process occurring at

a location with constant temperature, pressure, and (local) composition if a spatial gradient of chemical potential exists. During a chemical reaction, the concentrations of individual components may change, while the total amount of each elemental species remains constant [79]. In an ideal gas mixture, the chemical potential of each component is independent of the others. To determine the influence of a single component on the total Gibbs free energy, each species in an ideal gas mixture can be described by its standard state molar Gibbs free energy, supplemented by a pressure-dependent term accounting for the work associated with volume change [75, 80]:

$$\mu_i = \mu_i^\ominus + RT \ln \left(\frac{p_i}{p^\ominus} \right) \quad (2.6)$$

Where $\mu_i^\ominus$ is the chemical potential of substance i in the standard state at typically 1 bar and 298.15 K and p_i is the partial pressure of substance i . The standard state of a real gas is a hypothetical state in which the gas behaves ideally at pressure $p^\ominus$. More generally, the chemical potential of the pure substance i in the standard state depends on a known temperature and pressure ($\mu_i^*(T, p)$):

$$\mu_i(T, p, x) = \mu_i^*(T, p) + RT \ln(x_i) \quad (2.7)$$

The mole fraction of substance i in an ideal solution is determined by applying Raoult's law ($x_i = p_i/p$) [80]. When extending the concept of the chemical potential to a multicomponent system with n -components, the chemical potential of each component i becomes a function of the system's composition [79]:

$$\mu(T, p, x_i) = \sum_{i=1}^n x_i \mu_i(T, p, x_i) \quad (2.8)$$

However, when applying the principle of chemical potential to a heterogeneous catalytic system, the chemical potential is determined not only by the pressure, temperature, and composition of the reaction mixture at the inlet of a fixed-bed reactor. It is also influenced by gradients within the reactor [8]: By the progress of the reaction and its conversion, by the material transport to the catalyst particles and through the pores, and by the distribution of the active sites on the surface. The energy transport has a similar effect on the chemical potential. In summary, the dynamic change of a catalyst in response to the local chemical potential of the reactants in the reactor is a central aspect in the description of reaction systems in heterogeneous catalysis. Therefore, the chemical potential is the basis for the setup of the iso-potential coupling method of the IPOS concept.

2.3.2 Setup of Iso-Potential Coupling

In the present work, the concept of IPOS is presented and demonstrated using the spectroscopic method DRIFTS. Figure 2.1 shows the general setup to perform Iso-Potential Operando DRIFTS (IPO DRIFTS) measurements. The catalytic fixed-bed reactor is equipped

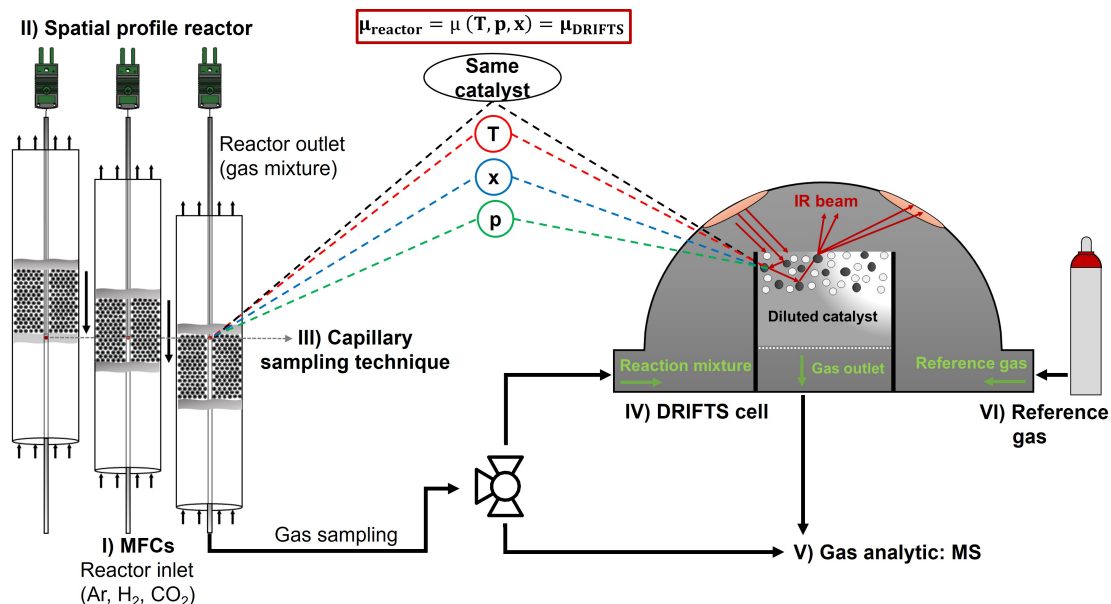


Fig. 2.1: Schematic overview of the IPO DRIFTS measurement technique: (I) Gas dosing system - set of Mass Flow Controllers (MFCs); (II) Spatial profile reactor - Compact profile Reactor (CPR); (III) Working principle of the spatially resolved capillary sampling technique; (IV) IR spectroscopy - DRIFTS cell; (V) Gas analytic - Mass Spectrometer (MS); (VI) Reference gas connection to the DRIFTS cell. Adopted and modified from [81]

with a capillary sampling technique (spatial profile reactor). A capillary is passed through the catalyst bed, allowing gas to be sampled through an orifice. A temperature measuring probe, for example, using a thermocouple or a pyrometer, can be inserted into the capillary to additionally record the temperature of the gas phase or the catalyst surface through an orifice. By changing the position of the capillary and thus the sampling orifice, a small portion of the reaction mixture is continuously removed along the fixed-bed and guided into a commercially available DRIFTS cell by connecting its inlet to the outlet of the sampling capillary. In the cell, the reaction mixture flows through a sample crucible filled with a small amount of the **same catalyst** that is used in the profile reactor. As soon as the reaction mixture sampled locally in the reactor leaves the reaction system through the orifice of the capillary and is separated from the catalyst, all catalytic reactions should be interrupted in order not to change the mole fractions of the species present in the gas

mixture, indicated by the vector (x). This also applies to the composition of the reaction mixture in the spectroscopic cell itself. To avoid significant changes in the composition of the reaction mixture in the cell due to additional reactions on the catalyst sample being analyzed, the contact time of the flowing gas mixture must be kept as short as possible. Expressed by the gas hourly space velocity (GHSV), the contact time of the reaction mixture with the catalyst sample in the DRIFTS cell should be several orders of magnitude higher than the corresponding value in the catalytic reactor to minimize additional conversion. Quantitative analyses using a mass spectrometer or gas chromatograph, connected both after the cell and the profile reactor, enable the investigation of differences in gas composition in addition to the study of structure–activity relationships. Transporting the gas mixture from the reactor through the capillary into the cell is associated with a pressure difference. The transfer system must be designed in such a way that the pressure drop through the connecting line is as small as possible to ensure a pressure in the cell (p) that is basically the same as the local pressure in the reactor. Finally, the catalyst sample in the spectroscopic cell is heated to the same temperature (T) that is measured locally at the sampling position in the reactor to mirror the same temperature profile along the fixed bed.

By exposing the catalyst in the DRIFTS cell to the reaction mixture with the same composition (x), temperature (T) and pressure (p) as was sampled and measured locally in the profile reactor, the same local chemical potential (iso-potential, $\mu_{\text{reactor}} = \mu_{\text{DRIFTS}}$) is transferred from the sampling position in the fixed-bed of the profile reactor to the same catalyst in the DRIFTS cell. The concept of IPO DRIFTS is based on the hypothesis that the catalyst in the spectroscopic cell adopts the same structure and surface adsorbates and exhibits the same reactivity when exposed to the same chemical potential as the catalyst locally in the reactor, according to Eq. (2.8). Consequently, the catalyst in the DRIFTS cell changes in the same dynamic manner as the catalyst locally in the reactor when the orifice of the sampling capillary is moved from the inlet to the outlet across the fixed-bed of the profile reactor, in response to the same sequence of chemical potentials. This allows a spectroscopic profile (IPOS profile) to be recorded that reflects the dynamic changes of the catalyst and the reaction process in the reactor. The movement of the sampling orifice from the inlet to the outlet of the fixed-bed is essential to observe the same chemical history on the catalyst in the spectroscopic cell as in the reactor. A reversed direction of movement could, for example, cause unforeseen irreversible changes in the catalyst structure or the surface adsorbates in the wrong chronological order. To observe irreversible processes, such as poisoning, fouling, sintering, solid-state processes, etc., on the catalyst in the

spectroscopic cell, sufficient measurement time must be planned at each spatial reactor coordinate until a possible change of state, as in the reactor, has occurred. The use of IPO DRIFTS profile measurements provides adsorbate profiles that offer a way to distinguish between reaction intermediates and spectator species by correlating them with the progress of reaction (structure–activity relationship). The concept is theoretically applicable to other spectroscopic, microscopic, or imaging methods where the cell can be adapted to the process conditions of the reactor.

2.4 IR Spectroscopy

IR spectroscopy allows the monitoring of vibrational and rotational modes of adsorbed and gaseous molecules, molecules in lattices (solids) or chemical bonds by perturbing them with electromagnetic light in the infrared range ($10 - 10000\text{ cm}^{-1}$). The interaction of IR light with matter is generally divided into three energy categories that cause molecular rotations or lattice vibrations in the far infrared (FIR) spectral range ($10 - 200\text{ cm}^{-1}$), molecular vibrations in the mid-infrared (MIR) spectral range ($200 - 4000\text{ cm}^{-1}$) and their overtones in the near infrared (NIR) spectral range ($4000 - 12500\text{ cm}^{-1}$) [82, 83]. The focus of surface analysis in heterogeneous catalysis is on vibrational spectroscopy of adsorbates in the MIR (or IR) range, with a typical absorption spectrum between $400 - 4000\text{ cm}^{-1}$ [84]. A brief overview is given below.

2.4.1 Fundamentals of IR Spectroscopy

Molecules can transition from the vibrational ground state (E_0) to excited vibrational energy states ($E_1, E_2, \dots$) by absorbing a quantum of energy from interacting IR radiation. The fundamental vibration of molecules corresponds to the transition from the vibrational quantum number $\nu = 0 \rightarrow 1$, which is mainly found in the MIR spectrum. Transitions to quantum numbers $\nu = 2, 3, \dots$ through overtones or combination modes occur at higher wavenumbers, a multiple of the fundamental frequency. The electromagnetic field of IR radiation exerts a force (excitation energy) on the charge centers of the molecule, causing the molecule's electromagnetic field to oscillate. For example, the excitation of a vibrational mode between two bonded atoms leads to periodic motion of the atomic nuclei around their center of mass, which changes the bond length or angle. A transition to a quantized discrete vibrational energy level only occurs if the frequency (ν) of the incident IR radiation exactly corresponds to the energy difference (ΔE_ν) between two quantized vibrational states of a molecule (e.g.

$E_{v=0} \rightarrow E_{v=1}$), according to Planck's (h) relation [85–87]:

$$\Delta E = E_{v+1} - E_v = h\nu = h \frac{c}{\lambda} = \tilde{\nu} h c \quad \text{with } \nu = \frac{c}{\lambda}, \tilde{\nu} = \frac{1}{\lambda} \quad (2.9)$$

Instead of the frequency of absorption (ν), the wavenumber ($[\tilde{\nu}] = \text{cm}^{-1}$) is commonly used in spectroscopy.

A nonlinear polyatomic molecule with N atomic nuclei has a total of $f = 3N$ degrees of freedom of motion, consisting of translational ($f_{\text{trans}} = 3$), rotational ($f_{\text{rot}} = 3$) and vibrational ($f_{\text{vib}} = 3N - f_{\text{trans}} - f_{\text{rot}} = 3N - 6$) degrees of freedom [87, 88]. As an example, the molecule of methane is used, which has nine degrees of vibrational freedom ($f_{\text{vib}} = 3 \cdot 5 - 6$) due to its five atoms ($N = 5$) and non-linear geometry. In contrast, linear polyatomic molecules exhibit one rotational degree of freedom less and therefore only have $3N - 5$ vibrational degrees of freedom. The vibrational degrees of freedom of a molecule indicate how many independent types of normal vibrations it can perform. In a normal vibration, the atoms involved move at the same specific frequency and in a fixed phase relative to each other. Depending on the type of vibrational movement, a distinction is generally made between symmetric (ν_s) and asymmetric (ν_{as}) stretching vibrations, which are accompanied by a change in bond lengths, and deformation vibrations (δ), in which the bond angles change [85]. The different vibration modes of molecules can show the same frequency despite different spatial coordinates of the atoms if they are equivalent due to symmetry. Vibrations of the same frequency are degenerate, and the number of vibrations of the same frequency indicates the degree of degeneracy [86]. Although methane has nine vibrational degrees of freedom, the tetrahedral symmetry properties of the molecule result in only four fundamental normal vibrations, called C–H vibrations [89]: a non-degenerate symmetric stretching vibration ($\nu_s(\text{C–H})$), a triply degenerate asymmetric stretching vibration ($\nu_{\text{as}}(\text{C–H})$), a doubly degenerate symmetric deformation vibration ($\delta_s(\text{C–H})$, scissoring), and a triply degenerate asymmetric deformation vibration ($\delta_{\text{as}}(\text{C–H})$, bending). However, not all normal vibrations of methane can be detected by IR spectroscopy. The selection rule for IR activity states that a spectroscopically observable transition to an excited vibrational energy state (typically with $\Delta v = \pm 1$) only occurs if the molecular vibration is accompanied by a periodic change in the electric dipole moment. Consequently, only the asymmetric stretching vibration and the asymmetric deformation vibration of methane are IR-active.

Each normal mode of vibration excited by IR radiation leads to a characteristic vibrational band in the IR spectrum. The mathematical model of a harmonic or anharmonic oscillator can be used to predict the position of IR bands theoretically. Conversely, the

vibrational frequencies of bands measured in the IR spectrum allow the vibrational energy to be estimated and thus provide information about the strength and type of chemical bond that is characteristic of the respective molecular structure and property. As an example, the vibrational energy of a diatomic molecule can be described using the model of a one-dimensional harmonic oscillator. It is assumed that the force acting between the atoms is proportional to the deflection and obeys Hooke's law like a mechanical spring, while the energy is quantized according to the Schrödinger equation [85, 87, 88]:

$$E_{\text{vib}} = \frac{E_v}{h c} = \tilde{\nu} \left(v + \frac{1}{2} \right) \quad \text{with } \tilde{\nu} = \frac{1}{2 \pi c} \sqrt{\frac{k}{\mu}} \quad (2.10)$$

where k is the force constant of the bond, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of a diatomic system and $\tilde{\nu}$ is the vibration wavenumber (also called vibration or vibrational frequency). For vibrational transitions in the harmonic oscillator, the selection rule $\Delta v = \pm 1$ applies to the vibration quantum number. This results in equidistant vibrational energy levels with a constant energy distance that corresponds to the wavenumber of the fundamental vibrational frequency (ν_0):

$$\begin{aligned} \Delta E_{\text{vib}} &= \frac{E_{v+1}}{h c} - \frac{E_v}{h c} \\ &= \tilde{\nu} \left((v+1) + \frac{1}{2} \right) - \tilde{\nu} \left(v + \frac{1}{2} \right) \\ &= \tilde{\nu}_0 \end{aligned} \quad (2.11)$$

I.e., in the IR spectrum, an absorption band is formed at the wavenumber of the fundamental vibration ($\tilde{\nu}_0$), which corresponds to the transition from the vibrational ground state ($v = 0$) to the first excited state ($v = 1$). The harmonic oscillator provides a good approximation for this type of transition [88]. By applying the harmonic oscillator model to methane, the wavenumber of the asymmetric stretching vibration, with a force constant of approximately 500 N m^{-1} and a reduced mass of about 0.923 amu , can be estimated to 3020 cm^{-1} [90], which is very close to the real band position of 3019 cm^{-1} [89]. Since the harmonic oscillator only considers diatomic bonds, the simple model cannot be applied to estimate the IR-active deformation vibration of methane, in which several atoms vibrate simultaneously.

In the harmonic oscillator model, the attractive force between the atoms increases indefinitely with increasing deflection, so that no dissociation is possible in this model [85]. In reality, the energy difference between neighboring vibration levels gradually decreases as the vibration level increases until the dissociation energy is finally reached. If the dissociation energy is exceeded, the vibrational energy is sufficient to overcome the elastic atomic bond, causing it

to break and the atoms to dissociate. To predict not only the fundamental vibrational bands of diatomic molecules, but also of complex molecules and their overtones and combination bands in the IR spectrum, the mathematical model of an anharmonic oscillator is used, whose selection rule includes transitions of $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ [91]. For a more realistic calculation of molecular vibrational frequencies, anharmonic models are used in quantum mechanical methods such as density functional theory (DFT) or post-Hartree-Fock methods [88]. They enable a more precise assignment of spectral bands of complex molecules, for example, the asymmetric deformation vibration of methane at a vibration frequency of 1306 cm^{-1} [89].

The absorbed energy of an incident IR radiation can also be distributed among quantized rotational energy states (E_J), resulting in a rotation of the molecule that can be described quantum-mechanically [92]. For the simplest case of a rotor, a rigid diatomic molecule, Schrödinger's equation applies [93]:

$$E_{\text{rot}} = \frac{E_J}{h c} = B J (J + 1) \quad \text{with } B = \frac{h}{8 \pi^2 c I} \quad (2.12)$$

where B is the rotational constant, $I = \mu r_0^2$ is the moment of inertia, defined by the bond length r_0 in equilibrium, and $J = 0, 1, 2, \dots$ is the rotational quantum number. Similar to the vibrational quantum number, a change in the rotational quantum number of a rotor is determined by the selection rule $\Delta J = \pm 1$, resulting in a quadratic increase in energy levels as the rotational quantum number increases, while the energy distances increase linearly – starting at $2B$ and rising by $2B$ each time [91]:

$$\begin{aligned} \Delta J = +1 : \quad \Delta E_{\text{rot}} &= \frac{E_{J+1}}{h c} - \frac{E_J}{h c} \\ &= B (J + 1) [(J + 1) + 1] - B J (J + 1) = 2 B (J + 1) \end{aligned} \quad (2.13)$$

$$\begin{aligned} \Delta J = -1 : \quad \Delta E_{\text{rot}} &= \frac{E_{J-1}}{h c} - \frac{E_J}{h c} \\ &= B (J - 1) [(J - 1) + 1] - B J (J + 1) = -2 B J \end{aligned} \quad (2.14)$$

Eq. (2.13) shows that the smallest possible angular momentum occurs through a transition from the ground state $J = 0$ to the state $J = +1$ with an energy of $2B \text{ (cm}^{-1}\text{)}$, which leads to an absorption band at this wavenumber in the IR spectrum – under the condition that the molecule has a permanent dipole moment [93]. Consequently, a quantized increase in rotational energy leads to an absorption spectrum containing bands at distances of $2B, 4B, 6B, \dots \text{ cm}^{-1}$, which are typically between $1 - 10 \text{ cm}^{-1}$ [75, 92]. Real (non-rigid)

diatomic or more complex molecules deviate from the idealized rigid rotor due to their inherent elastic chemical bonds. As a result of the centrifugal force, the bond length increases with increasing rotation, which reduces the rotational constant and causes the energy distances between the rotation levels to increase more slowly than in the idealized case [85]. A detailed explanation of non-rigid rotors is beyond the scope of this work and the reader is referred to the relevant literature [75, 91, 93, 94].

Vibrational transitions of free molecules (i.e., in the gas phase) are always coupled with rotational transitions [88]. If a vibrational transition is excited ($\Delta v = +1$), rotational transitions with $\Delta J = +1$ (R-branch) and $\Delta J = -1$ (P-branch) occur simultaneously. Therefore, the rovibrational spectrum (combined vibration-rotation spectrum) of small molecules shows a rotational fine structure, as transitions between quantized rotational levels divide the vibrational band into characteristic rotational lines [86]. For larger molecules, however, the individual rotational transitions are so close together that the fine structure can no longer be resolved spectrally.

The simplest model for rovibration is a harmonically vibrating rigid rotor, where vibration and rotation are considered independent and the total energy transfer is the sum of both [95]:

$$E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}} = \tilde{\nu} \left(v + \frac{1}{2} \right) + B J (J + 1) \quad (2.15)$$

A vibrational transition from the vibrational quantum number $v = 0 \rightarrow 1$ leads to a splitting in the IR spectrum in the form of two branches due to the coupling with rotational transitions: the P branch (cf. Eq. (2.14)) with characteristic absorption bands below the band center around the fundamental vibrational wavenumber ($\tilde{\nu}_0$), and the R branch (cf. Eq. (2.13)) with bands above it [93]:

$$\begin{aligned} \text{P branch:} \quad \Delta E_{\text{total}}(J = -1) &= \tilde{\nu}_0 - 2 B J \\ \text{R branch:} \quad \Delta E_{\text{total}}(J = +1) &= \tilde{\nu}_0 + 2 B (J + 1) \end{aligned} \quad (2.16)$$

A simple diatomic molecule such as CO has only two rotational axis and one vibrational degree of freedom, corresponding to an IR-active bond-stretching vibration along the molecular axis. This vibration induces a change in the electric dipole moment and gives rise to a characteristic rovibrational absorption band at a wavenumber of 2143 cm^{-1} , featuring well-resolved rotational fine structure in the form of P and R branches [92]. Due to the selection rule $\Delta J = 0$ being forbidden, a gap appears at the band center, where the Q

branch would otherwise occur. In linear, polyatomic molecules, however, this fine structure is usually no longer resolvable because the larger moment of inertia leads to a smaller rotation constant. Nonlinear, polyatomic molecules exhibit a significantly more complex

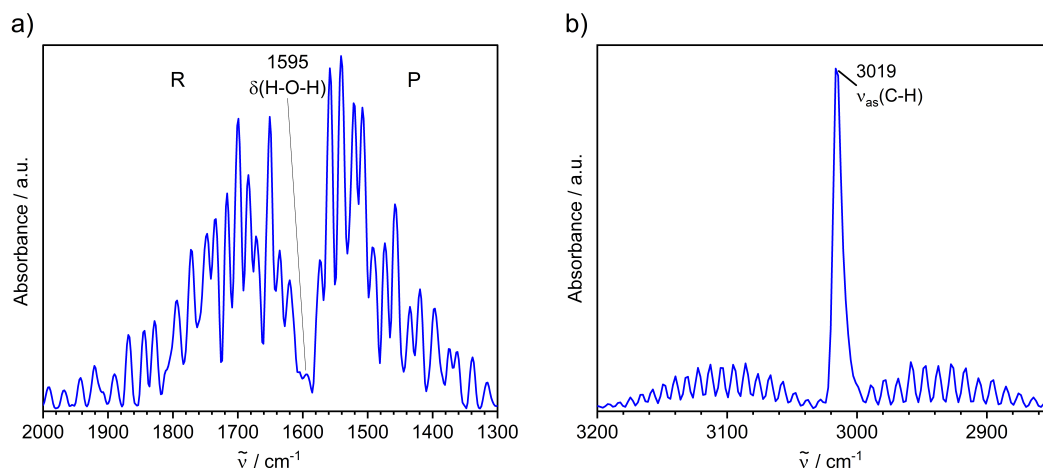


Fig. 2.2: (a) The characteristic IR absorption band of the symmetric bending vibration of water vapor ($\delta(\text{H-O-H})$) at 1595 cm^{-1} , exhibiting characteristic rovibrational fine structure with distinct P and R branches. (b) The IR absorption band of the asymmetric stretching vibration of methane at 3019 cm^{-1} , exhibiting quasi-rovibrational fine structure due to rotation–vibration coupling.

rovibrational spectrum, which is primarily determined by their molecular symmetry [85]. For instance, a simple nonlinear molecule such as water also displays the characteristic P and R branches in the IR spectrum of water vapor. However, due to its asymmetric geometry, the rotational fine structure is irregular and non-equidistant [86]. For illustration purposes, the rovibrational band associated with the symmetric bending vibration of water vapor ($\delta(\text{H-O-H})$) in the IR spectrum is shown in Figure 2.2a. For comparison, the asymmetric stretching vibration of methane ($\nu_{\text{as}}(\text{C-H})$) is given in Figure 2.2b. CH_4 is spherically symmetric, possessing three equal moments of inertia and no permanent electric dipole moment. As a result, pure rotational transitions are not observable in its IR spectrum [94]. Nevertheless, a quasi-rovibrational fine structure appears, which arises from the coupling between rotational and vibrational motions and the associated frequency shifts [92]. In adsorbed molecules, rotational motion is strongly hindered due to the bond to the surface. As a result, no rotational fine structure is observed in the IR spectrum. Instead, one or more broad vibrational bands appear, depending on the specific adsorption geometry (e.g., linear, bridged). A theoretical discussion of these effects is provided in Section 2.5.4.

2.4.2 Diffuse Reflection Spectroscopy

In analytical research using IR spectroscopy, infrared radiation is directed onto a sample. The incident light, with an initial intensity I_0 , undergoes several interactions with the sample: a portion is reflected as specular reflection (I_R) at the sample surface, scattered within the sample due to diffuse reflection (I_S), or absorbed by the sample (I_A), while the remaining portion is transmitted through the sample (I_T) [83]. These interactions form the basis of infrared spectroscopic analysis. Although the absorbed fraction contains molecular information in the form of characteristic vibrational energy transitions, it cannot be measured directly. Instead, the adsorbed radiation must be inferred from the difference between I_0 and one of the other measurable intensities, assuming that the remaining contributions are negligible or have been corrected accordingly. Diffuse reflection spectroscopy is a specialized technique within IR spectroscopy that analyzes the diffusely scattered radiation from a sample, as illustrated in Figure 2.3. It is particularly well-suited for inhomogeneous

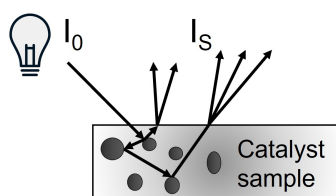


Fig. 2.3: Illustration of the diffuse reflection of IR radiation from a catalyst surface, which interacts with the radiation and scatters it in multiple directions.

powders or opaque materials with minimum sample preparation [47]. Since diffuse reflection spectra are governed by absorption within the diffusely scattering medium, they exhibit absorption-like band profiles similar to those seen in transmission spectra [86]. In transmission spectroscopy, the loss of transmitted intensity (I_T) by homogeneous samples due to absorption processes is described by the Beer-Lambert-Bouguer law and expressed as transmittance (T) [88]:

$$T = \frac{I}{I_0} = 10^{-\epsilon c l} \quad (2.17)$$

where I is the intensity of the beam after it has passed the sample and reached the detector, I_0 is the initial intensity of the beam incident on the sample, measured by the reference spectrum, ϵ is the decadic extinction coefficient, which describes how strongly a homogeneous sample absorbs light at a specific wavelength, c is the concentration of the absorbing species, and l is the optical path length through the sample. By applying a

logarithmic transformation, the absorbance (A) is obtained, which varies linearly with the concentration of the absorbing species [88]:

$$A = -\log(T) = \log\left(\frac{I_0}{I}\right) = \epsilon c l \quad (2.18)$$

This mathematical relationship between spectral response and analyte concentration enables the quantitative determination of molecular species in spectroscopic analysis. Similar to transmission spectra, diffuse reflectance spectra require a transformation into a form in which the reflectance $R(\tilde{\nu})$ is expressed as a quantity that correlates linearly with the concentration of the absorbing species [86]. Absorption and scattering phenomena in diffusely reflecting systems can be described using theoretical models such as the Schuster approximation (1905) or the generalized Kubelka-Munk theory (1931) [96]. The Schuster model describes the proportion of incident light that is reflected by the uppermost layers of a sample, which are theoretically assumed to be infinitely thin, flat, and parallel. However, this approximation is limited by the fact that back reflections are considered angle-independent, which leads to lower accuracy for real, diffusely scattering materials, especially when compared to more advanced models. The Kubelka-Munk approach offers a more comprehensive description of scattering by accounting for angular dependence and varying optical paths within a layer [96]. It applies to an optically infinitely thick, opaque layer – a condition that, in practice, can be achieved using fine powders at a sample thickness of just a few millimeters [97]. Under this assumption, the Kubelka-Munk function is defined as:

$$F[R_\infty(\tilde{\nu})] = \frac{(1 - R_\infty)^2}{2 R_\infty} = \frac{k}{s} \quad (2.19)$$

where $R_\infty(\tilde{\nu})$ denotes the fraction of incident light that is diffusely reflected from an optically infinitely thick sample layer, and k and s represent the absorption and scattering coefficients, respectively. Another common approach in the analysis of diffuse reflection spectra is to convert the reflectance $R(\tilde{\nu})$ to a pseudo-absorbance, typically using $\log(1/R)$ [70, 98–100].

To generate an absorption spectrum of scattering powders, a Fourier Transform Infrared (FTIR) spectrometer equipped with a diffuse reflectance accessory, known as a DRIFTS (diffuse reflectance infrared Fourier-transform spectroscopy) cell, is used. In the spectrometer, broadband infrared radiation is emitted by a thermal source and directed through a Michelson interferometer, where the beam is split into two optical paths of different lengths by a fixed and a moving mirror [88]. Upon recombination, the two beams interfere periodically and encode all infrared frequencies into a composite signal called an interferogram, which

varies depending on the optical path difference [87]. This beam then enters the DRIFTS cell, where the powdered sample diffusely scatters the incident radiation. Large ellipsoidal mirrors collect the scattered infrared light and focus it onto a detector optimized for the mid-infrared region [86]. The recorded interferogram is mathematically transformed into a single-beam spectrum via Fourier transformation. To obtain a conventional absorption spectrum (intensity or absorbance versus wavenumber), this spectrum is compared with a reference spectrum recorded under identical conditions without a sample, but using a reference material/'white standard' [88].

2.5 Adsorption on Solid Surfaces

Modern science assumes that catalytic reactions occur on the surface of the catalyst and therefore refers to a surface reaction, which is a sequence of elementary steps that together form a cyclic process. The process involves mass transfer of the reactants from the bulk fluid to the outer catalyst surface, followed by diffusion into the catalyst pores, the surface reaction and back diffusion of the products in the same way. Supposing that the overall reaction rate is not affected by diffusion limitations during these steps, it depends mainly on the surface reaction. This includes the adsorption of the reactant molecules onto the catalyst surface to form intermediates, the reaction itself, and the desorption of products, restoring an unaltered catalyst surface [50, 101]. Consequently, the adsorption process, as the first step of a surface reaction, is the critical step for the progress of the overall reaction [102]. Adsorption generally involves the attachment of molecules (adsorbates) from the surrounding gas atmosphere to the solid surface (adsorbent) of a catalyst. Catalytic adsorption and the related surface reaction are complex topics and differ by the chemical and physical properties of the metal surface on which they take place. In catalysis, these can be conductive (transition metals, e.g. Ni, Pt), insulating (e.g. Al_2O_3 , SiO_2) or semiconductive (e.g. NiO , MnO_2). Since typical industrial catalysts consist of a variety of components such as pure metals, metal oxides, or metal sulfides [1], adsorption and the effects on the vibrational properties of adsorbates will be explained below mainly in terms of transition metals for simplicity.

2.5.1 Historical Overview

In 1913, Sabatier theorized that the reaction molecules in a heterogeneously catalyzed reaction form unstable complexes as intermediates with the catalyst surface, which are stable enough to be formed in sufficient quantities, but at the same time unstable enough to

decompose and yield the product [1, 103]. Under optimal conditions, this process determines the selectivity and reaction rate of catalysis. Sabatier's proposal that catalytic reactions take place at the catalyst surface was not widely accepted until the mid-1920s, after the Langmuir isotherms for quantifying gas adsorption on surfaces (1915), Taylor's concept of active sites on a catalyst surface (1925), and the Langmuir-Hinshelwood formalism for describing reaction kinetics (1927) became popular. With the development of infrared spectroscopy in the 1950s and other following characterization techniques of surface species, the key role of the catalyst in stabilizing intermediates through adsorbate-surface bonds was linked to the structure and composition of the catalysts [102, 104]. When a molecule approaches a catalyst surface, it can be attracted to the adsorbent as an adsorbate and adsorbs without direct binding (physisorption) or forms a chemical bond (chemisorption) by overcoming the potential energy barrier.

2.5.2 Physisorption

Taylor classified adsorption according to their heats of adsorption and activation energies into reversible and irreversible processes with small ($< 40 \text{ kJ mol}^{-1}$) and large quantities ($> 40 \text{ kJ mol}^{-1}$), respectively [105, 106]. However, since weak chemical interactions also exist, adsorption must be distinguished according to both the type and energy of binding of the adsorbate to the adsorbent [107]. When a molecule approaches and collides with the catalyst surface, this can result in a loss of kinetic energy. If the energy exchange with the surface is high enough that the molecule does not leave the surface directly, a weak physical interaction comparable to molecular van der Waals forces can occur at a distance of a few angstroms ($3 - 4 \text{ \AA}$) [104, 108]. Van der Waals forces are attributed to polarization forces. When a molecule with a permanent, induced or transient dipole moment approaches the surface [109], the conduction band electrons of catalytic metal surface atoms rearrange to form an image dipole that reflects the original dipole of the approaching molecule [102]. The oppositely charged poles of the molecule and the polarized atoms of the catalyst surface result in a weak attractive potential without chemical bonding or significant change in the electronic structure of the adsorbate and adsorbent. Since the physisorption process has low adsorption energies and is independent of the adsorbent surface, it occurs between all adsorbates and adsorbents [104]. If the adsorbed molecule approaches too close to the surface atoms due to the attraction of van der Waals forces, their electron shells repel each other due to Pauli repulsion [107]. The Pauli principle states that no electrons (fermions) may be in the same energy state, i.e., not coincide in quantum numbers or states. These attractive and repulsive interactions determine the potential energy of the molecule

and can be described by the Lennard-Jones potential [110, 111]. For clarity, the Van der Waals interaction is shown in a simplified energy diagram in Figure 2.4 as a function of distance from the adsorbent surface. The sum of the attraction and repulsion is the total

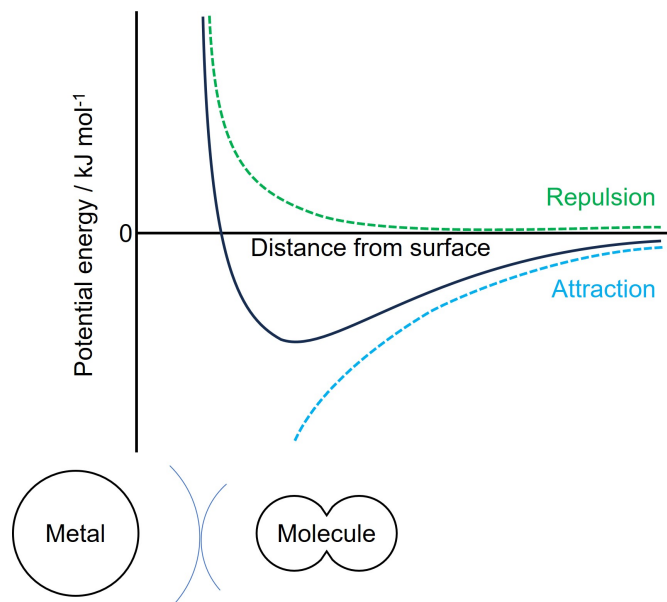


Fig. 2.4: Simplified one-dimensional potential energy diagram for physisorption of a molecule at a catalyst surface, showing the attractive van der Waals force and the repulsive force due to Pauli repulsion [111].

potential energy given as a solid line. At a greater distance (towards infinity) from the surface, the molecule is not attracted and has zero potential energy. The attractive force corresponds to a negative potential energy, indicated as a blue dotted line, and increases as the molecule approaches the surface. Before the electron shells of the molecule and the surface atoms begin to overlap, the Pauli repulsion, shown as a green dotted line, counteracts further convergence. If, for example, a molecule with filled valence bands, such as that of a noble gas, approaches the occupied orbitals of metal surface atoms, charge transfer by electrons is hindered. This results in a strong repulsive interaction with the molecular orbital, which partially compensates for the van der Waals attraction. At the minimum of the total potential energy, the equilibrium position of the adsorbate to the adsorbent is reached and reflects the weak physisorption energy. This molecular state is also considered as associative molecular adsorption, which locally approaches an empty surface site [52, 109].

The van der Waals forces can also extend to molecules above the nearest molecular layer to the surface, causing molecules to interact with sites already occupied. The weak

hold of the physisorbed state enables the diffusion of these molecules over the surface till they are locally adsorbed to an empty surface site. Since there is no activation energy barrier for the physisorption process, the molecule can be easily desorbed back into the gas phase after a sticking time if it still has sufficient kinetic energy perpendicular to the surface. Due to the weak bond to the surface, physisorbed molecules largely retain their spectroscopic properties from the gas phase. The degree of coverage, temperature and gas pressure can affect the sticking time of the adsorbed gas molecule. As a result of the weak bond to the surface, physisorption mainly occurs at low temperatures close to or below the boiling point of the gas atmosphere. Once the approaching molecule rearranges its electronic configuration and overcomes an activation energy barrier, the physisorption state can be a precursor to chemical adsorption, attracting the molecule more tightly to the surface [104, 106].

2.5.3 Chemisorption

The rearrangement in the electronic density of the adsorbed molecule and the surface of the adsorbent leads to a strong chemical force known as activated adsorption process or chemisorption. The chemisorption process is the key to a catalytic surface reaction, as chemisorbed molecules can serve as reaction intermediates. Langmuir distinguished adsorption into two different types [102, 112]: In non-dissociative molecular (associative) adsorption, the intact molecule is adsorbed on the catalyst surface. In contrast, dissociative adsorption breaks the molecular bond at the catalyst surface to form atoms, radicals or, in the case of the approach of polyatomic molecules, entire molecules are formed. A simplified model to qualitatively distinguish between molecular and dissociative adsorption is the Lennard-Jones potential energy diagram given in Figure 2.5a [110]. In this diagram, no separation is included between physisorption and associative chemisorption for molecular adsorption. The blue line represents the molecular adsorption as the diatomic molecule (M) approaches the surface according to the physisorption process in Figure 2.4. The weak attraction at greater distances is attributed to van der Waals forces, which trap the molecule and cause it to adsorb onto the surface. Closer attraction can be hindered by Pauli repulsion. The orange line represents the energy potential of two separated atoms, originating from a dissociated molecule in the gas phase, as they approach the surface. The dissociation energy causes the initial higher energy state (ΔE_{diss}). The interaction of the two atoms with the surface leads to a chemical bond and results in a lower chemisorption well than in physisorption. The negative enthalpy of adsorption determines the strength of the chemical bond between the molecule and the surface and is usually exothermic. By bringing

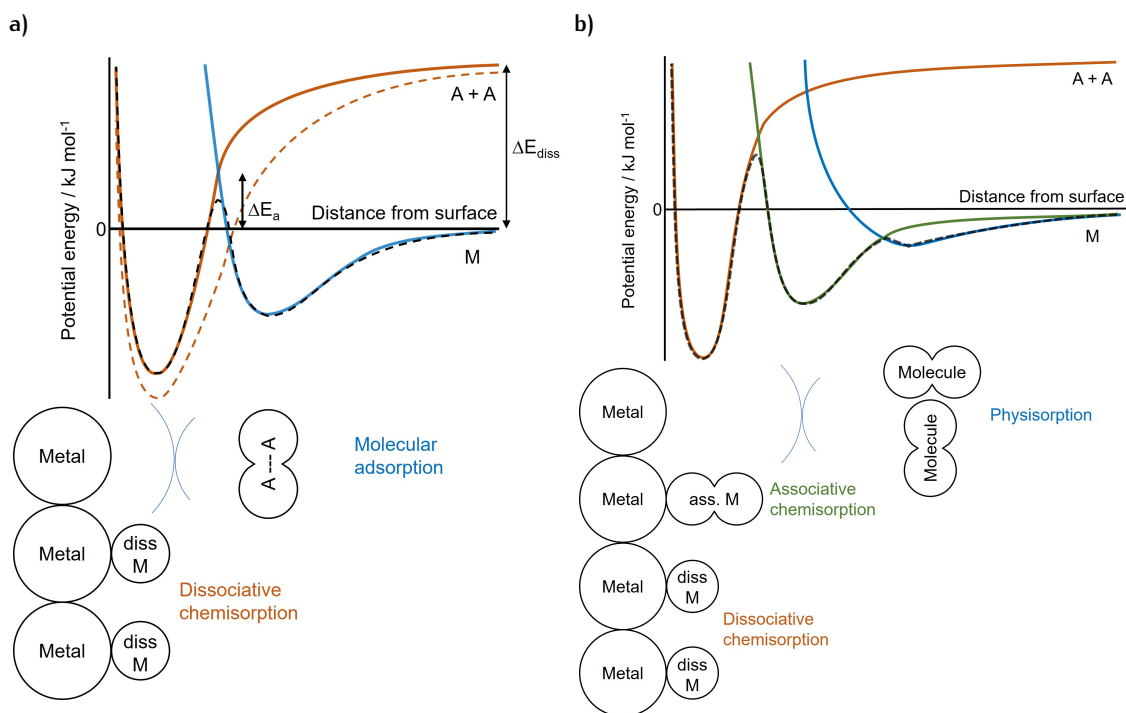


Fig. 2.5: Simplified one-dimensional potential energy diagram for the adsorption of a diatomic molecule approaching a surface: (a) Scheme of physisorption (blue) and dissociative chemisorption (orange) after Lennard-Jones [109]. (b) Scheme for the physisorption (blue), associative (green) and dissociative (orange) chemisorption on a catalytic metal surface [104].

the two systems together, the physisorbed molecule rearranges its electron structure and overcomes an activation energy barrier (ΔE_a) to cross over from the precursor state to the dissociated state. The black dotted line marks the connected process. Depending on whether the intersection between the molecular (blue line) and the dissociative adsorption line is above (orange line) or below (dotted orange line) the zero potential energy value, the dissociative chemisorption process is either activated with an energy barrier or occurs without an activation barrier. In the latter case, a direct dissociative adsorption of the molecule dominates, while overcoming an energy barrier above the zero potential depends on the thermal energy of the physisorbed molecule to rearrange the electronic structure and to chemisorption [113–115].

However, the Lennard-Jones diagram is only a one-dimensional approximation of the interaction energy between the adsorbate and the surface to illustrate the difference between physisorption and chemisorption. For example, the orientation of the approaching molecule relative to the surface and its structure are not considered. If the molecule

adsorbs perpendicular to the surface and the energy is not sufficient to activate dissociative adsorption, the molecule can be chemisorbed associatively instead [102]. Molecular binding to the surface is lower in energy and is preferred to dissociative adsorption because the dissociative state is unstable and short-lived. A transition between both states allows multiple configurations of adsorbed molecules. A simplified classification of the associative (green line) and dissociative chemisorption (orange line) in the potential energy diagram is shown in Figure 2.5b. The adsorption process follows the black dotted line. It starts with the physisorption precursor state (blue line), as already shown and described in Figure 2.5a. By rearranging the electron configuration of the physisorbed diatomic molecule and weakening the molecular bond, a chemical bond is formed with the surface. By overcoming an energy barrier, the bond of the associatively chemisorbed molecule breaks and dissociatively adsorbs with its molecular fragments on the catalyst surface [116].

2.5.4 Vibrational Properties of Adsorbates

The change in the stretching vibration between the atoms of an adsorbed molecule is an indicator of a weakening of the molecular bond, which results in a shift in the vibration frequency that differs from the original vibration property of the molecule in the gas phase. Using IR spectroscopy, for example, vibrational properties can be determined based on the frequency position in the absorption spectrum and can be traced back to the type of chemisorption bond [109]. To understand the interaction of the electronic configuration of adsorbates with the surface and how it affects the vibrational properties of adsorbates, a simple molecular orbital view of adsorbed carbon monoxide on d-metal is applied and discussed below.

The chemisorption of a CO molecule to a transition metal such as nickel or platinum can be described by a covalent bond. In the CO bond between a carbon and oxygen atom, a 5σ (or σ_{2p}) molecule orbital (MO) is formed as the highest occupied molecular orbital (HOMO). It is called the bonding orbital of the molecule. CO also has two lowest unoccupied molecular orbital (LUMO) $2\pi^*$ -MO (or π_{2p}^*), which are referred to as antibonding orbitals and are responsible for the binding strength of the molecule. Both the filled and empty electronic states of the frontier orbitals are mainly responsible for chemisorption on a metallic surface [50, 117]. The density of states of transition metals consists of a broad conduction band (sp band), which is delocalized and half-filled, and of localized and narrow d-bands. The occupancy of the d-bands up to the Fermi level (E_f), the highest occupied electronic energy level (by definition at 0 K), varies depending on the transition metal group;

hence, they are also termed d-metals [107, 118]. CO tends to approach most transition metal surfaces linearly via the carbon end because its HOMO (the 5σ -MO), which is localized on carbon, lies highest in energy and is well aligned with the metal Fermi level, facilitating donation of electron density (σ -donation) to the metal [50]. First, a strong sp-induced metal bond is initially formed with the σ -MO and π -MO of the adsorbate. Then, according to the Blyholder model schematically shown in Figure 2.6, the overlap of the occupied 5σ -MO of the adsorbed molecule with the partially filled d-band of the metal surface leads to an electron donation to the metal surface [119]. This donation contributes to the chemisorption strength of the carbon atom to the metal surface. With the increasing occupation of the d-band, the adsorption strength decreases and causes a Pauli repulsion [117]. In contrast, the interaction of the two unoccupied π^* -MO of the molecule with the d-band leads to attraction, but also to electronic back-donation from the surface to the adsorbate. The back donation from the metal surface fills up the two antibonding π^* -MO of the adsorbed CO molecule and weakens the bond between the carbon and oxygen atom. This process can promote dissociation. Therefore, certain transition metals adsorb CO dissociatively already at room temperature [120, 121]. With the increasingly filled d-band from Ti to Ni, the activation barrier for dissociative chemisorption rises and molecular adsorption is preferred. However, increasing the temperature or gas pressure can affect the orbital overlap and weaken the binding strength of the adsorbed molecule enough to favor dissociation. For instance, CO usually adsorbs in a molecular form on nickel surfaces as carbonyl surface species. The permanent dipole moment of the vertically bound CO is enhanced by the image dipole of the surface (adsorption-induced dipole), as mentioned in section 2.5.2. The absorption of IR radiation therefore leads to strong absorption bands in the IR spectrum. Parallel adsorption (horizontally aligned CO) on the surface would result in an image dipole that balances the dipole moment of the adsorbed CO, rendering it IR-inactive [86]. Heating to higher temperatures (500K) can result in dissociatively adsorbed states forming a metal carbide and oxide [122]. Defect sites on the metal surface can additionally promote dissociation.

The different d-band filling of the transition metals allows molecular adsorption of CO in various structural forms of adsorbed carbonyl species ($^*\text{CO}_{\text{ads}}$). Due to the electron occupancy of the molecular orbitals between the adsorbate and the transition metal, CO can be linearly adsorbed by the σ -bond on top of a surface atom. Moreover, the $2\pi^*$ -bonds favor bridged adsorption to two adjacent surface atoms or at threefold hollow sites $2\pi^*$ -bonds [107]. As the bonds and thus the bond strengths of the carbon atom to the metal atoms

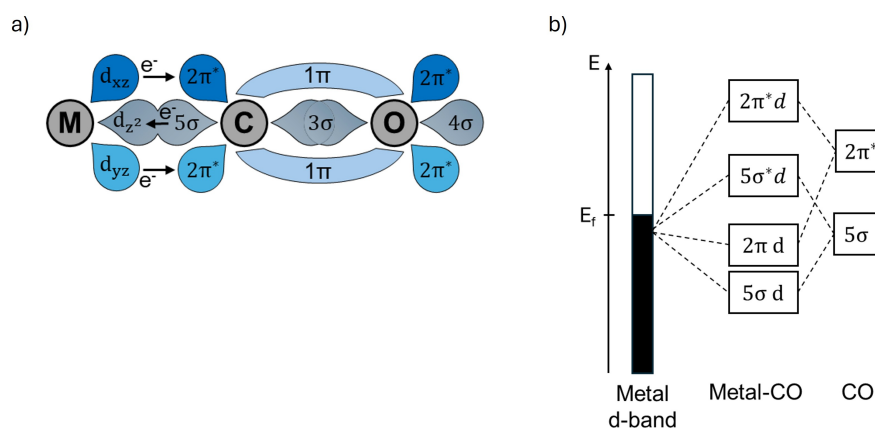


Fig. 2.6: Simplified Blyholder model of the CO chemisorption on a transition metal [123, 124]: a) Schematic illustration of σ -donation from the 5σ -MO of CO (HOMO) into the half-filled metal d-orbital (primarily the d_{z^2} orbital) of a transition metal atom (M), and π -back-donation from the occupied metal d-orbitals (d_{xz} , d_{yz}) into the two empty $2\pi^*$ -MO of CO (LUMO) [121]. b) Schematic electron configuration of the CO chemisorption to a transition metal. The 5σ -MO of CO, localized on carbon, lies close in energy to the metal Fermi level (E_f) within the d-band, which enables linear adsorption geometry [50].

increase due to the electron back-donation from the metal, the bond strength within $^*\text{CO}_{\text{ads}}$ decreases at the same time [123]. I.e., the bond length decreases and with it the frequency of the stretching vibration (cf. Eq. (2.10)), which leads to a shift to lower wavenumbers (mid-infrared) that can be indirectly assigned to the linearly, bridged, or triply bonded adsorbed CO. For example, upon adsorption of $^*\text{CO}_{\text{ads}}$ on a transition metal surface, the carbonyl stretching vibration is shifted by at least 100 cm^{-1} below the fundamental frequency of the stretching vibration of CO in the gas phase [86]. The IR absorption band of the stretching vibration of a gas-phase CO molecule is found at 2143 cm^{-1} [125]. The different adsorption forms of CO can be associated with shifts in wavenumbers to $2000 - 2130\text{ cm}^{-1}$ for linearly, $1880 - 2000\text{ cm}^{-1}$ for bridged, and below for 3-fold bonded species [119, 126]. Depending on the nature of both the adsorbate and the adsorbent, molecular adsorption and its IR absorption frequency can additionally be affected by the degree of surface coverage and the surface structure [123]. An opposite polarization or resonant vibrational dipole interaction between closely spaced $^*\text{CO}_{\text{ads}}$ on, for example, Pt can change the stretching vibration with increasing coverage and slightly shift the wavenumber by a few tens of cm^{-1} [127]. Other works have also observed that CO adsorbs first linearly bonded to Pt at low coverage and that multiply bonded CO becomes visible with increasing coverage [128, 129]. In addition to the number of adsorbate-adsorbent bonds, the coordination number

of surface metal atoms may also affect the frequency shift in the range of tens of cm^{-1} in both directions [130]. Catalytic surfaces are usually not planar but have a high proportion of sites with low coordination. These may be edges, corners, kinks, or defect sites that are coordinatively unsaturated and support electron donation or back donation, affecting the vibrational frequency of the adsorbate. The absence of neighboring surface atoms leads to less orbital overlap among them, resulting in a narrower d-band. The overlap of the d-band with an adsorbate results in a larger energy shift and thus a stronger bond, which weakens the molecular bond of the adsorbate [104]. The unsaturated adsorption sites exhibit a lower energy barrier to dissociation and are therefore assumed to be crucial active sites for heterogeneous catalysis. The chemical modification of the separated molecular fragments, e.g., of metal carbides or oxides by dissociatively adsorbed CO, leads to different vibration frequencies in the formation of new adsorbate-adsorbent bonds. Consequently, IR spectroscopy is an essential tool to study the chemical nature of surface adsorbates in heterogeneous catalysis. The position of vibrational frequencies provides information about the type, binding properties, and structure of adsorbed molecules or molecular fragments and indirectly allows conclusions to be drawn about the binding between adsorbate and adsorbent.

2.5.5 Adsorption Sites on Catalytic Support Surfaces

Most heterogeneous reactions occur on supported catalysts using metal oxides as support material [116]. Although support materials are chemically inactive, defects (e.g., oxygen vacancies, Brønsted and Lewis acid sites), impurities or spillover effects can form active sites on the support surface that participate in the surface reaction and may be responsible for adsorption processes from the gas phase [102]. The commonly used support materials are metal oxides, which offer a large surface area and high porosity, resulting in multiple adsorption sites at the interface between metal particles and support material. [131]. Thus, the metal-support interface is bifunctional and exhibits various active sites for the adsorption of reaction intermediates both on the support side and on the metal nanoparticles. The Metal Support Interaction (MSI) is decisive for the electronic and chemical properties of the catalysts and the surface chemistry in the reaction process [132]. The strength of the MSI can influence the reaction mechanism on the catalyst by triggering a realignment of the electron distribution within the metal particles and the support material as a result of differences in the Fermi levels, the highest energy levels occupied by electrons [133]. The charge transfer can modify the oxidation state of the metal particles or oxide supports and influence the adsorption strength of reactants, such as CO_2 , CO and H_2 , and their reaction

intermediates [133]. The Fermi level in transition metals is mainly located in the conduction band, which overlaps with the outermost orbital, the valence band. The electrons confined to that band are free to move into the conduction band and may be involved in the charge transfer [114]. As explained in the previous section, the conduction bands of transition metals share electrons with adsorbed molecules and mainly contribute to bonding, while the interaction of the d-bands plays a crucial role in the nature of the bonding. With metal oxides, on the other hand, adsorption depends on the electronic structure. Reducible metal oxides (e.g. TiO_2 or CeO_2) are semiconductors with a moderate band gap separating the valence band and conduction band, which prevents electrons from moving freely without external energy impact. However, the potential to form defect sites like oxygen vacancies can enhance the charge transfer and enable spillover effects [133]. With an oxygen vacancy, two electrons are left behind when an oxygen is removed from the lattice, e.g., by a reduction. These electrons cannot remain in the valence band because it is already occupied. Instead, they occupy energy states close to the conduction band, which provides a sufficient shift in electron density towards the adjacent metal particles and thus increases their adsorption strength towards reactants or intermediates.

The spillover effect is an interfacial phenomenon in catalytic reactions in which a reactant is adsorbed and activated on an initiator, typically the surface of a metal particle, and then migrates to the support surface [134]. Best known in catalysis is the hydrogen spillover effect, in which hydrogen is chemisorbed and dissociated on the metal particles. Spillover effects are only possible if the surface is littered with lattice defects or favored by hydrogen acceptors [135]. An activated hydrogen atom then diffuses to the adjacent support surface, where diverse interactions can occur. When the hydrogen splits through the spillover, the proton of the hydrogen atom (H^+) can bind to an oxygen anion (O^{2-}) and form a hydroxyl group. In contrast, the split electron reduces the metal cation that remains next to the O–H bond [136]. If, on the other hand, the hydrogen atom (proton plus electron) does not separate, it can migrate across the support surface due to the repulsive interaction with the oxygen anions until it forms a bridge bond with two of them [135]. The resulting basic sites on the support surface can participate in the reaction and change the reaction mechanism by binding reactants such as CO_2 .

Ionic bonds cause the adsorption on insulators such as alumina or silica in accordance with acid–base rules, as charge transfer is limited due to their insulating nature [102]. Nevertheless, support materials such as alumina promote the adsorption of CO_2 without the

requirement for greater electron distribution. The surface of alumina consists of structural defects with Brønsted and Lewis acid sites, the composition of which varies depending on the heat treatment [116]. The lattice effects result in coordinatively unsaturated metal ions that have fewer oxygen neighbors than in the ideal lattice. These electron-accepting Lewis acid sites can interact with hydrogen, reaction intermediates, or water. At low temperatures, water only adsorbs weakly on most transition metals and is desorbed again at room temperature. However, it can also adsorb dissociatively on the acidic sites of metal ions and form hydroxyl groups. Hydroxyl groups on metal oxide surfaces are ubiquitous and stable up to temperatures of 1000 K [137]. Brønsted acid sites, on the other hand, exhibit proton-donating capabilities, which can be caused by strong basic oxygen anions formed by defects in the lattice or by weak basic hydroxyl groups adsorbed on the surface. Acidic molecules such as CO_2 tend to bind weakly to strongly to these basic sites and form bicarbonates or carbonates on the surface [116].

2.6 CO_2 Methanation

2.6.1 History of Catalytic Methanation

The first investigations into the decomposition of carbon oxides into methane by electrical induction were carried out by Brodie in 1873 [45, 138]. In 1902, Sabatier and Senders discovered that both CO and CO_2 can be catalytically hydrogenated to methane in the presence of a nickel catalyst [51]. Historically, the catalytic methanation reaction initially gained importance in industry through the purification of CO from H_2 -rich feed gases during ammonia production [139]. In the 1970s to 1980s, the focus was on the industrial production of synthetic natural gas (SNG) using commercial CO methanation. To date (status 2022), 82 % of the world's primary energy consumption is based on fossil fuels, primarily oil and natural gas (NG), while renewables account for only a small share of about 7.5 % [140]. Since the 1950s, demand for natural gas has increased steadily, although known reserves of fossil fuels were only expected to last for around 60 years [141]. In the wake of the oil crisis in the 1970s, there was increased research in the United States and Germany into the industrial production of SNG using syngas from coal or biomass gasification through an efficient CO methanation process to become less dependent on imports [39]. In this period, several pilot projects and commercial scale-ups were developed, as well as concepts for fixed-bed or fluidized-bed methanation reactors, which are still in use today. Research groups such as Kopyscinski et al. [39] or Rönsch et al. [41] provide a comprehensive review of industrial developments in methanation processes.

In recent years, the focus of today's research has shifted to the thermal catalytic hydrogenation of CO₂ instead of CO [142, 143], which combines two possibilities: the reduction of greenhouse gas emissions, with CO₂ being the leading cause of the greenhouse effect, and the transition to a sustainable energy future through Power-to-Gas (PtG) concepts [144–146]. The transition from fossil fuels to renewable energies is being driven by increasing energy demand and the desire of many countries to switch to green technologies [147, 148]. The conversion of wind and solar energy into electrical energy dominates, but requires a direct storage capability for excess energy, as both energy sources are only available intermittently [40]. Accordingly, battery storage is needed, which is currently not feasible on a large scale [149]. The PtG technology appears to be a promising approach to capture chemically renewable energy in a long-term and large-capacity storage system. Green hydrogen, powered by electrolysis from excess renewable energy, is used to recycle captured carbon dioxide into methane, which can in turn be fed into the already existing natural gas grid as SNG. However, since PtG plants are not yet economically viable on an industrial scale, there are only a few demonstration plants such as the Audi e-gas plant in Germany [40]. Nevertheless, the hydrogenation of CO₂ remains a key reaction of the current research focus for many future concepts and projects [150, 151].

2.6.2 Fundamentals

The catalytic hydrogenation of CO₂ to CH₄, as given in Eq. (2.20), today known as the Sabatier reaction (referred to as CO₂ methanation in this work), is an eight-electron reduction process with 4 mol H₂ and 1 mol CO₂ reacting stoichiometrically to 1 mol CH₄ and 2 mol H₂O. According to Le Chatelier's principle, the exothermic and volume-reducing CO₂ methanation reaction is thermodynamically favored at lower temperatures (< 500 °C) and higher pressures (up to 30 bar) [45, 152]. To ensure significant conversion rates and yields even at more economical temperatures and operating pressures (e.g., atmospheric pressure), CO₂ methanation is mainly carried out in the range of 200 – 400 °C and with high H₂/CO₂ ratios [144]. In this reaction temperature range, other side reactions can proceed in parallel, such as the CO methanation reaction (cf. Eq. (2.21)), the reverse Water-Gas Shift (rWGS)

reaction (cf. Eq. (2.22)), or the Boudouard reaction (cf. Eq. (2.23)) [42, 45, 153, 154].



Of particular note is the work of Gao et al. [152], which provides a comprehensive overview of the side reactions that can occur during the CO_2 methanation reaction and their effects when pressure, temperature and the H_2/CO_2 ratio are varied. They observed both CO_2 conversion and selectivity toward CH_4 of more than 90 % at pressures above 10 bar and reaction temperatures below 450°C . At ambient pressure, the conversion rate drops to about 80 % at 450°C , while the selectivity remains above 90 %. At temperatures above 450°C , the rWGS (cf. Eq. (2.22)) reaction sets in and the concentration of CO increases, promoting the CO methanation. Since the CO methanation reaction dominates the CO_2 methanation, the concentration of unreacted CO_2 in turn increases, resulting in a lower CH_4 yield. With increasing CO, the deposition of carbon can occur as a result of the Boudouard reaction (cf. Eq. (2.23)). However, due to the high CH_4 selectivity, they did not observe any carbon deposition under the experimental reaction conditions, provided that the H_2/CO_2 feed ratio was equal to or greater than 4. Moreover, since the rWGS reaction is negligible at reaction temperatures below 350°C , CO methanation can likewise be regarded as insignificant under these conditions [152].

2.6.3 Chemical Equilibrium

The thermodynamics of a chemical reaction allows the prediction of optimal reaction conditions by providing information about whether and to what extent a reaction occurs voluntarily [75]. In contrast to irreversible reactions, in which a complete conversion of the reactants is possible, reversible reactions strive for a chemical equilibrium of forward and reverse reactions depending on the reaction conditions (pressure, temperature, initial composition). At equilibrium, the net change in the concentrations of the reacting species and the forming products is zero. Once an equilibrium composition is reached, the maximum possible, but probably incomplete, conversion is achieved [155]. Therefore, equilibrium calculations provide the maximum conversion that can be thermodynamically achieved for the respective reaction conditions. The change in free enthalpy (Gibbs energy) indicates whether the reaction is favored and to what extent it occurs spontaneously under the given

reaction conditions [75]. Since temperature, pressure and amounts of the species involved can change during the reaction, the free enthalpy depends on several thermodynamic state variables ($G(T, p, n_1, \dots, n_i)$, cf. Eq. (2.5)). When investigating chemical reactions, for example, in kinetic measurements, it is often necessary to precisely control the reaction conditions by keeping pressure ($V dp = 0$) and temperature ($-S dT = 0$) constant [77]. Under isothermal-isobaric conditions, the thermodynamic change of state of the reaction system can be described by the simplified Gibbs equation [75]:

$$dG = \sum_i \mu_i dn_i \quad (2.24)$$

whereby the change in Gibbs energy is a function of the chemical potentials of the components i (μ_i) involved, depending on their amounts of substance (n_i). By extending the equation with the extent of the reaction (ξ), the rate of change of the Gibbs energy per mole of reaction can be determined [79, 80]:

$$\begin{aligned} dG_{p,T,n} &= \left(\sum_i \nu_i \mu_i \right) d\xi \\ \Delta_R G &= \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_i \nu_i \mu_i \end{aligned} \quad (2.25)$$

$\Delta_R G_{j,T}$ is called the free enthalpy or Gibbs free energy of reaction j at reaction temperature T .

The dependence of the chemical potential of a species i (μ_i) in a reaction mixture on temperature and pressure can be expressed by its activity [156]:

$$\mu_i(p, T) = \mu_i^\ominus(p^\ominus, T) + R T \ln(a_i) \quad (2.26)$$

By combining Equations (2.25) and (2.26), the rate of change of Gibbs free energy per mole of reaction is given as follows [80]:

$$\Delta_R G = \sum_i \nu_i \mu_i^\ominus + R T \sum_i \nu_i \ln a_i \quad (2.27)$$

The activity of a gas species (a_i) is a dimensionless quantity. For ideal gas behavior, it can be described approximately as the "effective pressure" and replaced by the partial pressure

of the species (p_i) based on its standard state ($p^\ominus = 1 \text{ bar}$) [75]:

$$a_i = \frac{p_i}{p^\ominus} \quad (2.28)$$

Considering that the chemical potential of a species in the standard state ($\mu_i^\ominus$) is equivalent to the standard free enthalpy of formation ($\Delta_B G_{i,T}^\ominus$), the combination of the equations Eq. (2.25) and Eq. (2.26) results in the following [156]:

$$\Delta_R G = \sum_i \nu_i \Delta_B G_{i,T}^\ominus + R T \ln \left(\prod_i a_i^{\nu_i} \right) \quad (2.29)$$

Thereby, the difference between the standard free enthalpy of formation of reactants and products in their respective standard states at the corresponding reaction temperature is representative of the standard free enthalpy of reaction ($\Delta_R G_{j,T}^\ominus$) [157]:

$$\Delta_R G_{j,T}^\ominus = \sum \nu_i \mu_i^\ominus = \sum \nu_i \Delta_B G_{i,T}^\ominus \quad (2.30)$$

Under isothermal and isobaric conditions, a reaction system moves towards the minimum free enthalpy until the standard Gibbs free energy reaches zero at equilibrium ($(\Delta_R G)_{p,T} = 0$) [75]. If this is applied to Eq. (2.29) and converted into its general exponential form, the law of mass action is obtained with K as the thermodynamic equilibrium constant [158]:

$$\begin{aligned} \Delta_R G^\ominus &= -R T \ln \left(\prod_i a_i^{\nu_i} \right) \\ \Rightarrow K &= \left(\prod_i a_i^{\nu_i} \right)_{\text{eq}} = \exp \left(\frac{-\Delta_R G^\ominus}{R T} \right) \end{aligned} \quad (2.31)$$

In this context, the sign of $\Delta_R G^\ominus$ is an indication of the direction of the reaction [75]. For $\Delta_R G^\ominus < 0$, the reaction is spontaneous and the equilibrium position is shifted towards the product side ($K > 1$). In contrast, if $\Delta_R G^\ominus > 0$, the reaction occurs involuntary ($K < 1$). By simplifying the law of mass action for gaseous reaction systems with ideal gas behavior, the equilibrium constant is determined from the composition of a reaction system in the

chemical equilibrium [159]:

$$\begin{aligned}
 K &= \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i} \quad , \text{ with } p_i = x_i p \\
 &= \prod_i (x_i p)^{\nu_i} (p^\ominus)^{-\sum \nu_i} = \prod_i x_i^{\nu_i} \left(\frac{p}{p^\ominus} \right)^{\sum \nu_i} \\
 \Rightarrow K &= K_x \left(\frac{p}{1 \text{ bar}} \right)^{\sum \nu_i} \quad , \text{ with } K_x = \prod_i x_i^{\nu_i}
 \end{aligned} \tag{2.32}$$

Since the standard free enthalpy of reaction depends only on the reaction temperature, this also applies to the (true) thermodynamic equilibrium constant (K , cf. Eq. (2.31)). On the other hand, if the reaction involves a change in the amount of substance, the system pressure (p) can affect the equilibrium constant based on the mole fractions (K_x), shifting the equilibrium position but not the equilibrium constant (K) itself [75, 156]. As a result, K_x is the key factor in calculating the maximum conversion under the given reaction conditions at equilibrium.

For the study of the CO₂ methanation, if only the simple Sabatier reaction with the hydrogenation of CO₂ to CH₄ (cf. Eq. (2.20)) is considered, the equilibrium constant can be converted into a function of the extent of reaction using the stoichiometry given in Table 2.1:

$$K = \frac{x_{\text{CH}_4, \text{eq}} x_{\text{H}_2\text{O}, \text{eq}}^2}{x_{\text{H}_2, \text{eq}}^4 x_{\text{CO}_2, \text{eq}}} \frac{p^{\ominus 2}}{p^2} = \frac{4\xi^3 (\dot{n}_{\text{eq}})^2}{(\dot{n}_{\text{B},0} - \xi)(\dot{n}_{\text{A},0} - 4\xi)^4} \frac{p^{\ominus 2}}{p^2} \tag{2.33}$$

Assuming a stoichiometric feed ratio of the reactants, Eq. (2.33) can be simplified to:

$$K = \frac{\xi^3 (5 \text{ mol min}^{-1} - 2\xi)^2}{64(1 \text{ mol min}^{-1} - \xi)^5} \frac{p^{\ominus 2}}{p^2} \tag{2.34}$$

To determine the extent to which a reaction can take place under given reaction conditions and a specific composition of the reaction mixture, the equilibrium constant is to be identified from the standard Gibbs energy (cf. Eq. (2.31)). Eq. (2.30) can in turn be used to calculate the standard Gibbs energy from the standard free enthalpies of formation of the individual species, which are given in the literature for standard conditions [160]. However, the reaction conditions of catalytic reactions rarely correspond to standard conditions. Therefore, the free standard reaction enthalpy can alternatively be converted into the desired reaction

Tab. 2.1: Stoichiometric table for the CO₂ methanation reaction

Species	Symbol	ν_i	$\dot{n}_{i,0}$ mol min ⁻¹	$\dot{n}_{i,\text{eq}} = \dot{n}_{i,0} + \nu_i \dot{\xi}$ mol min ⁻¹	$x_{i,\text{eq}} = \frac{\dot{n}_{i,\text{eq}}}{\dot{n}_{\text{eq}}}$
H ₂	A	-4	$\dot{n}_{A,0}$	$\dot{n}_{A,0} - 4\dot{\xi}$	$\frac{\dot{n}_{A,0} - 4\dot{\xi}}{\dot{n}_{\text{eq}}}$
CO ₂	B	-1	$\dot{n}_{B,0}$	$\dot{n}_{B,0} - \dot{\xi}$	$\frac{\dot{n}_{B,0} - \dot{\xi}}{\dot{n}_{\text{eq}}}$
CH ₄	C	1	0	$\dot{\xi}$	$\frac{\dot{\xi}}{\dot{n}_{\text{eq}}}$
H ₂ O	D	2	0	$2\dot{\xi}$	$\frac{2\dot{\xi}}{\dot{n}_{\text{eq}}}$
Σ		-2	$\dot{n}_0 = \dot{n}_{A,0} + \dot{n}_{B,0}$	$\dot{n}_{\text{eq}} = \dot{n}_0 - 2\dot{\xi}$	

temperature using the Gibbs-Helmholtz equation:

$$\Delta G_R^\circ(T) = \Delta_R H^\circ(T) - T \Delta_R S^\circ(T) \quad (2.35)$$

The Hess (cf. Eq. (2.36)) and Kirchhoff (cf. Eq. (2.37)) theorems are used to determine the standard reaction enthalpy ($\Delta_R H_{j,T}^\circ$) and standard reaction entropy ($\Delta_R S_{j,T}^\circ$) for the gas components involved in the reaction, while the temperature dependence can be considered with the Shomate equation (cf. Eq. (2.38)) [161, 162].

$$\begin{aligned} \Delta_R H_{j,T}^\circ &= \sum_i \nu_i \Delta_B H_{i,T}^\circ \\ \Delta_R S_{j,T}^\circ &= \sum_i \nu_i S_{i,T}^\circ \end{aligned} \quad (2.36)$$

$$\begin{aligned} \Delta_R H_{j,T}^\circ &= \sum_i \nu_i \Delta_B H_{i,T}^\circ = \sum_i \nu_i \left(\Delta_B H_{i,T_0}^\circ + \int_{T_0}^T c_{p,i}(T) dT \right) \\ \Delta_R S_{j,T}^\circ &= \sum_i \nu_i S_{i,T}^\circ = \sum_i \nu_i \left(S_{i,T_0}^\circ + \int_{T_0}^T \frac{c_{p,i}(T)}{T} dT \right) \end{aligned} \quad (2.37)$$

$$\begin{aligned}\Delta_B H_{i,T}^\ominus &= \Delta_B H_{i,T_0}^\ominus + A t + B t^2/2 + C t^3/3 + D t^4/4 - E/t + F - H \\ S_{i,T}^\ominus &= A \ln(t) + B t + C t^2/2 + D t^3/3 - E/(2 t^2) + G\end{aligned}\quad (2.38)$$

The Shomate equation describes the specific heat capacity of a substance as a function of the temperature ($c_{p,i}(t)$ with $t = T/1000$) and provides a method for integrating the heat capacities in Kirchhoff's theorem. The values for the standard formation enthalpy, the entropy and coefficients A to H can be obtained from the NIST Chemistry Webbook [162] and are listed in Table 2.2 with respect to the Sabatier reaction (cf. Eq. (2.20)). Figure 2.7a shows

Tab. 2.2: Values for the variables of the Shomate equation for calculating the integrated heat capacity, adopted from [162, 163]

Species Scope	H ₂ 298 – 1000 K	CO ₂ 298 – 1200 K	CH ₄ 298 – 1300 K	H ₂ O 500 – 1700 K
$\Delta_B H_{i,T}^\ominus / \text{kJ mol}^{-1}$	0	−393.52	−74.87	−241.83
$S_{i,T}^\ominus / \text{J mol}^{-1} \text{K}^{-1}$	130.68	213.79	186.25	188.84
A	33.066178	24.99735	−0.703029	30.092
B	−11.363417	55.18696	108.4773	6.832514
C	11.432816	−33.69137	−42.52157	−2.53448
D	−2.772874	7.948387	5.862788	0.082139
E	−0.158558	−0.136638	0.678565	−250.881
F	−9.980797	−403.6075	−76.84376	223.3967
G	172.707974	228.2431	158.7163	−241.8264
H	0	−393.522400	−74.873100	−74.873100

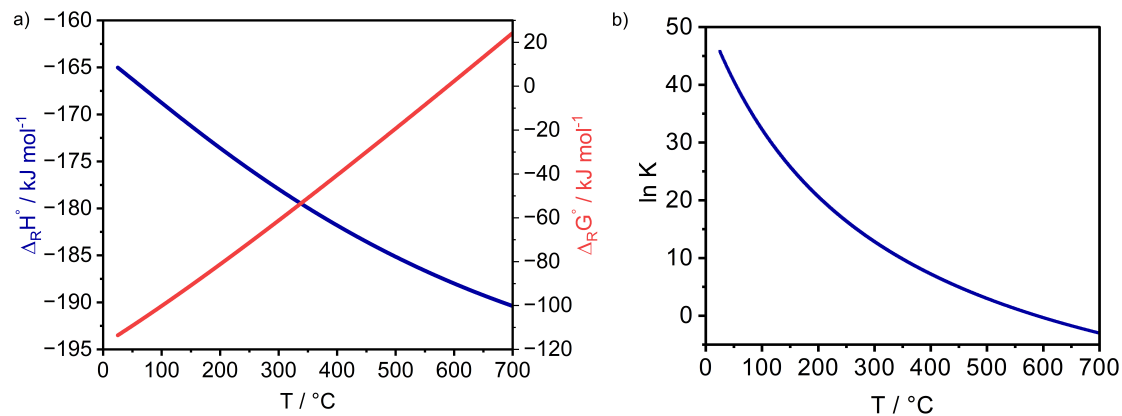


Fig. 2.7: (a) Standard reaction enthalpy (blue line) and standard Gibbs energy (red line) of the CO₂ methanation reaction as a function of certain reaction temperature range. (b) Logarithmized equilibrium constant as a function of the temperatures.

the standard reaction enthalpy ($\Delta_R H_{j,T}^\circ$, blue line) and resulting standard Gibbs energy ($\Delta_R G_{j,T}^\circ$, red line) as a function of reaction temperatures from 0 – 700 °C. The Sabatier reaction under standard conditions (1 bar) is characterized by an exothermic reaction , whereby a reaction energy of 165 kJ mol⁻¹ is released at 25 °C, and the intensity increases with rising temperature. Examining the standard Gibbs energy, the Sabatier reaction is favorable at low temperatures ($\Delta_R G_{j,T}^\circ < 0$ kJ mol⁻¹), with the equilibrium position shifted towards the product side. At approximately 590 °C ($\Delta_R G_{j,T}^\circ = 0$ kJ mol⁻¹), forward and reverse reactions are equally pronounced, resulting in a theoretical conversion of 50 %. In comparison, the equilibrium constant is 1 ($\ln K = 0$), which is shown logarithmically in Figure 2.7b. The equilibrium constant increases sharply towards lower temperatures ($K \gg 1$), indicating an almost complete conversion of the reactants. Conversely, with increasing temperature ($\ln K \rightarrow 0$), the equilibrium position shifts in favor of the reactants and the driving force of the Sabatier reaction decreases according to Le Chatelier's principle [75].

Once the equilibrium constant is given, the extent of the reaction can be calculated (cf. Eq. (2.34)) and used to determine the equilibrium conversion according to Eq. (2.39). Figure 2.8a shows the conversion of CO₂ in relation to the reaction temperature at varying pressures.

$$U_{\text{CO}_2, \text{eq}} = \frac{-\dot{\xi} \nu_{\text{CO}_2}}{\dot{n}_0} \quad (2.39)$$

For water, the Shomate equation parameters are valid only within a defined temperature

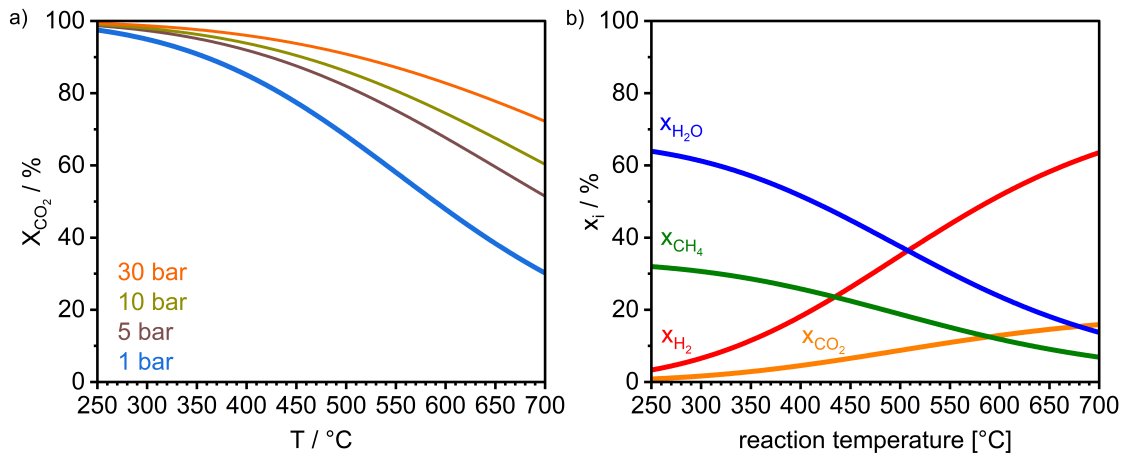


Fig. 2.8: (a) Equilibrium conversion of the CO₂ methanation reaction as a function of temperature at different pressures. (b) Equilibrium composition of the gas mixture at varying reaction temperatures in relation to a stoichiometric feed ratio and standard reaction pressure.

range, which restricts the applicability of the equation to temperatures above 250 °C. Since the Sabatier reaction (cf. Eq. (2.20)) is a volume-reducing reaction system ($5 \text{ mol} \rightarrow 3 \text{ mol}$), an increase in reaction pressure shifts the equilibrium position towards the product side in accordance with Le Chatelier's principle and thereby increases the maximum possible equilibrium conversion. Figure 2.8b illustrates the equilibrium composition in the form of the mole fraction as a function of the reaction temperature at standard reaction pressure ($p = 1 \text{ bar}$).

In the chemical equilibrium calculation above, only the Sabatier reaction (cf. Eq. (2.20)) was considered under the assumption of ideal gas behavior. In reality, however, CO₂ methanation constitutes a complex reaction network whose equilibrium can be influenced by various side reactions. To account for such complexities, the chemical equilibrium of the system can be determined using the Gibbs free energy minimization method [156]. For example, Gao et al. [152] or Yarbaş et al. [164] used this tool to analyze the equilibrium composition of the Sabatier reaction, including numerous side reactions. However, when the simplified equilibrium calculation is compared with the complex calculations in the literature, there are only slight deviations at lower reaction temperatures up to 450 °C, as described in Section 2.6.2.

2.6.4 Catalyst

It is a challenge to find a compromise between highly active and selective catalysts that work at thermodynamically favorable low temperatures and economic pressures with high stability and durability [154]. In the past, the activity and selectivity of various metals, mainly from Groups 8 to 10, have been investigated for their effectiveness in CO₂ methanation [42, 153, 165, 166]. Since the metals differ considerably in terms of their activity or selectivity, various rankings of their effectiveness have been published and reviewed [41, 154, 167]. Catalysts based on ruthenium (Ru) or rhodium (Rh) proved to be the most active metals for CO₂ methanation, as they react at low temperatures of around 200 °C with a high methane yield [168–170]. These noble metals are relatively resistant to fouling caused by coking or carbon deposition, a physical blockage of the active sites of the catalyst [171]. Consequently, they offer extended durability and stability for long-term use. Other noble metal-based catalysts, such as palladium (Pd) or platinum (Pt), also exhibit high activity but tend to favor the rWGS side reaction, which forms CO [167]. Overall, despite their high activity at low temperatures and stability over a wide temperature range, noble metals are unsuitable for commercial CO₂ methanation applications due to their high commodity prices

[151].

Catalysts supported with base metals such as iron (Fe), cobalt (Co) or nickel (Ni) are characterized by their low costs as well as their high CO₂ methanation activity. A significant drawback is the higher reaction temperatures above 300 °C required to overcome the kinetic barriers of the methanation process, and their varying selectivity for CH₄. Fe-based catalysts, commonly used in Fischer-Tropsch or ammonia synthesis, are highly reactive for CO₂ methanation [172]. However, during the CO₂ methanation reaction, iron carbides and carbon deposits form on Fe, blocking the active surface sites and deactivating the catalyst [173, 174]. Co-based catalysts show less activity than iron, but higher CH₄ selectivity. Nevertheless, the comparatively higher cost of Co relative to other base metals, along with its susceptibility to deactivation through sintering and coking at the elevated temperatures typical for CO₂ methanation, renders Co-based catalysts less attractive [154]. The most thoroughly researched and widely used are supported Ni-based catalysts, which demonstrate satisfactory activity and selectivity relative to their low cost [144, 175]. In most CO₂ methanation studies using reaction temperatures between 300 and 350 °C, carbon deposition or coking is less of an issue with Ni-based catalysts than with Fe- or Co-based catalysts [152, 176–178]. In contrast, poisoning and sintering of the active metal particles during the exothermic CO₂ methanation process is a known suffering, particularly when Ni is used [179, 180]. Nickel is prone to poisoning by impurities such as sulfur, which could occur when using a CO₂ feed stream from biogas plants for commercial methanation. Hydrogenated organic sulfur compounds chemisorb strongly and dissociatively to the active metal sites, which are thus blocked and deactivated ($\text{H}_2\text{S}(\text{g}) + \text{NiO}(\text{s}) \leftrightarrow \text{NiS}(\text{s}) + \text{H}_2\text{O}(\text{g})$) [41]. Industrial processes such as sulfur removal systems with scrubbers or guard beds for the purification of the feed gas offer opportunities for the prevention of poisoning [171]. Ni-based catalysts also suffer from thermal deactivation due to sintering of the metal particles, depending on the time the catalysts spend at high operating temperatures. In the literature, sintering processes have been observed mainly at the hot spots of catalytic fixed-bed reactors or accelerated by the presence of water [45, 154].

However, the catalytic performance and physico-chemical characteristics like stability are not only determined by the active metal, but also to a large extent by the choice of support type, the metal dispersion on the support, the metal loading and its particle size [179]. CO₂ methanation catalysts are mainly developed as supported catalysts using metal oxides, individually or as a composite. The use of materials such as zeolites or metal-organic

frameworks has also recently become attractive [151]. Several excellent reviews of CO₂ methanation catalysts have been reported in the literature, with the most commonly used supports being materials such as Al₂O₃, TiO₂, SiO₂, CeO₂ or ZrO₂ [43, 144, 153, 167, 175, 181]. Of these, γ -Al₂O₃ is the most frequently investigated material due to its well-studied and well-known surface structure and acid-base properties [41, 145]. As described in Section 2.5.5, the large surface area and porosity of metal oxide supports provide multiple catalytic adsorption sites at the metal-support interface for key reaction intermediates [131]. Depending on the strength and nature of the MSI, the number of exposed active sites is increased by maintaining high dispersion and stability of the particle size and suppressing the sintering of nickel [132]. Thus, the choice of support material can play a crucial role in the reaction mechanism.

Phenomena such as sintering or fouling during reaction alter both the concentration and structure of reactive centers on the metal nanoparticles, particularly through changes in the particle size and the accessibility to active surface sites, which can modify the catalyst's activity [50]. A classic measure of the structure-activity relationship is the turnover frequency (TOF), which quantifies the number of reactant molecules converted per active site and unit time under defined reaction conditions [53]. For instance, the chemisorption of σ -bond containing reactants at catalytically active sites can be promoted by specific surface atom configurations, such as step, edge, or corner atoms, which often exhibit enhanced reactivity due to their lower coordination and increased electronic unsaturation [50, 182]. Likewise, reactants containing π -bonds can exhibit stronger chemisorption and facilitated bond cleavage at defect sites [182]. Therefore, decreasing particle size through increased dispersion on the support material enhances the accessible surface area and, consequently, the number of these specific active surface sites [50, 183]. However, not all surface atoms of metal nanoparticles contribute equally to catalytic activity [54, 184]. For some reactions, the TOF remains unchanged despite variations in nanoparticle size [182]. Accordingly, it is common practice to represent the TOF as a function of particle size. For example, Vogt et al. [184] explored the CO₂ methanation on a Ni/SiO₂ catalyst with different Ni nanoparticle sizes between 1 and 7 nm, with the highest TOF occurring at about 2.5 nm. Hao et al. [185] investigated the CO₂ methanation using Ni/CeO₂ catalysts and demonstrated the structural sensitivity of the reaction by observing an increase in the TOF with decreasing Ni particle size in the range of 8 – 21 nm. However, with smaller Ni nanoparticles, they also exhibited a loss of catalytic activity, which was attributed to particle agglomeration and the formation of carbon deposits. Furthermore, the size of the nanoparticles influences their shape by

altering the distribution of exposed facets, corners, edges and steps. This determines the nature and stability of the adsorbed intermediates, which can ultimately dominate a reaction mechanism [186]. Additionally, the support material plays a decisive role in catalyst activity by not only promoting the formation of active sites at the metal-support interface, but also by enhancing the dispersion of metal nanoparticles and modifying their morphology [45, 179]. Consequently, CO₂ methanation is widely regarded as a structure-sensitive reaction, with catalytic performance governed by the size and shape of the metal nanoparticles, as well as their loading and dispersion on and through the specific support material. Nevertheless, the precise nature of this dependency remains the subject of ongoing debate in the literature [186, 187].

2.6.5 Reaction Mechanism

The reaction pathway of CO₂ methanation and its reaction intermediates are still a matter of debate in the literature. Many research results are already summarized in established review articles, e.g., in [42–46, 188]. In general, the catalytic hydrogenation of CO₂ to CH₄ requires the presence of two distinct types of active sites, which facilitate the adsorption and activation of H₂ and CO₂ on widely applied transition metal catalysts supported on metal oxides, such as alumina-supported nickel catalysts. While the activation of H₂ typically takes place on the metal nanoparticles, CO₂ activation can occur either at the active metal sites or at the metal-support interface [179]. The number of active sites that can be located on the catalyst surface gives rise to various theories about possible surface reaction intermediates [144, 153, 167, 175, 177]. The reaction mechanism can be classified into (A) the dissociative pathway or (B) the associative pathway, as shown schematically in Figure 2.9. Pathway (A) suggests the formation of carbonyl intermediates (*CO_{ads}), where methane is produced via the dissociative adsorption of CO₂ on active metal sites, followed by CO methanation. If CO₂ methanation proceeds concurrently with continuous CO dissociation (A1), the resulting fragments undergo consecutive hydrogenation to CH₄ or H₂O by hydrogen atoms formed through dissociatively adsorbed H₂ on the metal surface. In the absence of CO dissociation, it reacts directly with dissociatively adsorbed hydrogen atoms to yield methane and water via oxygenate intermediates (A2). In contrast, pathway (B) involves an associative adsorption of *CO_{2ads} primarily on surface oxygen or hydroxyl species covering the metal oxide support. Thus, carbonate (B1) or bicarbonate (B2) species are formed. Through hydrogen spillover effects at the metal-support interface, the carbonate and bicarbonate intermediates are hydrogenated to monodentate or bidentate formate and consecutively to methane.

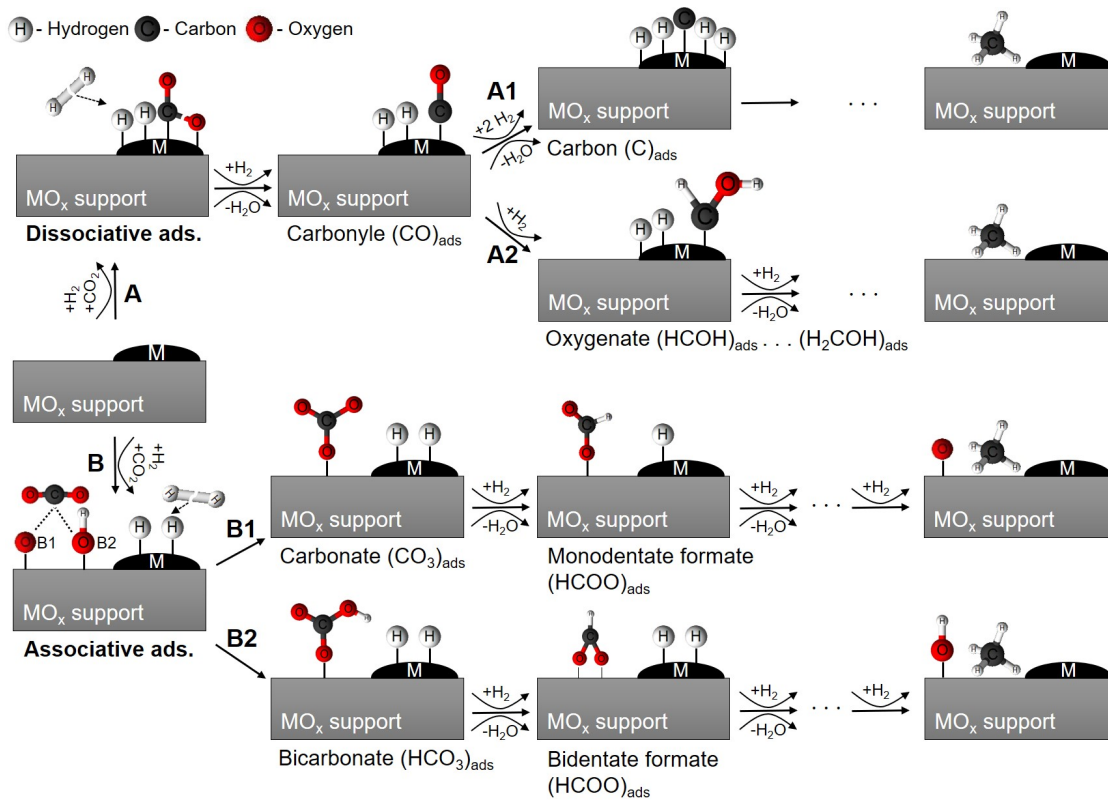


Fig. 2.9: Schematic description of the general CO₂ methanation reaction mechanism occurring on metal oxide supported catalysts. (A) Dissociative pathway: CO₂ dissociatively adsorbs as a carbonyl intermediate (CO_{ads}) on the metal particle and is hydrogenated to methane via carbon (A1) or oxygenate (A2). (B) Associative pathway: CO₂ associatively adsorbs as monodentate (B1) or bidentate (B2) formate intermediate (HCOO_{ads}) on the unreduced or reduced surface of the metal oxide support, respectively, and is hydrogenated to methane. Adopted from [81].

3 Material and Methods

In this chapter, the materials and methods used in this study to realize iso-potential DRIFTS measurements by coupling a DRIFTS cell with a profile reactor in operation are described in detail. First, a list of all the chemicals relevant to this study is provided (Section 3.1.1). The following section describes the preparation and characterization methods used for the catalyst in this work, demonstrating the novel technique through the CO₂ methanation reaction as a test reaction (Section 3.1.2). It also explains the equipment provided for this work, including the profile reactor in which the test reaction took place (Section 3.1.3) and the gas dosing system for the iso-potential *operando* DRIFTS measurements (Section 3.1.4). The mass spectrometric and IR spectroscopic analytical methods used to obtain concentration and adsorbate profiles are detailed in Section 3.1.5 and Section 3.1.6, respectively. Section 3.2 deals with the methodology of the iso-potential *operando* DRIFTS measurement technique: Based on the methodological approach for experimentally investigating a catalyst using DRIFTS measurements and the spectral information that can generally be obtained (Section 3.2.1), a workflow for iso-potential *operando* DRIFTS measurements can be derived (Section 3.2.2). General instructions for extracting spectral information about catalyst adsorbates from iso-potential *operando* DRIFTS measurements follow in Section 3.2.3.

3.1 Material

3.1.1 List of Chemicals

Table 3.1 lists the chemicals that were needed for catalyst synthesis, as well as the gases that were used for the reaction mixture, calibrations, or DRIFTS experiments.

3.1.2 Catalyst Synthesis and Characterization Methods

The catalyst synthesis was carried out as part of student research works by Thore Klinger [189] and Svenja Seiß [190]. In summary, a Ni catalyst was synthesized on a γ -Al₂O₃ support, a material widely regarded as suitable for the CO₂ methanation reaction in the

Tab. 3.1: List of chemicals used and their application for this work

Chemical	Chemical formula	Purity	Supplier	Application
Alumina spheres	$\gamma\text{-Al}_2\text{O}_3$	> 99 %	Sasol Germany GmbH	Cat. synthesis
Nickel nitrate hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	> 99 %	Sigma-Aldrich	Cat. synthesis
Argon	Ar	5.0 (> 99 %)	Westfalen AG	Internal standard
Carbon dioxide	CO_2	3.5 (> 99 %)	Westfalen AG	Reactant, calibrant
Hydrogen	H_2	5.0 (> 99 %)	Westfalen AG	Reactant, calibrant
Methane	CH_4	5.0 (> 99 %)	Westfalen AG	calibrant
Carbon monoxide	CO	5.0 (> 99 %)	Westfalen AG	DRIFTS
Calcium fluoride	CaF_2	> 99 %	Sigma-Aldrich	DRIFTS

literature [175]. Nickel loading was performed by incipient wetness impregnation of alumina particles in a rotary evaporator (Büchi, R-300), as described in [191]. The support particles, with a diameter of 300 – 400 μm and a specific surface area of 160 $\text{m}^2 \text{g}^{-1}$, were obtained by crushing and sieving 1 mm $\gamma\text{-Al}_2\text{O}_3$ spheres provided by Sasol Germany GmbH [192]. Residual water and entrapped air within the pores could be effectively removed by drying (50 °C) under reduced pressure (80 mbar). The precursor concentration of an aqueous nickel nitrate hexahydrate solution ($\text{pH} \approx 5$) was calculated for a theoretical weight loading (wt%) of 15 % nickel content and adjusted to match the pore volume of the alumina particles to be impregnated. In the work by Aziz et al. [180], it is mentioned that a Ni content of 10 to 20 wt% enables both high CO_2 conversion and a high methane yield. The precursor was dropped onto the alumina particles in several impregnation steps, each step being interrupted by three hours of drying at 50 °C and 80 mbar to remove the solvent. Although the pH value of the precursor solution was below the point of zero charge of alumina (PZC ≈ 8), which would likely cause a positive surface charge due to protonated hydroxyl groups adsorbed on the surface [193], the uptake of nickel nitrate was visually observed during the impregnation steps. It is assumed that the impregnation method, involving individual impregnation and drying steps, allowed the precursor solution to penetrate the pores of the support material through capillary forces. Also, the dissolution of aluminum atoms by the acidic precursor solution may be responsible for creating adsorption sites for nickel nitrate [194]. However, lower metal dispersion and relatively large metal particles are expected as

a result of the impregnation process. The impregnation was followed by a drying process at 60 °C for 12 h. The calcination step was carried out in a tubular furnace purged with synthetic air at 500 °C (heating ramp of 5 K min⁻¹) for three hours. Calcination temperature and time ensure the complete conversion of nickel nitrate to nickel oxide, accompanied by the formation of nitrogen oxides, which are removed during the calcination process [191]. This was followed by a reduction step in a 5 vol% H₂/N₂ atmosphere to reduce NiO to elemental nickel while preventing sintering of the nickel particles and maintaining a small particle size of nickel crystallite. A reduction temperature of 600 °C and a reduction time of 2 hours were selected for this step [195].

The Ni/ γ -Al₂O₃ catalyst characterization is performed with the freshly reduced catalyst. For comparison, some characterization methods were also conducted using a previously spent catalyst sample after the experiments were completed. A sample of the reduced catalyst was degassed at 350 °C for 6 h before BET surface area was determined by N₂-physisorption at 77 K using the static-volumetric method in an Autosorb IQ 2 (Quantachrome Instruments). With the same instrument, H₂-chemisorption at 35 °C was performed by the volumetric method to examine the accessible surface, dispersion, and crystallite size of the nickel metal particles on both the freshly reduced and spent catalyst samples. The settings for the treatment and chemisorption process are oriented towards DIN 66136-2 for determining the specific metal surface area of nickel with hydrogen as the penetration gas [196]. The percentage weight loading of nickel on the catalyst was analyzed by Optical Emission Spectroscopy with Inductively Coupled Plasma (ICP-OES) using an Optima 8300 DV (PerkinElmer) instrument. For the analysis process, the catalyst sample had to be in the liquid state. The dissolution was carried out in aqua regia using a microwave reaction system (Anton Paar, Multiwave Pro) at approximately 170 °C and 50 bar and then diluted with ultrapure water (Milli-Q) for the ICP-OES measurement. Morphological and compositional information of the reduced catalyst was studied using Scanning Transmission Electron Microscopy (STEM) combined with Energy Dispersive X-ray Spectroscopy (EDS). For this purpose, a sample of the reduced catalyst was dry-prepared by spreading the particles on a holey carbon film and analyzed with a JEOL JEM-F2000 TEM using a Gatan Metro camera. To obtain crystallographic information about the support and the metal particles, a spent catalyst sample was determined by X-ray Diffraction (XRD) measurements at beamline P21.1 at PETRA III (DESY, Hamburg). A silica reactor tube filled with the catalyst bed was placed in the synchrotron radiation, and diffracted X-rays were detected with a XRD 1621 N ES detector (PerkinElmer). The energy of the incident X-rays with fixed angles

was 101.6 keV, corresponding to a wavelength of 0.1221 Å. At an exposure time of 1 s, 60 images were captured and averaged. HighScore Plus software and reference patterns from the ICDD database were applied for the qualitative phase analysis [197]. In a further characterization step using Raman spectroscopy, the spent catalyst was examined after the reaction for carbonaceous deposits that may have been formed from CO by the Boudouard reaction (cf. Eq. (2.23)). The spent catalyst-filled silica reactor tube was positioned in the laser beam (frequency-doubled Nd:YAG laser) with a wavelength of 532 nm. With an attached microscope (Olympus, BX51WI), the laser spot could be directed externally onto the catalyst bed at the inlet and outlet of the reactor, providing two measurement points for comparing the possible carbon content after reaction with an unspent reference condition. Raman spectra were acquired using a triple filter Raman spectrometer (TriVista 557 S&I GmbH) with a liquid nitrogen-cooled CCD camera (Princeton Instruments) as the detector. To support the results of the Raman measurements, individual catalyst particles were also taken from the reactor tube at the inlet and outlet to determine carbon deposits by Laser-Induced Breakdown Spectroscopy (LIBS). The particles were placed on a movable sample holder of a LIBSpector (ARYELLE Butterfly, LTB Lasertechnik Berlin GmbH) and guided into a pulsed laser beam with a wavelength of 1064 nm (Q-switched Nd:YAG laser). The penetration of the beam vaporizes a part of the catalyst bulk and creates a plasma cloud. The radiation emitted by the plasma cloud was detected by an EMCCD camera and analyzed using Plasus Specline AMS software.

Details on the characterized catalyst are provided in the experimental section Section 4.3. The ICP-OES measurement was kindly performed by the Central Laboratory of the Hamburg University of Technology. The STEM-EDS analysis was done by Saleh Corji, a research assistant in M. Willinger's group at TU Munich. The XRD analysis was kindly realized by Birte Wollak, a research assistant of the Technical University of Hamburg, at DESY in Hamburg (Germany), a member of the Helmholtz Association HGF. Filip Vrljic and Diego Espinoza, research assistants at Hamburg University of Technology, conducted the Raman measurements and LIBS measurements, respectively.

3.1.3 Compact Profile Reactor

IPOS aims to analyze surface adsorbates along a catalytic fixed-bed in an optimized *operando* manner, with the reactor and spectrometer separated. To acquire adsorbate profiles spectroscopically, the reactor must provide local access to obtain the spatial gradients within the catalytic packed bed during CO₂ methanation over a Ni/γ-Al₂O₃ catalyst. An

overview of the reactor supplied by REACNOSTICS for this work is shown in Figure 3.1. A reaction gas mixture can be dosed to the profile reactor via an inlet, the product mixture can be discharged via an outlet, and gas samples can be taken via a separate analysis line (Figure 3.1, A). Inside the CPR housing, a reactor tube (Figure 3.1, B) with the capillary sampling technique (Figure 3.1, C) is located. The spatially resolved capillary sampling technique of the reactor represents the heart of the iso-potential coupling to the spectroscopic instrument. The reactor tube with a length of 180 mm, an outer diameter (OD) of 6 mm, and a wall thickness of 1 mm was made of fused silica (ilmasil PN, QSIL GmbH). Particles of the Ni/ γ -Al₂O₃ catalyst are filled into the reactor tube and fixed at the top and bottom with a layer of quartz wool to form the packed bed. An inner diameter (ID) of 4 mm for the reactor tube defined the diameter of the fixed-bed. A catalyst bed with a maximum length of 6 cm can be accommodated within it. The reactor tube is surrounded by a heating block with two heating cartridges and sensors to control the reaction temperature. This allows reaction temperatures of up to 500 °C to be achieved. The heating zone of the heating block is sufficiently long to preheat the connected gas supply to the desired reaction temperature before entering the catalyst bed. A guide rail beneath the heating block, connected to a high-precision stepper motor, enables axial displacement of the assembled reactor tube and the fixed catalyst bed in the micrometer range. A stainless-steel sampling capillary (700 μ m OD, 520 μ m ID) is centered through the catalyst packing and locked in place. The capillary has four lateral orifices (4 x 70 μ m) that are laser drilled (LaserMicronics GmbH) at a specific position offset by 90 degrees. In addition, an insulated type K Inconel thermocouple (OD 250 μ m, TMH Elektrotechnik GmbH) is inserted into the capillary and pinned in place with the tip aligned to the side sampling orifices. An internal heating system of the CPR, capable of reaching temperatures of up to 200 °C, prevented the condensation of water in the transfer lines and the sampling capillary in the housing. The temperatures in the reactor housing and catalyst bed, as well as the movement of the reactor tube, i.e., the movement of the sampling orifices through the catalyst bed, could be monitored and controlled via a control box (Figure 3.1, D).

By moving the reactor tube and the catalyst bed while keeping the capillary fixed, different measuring positions can be approached with the orifices, and local temperature measurements can be performed using the inserted thermocouple. At the same time, a small sample of the reaction mixture is continuously extracted and transferred via sampling lines to analytical instruments such as mass spectrometers or IR spectroscopy devices. Simultaneous analysis of the gas temperature and reaction mixture composition as a function of sampling positions

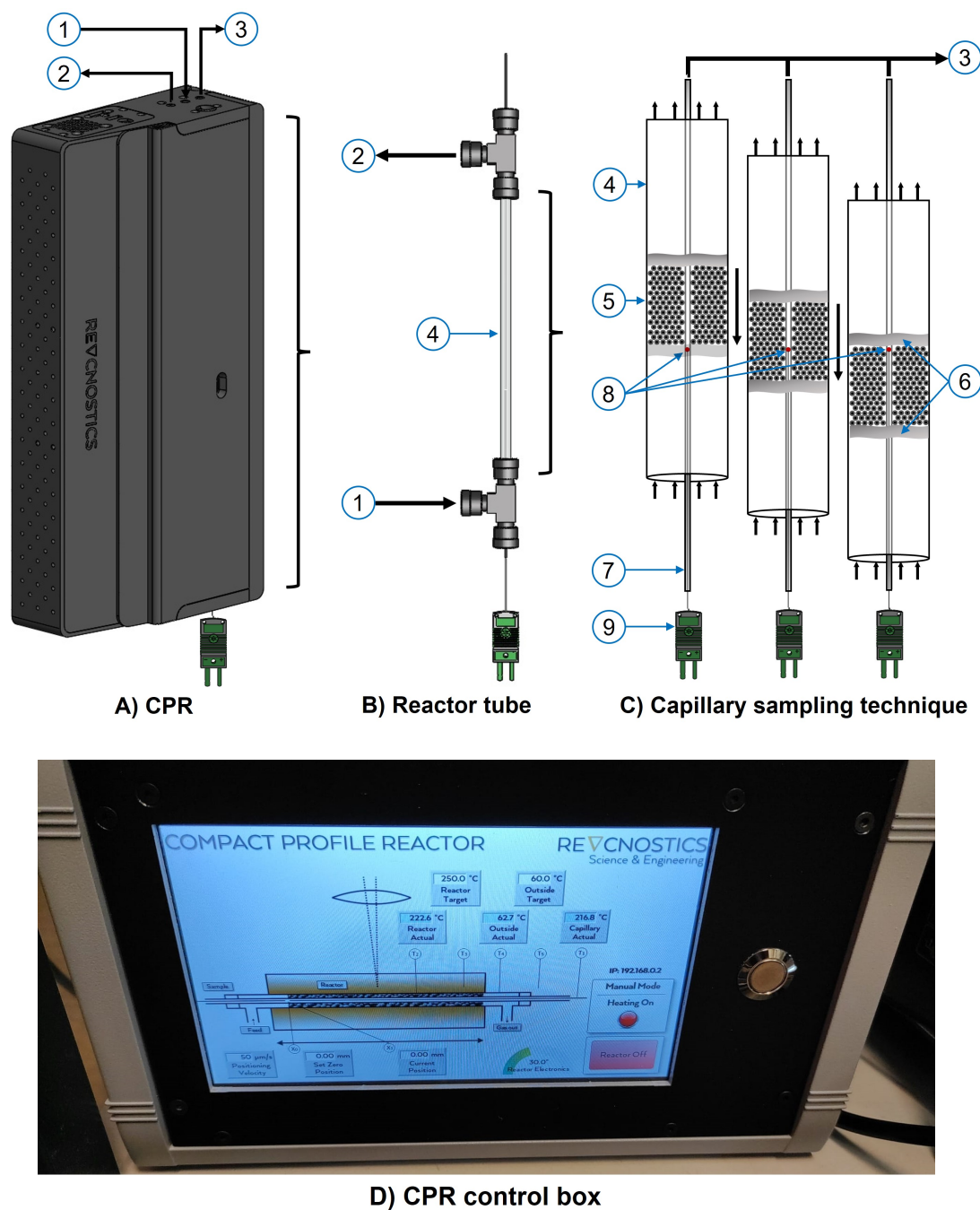


Fig. 3.1: Illustration of the Compact Profile Reactor (CPR, A–B) and its sampling capillary technique (C), controlled and monitored via a control box (D). The inner components are labeled with numbers 1 – 9: ① reactor inlet ② reactor outlet ③ gas sampling for analytics ④ reactor tube ⑤ catalytic fixed-bed ⑥ quartz wool ⑦ sampling capillary ⑧ sampling orifice ⑨ thermocouple

enables the measurement of a concentration and temperature profile throughout the catalytic fixed-bed. Therefore, a **profile run** is defined as a spatially resolved measurement of the catalytic fixed-bed in the CPR, where the gas mixture is sampled at desired measurement positions within the packing and directed to the analytics while a temperature profile is simultaneously recorded.

3.1.4 Gas Dosing System

Gas dosing to the reactor is accomplished by mass flow controller (MFC) modules, with the general setup shown in a CAD model and a flow chart in Figure 3.2a and Figure 3.2c, respectively. The gas supplies (cf. Table 3.1) are connected to the supply modules via pressure-regulated lines protected by a control valve, ensuring precise dosing of the gas flows for experiments or calibrations. Dosing was carried out with mass flow controllers (MFCs, Bronkhorst™) matched to the gases, which were assembled with safety fittings to form compact modules. The applied MFCs are listed, along with their serial numbers and maximum flow rates, in Table 3.2. On the gas supply side, the MFC modules were equipped with a filter (Swagelok), magnetic valve (Christian Bürkert GmbH & Co. KG) and pressure reducing valve (GCE-Druva) before the incoming gas enters the MFC. The magnetic valve is installed in the modules for flammable gases, such as hydrogen and methane. It serves as a safety device for the emergency shutdown of the gas supply in the event of a power supply interruption. The pressure regulator is used to maintain the line at a constant inlet pressure to the MFC for consistent regulation characteristics. A check valve, located directly behind the MFC, prevents gas from flowing back and thus damaging the device. Three gas outlets can be used separately via two 3-way ball valves.

For the experimental application, the MFC modules (cf. Table 3.2) are implemented in a compact table, as illustrated in Figure 3.2b. The MFCs are linked together via a built-in control box and power supply. They are controlled by a computer using Bronkhorst software. Gas dosing into the CPR is realized with a single supply line connected in series to the outlet ports of the MFC modules. The gas line was sufficiently long to ensure homogeneous mixing of the individual gas species before they entered the reactor. Calibration of the flow rates of each gas species is performed with a film flow meter upstream of the reactor inlet. In addition to the MFC modules installed in the gas dosing table, two further transportable modules for H₂ and CO are available. They are used separately for DRIFTS experiments.

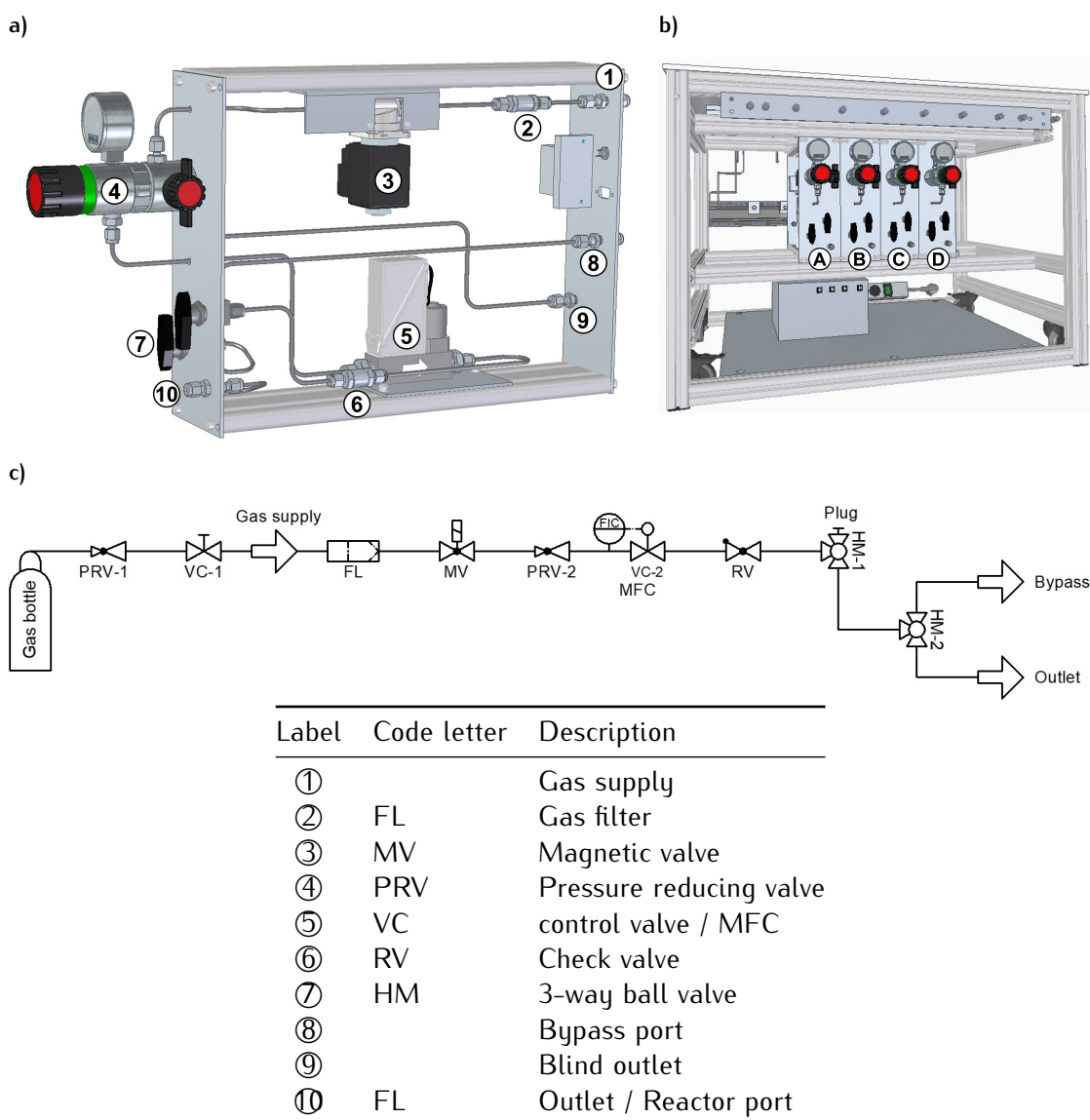


Fig. 3.2: CAD model (a) and flow chart (c) of the general setup of MFC modules and the implementation into a gas dosing table (b) containing different modules (A–C).

3.1.5 Mass Spectrometry

A quadrupole mass spectrometer (QMS 200 M2 with a Balzers Prisma QME 200, Pfeiffer Vacuum) was applied to determine the gas composition. For high-quality electron ionization analysis, the mass spectrometer (MS) is equipped with a Faraday cup and a secondary electron multiplier detector (QMA 200 M, Channeltron). The gas supply to the MS is enabled via a capillary installed in the sampling line. The sampling line is connected to

Tab. 3.2: Types and maximum flow rates of the MFCs (Bronkhorst™) used and the supplied gas species

MFC module	Species	Max. flow	MFC type
Ⓐ	Ar	50 ml/min	F-201-CV-500-RAD-11-V
Ⓑ	CO ₂	200 ml/min	F-201-CV-500-RAD-11-E
Ⓒ	H ₂	100 ml/min	F-201-CV-100-RAD-11-V
Ⓓ	CH ₄	50 ml/min	F-201-CV-050-RAD-11-V
portable	H ₂	50 ml/min	F-201-CV-050-RAD-11-V
portable	CO	50 ml/min	F-201-CV-050-RAD-11-V

a vacuum pump, allowing only small amounts of gas from the sampling line to enter the MS through the capillary. With this setup, larger volume flows can be handled through the sampling line without increasing the pressure or the feed to the measuring chamber of the MS, thereby maintaining measurement quality. The vacuum in the sampling line is regulated by a needle valve located upstream of the vacuum pump, thereby preventing any influence on upstream processes. Consequently, the vacuum in the sampling line can be considered negligible. Since water is a main product of the CO₂ methanation reaction, a small condensate trap (Neubert-Glas GbR) is installed in the sampling line upstream of the MS to avoid water adsorption effects and interference from capillary blockage during long-term measurements.

The gas composition was quantified using the internal standard method. By operating in an analog scan mode, a profile is displayed up to a mass-to-charge ratio of $m/z = 50$ amu. Figure 3.3a shows an example of the profile of a mass spectrum when measuring a methane-argon gas mixture. Minimal leakage could not be entirely avoided due to several pipe connections within the setup, resulting in slight background noise. However, reference subtraction eliminated most of the background noise, producing high-resolution spectra for quantification. The reference spectra were recorded before MS measurements were performed using pure argon as purge gas. For quantification, the peak areas to be determined were numerically integrated using the trapezoidal rule. Derived from a calibration curve, the peak area of a component could be converted to the molar flow rate by relating it to the internal standard. The calculation was carried out according to the following equation:

$$\frac{A_i}{A_{IS}} = m_c * \frac{\dot{n}_i}{\dot{n}_{IS}} \quad (3.1)$$

A_i and A_{IS} are integrated peak areas, while $\dot{n}_i$ and $\dot{n}_{IS}$ represent the molar flow rate of the component (i) and internal standard (IS), respectively. m_c stands for the multiplication factor, which is derived from the slope of the calibration curve. An example of a calibration curve for methane is shown in Figure 3.3b. Since the intercept approaches zero, it can be neglected when calculating the molar flow rates of a component as seen in the equation above.

Argon ($m/z = 40$ amu) was selected as the internal standard because, unlike nitrogen, it does not interfere with the mass fragments of CO_2 , the reactant, or CO, a possible byproduct of CO_2 methanation. The mass spectrometer was calibrated for mass-to-charge ratios (m/z) of 15 amu (CH_4) and 44 amu (CO_2) in binary mixtures with argon over a range of concentrations considered suitable for the reaction conditions. Although CH_4 has its central ionized peak at a mass-to-charge ratio of 16 amu (CH_4^+), it is affected by the fragments of CO_2 (O^+) and H_2O (O^+). Therefore, the non-sensitive mass-to-charge ratio of 15 amu (CH_3^+) was used for CH_4 detection. Further calibrations are not required for CO_2 methanation, as the amounts of water and hydrogen were calculated via stoichiometry by balancing oxygen and hydrogen, respectively. Carbon monoxide was considered a possible by-product and calculated by closing the carbon balance. Further details on calculating mass balances and determining product composition are presented in the results (4.2.2). The calibration of the

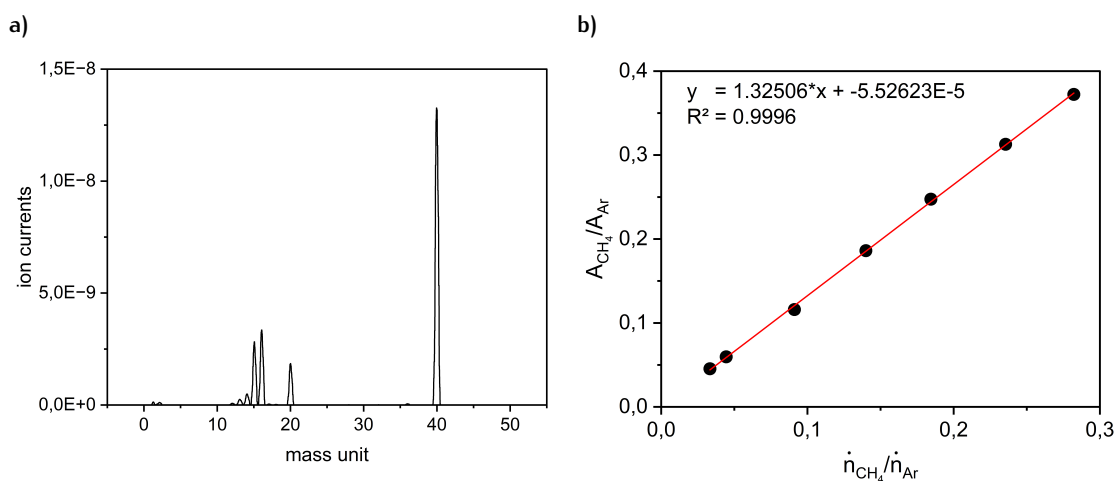


Fig. 3.3: (a) A sequence of a mass spectrum during calibration of a methane–argon gas mixture. (b) Calibration line of the integrated peak area ratios of CH_4 to the internal standard Ar.

MS is performed in the same configuration as the actual experiments (Section 4.1), using the reactor setup with an empty reactor tube at room temperature and ambient pressure. Mass flow controllers dose the gas mixtures to the reactor and through the sampling line to the

MS. Prior to the experiments, the CO₂ calibration was checked by a two-point calibration of the reaction mixture entering the reactor and the calibration factor was adjusted in case of deviations to ensure a high-quality evaluation. Using the known molar flow rate of CO₂ at the reactor inlet, a two-point calibration line was formed through the zero point, as the calibration line for CO₂ ran through the zero point, similarly to the calibration line for CH₄ in Figure 3.3b.

3.1.6 FTIR Spectroscopy

For catalyst surface analysis, IR spectra were recorded with a FTIR spectrometer (Vertex70, Bruker). A picture of the IR setup is shown in Figure 3.4a. The sample chamber in the IR spectrometer is a Praying Mantis™ high-temperature reaction chamber (DRIFTS cell, Harrick) with ZnSe windows placed into a mirror collector assembly (Praying Mantis™ Diffuse Reflection Accessory, Harrick). The key components are the horizontal and ellipsoidal mirrors, metaphorically aligned like a praying mantis. The beam enters the sample

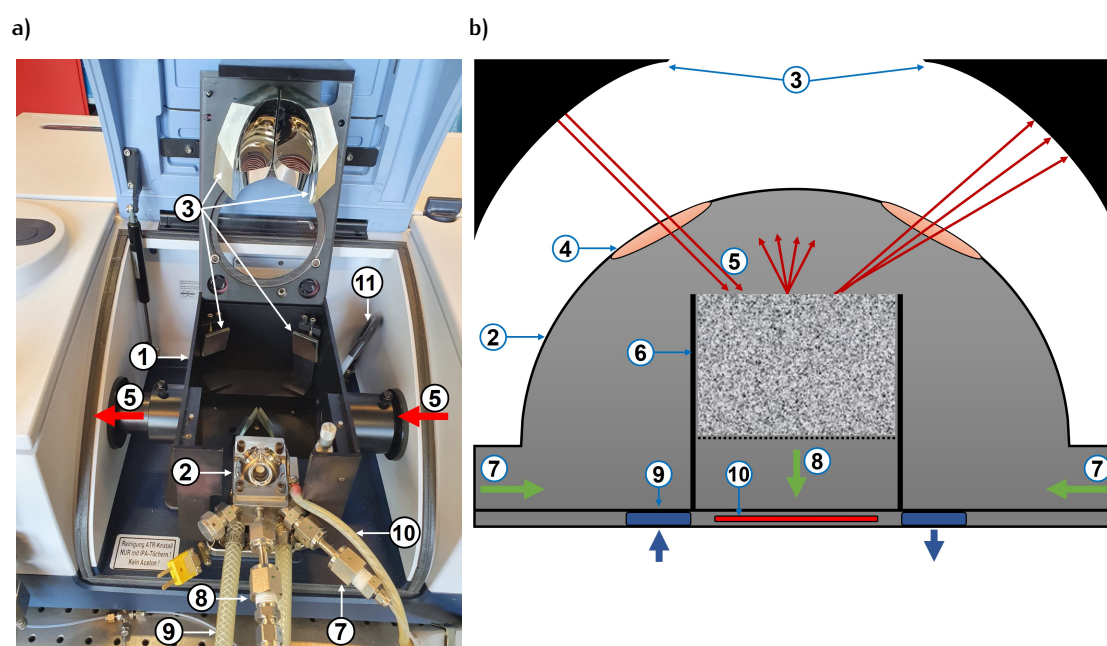


Fig. 3.4: (a) Setup of the IR spectrometer equipped with the components to obtain DRIFTS spectra. (b) Illustration of the DRIFTS chamber for a detailed overview. For explanation, the components are labeled with numbers 1 – 9: ① mirror collector assembly ② DRIFTS cell ③ mirrors ④ ZnSe-windows ⑤ MIR radiation ⑥ sample cup ⑦ gas inlet port ⑧ gas outlet port ⑨ water-cooling system ⑩ heating system ⑪ purge gas supply

chamber through the right optical access port, which is separated from the interferometer

compartment by an IR-transparent sample compartment window made of KBr, as indicated by a red arrow. The special mirror arrangement directs the beam into the DRIFTS cell on the probe. The mirrors then transmit the radiation diffusely reflected by the sample to a detector in the left compartment, which is also separated by a window. A deuterated L-alanine-doped triglycine sulfate (DLaTGS) detector with a KBr window is installed as standard, providing a nominal spectral range of $12000 - 250\text{ cm}^{-1}$. However, the accessible MIR range is restricted to $4000 - 400\text{ cm}^{-1}$. Since the IR radiation from the broadband MIR source passes through the interferometer's built-in KBr beamsplitter, the spectrometer housing windows, and the ZnSe windows of the DRIFTS cell, the effective spectral range is further limited to approximately 500 cm^{-1} . The DRIFTS cell is designed for temperatures and pressures up to $900\text{ }^{\circ}\text{C}$ and 30 bar, respectively. A cylindrical stainless steel sample cup is integrated into the DRIFTS cell and can be filled with a catalyst sample. A thin stainless steel sieve plate with a mesh size smaller than $100\text{ }\mu\text{m}$ is placed at the bottom of the sample cup, allowing the catalyst sample to be securely fixed in space. When Gas flows through the body of the DRIFTS cell, it enters via the gas inlet port and passes vertically through the sample cup and the catalytic fixed bed contained within, similar to a reactor tube. The cell features a heating cartridge and a Type-K thermocouple, both of which can be controlled and monitored via a control box. As the device does not feature a temperature probe directly in the sample, a separate calibration measurement was performed by placing a thermocouple directly in the sample and correlating its temperature reading with the temperature of the heating cartridge. A cooling system runs through the cell body, which operates with water. Cooling of the outer walls of the cell is necessary to prevent influencing the IR measurements by background radiation from the hot walls or by the expansion of the metal, which would displace the measurement position. For measurements, the chamber containing the DRIFTS cell can be purged either with air dried by a purge gas generator or with nitrogen, to minimize background interference from water vapor and CO_2 present in the surrounding atmosphere. With default settings, the spectrometer operates at a resolution of 4 cm^{-1} , with 64 scans per run, and transmits the data to an OPUS-based software system for the evaluation of the detected IR spectra. The detector registers maximum signal intensities when the recombined beams undergo constructive interference and minimum intensities when they undergo destructive interference, arising from the relative phase differences introduced within the interferometer. By summing the interference contributions at each optical path difference for all wavelengths, an interferogram is obtained. This interferogram is then mathematically transformed using a Fourier transformation to yield an IR spectrum, typically displayed as absorbance versus wavenumbers.

The standard IR measurement procedure begins with recording a reference spectrum, commonly referred to as the background spectrum. In a subsequent step, the sample spectrum is acquired under identical conditions. The final reflection spectrum is then obtained by dividing the sample spectrum by the reference spectrum, in accordance with the Beer-Lambert-Bouguer law explained discussed in Section 2.4.2. In the context of diffuse reflectance measurements using a DRIFTS cell, the term transmittance (T) is formally analogous to reflectance (R). It represents the ratio between the intensity of the diffusely reflected radiation from the sample (I) and the intensity of the incident beam recorded in the background measurement (I_0). In DRIFTS measures, the reference spectrum is recorded without the sample, but with a non-absorbing and chemically inert reference material (or 'white standard') placed in the DRIFTS cell. Calcium fluoride (CaF_2) was used as the reference material/'white standard' due to its properties of being chemically inert, temperature-resistant, nonhygroscopic and quasi-insoluble in water. It is also characterized by transparency to IR radiation over a broad wavenumber range, except for strong absorption below 1100 cm^{-1} [85, 86]. Consequently, the spectral range for MIR measurements was restricted to $4000 - 1200\text{ cm}^{-1}$. According to the literature, it is common to visualize DRIFTS spectra by transforming the intensity of the reflectance into a pseudo-absorbance or using the Kubelka-Munk function [70, 98–100]. In this work, IR spectra are expressed exclusively as absorbance spectra by applying the negative logarithm to the reflectance spectra (R), titled as pseudo-absorbance (A) transformation:

$$A = -\log_{10}(R) = \log_{10}\left(\frac{1}{R}\right) \quad (3.2)$$

The transformation to an adsorption spectrum is performed automatically by the software. It produces a spectrum with the wavenumber as the abscissa and the pseudo-absorbance as the ordinate, hereinafter referred to as "absorbance" for the sake of simplicity.

3.2 Methodology of Iso-Potential Operando DRIFTS

In the preceding sections, the materials required for this study were described in detail. The following section outlines the methodological approach for investigating adsorbates on catalysts under reaction conditions using DRIFTS, as initially published in [81].

3.2.1 Methodical Approach for the Measurement of Adsorbates using DRIFTS

Typically, three spectra are required in DRIFTS experiments to obtain adsorbed species of a catalyst surface in the IR spectrum [100]. Starting with a reference spectrum (I_0) measured with a 'white standard' in the DRIFTS cell. The second spectrum is obtained from the catalyst without adsorbates (I_{cat}). When a catalyst sample is treated in the DRIFTS cell with a reducing or oxidizing gas (depending on the catalyst) at the target temperature, and subsequently purged with a non-absorbing inert gas, the resulting reflectance spectrum reveals a catalyst surface essentially free of adsorbates ($R_{\text{cat}} = I_{\text{cat}}/I_0$). A third sample spectrum, obtained after exposing the catalyst to an adsorbing gas ($I_{\text{cat+abs}}$) at the target temperature and subsequently purging with a non-absorbing inert gas, provides a reflectance spectrum that conveys information on both the adsorbates on the catalyst surface and the IR absorption of the catalyst bulk ($R_{\text{cat+abs}} = I_{\text{cat+abs}}/I_0$). In the study by Sirita et al. [100], the relative reflectance is defined as the sample spectrum of the catalyst with adsorbates in relation to the reference spectrum of the adsorbate-free catalyst:

$$R' = \frac{R_{\text{cat+abs}}}{R_{\text{cat}}} = \frac{I_{\text{cat+abs}}/I_0}{I_{\text{cat}}/I_0} = \frac{I_{\text{cat+abs}}}{I_{\text{cat}}} \quad (3.3)$$

Consequently, only two spectra are required to capture the vibrational bands of the adsorbed species on the catalyst surface, with the addition of a reaction gas mixture yielding the sample spectrum (here referred to as the third spectrum). However, the resulting spectrum not only contains spectroscopic information of the adsorbed species on the catalyst surface but is also affected by spectral contributions unrelated to the catalyst adsorbates. This includes all spectral features that do not correspond to the vibrational bands of surface-bound species on the active metal and support sites, thereby complicating the characterization. Taking this into account, the iso-potential *operando* DRIFTS measurement technique must address two challenges: I) undesired spectroscopic information must be removed from the raw data as accurately as possible to highlight the catalyst adsorbates in the acquired DRIFTS spectra and obtain clear adsorbate spectra, and II) the catalytic conversion in the DRIFTS cell must be minimized to prevent reaction-induced changes to the catalyst surface. The latter can be experimentally avoided by highly diluting the catalyst sample in the DRIFTS cell with a chemically inert reference material/'white standard'. For this purpose, CaF_2 was used as 'white standard'. Further details on the dilution of the catalyst sample for DRIFTS measurements can be found in Section 4.2.1. For the spectral acquisition of a diluted catalyst sample, all potential sources of infrared absorption that may arise during DRIFTS

measurements of the sample and reference spectra are first identified and illustrated with examples from DRIFTS measurements of a Ni/ γ -Al₂O₃ catalyst under CO₂ methanation reaction conditions:

- a) **Adsorbed species on the catalyst surface and catalyst support surface under reaction atmosphere:** This is the desired information to be derived from the sample spectrum of the diluted catalyst under reaction conditions.
- b) **Adsorbed species on the diluent under reaction atmosphere:** Since the catalyst sample is diluted with a white standard, surface adsorbates may also form on the diluent under the reaction gas atmosphere and appear as vibrational bands in the acquired DRIFTS spectra. This undesired spectral signature must be removed.
- c) **IR absorption of the bulk of the catalyst, the catalyst support and the diluent/'white standard':** The bulk material in the DRIFTS cell interacts with the penetrating infrared radiation and attenuates the intensity to some extent, resulting in undesired spectral bands in the IR spectrum. In the present study, CO₂ methanation over a Ni/ γ -Al₂O₃ catalyst diluted in CaF₂ is used as a model reaction, wherein the reaction gas mixture from the reactor is introduced into the DRIFTS cell. Accordingly, the composition of the gas mixture varies along the reactor, ranging from the reactants CO₂, H₂, and inert gas at the inlet of the catalyst bed to the reaction mixture at the outlet, which contains CO₂, H₂, CH₄, H₂O, CO, and inert gas. The bulk structures of the chemically inert materials used as the catalyst support (γ -Al₂O₃) and the diluent/'white standard' remain unchanged by the reaction mixtures. In contrast, H₂ can maintain the active nickel component in its reduced elemental state, whereas gas species such as CO₂ or H₂O may oxidize nickel to nickel oxide. Consequently, the IR absorption of the catalyst bulk may vary depending on the gas composition to which it is exposed. Although the variations in IR absorption of the catalyst bulk due to chemical changes cannot be eliminated from the raw DRIFTS spectra, they can be quantified relative to a reference state for comparison, following the procedure described in Eq. (3.3). By performing a reference measurement of the catalyst with a favorably chosen reference gas – e.g., pure H₂ as employed in the present study – several spectroscopic advantages can be achieved:
 - Gaseous H₂ is IR-inactive and does not produce spectral signatures in DRIFTS measurements. While molecularly adsorbed H₂ exhibits only weak, negligible IR-active vibrational bands in the MIR region, dissociatively adsorbed H₂ gives rise to strongly IR-active modes, which are typically observed in the NIR or FIR regions and are not relevant in this context.

- H_2 is the major component of the reactants for CO_2 methanation, so the reference state of the catalyst is probably similar to the state of the catalyst under the reaction gas atmosphere.
 - H_2 has a reducing effect on the active component nickel and keeps it in its metallic state, which is IR-silent.
- d) **Adsorbed species on the catalyst surface and catalyst support surface under reference gas atmosphere:** DRIFTS measurements of the catalyst sample under a reference gas atmosphere result in different adsorbates on the catalyst and catalyst support than under reaction conditions. This may result in deviations such as negative or residual spectral bands in the difference spectrum when the reference state spectrum is subtracted from that of the reaction state. In the test reaction, for instance, if the active component nickel were present in an oxidized state under the reaction atmosphere, hydrogen could chemisorb on nickel oxide, giving rise to OH-stretching vibrational bands in the IR spectrum. Under reference conditions, however, H_2 binds to reduced nickel. Nevertheless, H-stretching vibrations are not visible in the MIR region and do not appear as spectral signatures in the DRIFTS spectrum. Thus, when the reference spectrum of the diluted catalyst is subtracted from its sample spectrum under reaction conditions, the OH bands are retained in the difference spectrum. Consequently, the use of a different reference gas could alter the DRIFTS spectrum due to the formation of different adsorbates on the catalyst and possibly generate negative bands in the difference spectrum when subtracted from the spectrum of the sample in the reaction state.
- e) **Adsorbates on the diluent under reference gas atmosphere:** DRIFTS measurements of the diluent/‘white standard’ under a reference gas atmosphere result in different adsorbates than under a reaction atmosphere, which can lead to deviations in the difference spectrum. However, in the context of the present application, it is not expected that the reference gas hydrogen will cause IR-visible adsorbates on the white standard.
- f) **IR absorption of the gas phase exposed to the catalyst:** A significant source of undesired IR absorption arises when IR radiation penetrates the gas phase of the DRIFTS cell exposed to the catalyst. The spectral signature appears in the spectrum as rovibrational bands of gas molecules. The IR absorption of the gas phase increases with concentration (or pressure) and can become so dominant that it completely obscures the spectral signature of the adsorbates. Consequently, the IR absorption of the gas phase must be removed from the sample spectrum of the diluted catalyst under reaction conditions.
- g) **Instrument function:** As the infrared light travels along the optical path from the source

to the detector, the intensity of the IR radiation is attenuated by optical elements of the spectrometer and absorbed by the optical windows of the DRIFTS cell and by gas molecules in the optical path outside the DRIFTS cell, such as water vapor or carbon dioxide. Impurities on the optical windows, caused by dust, also affect the recorded DRIFTS spectrum. These undesired absorptions must also be removed from the raw data by measuring a reference.

3.2.2 Iso-Potential Operando DRIFTS Workflow

By coupling the CPR with the DRIFTS cell, gas samples can be taken at various measurement positions within the catalytic fixed-bed and directed into the DRIFTS cell during the reaction. Once the fixed-bed has been completely passed through, the iso-potential coupling method using DRIFTS provides a spectroscopic profile (DRIFTS profile) of the surface adsorbates on the catalyst, which hypothetically reflects the surface profile of the fixed-bed in the reactor. In total, as described in Section 3.2.1, four separate DRIFTS measurements have to be performed at each measurement position in the CPR to obtain an adsorbate profile from the sum of adsorbate-only spectra:

- Two DRIFTS measurements (sample/'white standard' spectrum) in which the DRIFTS cell is connected with the reactor through iso-potential coupling and is filled on the one hand with the diluted catalyst sample or on the other hand with the pure diluent/'white standard'. Both the sample and the diluent are exposed to the reaction gas mixture by sampling from the CPR at the preferred measurement positions. To establish the same measurement conditions as at the measurement positions in the CPR, the DRIFTS cell must be adapted to the locally measured reactor temperature (T_r) and pressure (p_r).
- Two DRIFTS measurements (reference spectra) in which the DRIFTS cell is filled with the diluted catalyst sample or the pure diluent/'white standard' and purged with the reference gas at the local reactor pressure (p_r) and temperature (T_r).

Since the Harrick DRIFTS cell design only provides for one test chamber (cf. Section 3.1.6), only one DRIFTS spectrum can be recorded at a time. Consequently, the DRIFTS measurements of the sample, 'white standard' and reference spectra are carried out in sequence. For switching from the diluted catalyst sample to pure diluent, the cell must be opened and repacked. Each time the chamber is opened, the respective sample requires renewed pretreatment. To avoid the considerable experimental effort associated with repeatedly changing samples and gas supplies in the DRIFTS cell, the four DRIFTS measurements are assigned to separate profile measurement sequences.

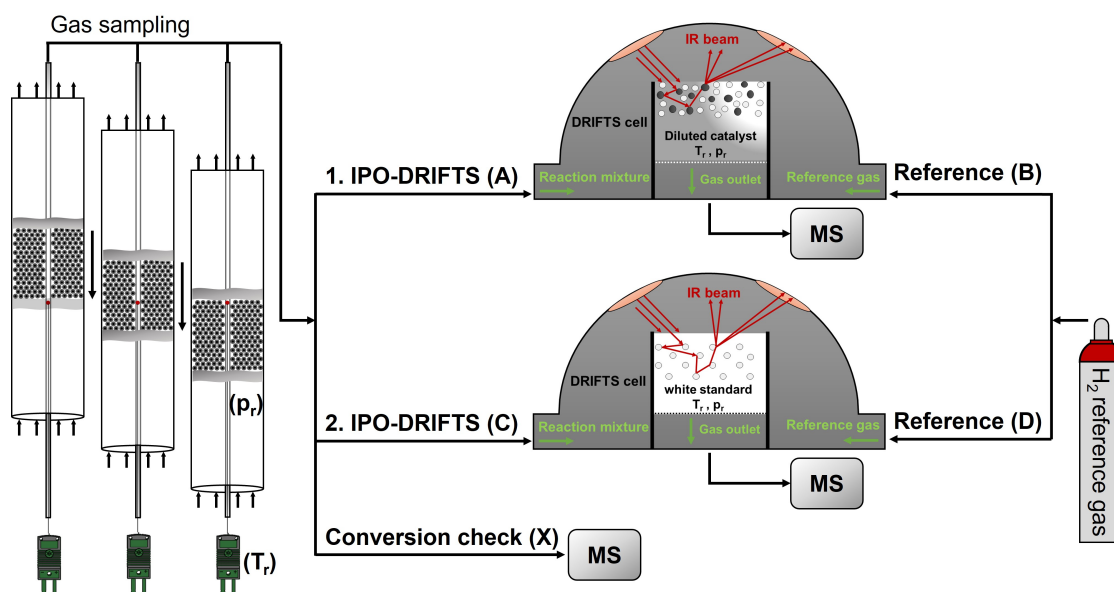


Fig. 3.5: Illustration of the iso-potential *operando* DRIFTS workflow. Adopted and modified from [81].

Taking all these aspects into account, the workflow for iso-potential *operando* DRIFTS measurements can be visually summarized and illustrated in Figure 3.5. In the first series of IPO DRIFTS and reference measurements (A and B), the DRIFTS cell is filled with a small amount of the same catalyst as in the reactor and highly diluted with the diluent/‘white standard’ (CaF_2). In a second set of IPO DRIFTS and reference measurements (C and D), the DRIFTS cell is filled with the reference material/‘white standard’ (CaF_2) only. To ensure that neither the diluted catalyst nor the diluent alone, nor the interior of the DRIFTS cell induces a significant change in the chemical composition of the reaction mixture that could affect the iso-potential measurement, the local reactor conversion at each measurement position is compared with the corresponding conversion measured downstream of the DRIFTS cell using a mass spectrometer. The conversion check (X) in the reactor was measured separately with the MS in an additional profile measurement that bypassed the DRIFTS cell. However, it is essential to record the profiles from the reactor inlet to the outlet, rather than in the opposite direction, to ensure that the catalyst in the DRIFTS cell experiences a history almost identical to that of the catalyst in the reactor, particularly in cases where structural or adsorbate-related changes are irreversible.

3.2.3 Extraction of Catalyst Surface Adsorbate Spectra

The information content of the four spectra recorded during IPO DRIFTS measurements at any measurement position in the reactor is described schematically in the following using CO₂ methanation on a Ni/ γ -Al₂O₃ catalyst. First, the bulk and surface state of the catalyst sample is discussed. Next, the process of removing gas phase absorption from DRIFTS spectra is explained. Finally, it is shown how to extract the adsorbate spectra.

In terms of the bulk and surface state of the catalyst, the catalyst sample is highly diluted in a 'white standard' (CaF₂) and exposed to the reaction mixture sampled from the reactor in a series of IPO DRIFTS measurements (A). The pressure and temperature in the DRIFTS cell are matched to the reactor pressure (p_r) and to the same temperature (T_r) as measured locally in the reactor. In another measurement sequence, the diluted catalyst sample is exposed to the reference gas under the same conditions (B), i.e., reactor pressure and local temperatures are adopted. The purpose of analyzing the catalyst under a reference gas is to provide a defined reference state (e.g., reduced or oxidized) for both the active metal and the support material, thereby identifying chemical changes in the bulk structure of the catalyst. The spectral information that can be included in a DRIFTS spectrum for each of these measurements is summarized in Figure 3.6. A drawing of the DRIFTS cell, along with its measurement conditions for the particular spectrum to be measured, is attached. The spectral signatures in the DRIFTS spectra, which can change as they pass through the catalyst bed in the reactor, are indicated by x for the surface species, y for the gas phase and z for the bulk phases. The IR absorptions under reference conditions are designated as 0 and are identical in content at every measurement position in the reactor for the respective temperature and pressure values. Reference measurements at different temperatures – and pressures in the case of pressure fluctuations in the reactor – are necessary to correlate the reaction conditions with the reference conditions; otherwise, the baseline in the spectra may shift, preventing comparison. Instrument effects and absorptions in the beam path outside the DRIFTS cell, which occur in both the reaction and reference gas measurements, are designated as 1 and should ideally be identical if the measurements are performed at short intervals. To illustrate a possible chemical change in the catalyst bulk in Figure 3.6, the nickel particle is colored blue under the reaction atmosphere (Figure 3.6 A), black under the reference gas atmosphere of hydrogen (Figure 3.6 B), and orange in the difference spectrum (A'_1) of both.

When a reflectance spectrum obtained by IPO DRIFTS measurements under reaction

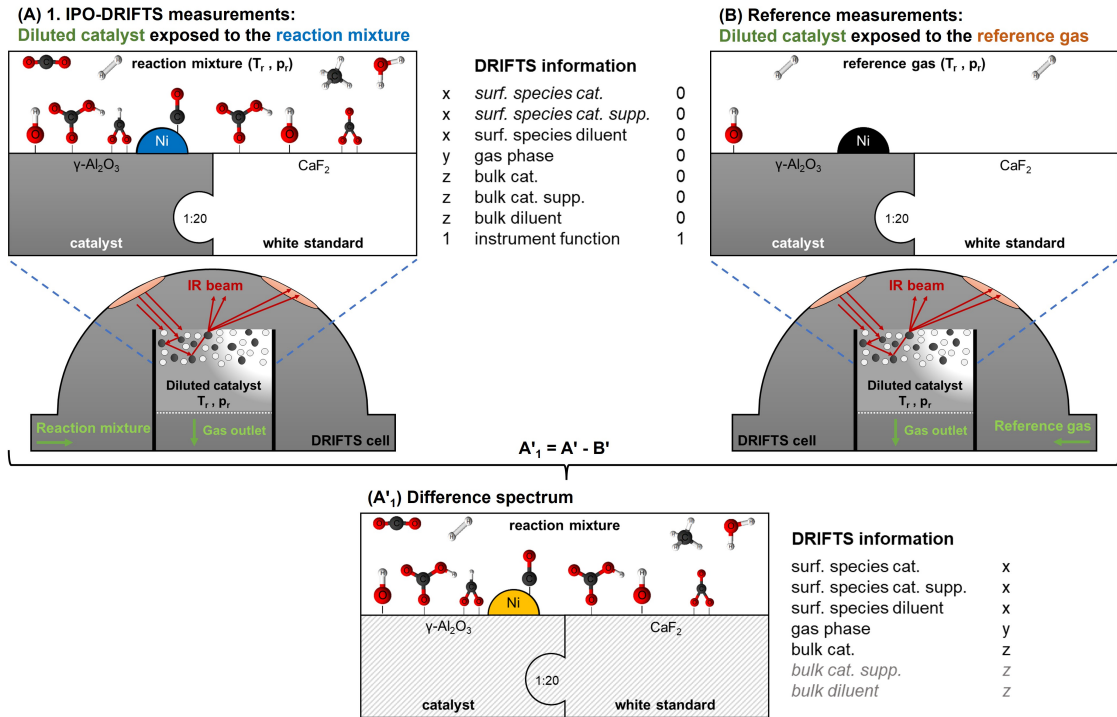


Fig. 3.6: Schematic illustration of the bulk and surface state of a Ni/γ-Al₂O₃ catalyst in an iso-potential *operando* DRIFTS measurement during CO₂ methanation. The DRIFTS cell is filled with a small amount of catalyst highly diluted in a diluent/‘white standard’ and exposed to the reaction mixture sampled locally from the reactor or to a reference gas. Temperature and pressure are adapted to the local reaction conditions (T_r , p_r) in the reactor. IR-absorptions, which can change when scanning through the reactor, are designated with x for the surface species, y for the gas phase and z for the bulk phases. IR-absorptions under reference conditions are denoted by 0. Instrument effects and absorptions in the beam path outside the DRIFTS cell are denoted by 1. (A) Iso-potential *operando* DRIFTS measurement, (B) reference measurement, (A₁) spectrum difference. Adopted and modified from [81].

conditions (A) is referenced to the reflectance spectrum acquired under reference conditions (B) according to Eq. (3.3), the resulting difference spectrum (A₁) ideally eliminates the undesired spectral signatures. By scanning the entire fixed-bed in the reactor (CPR), a profile of DRIFTS reflectance spectra is obtained. To facilitate the visual interpretation of a differentiated reflection spectrum, it can be transformed into an absorbance spectrum, which is permissible according to the following transformation derived from Eq. (3.2):

$$\begin{aligned} A'_1 &= -\log_{10}(R'_1) = -\log_{10}\left(\frac{A}{B}\right) = -\log_{10}(A) - (-\log_{10}(B)) \\ &= A' - B' \end{aligned} \quad (3.4)$$

However, spurious IR bands may remain in the difference spectrum if the bulk state of the catalyst under the reaction atmosphere differs from the reference state. Ideally, if the catalyst bulk in the reaction atmosphere is the same as under reference conditions, its IR absorption in the difference spectrum will cancel out exactly ($z = 0 \rightarrow 0 - 0 = 0$). The same principle applies to the bulk structure of the catalyst support and the diluent. In the present application, it is assumed that the bulk structure of both the catalyst support ($\gamma\text{-Al}_2\text{O}_3$) and the 'white standard' (CaF_2) remains unchanged under reaction and reference conditions, such that their bulk IR absorption cancels out in the difference spectrum. Therefore, in both illustrations, (Figure 3.6 A) and (Figure 3.6 B), the bulks are shown in dark gray and white, respectively, and shaded in the difference spectrum (Figure 3.6 A'₁). Similarly, the IR absorptions of the bulk structure are grayed out in the spectral information listed for the difference spectrum. The IR absorptions from surface adsorbates on the catalyst, both on the active component (Ni) and on the support material ($\gamma\text{-Al}_2\text{O}_3$), and on the white standard (CaF_2) are visible in the reflectance spectra. In contrast to the spectral information about the bulk IR absorption, these absorptions are retained in the difference spectrum. Furthermore, IR absorptions caused by optical components and molecules in the beam path outside the DRIFTS cell, referred to as 'instrument function', are detectable but are canceled out in the difference spectrum. The main perturbation remaining in the difference spectrum, which may lead to misinterpretation of the spectral information of the adsorbed species, arises from the IR absorption of the gas molecules surrounding the catalyst in the DRIFTS cell. Since the rovibrational bands of the gas phase absorption are broader than the vibrational bands of the adsorbed species, they can provide spectral overlapping. In the present application, the IR absorption of the gas phase under reaction conditions is obtained as absolute absorption because the reference gas H_2 is IR-inactive and does not introduce band cancellation during subtraction.

To remove the gas phase IR absorptions, the DRIFTS cell is filled with the pure diluent/'white standard' (CaF_2) and first exposed to the reaction mixture sampled from the reactor along the fixed-bed, followed by exposure to the reference gas in a second set of measurements. The pressure and temperature in the DRIFTS cell are again adjusted to match the reactor pressure (p_r) and the same temperature (T_r) as measured locally in the reactor. The spectral information, which may be present in a DRIFTS spectrum for each of these measurements, is summarized in Figure 3.7. The spectral signatures retained in the measured spectra arise from IR absorptions of surface species adsorbed on the diluent/'white standard' (x), the IR absorptions of the reaction gas phase (y), and the bulk IR absorption of the diluent (z). The transformed difference spectrum (Figure 3.7 A'₂) is obtained by

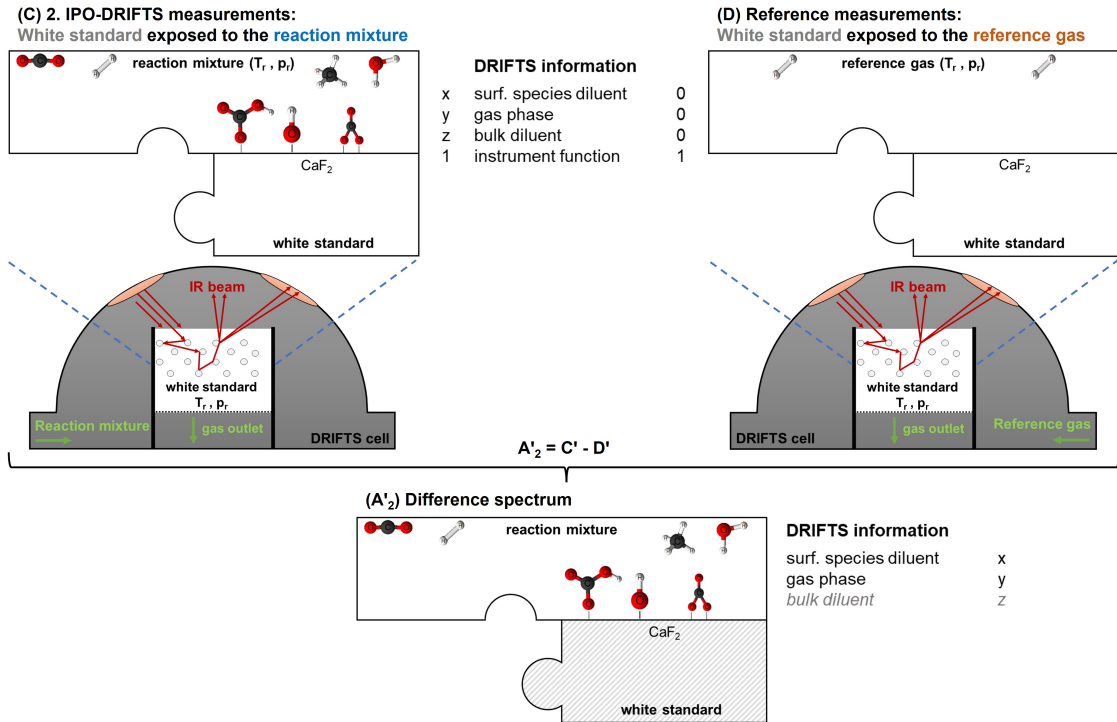


Fig. 3.7: The removal of IR absorption in the gas phase during an iso-potential *operando* DRIFTS measurement for CO₂ methanation on a Ni/ γ -Al₂O₃ catalyst is illustrated schematically. The DRIFTS cell is filled with pure diluent/'white standard' and exposed to the reaction mixture sampled locally from the reactor along the fixed-bed, as well as to a reference gas separately. Temperature and pressure are adapted to the reaction conditions of the local measurement positions in the reactor (p_r, T_r). IR absorptions that can vary along the fixed bed on the catalyst are designated as x for surface species, y for the gas phase, and z for the bulk phases. IR absorptions under reference conditions are denoted as 0, while instrumental effects and absorptions in the beam path outside the DRIFTS cell are denoted as 1. (C) Iso-potential *operando* DRIFTS measurement, (D) reference measurement, (A'₂) spectrum difference. Adopted and modified from [81].

referencing the reflectance spectrum of an IPO DRIFTS measurement to its corresponding reference measurement (Figure 3.7 D), following the transformation defined in Eq. (3.2):

$$\begin{aligned} A'_2 &= -\log_{10}(R'_2) = -\log_{10}\left(\frac{C}{D}\right) = -\log_{10}(C) - (-\log_{10}(D)) \\ &= C' - D' \end{aligned} \quad (3.5)$$

By scanning the entire catalyst bed in the reactor, a profile of DRIFTS absorbance spectra is acquired, containing IR absorptions of both the gas phase and surface species on the diluent/'white standard', as illustrated in this application.

To extract spectral information on surface adsorbates and bulk catalyst changes, the data of the difference spectrum shown in Figure 3.7 (A'_2) are subtracted from those of the difference spectrum in Figure 3.6 (A'_1) as a final data processing step. This procedure is illustrated schematically Figure 3.8. In this case, the difference spectrum is generated

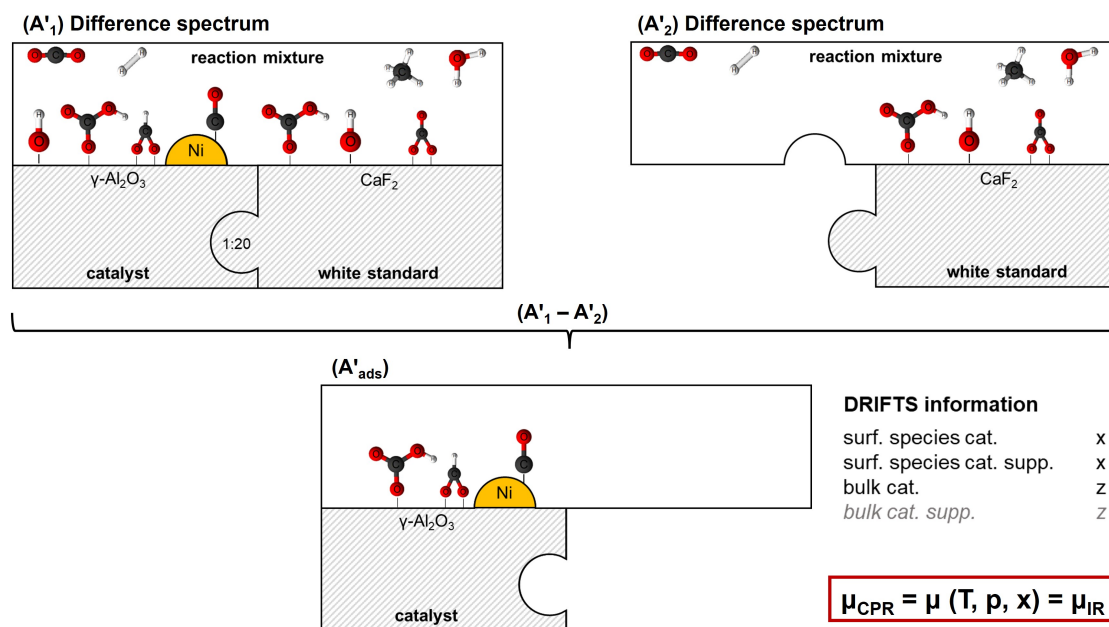


Fig. 3.8: Surface adsorbates and bulk catalyst changes are extracted by calculating a subtraction spectrum (A'_{ads}) from the difference spectra ($A'_1 - A'_2$). The resulting absorbance spectrum contains the IR absorptions of adsorbates on both the catalyst and support surfaces (x), as well as the bulk absorptions of the catalyst and support (z) relative to the reference state. Adopted and modified from [81].

by subtracting the transformed absorbance spectrum ($A'_1 - A'_2$) instead of dividing the reflectance spectra, as this allows for an optical interpretation of the obtained adsorbate spectrum without additional spectral transformation. This is permitted by the following transformation, derived from Equations (2.18) and (3.3):

$$R'_{\text{ads}} = \frac{R'_1}{R'_2} = \frac{A/B}{C/D}$$

$$A'_{\text{ads}} = -\log_{10}(R'_{\text{ads}}) = -\log_{10}\left(\frac{R'_1}{R'_2}\right) = -\log_{10}(R'_1) - (-\log_{10}(R'_2)) \quad (3.6)$$

$$= A'_1 - A'_2$$

The spectral signatures retained in the measured spectra arise from IR absorptions of the catalyst surface and the support surface (x), together with bulk absorptions of the catalyst

and support (z) relative to the reference state. In this step, all spectral contributions from IR absorptions of the reaction gas atmosphere (y), the main diluent (z), and the surface adsorbates on the diluent (x) are eliminated. By calculating all adsorbate spectra from the difference spectra obtained during reactor scanning through a set of IPO DRIFTS and reference measurements, a profile of adsorbate spectra can be derived. Owing to the iso-potential coupling of the DRIFTS cell with the reactor ($\mu_{\text{CPR}} = \mu(T, p, x) = \mu_{\text{IR}}$), this adsorbate profile reflects the same adsorbates present along the catalytic fixed-bed in the profile reactor (CPR).

4 Results and Discussion

4.1 Experimental Setup

The experimental setup, which meets the requirements for IPOS using DRIFTS, is shown in a simplified Piping and Instrumentation Diagram (P&ID) in Figure 4.1 and follows the concept already illustrated schematically in Figure 2.1. A Compact Profile Reactor (CPR, Reacnostics GmbH) specifically designed for spatially resolved measurements within a catalytic fixed-bed was employed. The technical specifications and operating principle of the CPR (II), together with the capillary sampling method for analyzing a fixed-bed of catalyst particles (III), are described in detail in Section 3.1.3 and references [32, 35]. An upstream gas dosing system, consisting of MFC modules (I), comprises a series of mass flow controllers (MFCs, Bronkhorst) installed in a rack with safety fittings (cf. Figure 3.2c), and supplies the CPR with the reaction gases – H_2 , CO_2 , and inert gas Ar. For MS calibration and preliminary IR tests, the gas dosing system is additionally equipped with MFC modules for CO and CH_4 . The complete list of gases and their respective applications is provided in Table 3.1, while a summary of the MFCs employed is presented in Table 3.2. An electronic pressure controller (II-1, EL-PRESS from Bronkhorst) located at the reactor outlet maintains a constant pressure within the reactor. Since the electronics in the pressure regulator are not designed for heating, an upstream wash bottle traps the condensation water produced during the CO_2 methanation reaction. This prevents measurement fluctuations due to phase mixing of the effluent reaction mixture in the downstream pressure regulator. The gas sampled along the catalyst bed in the CPR is directed through a customized sampling line switching module, tailored to the experimental workflow of the IPO DRIFTS measurements as illustrated in Figure 3.5. This module enables various configurations linking the CPR to the DRIFTS cell (IV) and the MS (V), as well as to the H_2 reference gas supply (VI). Two 4-port switching valves (C4UWE from Vici Valco) offer four different control options with the following configurations:

HM-1 (ON)/ HM-2 (ON): The gas mixture sampled from the CPR is first directed through the DRIFTS cell for IPO DRIFTS measurements and then forwarded to the MS. During

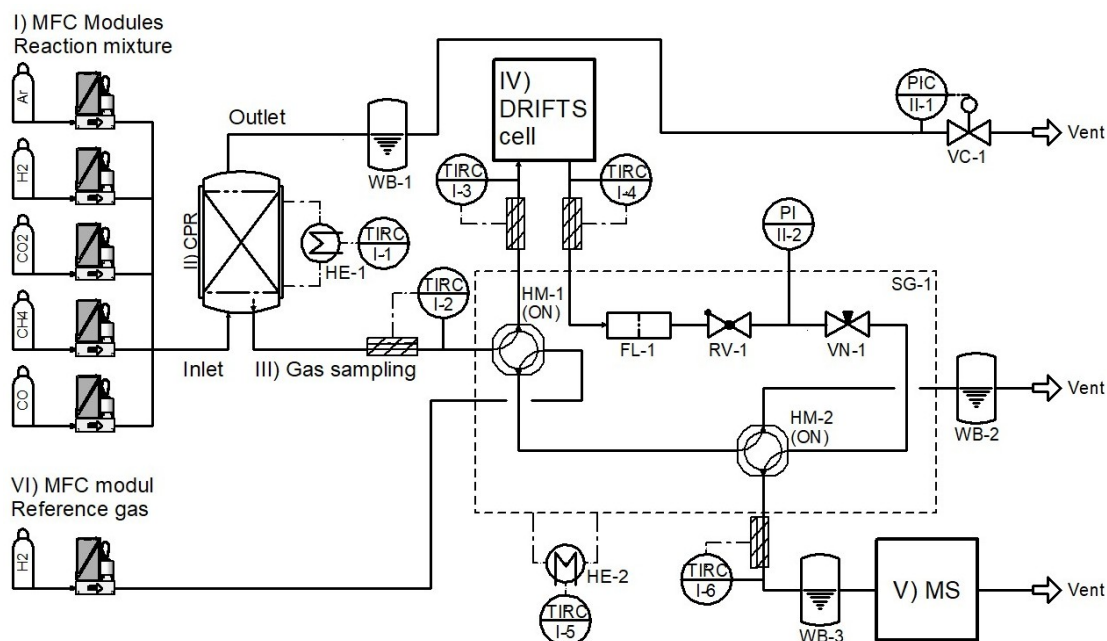
operation, the DRIFTS cell is filled with either the catalyst sample (cf. Figures 3.5 and 3.6, A) or the reference material/'white standard' (Figures 3.5 and 3.7 C), while the parallel reference line is continuously purged with the reference gas (H_2).

HM-1 (OFF)/ HM-2 (ON): The gas mixture sampled from the CPR is directed into the vent, while the reference gas is supplied to the DRIFTS cell and subsequently passed through the downstream MS into the vent. During operation, the DRIFTS cell is filled with either the catalyst sample (cf. Figures 3.5 and 3.6, B) or with the reference material/'white standard' (Figures 3.5 and 3.7 D). MS analysis of the gas stream allows continuous monitoring of the system to verify complete purging of the lines with the reference gas (H_2).

HM-1 (OFF)/ HM-2 (OFF): The gas mixture sampled from the CPR is directed into the MS, bypassing the DRIFTS cell, to perform a conversion check along the catalytic fixed-bed and to determine temperature and molar flow rate profiles (cf. Figure 3.5, X). In parallel, the DRIFTS cell can either be purged with the reference gas (H_2) or refilled with a new sample.

HM-1 (ON)/ HM-2 (OFF): The gas mixture sampled from the CPR is directed through the DRIFTS cell directly into the vent, while the MS is purged with the reference gas (H_2). In case of operational issues, such as blockages caused by condensed water, the MS could be disconnected from the system and cleaned without interrupting the experiment.

The entire sampling line must be permanently heated to prevent changes in the gas composition caused by water condensation. The transfer lines are equipped with heating tubes or heating wires (I-X, Hillesheim GmbH), and the sampling line switching module is installed in a heating cabinet (SG-1, FD56 from Binder) with insulated side access openings. A filter (FL-1) and a check valve (RV-1) are positioned in the sampling line downstream of the DRIFTS cell. The fittings serve as a safety measure to prevent particles from being absorbed into the lines or the sample in the DRIFTS cell from being disturbed during replacement or upon changes in the gas supply. Additionally, a restrictor (VN-1), similar to a needle valve, is mounted downstream to stabilize the cell pressure, which is monitored by an integrated pressure transmitter (II-2, WIKA). This arrangement ensures a constant sample flow through both the sampling line and the cell. A small cooling finger (WB-3) is installed in the sampling line to the MS, located behind the heated parts, to trap condensation. Thereafter, it is no longer necessary to heat the last section of the sampling line to the MS, since the suction vacuum generated by the MS is sufficient to prevent water condensation. The length of the sampling line to the MS is carefully selected to ensure that the pressure in the system upstream of the cooling finger remains undisturbed.



Code letter	Designation	Description	Manufacturer
I)	MFC Modules	Section 3.1.4	Bronkhorst™
II)	CPR	Section 3.1.3	Reacnostics GmbH
III)	Gas sampling	Section 3.1.3	Reacnostics GmbH
IV)	DRIFTS	Section 3.1.6	Harrick
V)	MS	Section 3.1.5	Pfeiffer Vacuum
	HE	Heat exchanger	-
	WB	Wash bottle	Neubert-Glas GbR
	FL	Filter	Hy-Lok D
	RV	Lift check valve	Hy-Lok D
	VN	Needle valve (Restrictor)	-
	HM	Multi-way ball valve	Vici Valco
	SG	Furnace	Binder
I-X	TIRC	Temperature control with indication and recording	Hillesheim GmbH
II-1	PIC	Pressure control with indication	Bronkhorst
II-2	PI	Pressure indication	WIKA

Fig. 4.1: A simplified piping and instrumentation diagram of the experimental setup with the associated parts list.

4.2 Experimental Conditions and Procedures

Table 4.1 summarizes the experimental conditions for the reactor (CPR) and for the DRIFTS cell, which were coupled in this work to carry out IPO DRIFTS measurements. Preliminary

Tab. 4.1: Experimental parameter list of the iso-potential *operando* DRIFTS measurements. Adopted and modified from [81].

Experimental parameters	CPR	DRIFTS cell	Unit
L_{bed}	30	2	mm
d_{bed}	4	4.7	mm
d_{cat}	300 – 400	100 – 200	μm
T_{reactor}	320	–	$^{\circ}\text{C}$
T_{catalyst}	measured locally	adapted to CPR	$^{\circ}\text{C}$
p	1.1	1.0	bar
m_{cat}	330	2.4	mg
$\dot{V}_0$ (STP)	120	6	ml min^{-1}
WHSV	20×10^3	139×10^3	$\text{ml/g}_{\text{cat}}/\text{h}$
Ar/H ₂ /CO ₂ feed ratio	3/4/1	3/4/1	–

tests with the Praying Mantis DRIFTS cell (Harrick Scientific) revealed that the empty cell exhibits a low, temperature-dependent blank activity with the gas phase, which can be attributed to its metallic interior. This finding is consistent with observations reported by other researchers [72]. To minimize this blank reactivity in the experiments conducted in this study, the heating temperature was maintained below 350 $^{\circ}\text{C}$. In addition, due to the highly exothermic nature of the CO₂ methanation reaction, the presence of a temperature maximum within the catalytic fixed bed of the reactor tube in the CPR cannot be entirely excluded, despite effective heat dissipation through the reactor housing. Therefore, the reaction temperature was defined to prevent the target temperature in the DRIFTS cell from rising above the limit value and causing significant blank reactivity. Based on preliminary reaction tests in the CPR and literature reports, which indicate that optimal CO₂ methanation conversions are achieved at reaction temperatures between 200 – 400 $^{\circ}\text{C}$, conducting the experiments at a reaction temperature of 320 $^{\circ}\text{C}$ represents an acceptable compromise. Furthermore, to minimize the conversion caused by the catalyst sample in the spectroscopic cell, its weight hourly space velocity (WHSV) was set as high as possible, at least several orders of magnitude higher than the corresponding value in the reactor. With a total inlet flow of $\dot{V}_{0,\text{CPR}} = 120 \text{ ml min}^{-1}$ into the CPR (adjusted at standard temperature and pressure (STP), 25 $^{\circ}\text{C}$ and 1 atm), a corresponding sample flow of 5 % ($\dot{V}_{0,\text{DRIFTS}} = 6 \text{ ml min}^{-1}$) was provided. A catalytic fixed-bed of 0.33 g was used for the experiment, resulting in a WHSV_{CPR} of

approximately $20000 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ in the tube reactor, while a sevenfold $\text{WHSV}_{\text{DRIFTS}}$ can be obtained in the DRIFTS cell. To achieve a high flow rate through the reactor under laboratory conditions, an inert gas was added to the feed. Not least, to facilitate gas composition analysis using the MS via the internal standard method. The feed ratio of the gas mixture was set to $\text{Ar} : \text{H}_2 : \text{CO}_2 = 3 : 4 : 1$ to ensure that the equilibrium conversion exceeding 90 % remains thermodynamically feasible at the specified reaction temperature of 320°C (cf. Figure A.1). Calculations of the chemical equilibrium under the chosen reaction conditions are provided in Section A.1. In gas phase reactions, the concentration of reacting species is directly proportional to the total pressure. A pressure drop in the catalytic fixed-bed can negatively impact reactor operation by limiting both throughput and conversion, as well as reducing the reaction rate [53]. The CPR was operated at 1.1 bar, slightly above ambient pressure, to create a slight pressure gradient for a constant and undisturbed gas sample flow into the DRIFTS cell, which was maintained at near-ambient pressure. The Ergun equation indicates that no significant pressure drop was expected in the packed porous bed under the experimental reaction conditions, as shown in Section A.2.

As discussed in Sections 3.2.2 and 3.2.3, in accordance with the IPO DRIFTS workflow, two separate IPO DRIFTS measurements were performed at each measurement position within the catalyst bed of the CPR (cf. Figure 3.5, A and C). Simultaneously, the conversion profiles were recorded using mass spectrometry. The corresponding reference measurements were conducted under a hydrogen flow serving as the reference gas (cf. Figure 3.5, B and D). Additionally, a reference conversion profile along the catalyst bed within the CPR was recorded using mass spectrometry (cf. Figure 3.5, X), bypassing the DRIFTS cell to exclude it from the flow path. Temperature profiles of the catalyst bed are monitored both during the IPO DRIFTS measurements and during the conversion check measurement.

At the beginning of the experimental procedure, the reactor tube of the CPR was filled with the pre-reduced $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst (300 – 400 μm) and sealed with a layer of quartz wool at each end of the bed to form a 30 mm catalytic fixed-bed. The reactor tube, filled with catalyst, was mounted in the CPR and purged with Ar at atmospheric pressure to record at least 20 reference spectra using the MS. The inert gas was sampled via the capillary sampling line according to the setup configuration (X) shown in Figure 3.5. Subsequently, the heating block of the CPR was slowly heated up to the set reaction temperature of 320°C under a 5 vol% H_2 atmosphere in Ar. Once the reaction temperature was reached, the gas stream was switched to the reaction mixture, and the catalyst was allowed to attain

steady state over the course of one hour. A catalyst sample, approximately 2.4 mg from the same batch used for the CPR, was highly diluted in CaF_2 (Sigma-Aldrich, > 99 % purity) at a dilution ratio of 1 : 20 and applied as a thin, 2 mm high, uncompressed layer on a bed of pure CaF_2 in the sample cup of the DRIFTS cell. Further details of the packing procedure are provided in the following section (cf. Section 4.2.1). The catalyst sample was treated in the DRIFTS cell under a hydrogen gas atmosphere at 500 °C for one hour to remove residual traces of water and adsorbates that may have formed due to exposure to ambient air. After this pretreatment step, the reference measurement was carried out (cf. Figure 3.5, B), followed by the IPO DRIFTS measurements (cf. Figure 3.5, A). In the lack of a DRIFTS cell with multiple sample compartments, all measurements in this experiment must be performed sequentially, which risks temporal changes in the CPR or in the DRIFTS cell. To minimize the time delay between the separate measurements, the reference measurement (cf. Figure 3.5, B) was conducted at an average temperature representative of the catalyst bed. The reference measurement involves analyzing the diluted catalyst sample in the DRIFTS cell under a hydrogen reference atmosphere. The average temperature was determined from previous test profile measurements using the CPR and confirmed by evaluating the temperature profiles obtained in this experiment. Since the temperature varied only modestly along the catalyst bed between 320 – 343 °C (cf. Figure 4.14), performing the reference measurement at an average temperature of 330 °C was an acceptable compromise. The reference spectrum (B) was recorded and subsequently used in the data analysis to extract surface adsorbate profiles from the IPO DRIFTS measurements. This approach generated a slight baseline shift in the IR spectra during the extraction of the surface adsorbate profiles, which could be compensated for by the IR software. For larger temperature fluctuations within the catalyst bed in the CPR, it was necessary to record the DRIFTS reference spectra for each temperature value. This would have required reference measurements at every position in the catalyst bed.

In the first set of IPO DRIFTS measurements (cf. Figure 3.5, A), the diluted catalyst sample was examined in the DRIFTS cell under reaction conditions at each defined measurement position in the fixed-bed of the CPR, while quantitative gas analysis was performed using the MS connected in series. The sampling line from the reactor, via the DRIFTS cell, to the MS was purged with the reaction mixture for at least 20 minutes at each measurement position to ensure complete gas exchange in the spectral chamber, establish steady state conditions, and enable high-quality measurements. Three DRIFTS spectra were acquired at 5-minute intervals, and 20 scans were performed with the MS. In a subsequent data

processing step, the DRIFTS spectra were checked for steady-state behavior, and a final spectrum was selected for each IPO DRIFTS measurement. The 20 MS data were then used to calculate a concentration average from the CO₂ and CH₄ peaks, based on the Ar peak as an internal standard. Further details on the mass spectrometry analysis are provided in Section 4.2.2. After passing through an entire IPO DRIFTS profile from the inlet to the outlet of the fixed-bed in the CPR, the diluted catalyst sample in the DRIFTS cell was replaced with pure CaF₂ and pre-treated with flowing hydrogen under the same conditions as described above. The reference spectrum of the reference material/'white standard' was then recorded at the average temperature (cf. Figure 3.5, D). Concurrently, the CPR was positioned for the first set of measurements (A) by aligning the sample capillary orifice with the inlet of the catalyst bed. In the second set of measurements, IPO DRIFTS measurements of the pure reference material/'white standard' were conducted under reaction conditions at the same measurement positions in the CPR, following the experimental procedure described above and according to the setup configuration shown in Figure 3.5 (C). Measuring the profiles from the reactor inlet to the reactor outlet was essential to ensure that the catalyst in the DRIFTS cell undergoes the same exposure history as the catalyst in the reactor. After resetting the CPR, the conversion check was performed in a separate set of measurements (cf. Figure 3.5, X), bypassing the DRIFTS cell and connecting directly to the MS. The experimental procedure was replicated as in the previous IPO DRIFTS measurements.

4.2.1 Catalyst Dilution for DRIFTS Measurements

To minimize the conversion of the catalyst sample with the reaction mixture in the crucible of the DRIFTS cell and to increase the contribution of diffuse reflectance for measurable absorbance bands of surface adsorbates, a dilution material can be added to the catalyst sample [87, 97–99]. The dilution material must be of low self-absorption to weaken the absorption power of the black catalyst body and ensure deeper penetration of diffuse IR scattering. Since CaF₂ was already employed as a reference material/'white standard' due to its favorable properties – IR transparency, chemical inertness, thermal stability, non-hygroscopicity, and quasi-insolubility in water (cf. Section 3.1.6) – it was also used to dilute the catalyst sample to a high degree. The dilution was experimentally investigated through a series of measurements of different dilution ratios of the catalyst in CaF₂, with the aim of determining the optimal dilution ratio that yields the best IR spectral resolution.

Figure 4.2 illustrates the procedure used to load the catalyst sample into the DRIFTS cell. The cell was filled with a thin layer of finely ground catalyst sample diluted with an equally

finely ground CaF_2 , and then placed on top of a layer of pure CaF_2 to complete the filling of the sample cup. Since diffuse reflectance is affected by particle size, packing density, and

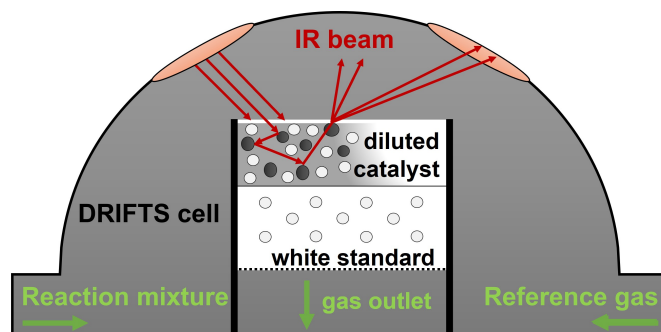


Fig. 4.2: Illustration of the DRIFTS cell prepared for IPO DRIFTS or reference measurements of a catalyst sample under a flowing reaction gas mixture or reference gas. The cell is filled with a small layer of a finely ground catalyst sample diluted in likewise finely ground CaF_2 on top of a layer of pure CaF_2 .

homogeneity of the sample, the catalyst and dilution material are crushed to a sieve fraction of $100 - 200 \mu\text{m}$ [198]. As the penetration depth of the IR radiation into the upper layer of the sample is less than $200 \mu\text{m}$ [199], the diluted catalyst was filled into the crucible as a thin, non-compressed layer of 2 mm in height (bed length). The samples in the DRIFTS cell are exposed to a gas mixture of Ar, H_2 , and CO_2 with a feed ratio of $\text{H}_2 : \text{CO}_2 = 4 : 1$. The flow rate was maintained at 6 ml min^{-1} (STP) and a set temperature of 320°C , as specified by the reaction conditions (cf. Table 4.1). Figure 4.3 presents the corresponding DRIFT spectra for a dilution ratios of 1:10 (blue spectrum), 1:20 (orange spectrum) and 1:50 (green spectrum) of mass catalyst to mass CaF_2 ($m_{\text{cat}} : m_{\text{CaF}_2}$). It is observed that the conversion of the reactants is proportional to the forming intensities of the CH_4 bands at 3019 cm^{-1} and 1306 cm^{-1} . The CO_2 conversion is lowest at a dilution ratio of 1:50 (green spectrum), as indicated by the weak CH_4 band intensities at 1306 cm^{-1} and 3019 cm^{-1} . This provides a reasonable approximation of iso-potential conditions but is accompanied by very low intensities of the surface adsorbate bands. In particular, the carbonyl bands at 2010 , 1915 and 1863 cm^{-1} approach the detection limit and become indistinguishable, as they are no longer resolved. At a dilution ratio of 1:10 (blue spectrum), the carbonyl bands and the formate bands between $1300 - 2600 \text{ cm}^{-1}$ were clearly differentiated and well resolved. However, the intense CH_4 bands indicate substantial CO_2 conversion in the DRIFTS cell. This would result in a chemical composition in the DRIFTS cell that differs significantly from the local composition in the CPR under such IPO DRIFTS measurement conditions. A suitable compromise between the two dilution ratios is a ratio of 1:20 (orange spectrum), at

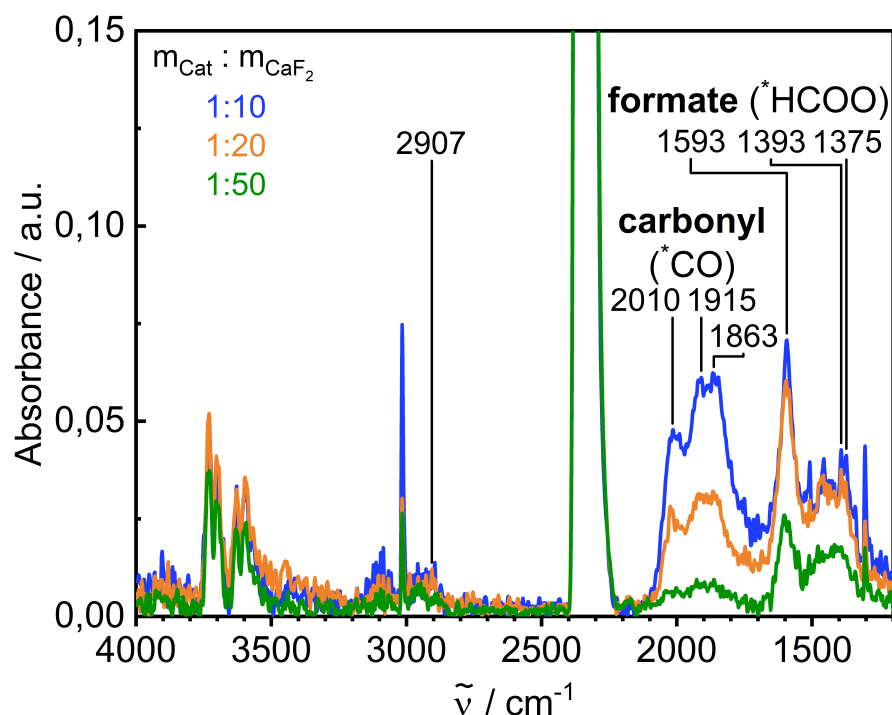


Fig. 4.3: DRIFT spectra of a finely ground catalyst sample (Ni/ γ -Al₂O₃ catalyst) diluted in a likewise finely ground reference material/‘white standard’ (CaF₂) under reaction conditions (Ar, H₂ and CO₂ feed with H₂ : CO₂ = 4 : 1, 6 ml min⁻¹ flow rate, 320 °C set temperature). At a dilution ratio of 1:20 by mass (green spectrum), the surface adsorbate bands of carbonyl and formate are well resolved and clearly detectable, while an acceptably low CO₂ conversion is observed, as evidenced by the small CH₄ bands at 3019 cm⁻¹ and 1306 cm⁻¹. Adopted and modified from [81].

which both carbonyl and formate bands remain resolved and clearly discernible, while CO₂ conversion remains relatively low. Accordingly, for all IPO DRIFTS measurements in this work, the catalyst sample was diluted with CaF₂ at a ratio of 1:20.

4.2.2 Gas Analysis and Mass Balance

Quantitative gas analysis was carried out using a calibrated MS, with the mass-to-charge ratios of 15 amu (CH₄) and 44 amu (CO₂) monitored, and 40 amu (Ar) employed as the internal standard. H₂O, CO and H₂ were determined stoichiometrically by closing the O⁻, H⁻ and C⁻ balances, with CO included as a potential byproduct. No other carbonaceous byproducts were detected, as confirmed by the catalyst characterization reported in Section 4.3. Figure 4.4 shows a typical spectrum excerpt recorded in an analog mode with the MS by sampling the gas mixture at the inlet and outlet of the catalytic fixed-bed in

the CPR, according to the setup configuration (X) (cf. Figure 3.5). The observed peaks were assigned to key fragments of ionized molecules, as summarized in Table 4.2, along with their parent molecules. From these data, six distinct species ($S = 6$) can be identified in the reaction system. From the table, it can be concluded that CH_4 at 15 amu and CO_2 at 44 amu are the most straightforward mass-to-charge ratios to quantify relative of Ar at 40 amu, as other fragments do not significantly influence them. To demonstrate that only the measurement of the molar flow rates of CO_2 and CH_4 is required to fully describe the reaction system, the 'key species' (R) can be determined using the elemental species matrix (ESM):

$$ESM = \begin{matrix} & \text{Ar} & \text{H}_2\text{O} & \text{CO} & \text{H}_2 & \text{CO}_2 & \text{CH}_4 \\ \begin{matrix} \text{C} \\ \text{H} \\ \text{O} \\ \text{Ar} \end{matrix} & \begin{pmatrix} 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 2 & 0 & 2 & 0 & 4 \\ 0 & 1 & 1 & 0 & 2 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \end{matrix}$$

By returning the reduced row echelon form (mathematical code: `rref`) of the ESM

$$rref(ESM) = \begin{matrix} & \text{Ar} & \text{H}_2\text{O} & \text{CO} & \text{H}_2 & \text{CO}_2 & \text{CH}_4 \\ \begin{matrix} \text{C} \\ \text{H} \\ \text{O} \\ \text{Ar} \end{matrix} & \left(\begin{array}{cccc|cc} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & -1 & 3 \end{array} \right) \end{matrix}$$

using Gauss-Jordan elimination, a rank of 4 can be deduced and regressed on the number of 'non-key species' (nR). Finally, two 'key species' are obtained by subtracting the number of 'non-key species' from the number of all species ($R = S - nR$). The following stoichiometric correlation is expressed in matrix notation to calculate the molar changes of the 'non-key species' ($\Delta \dot{n}_2$) based on the measured molar changes of the designated 'key species' CO_2

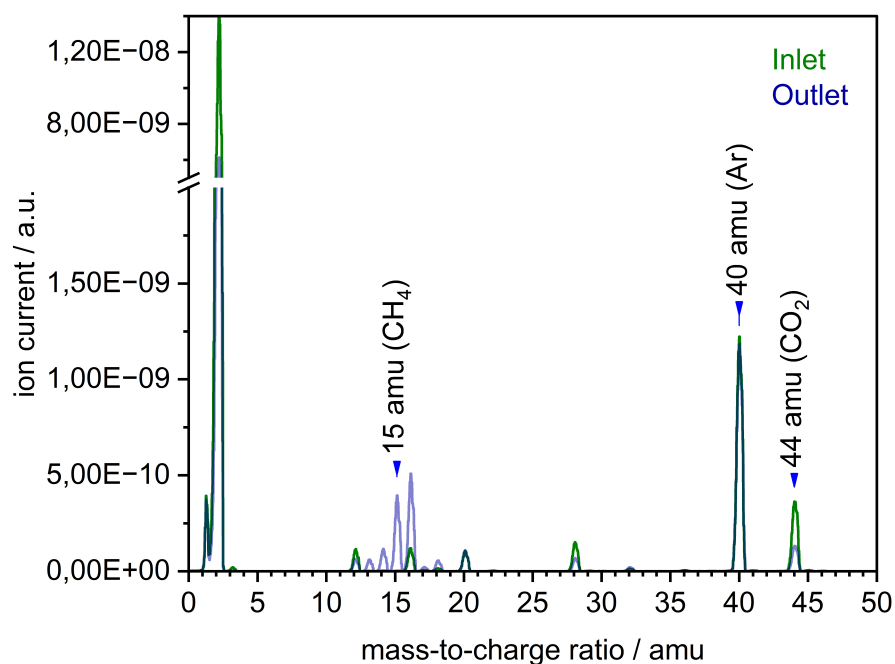


Fig. 4.4: Excerpt of mass spectrometry data of the reaction mixture sampled at the inlet and outlet of the catalytic fixed-bed in the CPR.

Tab. 4.2: Clarification of the fragment ions observed with the mass spectrometer.

mass-to-charge ratio (amu)	key fragments	probable parent molecules
1	H^+	H_2 , H_2O , CH_4
2	H_2^+	H_2
12	C^+	CH_4 , CO_2 , CO
13	CH^+	CH_4
14	CH_2^+ , CO^{++}	CH_4 , CO
15	CH_3^+	CH_4
16	CH_4^+ , O^+	CH_4 , H_2O
17	OH^+	H_2O
18	H_2O^+	H_2O
20	Ar^{++}	Ar
28	CO^+	CO_2 , CO
40	Ar^+	Ar
44	CO_2^+	CO_2

and CH₄ ($\Delta\dot{n}_1$):

$$\begin{array}{c} \text{C} \\ \text{H} \\ \text{O} \\ \text{Ar} \end{array} \begin{pmatrix} \text{Ar} & \text{H}_2\text{O} & \text{CO} & \text{H}_2 & \text{CO}_2 & \text{CH}_4 \\ 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 2 & 0 & 2 & 0 & 4 \\ 0 & 1 & 1 & 0 & 2 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} \Delta\dot{n}_{\text{Ar}} \\ \Delta\dot{n}_{\text{H}_2\text{O}} \\ \Delta\dot{n}_{\text{CO}} \\ \Delta\dot{n}_{\text{H}_2} \\ \Delta\dot{n}_{\text{CO}_2} \\ \Delta\dot{n}_{\text{CH}_4} \end{pmatrix} \begin{matrix} \Delta\dot{n}_1 \\ \Delta\dot{n}_2 \end{matrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$\underbrace{\hspace{10em}}_{\text{ESM1}} \quad \underbrace{\hspace{10em}}_{\text{ESM2}}$

$$\begin{pmatrix} \text{ESM1} & \text{ESM2} \end{pmatrix} \begin{pmatrix} \Delta\dot{n}_1 \\ \Delta\dot{n}_2 \end{pmatrix} = \text{ESM1} \cdot \Delta\dot{n}_1 + \text{ESM2} \cdot \Delta\dot{n}_2 = 0$$

$$\Rightarrow \Delta\dot{n}_1 = \text{ESM1}^{-1} \cdot (-\text{ESM2}) \cdot \Delta\dot{n}_2$$

The molar changes of CO₂ and CH₄ were determined from the differences between their known molar flow rates at the inlet of the CPR ($\dot{n}_{i,0}$) and the molar flow rates measured by the MS at each position in the catalyst bed up to the outlet ($\dot{n}_i$). The conversion of MS peak areas to molar flow rates was performed using Eq. (3.1), as described in Section 3.1.5. Applying this methodology, the C-, H-, and O-balances were closed for all experiments, with average deviations of up to 5 %. To assess the catalytic performance, the CO₂ conversion (X_{CO_2}) was calculated from the molar flow rates at the reactor inlet and outlet:

$$X_{\text{CH}_4}(\%) = \frac{\dot{n}_{\text{CO}_2,0} - \dot{n}_{\text{CO}_2}}{\dot{n}_{\text{CO}_2,0}} \cdot 100 \quad (4.1)$$

The selectivity for the product CH₄ is determined by

$$S_{\text{CH}_4}(\%) = \frac{m_{\text{CH}_4} \cdot \dot{n}_{\text{CH}_4}}{\sum m_k \cdot \dot{n}_k} \cdot 100 \quad (4.2)$$

where m_{CH_4} denotes the number of carbon atoms in CH₄, m_k the number of carbon atoms in each carbonaceous species k present in the system, $\dot{n}_k$ the corresponding molar flow rate of the species present in the reaction mixture, and $\dot{n}_{\text{CH}_4}$ denotes that of CH₄.

4.3 Catalyst Characterization

The results of the experimental methods used to characterize the Ni/ γ -Al₂O₃ catalyst in this study, as described in Section 3.1.2, are presented below.

4.3.1 ICP-OES

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis was used to determine the Ni concentration after dissolving a 40 mg catalyst sample in aqua regia. The digestion solution was diluted to a final volume of 25 ml to prevent extensive corrosion of the metal parts of the spectrometer. Samples taken for analysis were additionally diluted (by a factor of 10 with MilliQ water) to minimize matrix effects, e.g., plasma discontinuities between different samples due to the potentially different presence of readily ionizable elements such as K or Cs. For a multiple determination, four samples were analyzed and evaporated in the spectrometer using an argon plasma at approximately 8000 K, and then excited to optical emission. The emitted radiation characteristic of nickel in the UV region, at about 221 – 231 nm, was detected and quantified by referencing the peak area of the Ni signal to a calibration measurement using a standard solution of nickel nitrate (Merck IV). The calibration curve of the standard solution and an excerpt of the ICP-OES measurement of Ni are given in Figure 4.5. Quantification results in a Ni concentration of 22.19 mg L^{-1} in the diluted analyte dissolution, corresponding to a total Ni concentration of 138.7 g kg^{-1} in the sample ($22.19 \text{ mg L}^{-1} \cdot 10 \cdot \frac{25 \text{ ml}}{40 \text{ mg (sample)}} = 138.7 \frac{\text{g (Ni)}}{\text{kg (sample)}}$). Consequently, the freshly reduced Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst used in the present work has a weight loading of 13.8 % Ni.

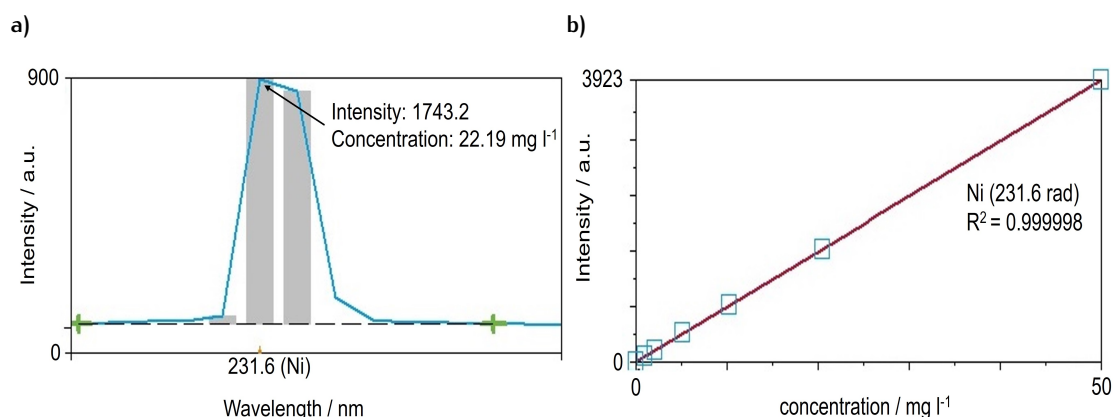


Fig. 4.5: ICP-OES analysis of a freshly reduced Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst sample dissolved in aqua regia. The emitted plasma radiation was detected in the UV region characteristic of Ni (a) and quantified using a reference measurement with a standard solution (b).

4.3.2 Physisorption Analysis

Brunauer-Emmett-Teller (BET) analysis of the freshly reduced and outgassed catalyst was employed to determine the specific surface area corresponding to the adsorption capacity

of the catalyst. The BET isotherm is shown in Figure 4.6 as a segment of the adsorption

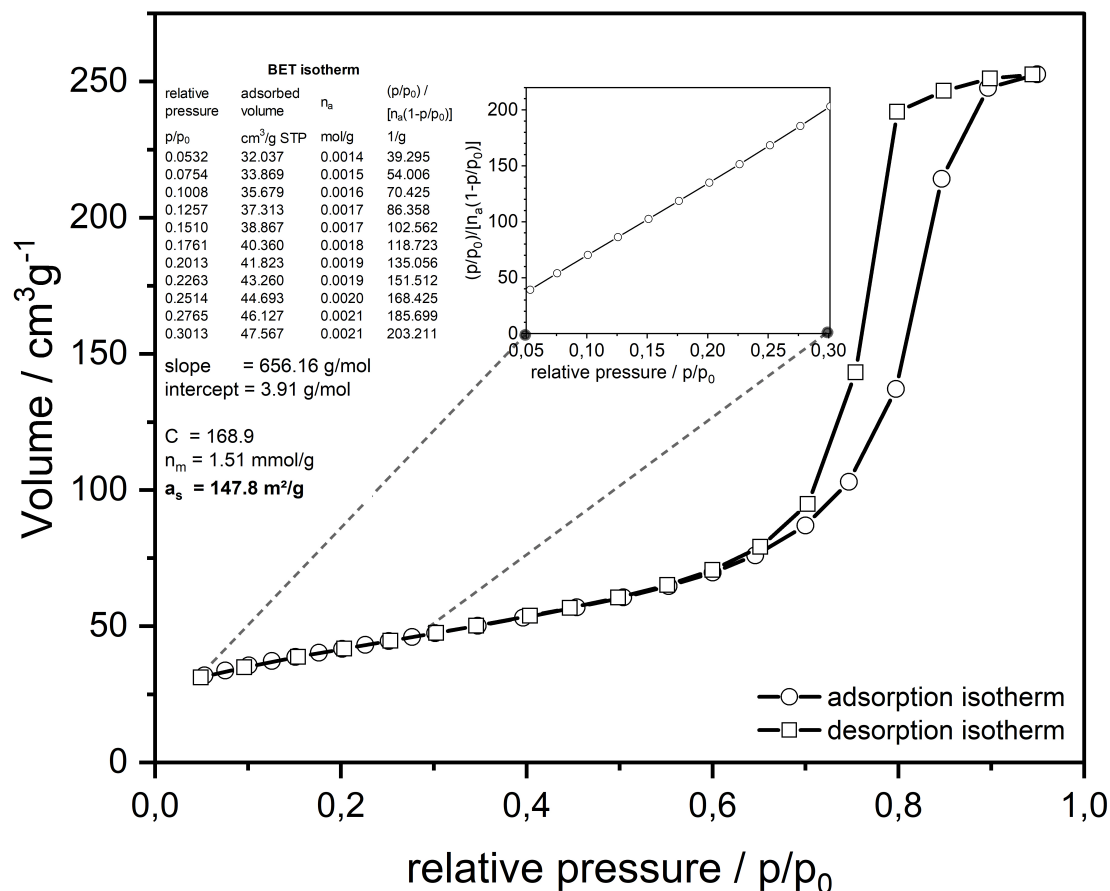


Fig. 4.6: Nitrogen adsorption-desorption isotherms of the freshly reduced Ni/γ-Al₂O₃ catalyst. The adsorption and desorption isotherms display a type IV hysteresis loop, characteristic of mesoporous materials.

isotherm obtained by N₂-physisorption, along with the corresponding desorption isotherm. Within the relative pressure range of $p/p_0 \approx 0.05 \dots 0.35$, the adsorption isotherm was linearized using

$$\frac{p/p_0}{n_a(1-p/p_0)} = \frac{1}{C n_m} + \frac{C-1}{C n_m} \frac{p}{p_0}$$

yielding the linearized BET isotherm [200]. n_a is the specific amount of adsorbed nitrogen at standard conditions (STP) based on the dosed volume at the relative pressure values obtained from the adsorption isotherm. n_m is the monolayer capacity of the adsorbate, and C is the BET constant derived from the slope (s) and intercept (i) of the linearized BET

isotherm:

$$n_m = \frac{1}{s + i} \quad C = \frac{s}{i} + 1$$

The constant C is related to the interaction between the catalyst and the adsorbate, and thus reflects the heat of adsorption. Higher C values correspond to increased adsorption due to a larger specific surface area [201]. For C values in the range of 100 – 200, complete monolayer coverage is already evident from $p/p_0 \approx 0.1$, providing a good straight-line fit in the BET plot. Values of C above 200 may indicate the presence of micropores [200]. The specific surface area (a_s) is calculated from the monolayer capacity and the cross-sectional area of nitrogen ($a_m(\text{N}_2) = 0.162\text{nm}^2$):

$$a_s = n_m \cdot a_m \cdot N_A$$

The results, summarized in Figure 4.6, indicate a reduction in the specific surface area of the coated catalyst ($148\text{m}^2\text{g}^{-1}$) compared with the reference surface area of the pure support ($160\text{m}^2\text{g}^{-1}$), as specified by the manufacturer (Sasol). The adsorption and desorption isotherms exhibit a hysteresis loop (type IV) that is characteristic of mesoporous materials [201].

4.3.3 STEM-EDS Mapping

STEM was applied in combination with EDS to investigate the crystallite size of Ni coated on $\gamma\text{-Al}_2\text{O}_3$ using a freshly reduced sample. Figure 4.7 maps various STEM-EDS detection modes to separately highlight the nickel and alumina phases of catalyst particles spread on a holey carbon film. Secondary electron (SE) detection enables the examination of the catalyst surface topology, revealing nickel particles on the alumina support through bright contrast that highlights the 3D structure. In Figure 4.7, a color-coding scheme is applied, with nickel particles and alumina highlighted in green and red, respectively. In the dark-field (DF) image, which is formed by detecting the scattered electrons, the diffraction contrast associated with atomic number allows for more intense color gradation between nickel and alumina. As a result, the heavier nickel particles are displayed brighter than the alumina. The color gradation can be used to specifically filter out the alumina, as shown in Figure 4.7b. In the bright-field (BF) image presented in Figure 4.7c, the contrast is reversed, with nickel particles appearing darker than the alumina due to diffraction effects. In the bottom images, nickel particles are highlighted and scaled in high-contrast overview images, with the dosage rate and total dose indicated in yellow. The average crystallite size is observed to range from approximately 10 to 12 nm.

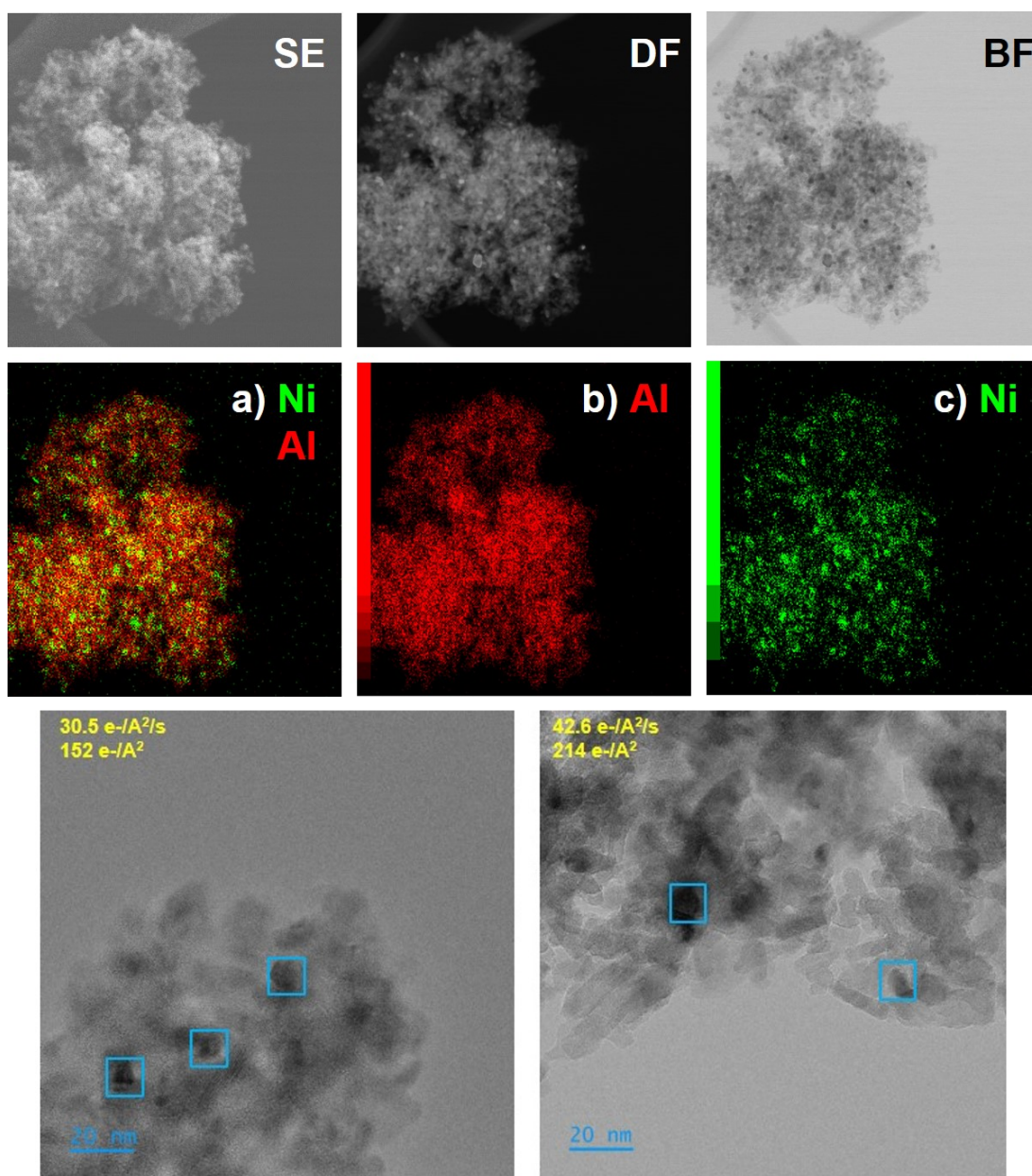


Fig. 4.7: STEM-EDS images of freshly reduced Ni/ γ -Al₂O₃ catalyst particles spread on a holey carbon film using different detection modes to visualize the single catalyst phases: a) Secondary Electron (SE) detection, b) Dark Field (DF) imaging, c) Bright Field (BF) imaging. High-contrast overview images (bottom) show an average crystallite size of the framed nickel particles to be about 10 nm to 12 nm (below). Adopted from [81]

4.3.4 Chemisorption Analysis

Volumetric chemisorption analysis method using H_2 as the adsorbent was performed to determine the specific metal surface area of the active Ni component, its metal dispersion, and the average crystallite size for both the freshly reduced and spent Ni/ γ - Al_2O_3 catalyst sample after the reaction. The results of the chemisorption measurements are presented in Figures 4.8 and 4.9, respectively. Both samples were subjected to surface cleaning prior to analysis by heating to above $450^\circ C$ for two hours in a hydrogen atmosphere. After evacuation under vacuum for 30 minutes, they were cooled to the adsorption temperature under a helium atmosphere. To suppress multilayer adsorption on Ni and physisorption on the support material, a moderate adsorption temperature of $35^\circ C$ was applied, as suggested in [196]. The complete treatment protocol is provided in the corresponding figures. However, the contribution to physisorption causing multilayer uptake be prevented entirely, and measurements of two isotherms (a and b) are required to determine the fraction of chemisorbed atoms (chemisorption of H_2 molecules leads to dissociative adsorptions). The combined isotherm (a) reflects gas uptake from both physical and chemical adsorption, whereas the weak isotherm (b) corresponds solely to weakly bound H_2 molecules attributable to physisorption. Following the measurement of isotherm (a), a pressure reduction induces desorption of the physically adsorbed molecules, leaving only the strongly chemisorbed atoms bound to Ni. Consequently, the second measurement, isotherm (b), represents the recovery of weakly bound adsorbates. The difference of (a – b) results in the strong isotherm (c), which represents gas absorption through chemisorption. By extrapolating the isotherm plateau of (c), the hydrogen monolayer coverage capacity ($n_m = \frac{V_m}{22.41 L mol^{-1}}$) can be derived from the y-axis intercept, which corresponds to the saturation volume (V_m). Based on the chemisorbed monolayer volume, the specific metal surface area of Ni (S_{Ni}) per gram of catalyst sample and its metal dispersion (D) can be calculated using the following equations [202]

$$S_{Ni} = \frac{n_m \cdot N_A \cdot a_{Ni}}{x} \quad D = \frac{n_m \cdot M(Ni)}{W \cdot x}$$

where a is the space occupied by the metal atom on the surface ($a_{Ni} = 6.49 \cdot 10^{-20} m^2$), x is the stoichiometric factor of the H_2 -chemisorption reaction ($x = 0.5$), N_A is the Avogadro constant, W is the analyzed weight loading of the catalyst ($W = 13.7$ wt-%) and $M(Ni)$ is the molecular weight of Ni. The average crystallite size of Ni particles (d_{Ni}) on the catalyst is calculated from the metal surface area and the shape factor (f) for spherical or cubic crystallites [202]:

$$d_{Ni} = \frac{f \cdot W}{S_{Ni} \cdot \rho_{Ni}}$$

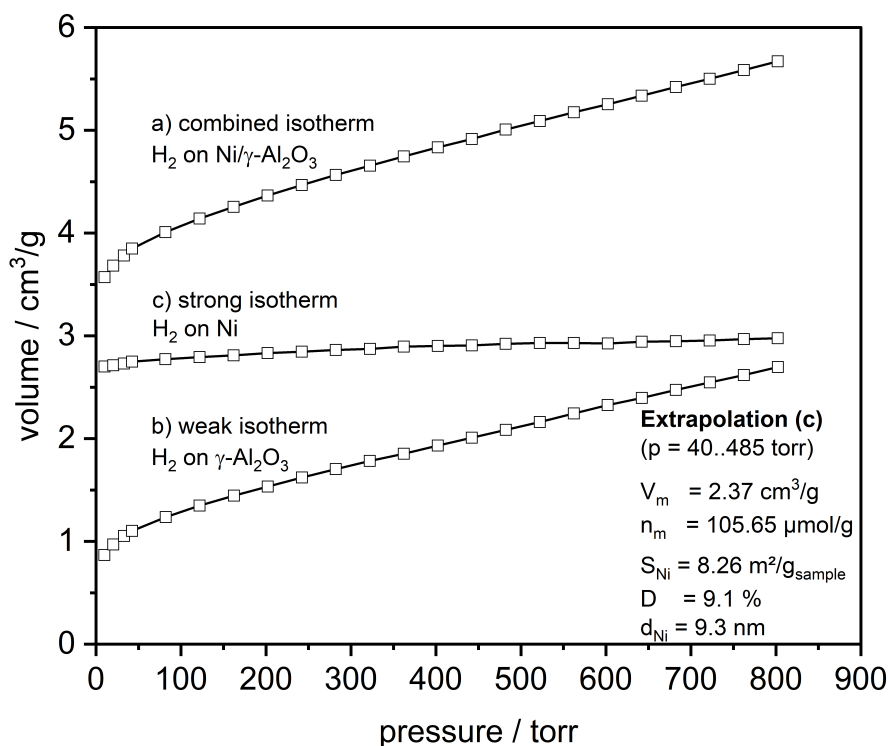


Fig. 4.8: Hydrogen adsorption isotherms for nickel dispersed on alumina, measured using a calcined Ni/γ-Al₂O₃ catalyst sample freshly reduced under a hydrogen atmosphere. a) Total H₂ chemisorption isotherm. b) H₂ adsorption isotherm on alumina. c) H₂ chemisorption isotherm on Ni. The reduction treatment was performed following the procedure in [196]. Adopted from [81].

Treatment protocol of the freshly reduced Ni/γ-Al₂O₃ catalyst:

1. Ramp temperature to 100 °C at 5 °C/min
2. Evacuate for 30 min
3. Change gas to hydrogen
4. Flow until setpoint
5. Ramp temperature to 600 °C at 5 °C/min
6. Flow gas for 100 min
7. Flow gas for 120 min
8. Evacuate for 30 min
9. Change gas to helium
10. Flow until setpoint
11. Force cool furnace to 35 °C (soak, stabilize)
12. Evacuate for 30 min

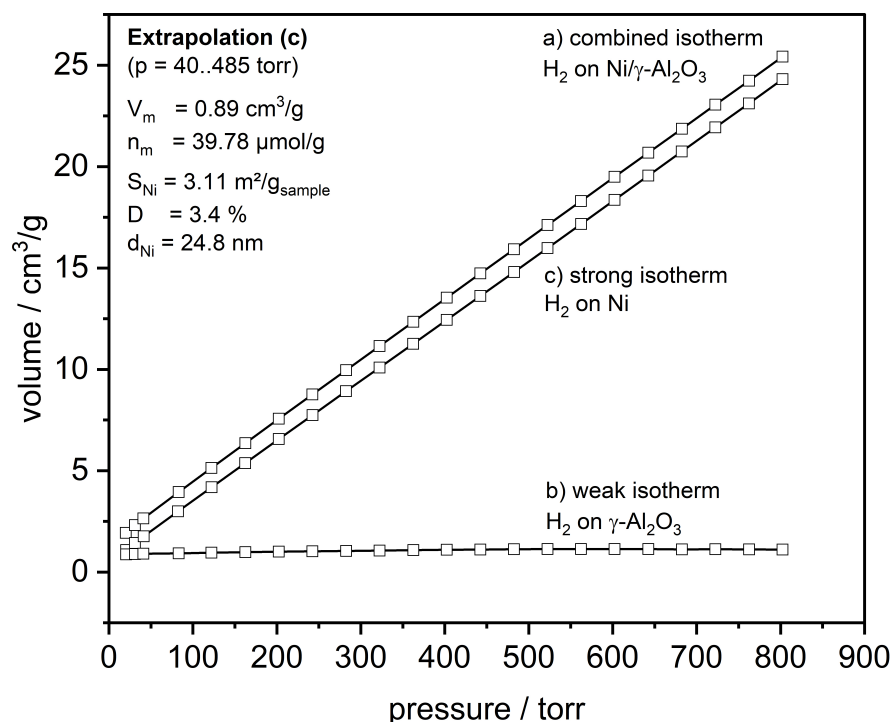


Fig. 4.9: Hydrogen adsorption isotherms for nickel dispersed on alumina, measured using a spent $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst sample treated under a hydrogen atmosphere. a) Total H_2 chemisorption isotherm. b) H_2 adsorption isotherm on alumina. c) H_2 chemisorption isotherm on Ni . The reduction treatment was performed following the procedure in [196]. Adopted from [81].

Treatment protocol of the spent $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst:

1. Ramp temperature to 100°C at $5^\circ\text{C}/\text{min}$
2. Evacuate for 30 min
3. Change gas to hydrogen
4. Flow until setpoint
5. Ramp temperature to 450°C at $5^\circ\text{C}/\text{min}$
6. Flow gas for 70 min
7. Flow gas for 120 min
8. Evacuate for 30 min
9. Change gas to helium
10. Flow until setpoint
11. Force cool furnace to 35°C (soak, stabilize)
12. Evacuate for 30 min

Since at least one crystallite plane of the active Ni component is in contact with the support surface, the shape factor is assigned to the remaining $f = 5$ exposed faces. ρ_{Ni} denotes the metal density. The results are summarized in the diagrams of Figures 4.8 and 4.9. Comparison of the crystallite size of Ni in a freshly reduced catalyst sample, measured both by H_2 -chemisorption and TEM, yields an average diameter of approximately 10 nm. In contrast, after the reaction, the coverage capacity of the hydrogen monolayer decreased, accompanied by an almost threefold increase in Ni crystallite size, with a corresponding decrease in Ni dispersion and specific Ni surface area. This indicates a sintering of the nickel particles during the reaction; however, no measurable decline in catalytic performance was observed during the experiments.

4.3.5 X-ray Diffraction

XRD patterns were recorded in a transmission mode over a 2θ range from 0 to 7° at an X-ray energy of 101.6 keV ($\lambda = 0.122 \text{ \AA}$) and detected using a 2D $410 \times 410 \text{ mm}^2$ Perkin Elmer XRD1621 with a pixel size of $200 \times 200 \text{ }\mu\text{m}^2$ to determine the phases of the spent Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. Images were converted into XRD patterns using the pyFAI package⁴¹ after correction with previously acquired dark images and flat-field referencing [35, 203]. The averaged images, presented in Figure 4.10, correspond to three distinct measurement locations. After the experiments, the silica reactor tube filled with catalyst was removed and analyzed *ex situ* at the inlet, center, and outlet of the fixed bed, with no significant differences observed between the locations. Phases are qualitatively analyzed using HighScore Plus software by comparing them to reference patterns from the ICDD database and shown in the diffractogram of Figure 4.11 [197]. For comparison, a baseline correction was applied to one of the averaged XRD curves. The broad, unlabeled signal at approximately $1.2 - 2^\circ$ is characteristic of the fused silica used for the reactor tube. All other signals in the diffractogram were assigned to nickel or alumina ($\gamma\text{-Al}_2\text{O}_3$) by reference matching with the software, confirming that no phase transformation of the catalyst occurs during the reaction.

4.3.6 Raman Spectroscopy

Following the experimental measurements, *ex situ* Raman spectroscopy was performed to identify possible carbon deposits in the spent catalyst bed, which may arise as a by-product of CO through the Boudouard side reaction (cf. Eq. (2.23)). The measurements were carried out by positioning the fused silica reactor tube containing the spent catalyst into the laser beam at the inlet and outlet of the fixed-bed, with the corresponding results presented

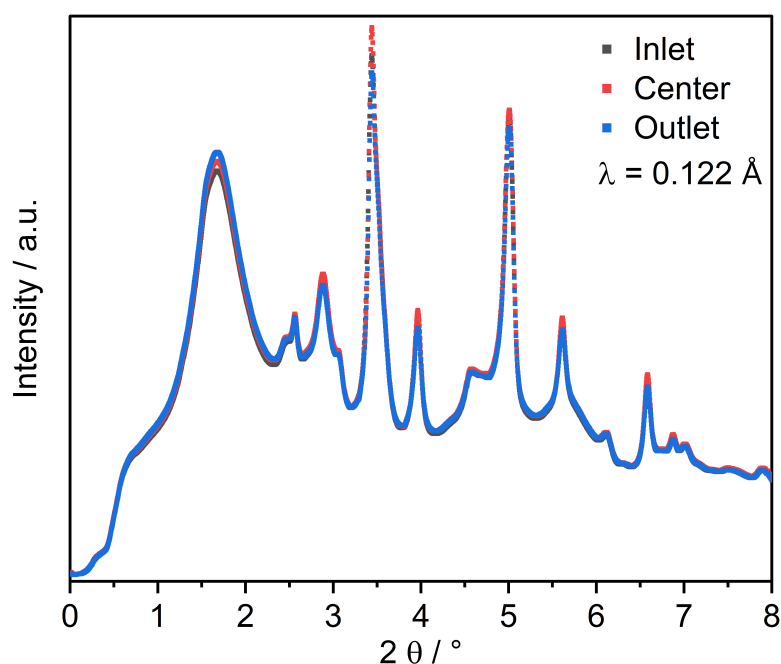


Fig. 4.10: X-ray diffraction patterns were carried out *ex situ* at three different measurement locations of the catalytic fixed-bed in a transmission mode over a 2θ range from 0 to 7° and converted to XRD images. The curves were averaged and represent the inlet, center, and outlet of the catalyst bed, revealing no significant differences between the positions. The measurements were performed at the beamline P21.1 at PETRA III (DESY, Hamburg). Adopted from [81].

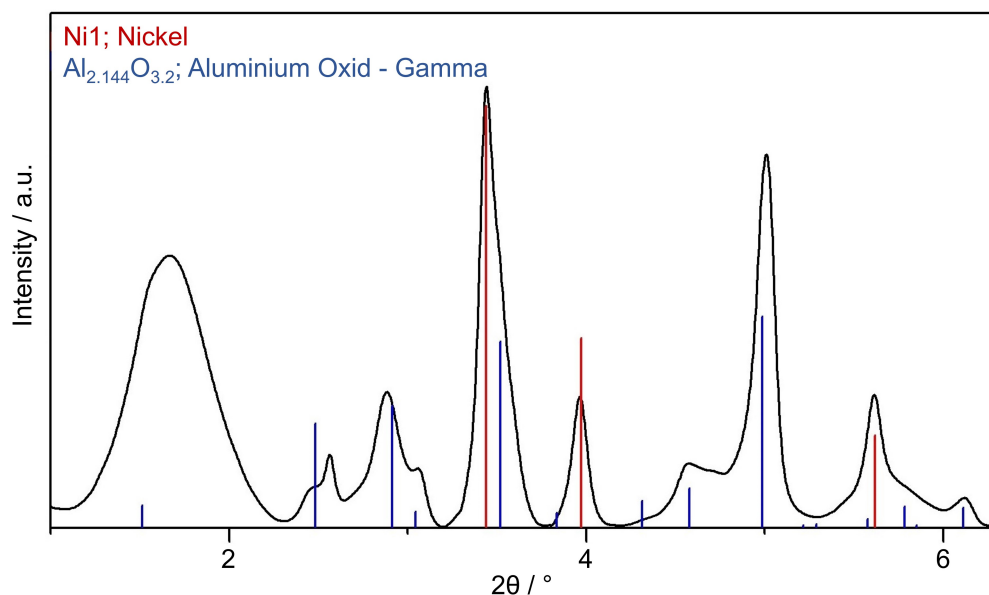


Fig. 4.11: HighScore Plus software was used to perform a qualitative phase assignment of the X-ray diffraction patterns by comparing them with reference patterns from the ICDD database. Adopted from [81].

in Figure 4.12. The silica material of the reactor tube causes the strong signals below

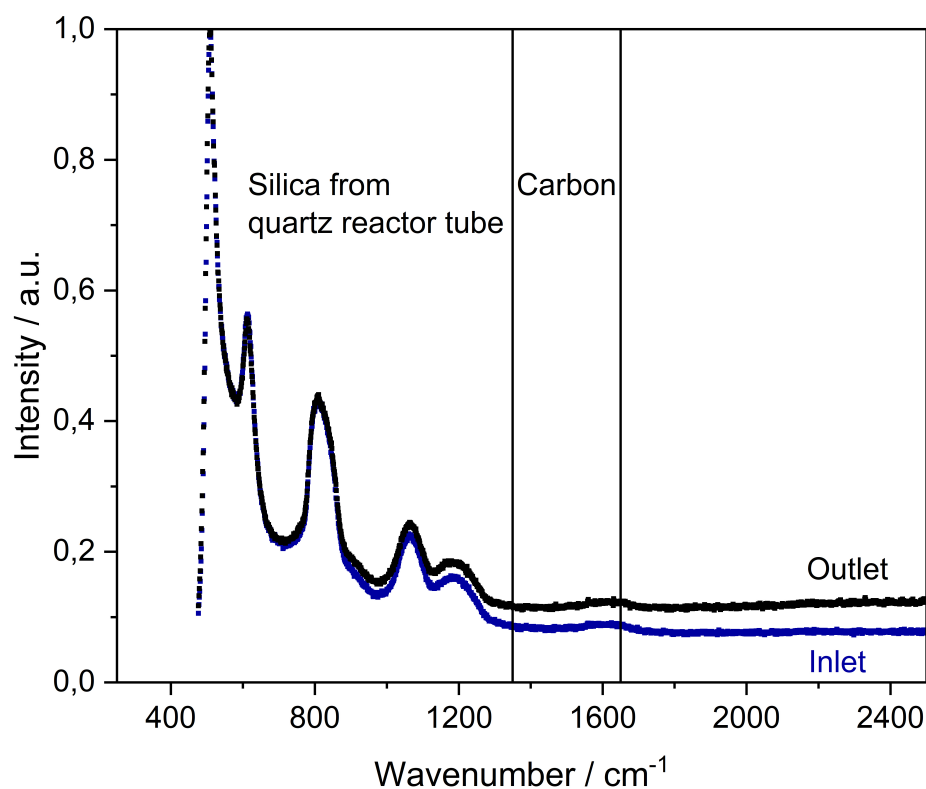


Fig. 4.12: Ex situ Raman spectroscopy was performed on the spent catalyst in the reactor tube to detect potential carbon deposits formed as by-products during the reaction. The spectra correspond to the inlet and outlet of the catalyst bed, with no significant carbon signals detected.

1300 cm^{-1} [33]. No band signals characteristic of disordered and amorphous carbonaceous material are detectable in the range from $1350 - 1620\text{ cm}^{-1}$ [204]. This is consistent with literature reports indicating that no coking occurs under methanation conditions [152, 205], provided that carbon monoxide formation remains negligible and methane selectivity approaches 100 %. These findings are further supported by the experimental evaluation presented in Section 4.4.1.

4.3.7 LIBS

To confirm the Raman measurements, *ex situ* Laser-Induced Breakdown Spectroscopy (LIBS) analysis was additionally employed, which also indicated the absence of carbonaceous deposits formed during the reaction. In contrast to the Raman measurements, in which the spent catalyst was analyzed externally through the quartz glass reactor tube, the LIBS

analysis was performed on individual catalyst particles removed from the center of the filled reactor tube at the inlet and outlet of the fixed-bed and examined in a LIBS spectrometer. The LIBS spectrum of a particle measured at the inlet is shown in Figure 4.13a, and that at the outlet in Figure 4.13b. The light emitted from the resulting plasma generated by laser ablation was collected and recorded in the UV region, as the most characteristic lines of carbon are visible at 193 and 247.9 nm [206, 207]. Peaks of a band are observed in the 300 – 320 nm region, which can be attributed to aluminum signals at 308.2 and 309.2 nm [207, 208]. The peaks observed between 220 and 240 nm form a broad, rising band and can be assigned to the characteristic fingerprint of elemental nickel, as confirmed by a reference measurement of a pure nickel sample. No additional peaks is observed, and consequently, no carbon signal was detected in the LIBS spectra at either the inlet or the outlet of the catalyst bed.

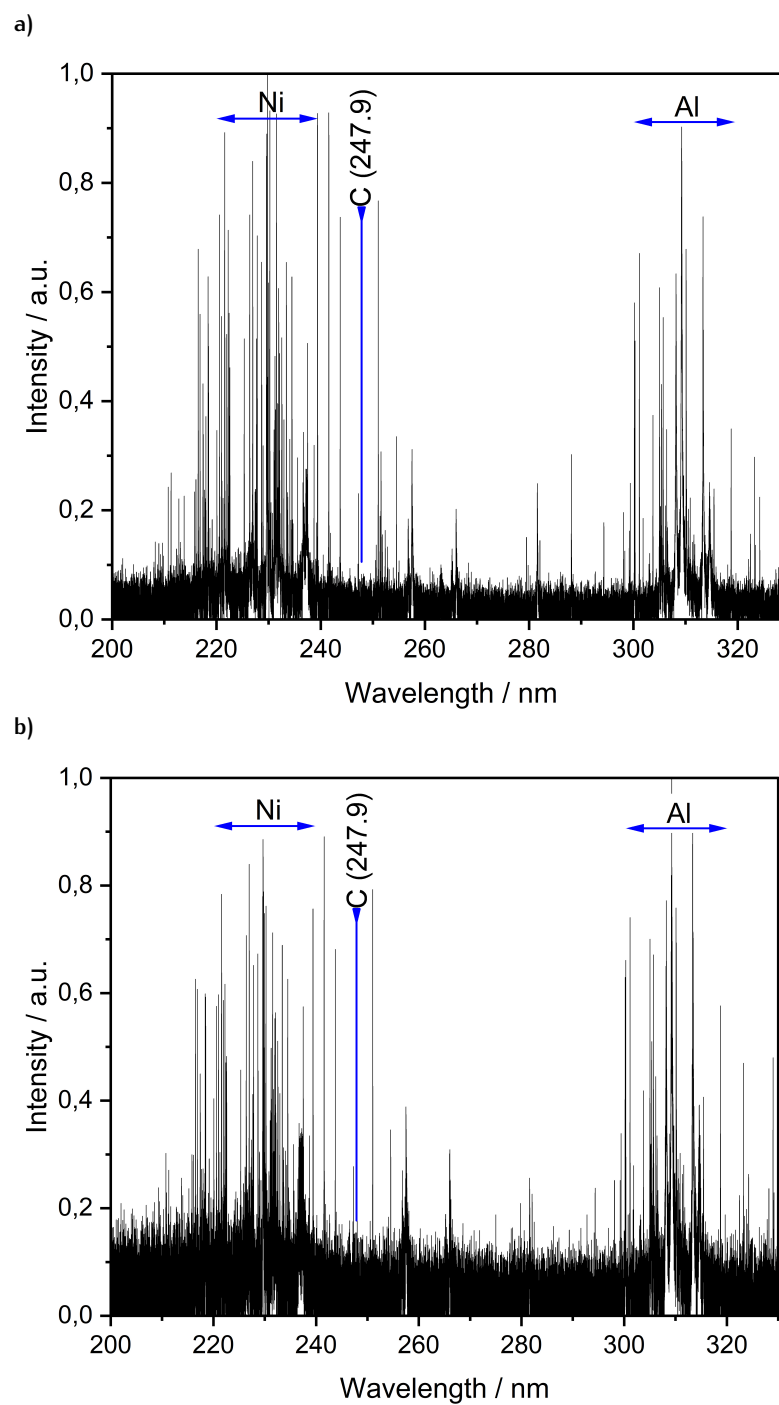


Fig. 4.13: Ex situ LIBS analysis of spent catalyst particles extracted from the packed reactor tube after the reaction at the inlet (a) and outlet (b) of the fixed-bed.

4.4 Iso-Potential DRIFTS Profiling

This section presents the results of the IPO DRIFTS profile measurements and the corresponding extracted adsorbate profiles, which were first published in [81]. The experimental workflow and corresponding setup configuration are described in Sections 3.2.2 and 4.1, respectively. The theoretical information content of the following IPO DRIFTS measurements is already defined in Section 3.2.3 and provides the basis for data analysis and processing. Contrary to the described experimental procedure in Section 4.2, the results of the IPO DRIFTS measurements are presented in reverse order in Section 4.4.1 to Section 4.4.4 to better illustrate the correlation of the measurements to the reader. Section 4.4.1 begins with the local 'conversion check' (X) in the reactor, measuring temperature and molar flow rate profiles. In Section 4.4.2, the CO₂ conversion profiles of the IPO DRIFTS measurements (A, C) are compared with the local reactor conversion (X) to verify that the composition of the reaction mixture was not altered while passing through the DRIFTS cell and thus did not influence the results. The IPO DRIFTS measurements of IR absorption in the gas phase are discussed in Section 4.4.3, while the measurements of the bulk and surface states of the highly diluted catalyst are described Section 4.4.4. Section 4.4.5 deals with the data processing step for extracting surface adsorbates and bulk catalyst changes from the measured IPO DRIFTS data.

4.4.1 Temperature and Gas Composition Profiles in the CPR (X)

The results of the temperature and gas composition profiles measured axially through the CPR are presented in Figure 4.14. Gas analysis was conducted via mass spectrometry using the setup configuration shown in Figure 3.5 (X) and is referred to as the 'conversion check'. Figure 4.14a details the profiles of the molar flow rates of the species contained in the reaction mixture at different measurement positions through the catalyst bed. H₂O, H₂ and CO were calculated stoichiometrically from the components CO₂ and CH₄, as described in Section 4.2.2. The gray area marks the measurement positions right before entering the catalyst bed, which extends from 0 mm to 30 mm. The flat species profiles, which remain constant before entering the catalyst bed without significant fluctuation, indicate the absence of axial species dispersion. However, H₂ represents a large proportion of the reaction mixture at the entrance to the catalyst bed. The diffusion coefficient of a molecule is inversely proportional to the square root of its molecular weight (cf. Equations (A.10) and (A.11)). Consequently, H₂ diffuses faster than all other components of the reaction mixture, as it is a lightweight molecule. Therefore, the potential for axial dispersion requires

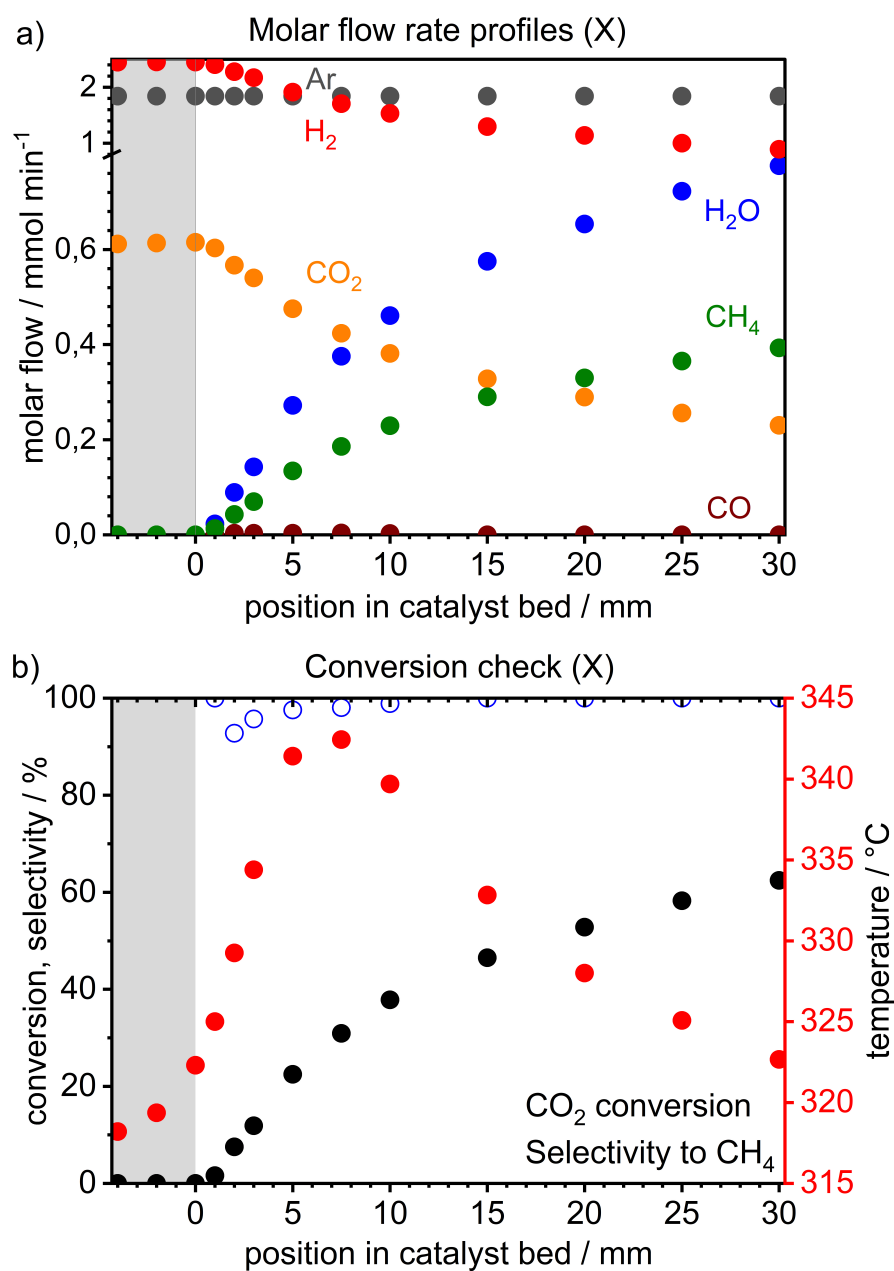


Fig. 4.14: Spatially resolved temperature and concentration profiles measured in the Compact Profile Reactor (CPR) during CO₂ methanation over the Ni/ γ -Al₂O₃ catalyst: (a) Molar flow rate profiles of the species. (b) Profiles of temperature, CO₂ conversion, and CH₄ selectivity. Experimental conditions are provided in Table 4.1. Adopted and modified from [81].

further investigation and is discussed in Section A.3. The calculation results in a high Bodenstein number, owing to the high total flow rate within the catalyst bed, indicating that

an axial dispersion of the gas flux can be neglected. Within the bed, samples were taken at intervals of 1 – 2.5 mm up to 10 mm, and every 5 mm thereafter. The highest methane formation rate, indicated by the most significant slope of the CH₄ profile, occurs between measurement positions 1 and 5 mm and gradually decreases thereafter. To determine a reduction in the reaction rate in this region, which could prevent a sufficiently high degree of conversion, the Mears and Weisz-Prater criteria are used to determine mass transport limitations in the catalyst bed. The results are provided and discussed in Sections A.4 and A.5. The observed variations in the molar flow rates of the individual species, as shown in Figure 4.14a, can be well approximated by a single stoichiometric equation corresponding to the Sabatier reaction (cf. Eq. (2.20)). The molar flow rates of CO are close to zero and within the accuracy of mass spectrometric product analysis. If at all, CO is only formed in trace amounts through the reverse water-gas shift reaction (rWGS, cf. Eq. (2.22)) [152, 209]. Carbonaceous deposits, which may have formed from traces of CO through the Boudouard reaction (cf. Eq. (2.23)), were examined after the experiments using Raman spectroscopy on a spent catalyst. As described in Section 4.3, no carbonaceous deposits were observed, consistent with literature reports [152, 205] indicating that coking does not occur under the reaction conditions employed in this work, provided that CO formation is negligible and CH₄ selectivity approaches 100 %.

Figure 4.14b presents the temperature profile along with the progression of CO₂ conversion and CH₄ selectivity throughout the catalyst bed. Conversion and selectivity were calculated using Equations (4.1) and (4.2), respectively, based on the molar flow rate profiles from Figure 4.14a. 4 mm before the catalyst bed begins, graphically signed at the measurement position of –4 mm, the gas temperature reaches a measured value of 318 °C. The slight deviation from the set reactor temperature of 320 °C indicates that the reaction mixture was effectively preheated before entering the catalyst bed. In contrast to the molar flow rate profiles of the species, the temperature profile indicates a slight increase even before the catalyst bed, suggesting axial thermal dispersion under these conditions. The temperature profile rises quickly within the catalyst bed, forming a temperature maximum of approximately 343 °C between measurement positions 5 and 7.5 mm, due to the heat production of the exothermic reaction. As the conversion decreases, the heat production of the reaction also decreases, reaching a temperature value of 323 °C at the end of the catalyst bed, which indicates good heat dissipation of the CPR and almost isothermal reactor operation. The CO₂ conversion increases continuously from 0 % at the entrance to 63 % at the end of the catalyst bed. Compared to the chemical equilibrium calculation for

the experimental reaction conditions discussed in Section A.1, the total conversion observed at the end of the catalyst bed in the profile measurement is significantly lower than the theoretically predicted equilibrium. Consequently, the CO_2 methanation reaction is not constrained by the defined experimental conditions, remains thermodynamically feasible, and exhibits an equilibrium position strongly shifted toward the products. The highest CO_2 consumption rate or methane formation rate corresponds to the slope of the profile between 2 and 5 mm, and then gradually slows down. The CH_4 selectivity remains close to 100 % throughout the bed, regardless of CO_2 conversion. Only some data points at 2 – 5 mm fluctuate below 100 %, which can be attributed to the zone with the steepest gradients in molar flow rate and temperature. These discrepancies are most likely caused by analytical inaccuracies arising from steep gradients and rounding errors. Since CO was not directly measured but calculated from the carbon and oxygen atom balances, and the CH_4 selectivity at 8 mm is close to 100 %, analytical errors are the more probable source.

4.4.2 Conversion Profiles with and without the DRIFTS cell

For accurate IPO DRIFTS profile measurements, the diluted catalyst sample in the DRIFTS cell must be exposed to the same chemical potential as the catalyst within the reactor tube of the CPR, which requires minimizing changes in the chemical composition of the sampled reaction mixture. Alterations in the chemical composition of the sampled reaction mixture may occur within the transfer system and within the DRIFTS cell itself. To ensure that neither the diluted catalyst sample (cf. Figure 3.5, A) nor the diluent alone (cf. Figure 3.5, B) experiences a noticeable change in the chemical composition of the reaction mixture, the local reactor conversion at each measurement position in the fixed-bed (cf. Figure 3.5, X) is compared with the corresponding conversion downstream of the DRIFTS cell, which is connected in series. Gas analysis was performed by mass spectrometry, and Figure 4.15 summarizes the results of the three different CO_2 conversion profiles. A scheme of the experimental configuration for the respective profile measurements is included in the figure and corresponds to the workflow description in Section 3.2.2. Starting 4 mm in front of the catalyst bed, samples were taken every 1 – 2 mm up to 10 mm into the catalyst bed and then in intervals of 10 mm until the end of the catalyst bed at 30 mm. A comparison of the profiles reveals that the CO_2 conversion values measured downstream of the DRIFTS cell, connected in series (A and C), are higher than those obtained with the CPR alone (X).

Deviations in the conversion data are attributed to blank reactivity on the metallic surfaces of internal components in the Praying Mantis DRIFTS cell (Harrick Scientific), consistent

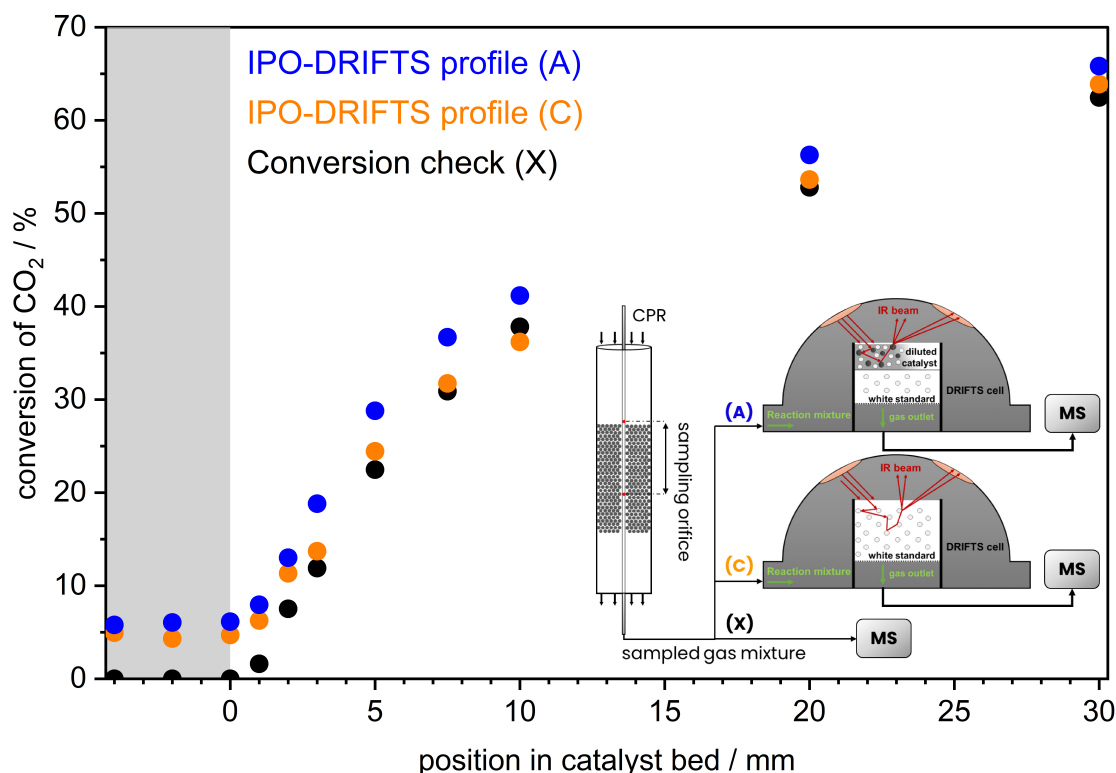


Fig. 4.15: Comparison of spatially resolved CO_2 conversion profiles measured with and without the DRIFTS cell connected in series to the CPR: DRIFTS cell filled with the catalyst sample diluted in CaF_2 (blue points). DRIFTS cell filled solely with the reference material/‘white standard’ CaF_2 (orange points). CPR operated alone, bypassing the DRIFTS cell (black points). Experimental conditions are provided in Table 4.1. Adopted and modified from [81].

with observations reported by other authors [72]. This is particularly noticeable in the measurement data of the IPO DRIFTS profile (C) involving the DRIFTS cell filled with the pure white standard (orange points), as CaF_2 is chemically inert and cannot cause any additional CO_2 conversion. At -4 mm, i.e., 4 mm before the catalyst bed begins, up to 2 mm inside the bed, the CO_2 conversion values are approximately 5 % higher than the conversion profile of the CPR alone (X, black points). The respective molar flow rate profiles of the IPO DRIFTS measurement (C) are given in Figure 4.16a and exhibit traces of H_2O and CO formed at the beginning of the catalyst bed. These traces are assumed to result from the interaction of the gas mixture with the metallic surfaces of the internal cell components following the rWGS reaction (cf. Eq. (2.22)), with subsequent conversion of CO to CH_4 via CO methanation (cf. Eq. (2.21)); however, the latter could not be clearly detected by MS. As the CO_2 conversion increases, starting at 1 mm within the catalyst bed of the reactor (X,

black points), the blank activity becomes less critical and the respective CO₂ conversion profiles converge.

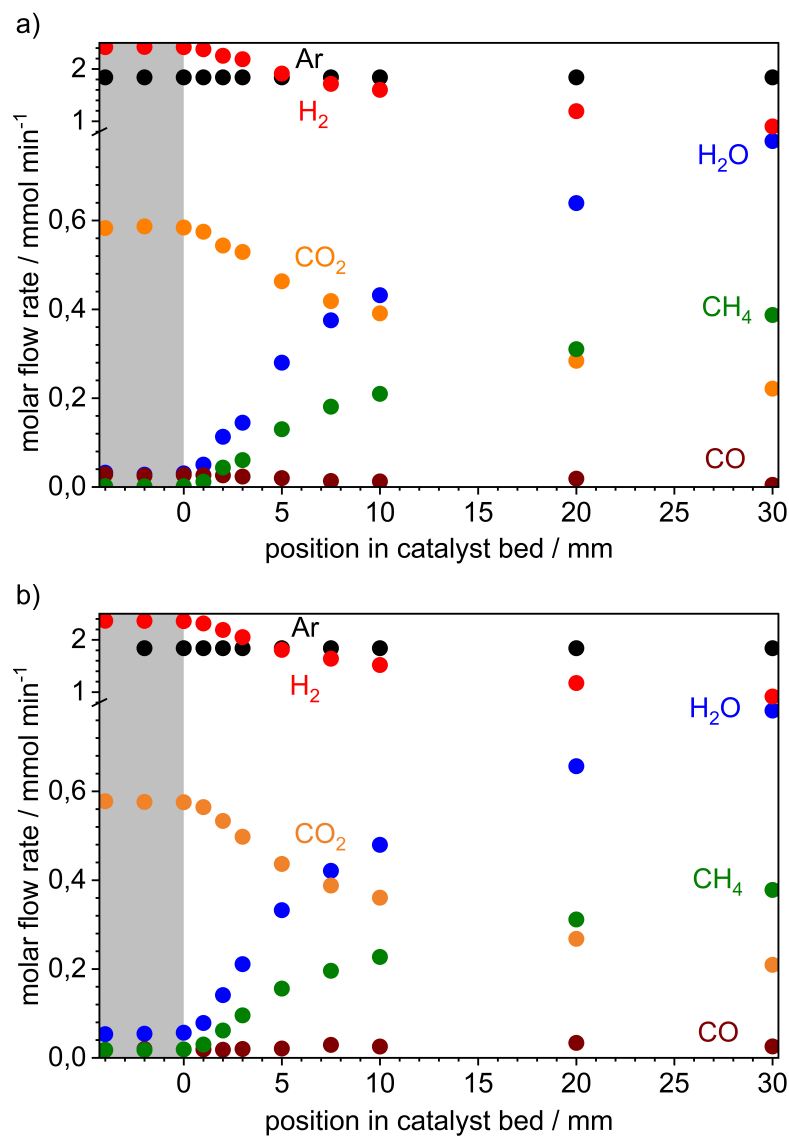


Fig. 4.16: Spatially resolved molar flow rate profiles from IPO DRIFTS measurements obtained downstream of the DRIFTS cell, which is connected in series with the CPR and filled with a) the diluent alone (C), and b) the diluted Ni/ γ -Al₂O₃ catalyst sample (A). Experimental conditions are provided in Table 4.1. Adopted and modified from [81].

Another source of deviating reactivity in an IPO DRIFTS measurement is the additional conversion caused by the catalyst sample in the spectroscopy cell. As discussed in Section 4.2.1, the catalyst sample in the DRIFTS cell is diluted with CaF₂ to detect adsorbate

signals of sufficient quality and minimize the conversion. An acceptable compromise was found with a catalyst dilution ratio of 1:20 by weight. The most substantial deviations in the conversion profile when analyzing the diluted catalyst sample in the DRIFTS cell are observed when the reaction rate is highest, i.e., deviations of about 8 % higher than with the CPR alone, particularly in the range of 1 – 5 mm within the catalyst bed (A, blue points). As the reaction rate in the reactor declines with decreasing reactant concentration and temperature, the additional CO₂ conversion in the DRIFTS cell becomes less significant, causing the profile to converge toward that of the CPR alone (X, black points). This is also evident from the molar flow rate profiles shown in Figure 4.15b. The traces of CH₄ and H₂O that formed at the measurement positions in front of the catalyst bed can be attributed to the CO₂ methanation reaction that occurred in the DRIFTS cell using the diluted catalyst sample.

In summary, the conversion profiles of the IPO DRIFTS measurement, with the diluted catalyst sample added to the DRIFTS cell or with the diluent alone, affected the chemical composition of the reaction mixture to a slight conversion difference within the accuracy of the mass spectrometric product analysis. The most substantial deviations due to the additional conversion of the catalyst sample are observed at the highest reaction rate, ranging from 1 – 5 mm. As the reaction rate in the reactor declines with decreasing reactant concentration and temperature, the additional CO₂ conversion in the DRIFTS cell likewise diminishes and gradually converges toward the CPR profile. The deviations observed with the CaF₂-filled DRIFTS cell, which are attributed to blank activity, are particularly noticeable before the catalyst bed begins and become less significant with increasing CO₂ conversion within the fixed-bed. However, the deviations in chemical composition between the reactor and the DRIFTS cell are minor and do not compromise the proof of concept of the IPOS method

4.4.3 IPO DRIFTS measurements of the Diluent (C, D)

According to the workflow described in Section 3.2.2 for an IPO DRIFTS measurement, three main IR absorption interferences occur when analyzing a diluted catalyst sample (cf. Figure 3.6): Undesired contributions by the adsorbed species on the surface of the diluent (x), the gas phase species in the reaction mixture exposed to the catalyst (y), and the IR absorption of the bulk phase of the diluent/‘white standard’ (z). To remove interfering spectral contributions and obtain a pure IR spectrum of the adsorbates on the catalyst surface, IPO DRIFTS measurements were performed according to the procedure illustrated in Figure 3.7. The DRIFTS cell was filled with the pure ‘white standard’/diluent

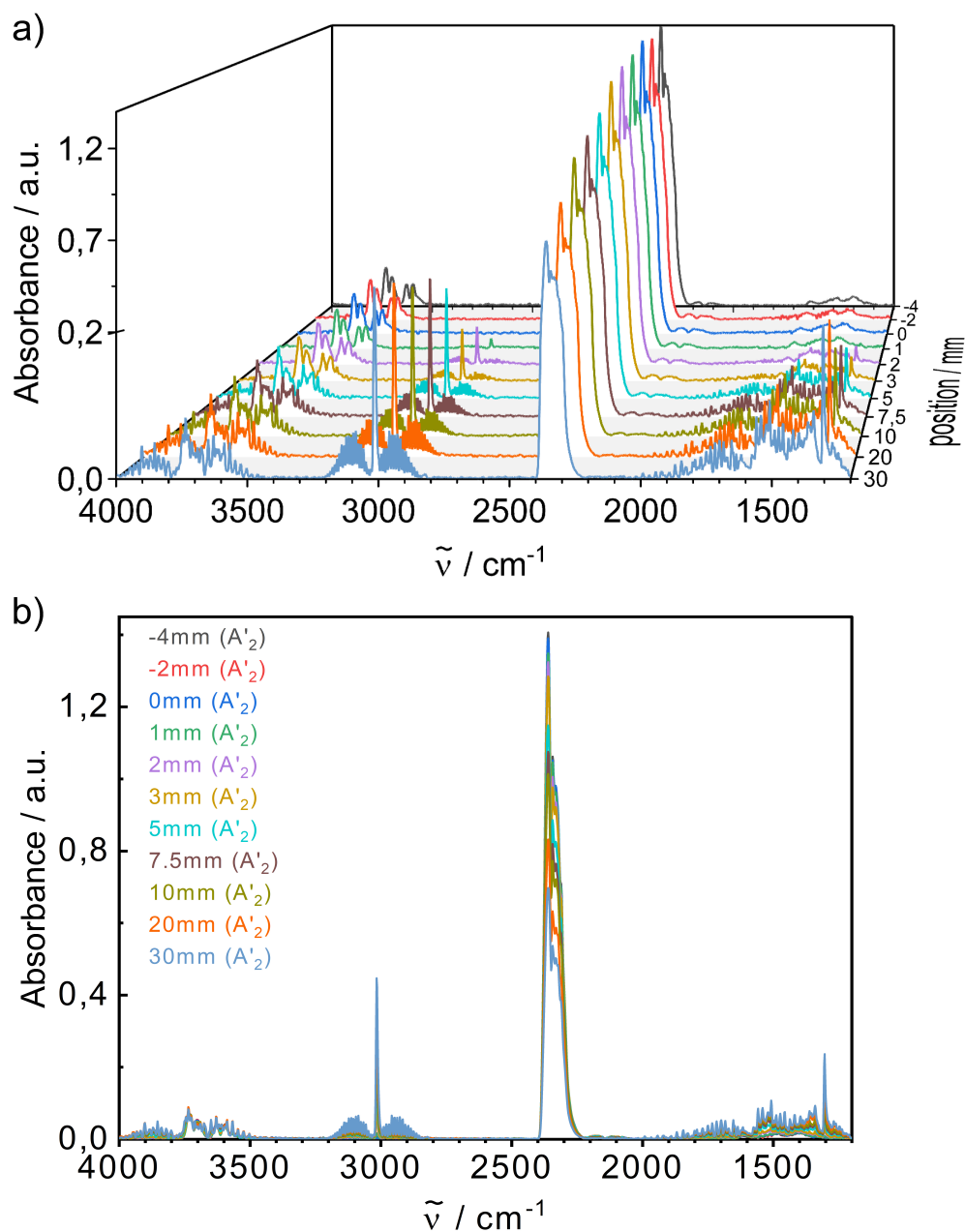


Fig. 4.17: Absorbance spectra (A'_2) (cf. Figure 3.7, $C' - D'$), obtained from the difference between the IPO DRIFTS measurements (C') with the DRIFTS cell filled with the pure diluent/'white standard' exposed to the reaction mixture and the corresponding reference measurements (D') under H_2 . (a) Waterfall plot of the referenced absorbance spectra as a function of the wavenumber and the measurement positions along the catalyst bed in the CPR. The vertical absorbance axis is split to visualize strong and weak bands. (b) Plot of absorbance as a function of wavenumber, illustrating the decrease in concentration of the observed gas phase species of the reaction mixture. Experimental conditions are provided in Table 4.1. Adapted and modified from [81].

material (CaF_2) and exposed to the reaction mixture locally sampled from the CPR along the fixed-bed (cf. Figure 3.5, C). In a separate set of measurements, reference spectra of the 'white standard' were recorded under flowing H_2 as the reference gas (cf. Figure 3.5, D). To minimize the time delay between the IPO DRIFTS profile measurements of the diluent and the catalyst sample, the individual reference measurements were conducted at the average temperature established within the catalyst bed under reaction conditions (cf. Section 4.2). Figure 4.17 provides the absorbance spectra (cf. Figure 3.7, A'_2), derived from the difference between the IPO DRIFTS profile spectra (C) and the IR spectrum of CaF_2 as a 'white standard' in the reference state (D).

The waterfall plot in Figure 4.17a displays the referenced DRIFTS spectra of the IR gas absorption as a function of absorbance, plotted against the wavenumber in the range of 4000 to 1200 cm^{-1} , and against the measurement positions within the catalyst bed of the CPR. For comparison, Figure 4.17b represents the same data, with the spectra superimposed directly to illustrate changes in the band intensities of the observed gas species CO_2 , CH_4 and H_2O in the reaction mixture. In Figure 4.18, three representative IR spectra obtained at 1, 3 and 30 mm along the catalyst bed are shown, and prominent bands are assigned for detailed examination and interpretation. The most prominent IR absorption band at 2349 cm^{-1} corresponds to the asymmetric stretching vibration (ν_{as}) of gaseous CO_2 , with combination vibrations ($2\delta + \nu_{\text{as}}$, $\nu_{\text{s}} + \nu_{\text{as}}$) of lesser intensity at higher wavenumbers in the range of $3500 - 3800\text{ cm}^{-1}$ [89, 210]. The other intense bands at 3019 cm^{-1} and 1306 cm^{-1} represent the degenerate stretching vibration (ν_{as}) and the equivalent deformation vibration (δ) of CH_4 , respectively [89]. The band intensity of CO_2 is highest at the measurement position, located -4 mm before the catalyst bed begins, and remains constant until it reaches the entrance at 0 mm . Within the catalyst bed, the CO_2 band intensity decreases progressively, showing only a slight reduction up to 3 mm , followed by a pronounced decline toward the end of the bed. The opposite trend is observed for CH_4 , which is initially absent in the catalyst bed and increases gradually as the reaction initiates. From 5 mm , the intensity of the CH_4 band rises sharply until the end of the catalyst bed. In Figure 4.19, the integrated IR band areas (green symbols) of CO_2 (2349 cm^{-1}) and CH_4 (3019 cm^{-1}) are compared with the corresponding mole fractions (orange symbols) obtained by MS at the different axial positions in the catalytic fixed-bed of the CPR. To permit a direct comparison on a common scale, all curves are normalized to their respective maximum values, highlighting the close correlation between the data sets. As described by the extinction law (cf. Eq. (2.18)), a change in the concentration of

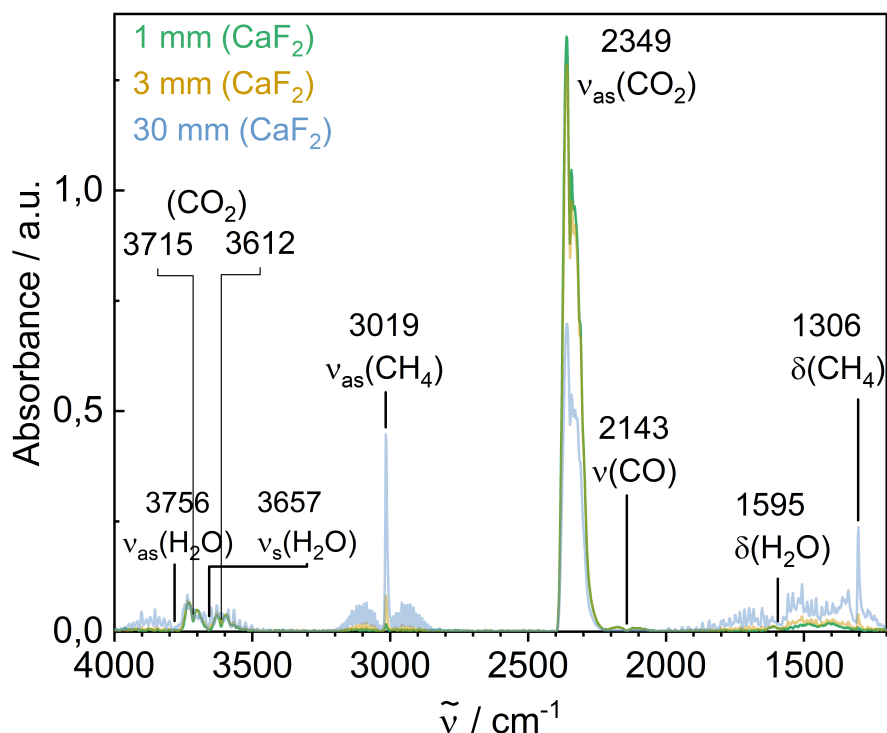


Fig. 4.18: Absorbance spectra (A'_2) at measurement positions 1, 3 and 30 mm (cf. Figure 3.7, $C' - D'$), obtained from the difference between the IPO DRIFTS measurements (C') with the DRIFTS cell filled with the pure diluent/'white standard' exposed to the reaction mixture and the corresponding reference measurements (D') under H_2 . Experimental conditions are provided in Table 4.1. Adapted from [81].

a gas species is proportional to a change in the intensity of the associated IR absorption band, resulting in this correlation. A slight offset is observed between the two curves. The normalized DRIFTS profile of CO_2 (green circles) is consistently slightly higher than the corresponding normalized concentration profile obtained from the reactor (orange circles). This discrepancy is attributed to the considerable time interval between the measurements of the two profiles, resulting in a minor experimental inaccuracy. For CH_4 , the normalized DRIFTS profile (green squares) differs from the normalized MS profile (orange squares) only within the first third of the catalyst bed, corresponding to the region of the highest CH_4 formation rate and steepest temperature increase. At the remaining measurement positions, however, both profiles are almost congruent. Since CaF_2 is chemically inert, the additional CH_4 detected by DRIFTS must have been formed within the DRIFTS cell itself, confirming the blank activity discussed in Section 4.4.2. This assumption is supported by a small rovibrational band of the stretching frequency of gaseous CO, which is visible in

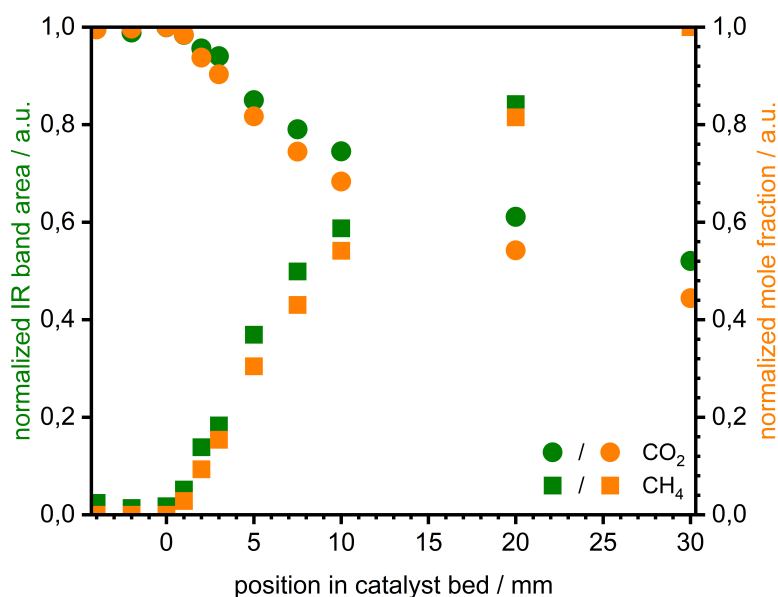


Fig. 4.19: Comparison of the integrated and normalized band areas of CO₂ (2349 cm⁻¹, green circle) and CH₄ (3019 cm⁻¹, green square) with the normalized mole fraction profiles of CO₂ (orange circle) and CH₄ (orange square) in the reactor. IR measurements were conducted following the workflow in Figure 3.5 (C), with the DRIFTS cell filled with the reference material/‘white standard’ (CaF₂), while mole fraction profiles were measured by MS according to the workflow in Figure 3.5 (X). Experimental conditions are provided in Table 4.1. Adapted and modified from [81].

the Figure 4.18 at 2143 cm⁻¹ [125]. Its band intensity is highest at -4 mm, i.e., 4 mm in front of the fixed-bed, and decreases as it moves inward. This is consistent with the traces of CO shown in Figure 4.16a. As already suggested in Section 4.4.2, CO is formed via the rWGS reaction on the metallic components in the DRIFTS cell and subsequently converted to CH₄ through CO methanation. Water is a major product of the CO₂ methanation process and is represented by two typical vibrational bands at approximately 1600 and 3600 cm⁻¹. From 3 mm onward, the water vapor bands gradually increase and begin to overlap with the CO₂ combination bands, forming a broad feature. At about 10 mm, a characteristic water vapor spectrum is fully established. Water vapor exhibits three rovibrational bands: symmetric (ν_s) and asymmetric (ν_{as}) O–H stretching vibrations, centered at approximately 3657 and 3756 cm⁻¹, respectively, and the H–O–H bending vibration (δ) around 1595 cm⁻¹, which overlaps a broad spectral range from 1200 to 1800 cm⁻¹ [211]. The latter broad band is particularly relevant in the present context, as it overlaps with the IR absorption bands of potential surface species formed during CO₂ methanation on the Ni/ γ -Al₂O₃ catalyst. Before the water vapor spectrum becomes prominent, three small bands are visible at 1610, 1481 and 1408 cm⁻¹, which are best seen in the spectrum

recorded at 1 mm in Figure 4.18, but are not labeled. However, the bands are too broad for accurate assignment and interpretation. The positions of the bands indicate carbonate-like vibrations of surface species on the reference material/‘white standard’ (CaF_2), presumably caused by the interaction of CO_2 with adsorbed hydroxyl groups on surface defects [212, 213].

In summary, the spectral information about the surface species on the diluent and in the surrounding gas phase, which was obtained from the CPR, was derived from the referenced absorption spectra of the IPO DRIFTS measurements using the DRIFTS cell filled with the pure reference material/‘white standard’ (cf. Figure 3.7). Spectral signatures of bulk IR absorption by the diluent are absent in the DRIFTS spectra, as CaF_2 was inert to the reaction mixture and did not undergo any structural changes upon exposure to it. Spectral influences due to ‘instrument functions’ have already been eliminated from the IPO DRIFTS spectra by referencing.

4.4.4 IPO DRIFTS measurements of the diluted Catalyst Sample (A, B)

Following the IPO DRIFTS profile measurements of the pure diluent, the catalyst sample is analyzed using the same procedure by placing a 2 mm layer of a 1:20 diluted catalyst- CaF_2 mixture into the sample cup of the DRIFTS cell, which was pre-filled with a bed of pure CaF_2 (cf. Section 4.2). After purging the cell with H_2 as reference gas at the average temperature of the catalyst bed to record the reference measurement (cf. Figure 3.5, B), the sampling flow of the CPR was switched to the inlet of the DRIFTS cell to measure an IPO DRIFTS profile along the fixed bed (cf. Figure 3.5, A). The absorbance spectra resulting from the referenced DRIFTS measurements using the diluted catalyst sample are given in Figure 4.20 and contain the spectral information summarized in Figure 3.6 ($A'_1 = A' - B'$): The adsorbed species on the catalyst surface (x), the IR absorption of the bulk phase of the catalyst (z), and the undesired contributions recorded during the IPO DRIFTS profile measurements of the diluent (cf. Figure 3.7) and already described in Section 4.4.3.

The waterfall plot in Figure 4.20a and the superimposed plots in Figure 4.17b display the same data, but in different views to better illustrate the decrease in band intensity of the observed spectral signatures and to facilitate data interpretation. Similar to the absorbance spectra using pure CaF_2 (cf. Section 4.4.3), the IPO DRIFTS spectra recorded for the diluted catalyst are predominantly influenced by the IR absorption bands of the gas phase species CO_2 , CH_4 , CO and H_2O , which constitute the reaction mixture. The weak vibrational band at 2143 cm^{-1} (not labeled) indicates traces of gaseous CO and is most pronounced

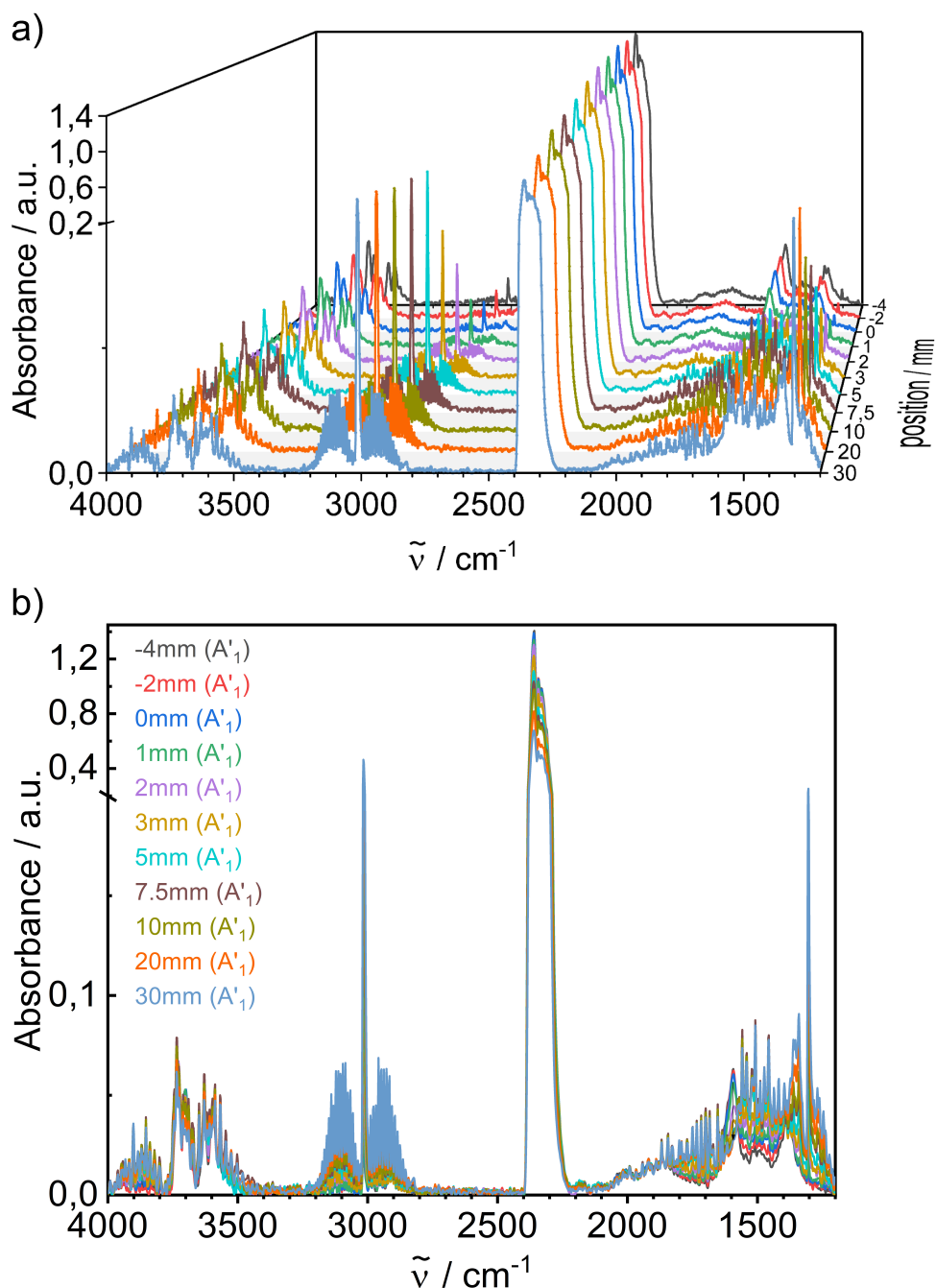


Fig. 4.20: Absorbance spectra (A'_1) (cf. Figure 3.6, $A' - B'$), obtained from the difference between the IPO DRIFTS measurements (A') with the DRIFTS cell filled with the diluted catalyst sample exposed to the reaction mixture and the corresponding reference measurements (B') under H_2 . (a) Waterfall plot of the referenced absorbance spectra as a function of the wavenumber and the measurement positions along the catalyst bed in the CPR. (b) Plot of absorbance as a function of wavenumber, illustrating the decrease in concentration of both gas phase species in the reaction mixture and adsorbed species on the catalyst surface. The vertical absorbance axis is split to visualize strong and weak bands. Experimental conditions are provided in Table 4.1. Adapted from [81].

upstream of the catalyst bed. As discussed in the previous sections, it is assumed that CO_2 reacted with the metallic components in the DRIFTS cell and formed CO through the rWGS reaction (cf. Eq. (2.22)). As the measurement progresses further into the catalyst bed, the CO concentration in the DRIFTS cell decreases rapidly due to its conversion back to CH_4 via CO methanation Eq. (2.21), thereby becoming spectrally and kinetically less relevant. The band intensities of CO_2 (2349 cm^{-1} , not labeled) and CH_4 (3019 cm^{-1} , not labeled) are consistent with the trend of the molar flow rate profiles measured with MS along the fixed-bed (cf. Figure 4.14a). To allow a comparison on the same scale, the integrated band areas of CO_2 (green circle) and CH_4 (green squares) are normalized to their respective maximum values and plotted in Figure 4.21 against the likewise normalized mole fractions of CO_2 (orange circles) and CH_4 (orange squares) measured in the CPR (cf. Figure 3.5, X). A general correspondence between the two curves is observed, with a slight

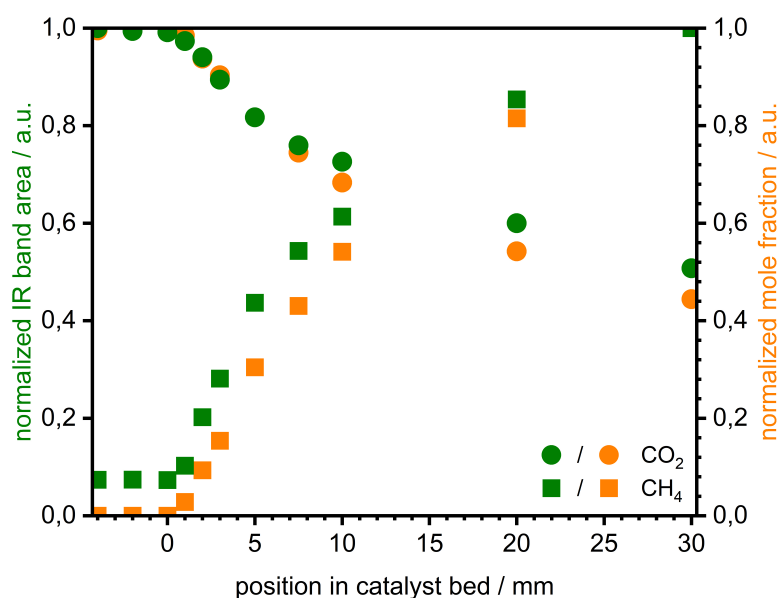


Fig. 4.21: Comparison of the integrated and normalized IR band areas of CO_2 (2349 cm^{-1} , green circles) and CH_4 (3019 cm^{-1} , green squares) with the normalized mole fraction profiles of CO_2 (orange circles) and CH_4 (orange squares) in the reactor. IR measurements were conducted following the workflow in Figure 3.5 (A), with the DRIFTS cell filled with the diluted catalyst sample. The mole fraction profile was obtained by mass spectrometry according to the workflow in Figure 3.5 (X). Experimental conditions are provided in Table 4.1. Adapted and modified from [81].

offset. The normalized DRIFTS profile of CO_2 (green circles) is in close agreement with the corresponding normalized concentration profile obtained from the reactor (orange circles). Small deviations are observed at higher measurement positions and can, once again, be attributed to the considerable time interval between the acquisition of the two profiles,

resulting in a minor experimental uncertainty. The discrepancy between the DRIFTS and MS data for CH_4 is more pronounced due to additional CO_2 conversion by the catalyst in the cell; nevertheless, it remains sufficiently small to uphold the validity of the IPOS methodology as a proof of concept. Three IR spectra from measurement positions at 1, 3 and 30 mm within the catalyst bed are selected for detailed interpretation of the DRIFTS profile data and are presented in Figure 4.22. The prominent bands are labeled, except for the IR absorption of the surrounding gas species, which corresponds to that shown in Figure 4.18. Broad bands appear in the range of 1200 to 2060 cm^{-1} , characteristic of the

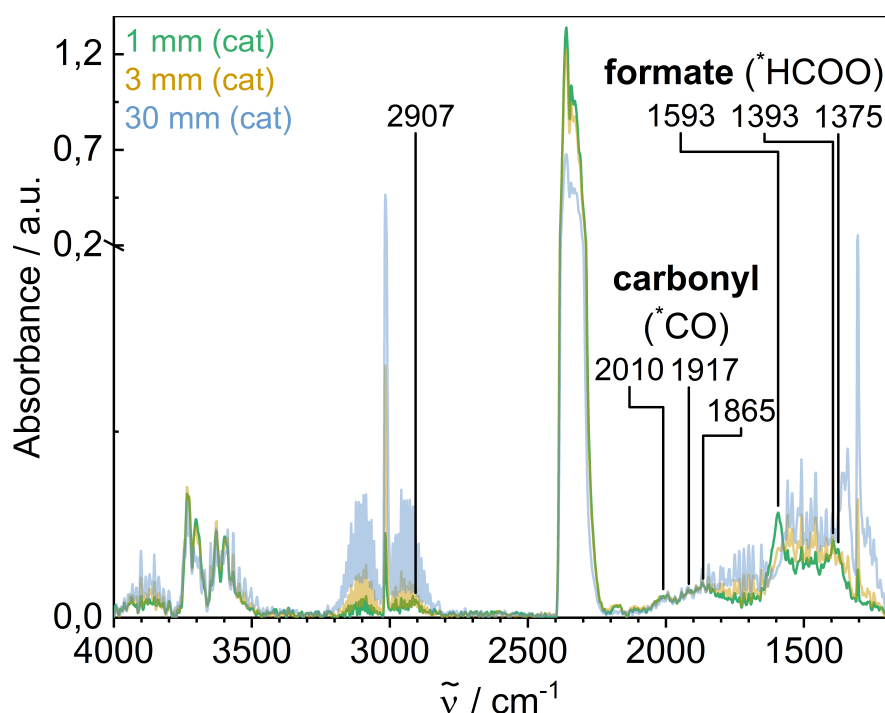


Fig. 4.22: Absorbance spectra (A_1) at measurement positions 1, 3 and 30 mm (cf. Figure 3.6, $A' - B'$), obtained from the difference between the IPO DRIFTS measurements (A') with the DRIFTS cell filled with the diluted catalyst sample exposed to the reaction mixture and the corresponding reference measurements (B') under H_2 . Experimental conditions are provided in Table 4.1. Adapted from [81].

vibrations of surface species derived from adsorbed CO_2 . In the literature, numerous authors have already conducted IR studies on CO_2 methanation and observed various adsorbed carbon species within this wavelength range [214–217]. Depending on the active metal components, the catalyst support material, or the reaction conditions used in the reactor, these surface adsorbates can be either spectators or reaction intermediates. Starting from the measurement position at 1 mm, the most pronounced band is located at 1593 cm^{-1} .

According to the review by Busca and Lorenzelli [218], along with the references cited therein, this band can be attributed to the asymmetric stretching vibration $\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$ of surface-adsorbed formate ($^*\text{HCOO}_{\text{ads}}$). Formate species are formed via the hydrogenation of chemisorbed carbonate species, a process theoretically facilitated by the spillover of hydrogen atoms from the Ni particles. As described in Section 2.5.5, carbonate and bicarbonate species are formed by the chemisorption of CO_2 on O- and OH-groups of $\gamma\text{-Al}_2\text{O}_3$, respectively. Consequently, the formate species are most likely located on the support surface or near the metal-support interface. The minor band at 2907 cm^{-1} and the shoulder that occurs at 1375 cm^{-1} are also attributed to formate and represent the symmetric stretching vibrations $\nu_{\text{s}}(\text{C}-\text{H})$ and $\nu_{\text{s}}(\text{O}-\text{C}-\text{O})$, respectively [219]. The band at 1392 cm^{-1} is reported in the literature as the bending vibration $\delta(\text{C}-\text{H})$ of adsorbed formate on metal oxides [220–223]. A summary of the assigned formate bands (1375 , 1392 , 1593 and 2907 cm^{-1}) is provided in the work by Fujita et al. [224], which investigates the methanation reaction on alumina-supported nickel catalysts. The proposed bands for bidentate formate show the closest agreement with the experimental observations of this study and are frequently cited as references for interpreting IR spectra in other CO_2 methanation research. Additional CO_2 surface species are indicated by the broad feature observed between 2050 and 1700 cm^{-1} . The weak peaks at 2010 and 1863 cm^{-1} , along with the shoulder at approximately 1915 cm^{-1} , can be allocated to different types of adsorbed carbonyl species ($^*\text{CO}_{\text{ads}}$) at nickel sites [225]. The bands above 2000 cm^{-1} are assigned to stretching vibrations of linearly bound ($^*\text{CO}_{\text{lin}}$), whereas the bands below correspond to stretching vibrations of bridged-bound ($^*\text{CO}_{\text{br}}$) [119, 226]. More specifically, $^*\text{CO}_{\text{ads}}$ can be adsorbed in a bridged configuration at 1915 cm^{-1} and in a threefold configuration at ($^*\text{CO}_{3\text{-fold}}$) at 1863 cm^{-1} [227, 228]. The weak oscillations between 1400 and 1500 cm^{-1} (not marked in Figure 4.22) cannot be clearly attributed to other surface adsorbates, but probably originate, as mentioned in the previous section, from carbonaceous adsorbates on the diluent (CaF_2) as mentioned in previous section. However, they are covered by the broad water vapor bending vibration at 1595 cm^{-1} and become unidentifiable. Other characteristic IR absorption of adsorbed surface species cannot be derived from these spectra.

In summary, the spectral information presented in the referenced absorbance spectra (A'_1) of the IPO DRIFTS measurements using the DRIFTS cell filled with the diluted catalyst sample is consistent with the theoretical predictions illustrated graphically in Figure 3.6. Besides the spectral signatures of the gas molecules from the sampled reaction gas mixture (y), the DRIFTS profile shows the vibrational bands of surface adsorbates on the catalyst,

the catalyst support, and on the diluent (x). Spectral signatures indicative of changes in the bulk phase of the active metal component Ni (z) cannot be confidently deduced from the spectra; however, the observed increase in intensity of the OH-vibrational band between $3500 - 3800\text{ cm}^{-1}$ may provide a possible indication: due to an oxidizing effect of the gas mixture during the reaction, the nickel oxide formed could adsorb hydrogen and appeared in the spectrum as OH-vibrational band. As water production increased with conversion, i.e., along the catalyst bed, the OH-vibrational band cannot be distinguished from that of water vapor molecules. No bulk changes of the catalyst support or the diluent are observed in the DRIFTS spectra, as CaF_2 or alumina are inert to the reaction gas mixture and do not undergo chemical transformations. Spectral influences caused by 'instrument functions' were previously eliminated by the data processing step, which involved referencing the IPO DRIFTS spectra (A) to the respective reference measurements (B).

4.4.5 Extraction of the Catalyst Surface Adsorbate Spectra

In a final data processing step (cf. Figure 3.8), the adsorbate profile (A'_{ads}) is extracted to isolate the IR absorption bands of the surface species on the catalyst and plot them as a function of reactor length. The difference between the referenced absorbance spectra derived from the IPO DRIFTS measurements using the DRIFTS cell filled with either the catalyst sample (A'_1 , cf. Figure 3.6) or the pure diluent (A'_2 , cf. Figure 3.7) results in an adsorbate profile that is shown in Figure 4.23 as a waterfall plot (a) or, for a better overview, as a superimposed graph (b). The calculation almost eliminates the rovibrational bands of the gas molecules from the reaction mixture (CO_2 , CH_4 , CO , H_2O). Discrepancies between the bands or the baseline to be subtracted result in residual gas phase contributions, which appear in Figure 4.23b as sharp interference bands or even negative bands, manifesting as data gaps in the evaluation shown in Figure 4.23a. One of the main sources of deviation can be attributed to the DRIFTS cell and its operational workflow. Owing to its single-chamber design, the IPO DRIFTS measurements of the diluent and the diluted catalyst had to be performed sequentially, requiring sample replacement by opening the Harrick DRIFTS cell during the experiment. This procedure resulted in an approximate time offset of about 8 hours between two corresponding measurement points. Despite the very good reproducibility of the reactor profiles, minor variations in the catalyst reactivity over time were unavoidable, which caused in slight differences in the gas atmosphere within the DRIFTS cell when measuring the catalyst and the diluent. The second factor contributing to the under- and overcompensation of gas phase signals is the limitation of ideal iso-potential conditions due to practical constraints. Even at high dilution, the catalyst in the DRIFTS cell leads to

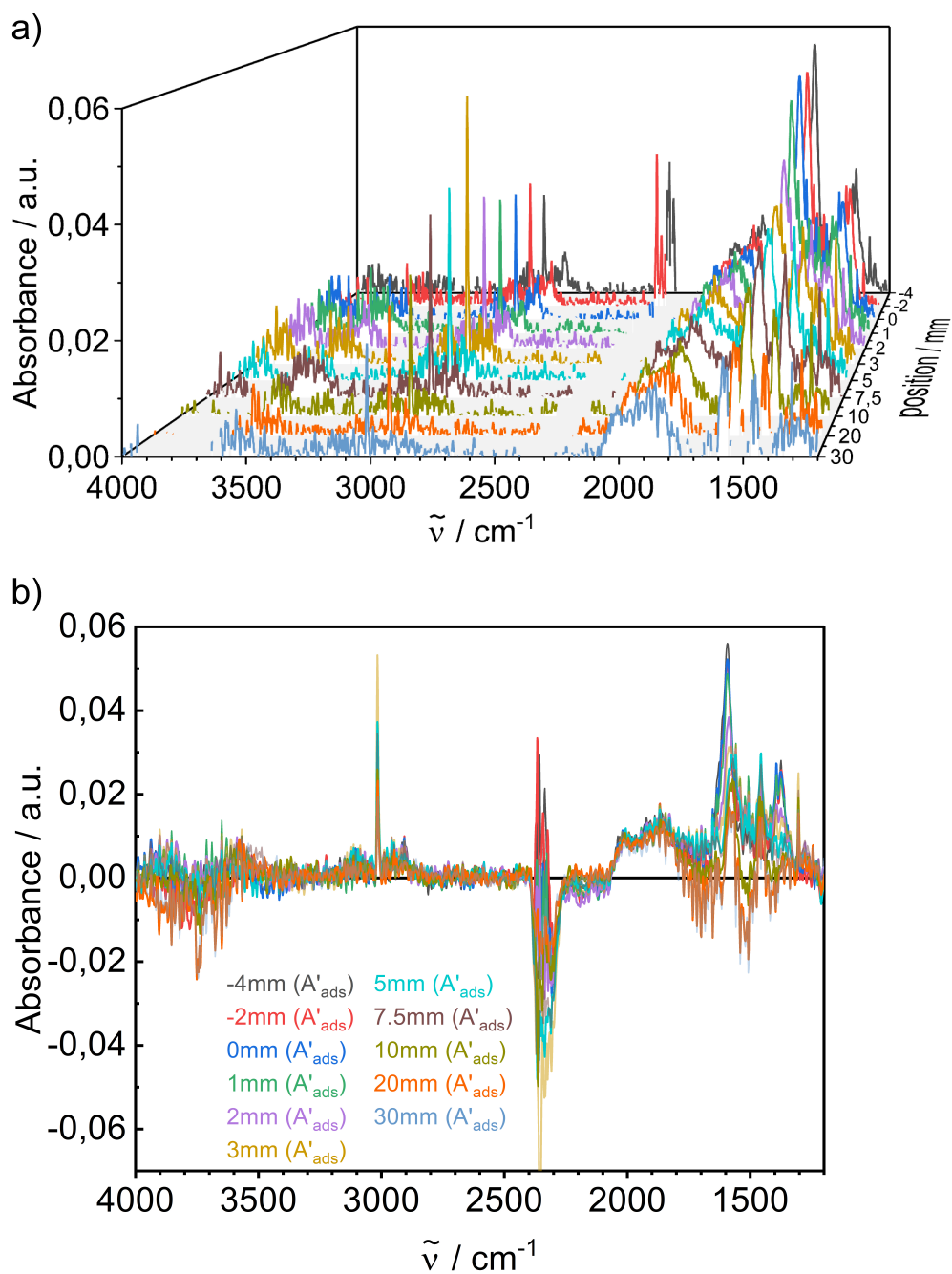


Fig. 4.23: Calculated absorbance spectra (A'_{ads}) highlighting the IR absorption of the surface adsorbates along the catalyst bed in the CPR. (a) Waterfall plot of the absorbance spectra as a function of wavenumber and axial measurement position within the fixed bed. (b) Plot of absorbance as a function of wavenumber, illustrating the decrease in concentration of the observed surface adsorbates. Experimental conditions are provided in Table 4.1. Adapted from [81].

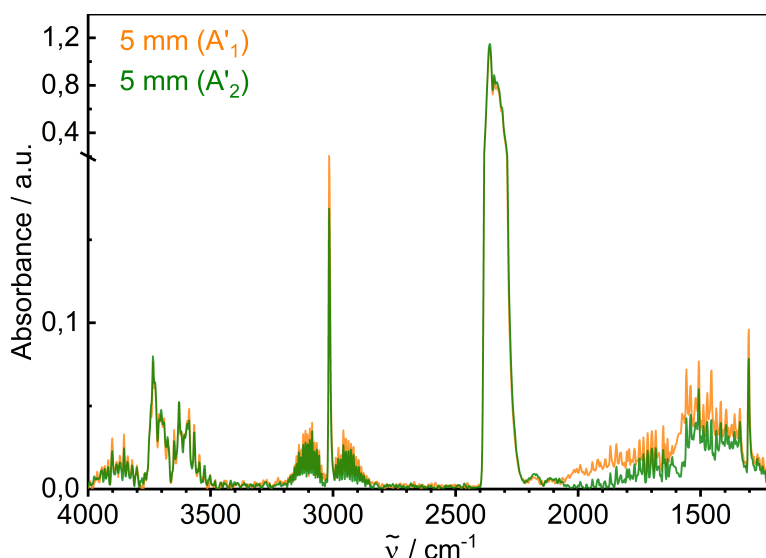


Fig. 4.24: Referenced IR spectra recorded at 5 mm inside the catalyst bed, obtained by sampling the reaction mixture into the DRIFTS cell filled with the pure diluent CaF_2 (green spectrum) and with the diluted catalyst (orange spectrum). Experimental conditions are provided in Table 4.1. Adapted and modified from [81].

a small but still measurable conversion. This results in a slightly lower concentration of reactants and a slightly higher concentration of products in the gas phase when comparing the DRIFTS measurements with the cell filled with the diluted catalyst to those with only the diluent. To illustrate the deviations more clearly, Figure 4.24 shows a superimposition of two corresponding absorbance spectra from the IPO DRIFTS profiles obtained at a measurement position of 5 mm using the DRIFTS cell filled with the diluted catalyst (orange spectrum) and with the pure diluent CaF_2 (green spectrum). Slight deviations can be observed in the orange spectrum of the band intensities for the gas species, which are attributed to reactions occurring on the catalyst sample within the DRIFTS cell. Compared to the spectrum of the pure diluent, the IR absorption bands of the reaction products CH_4 and H_2O appear with higher intensity, whereas those of CO_2 are attenuated. If the two non-congruent spectra are subtracted from each other, undercorrected bands remain for methane at 3016 and 1306 cm^{-1} and for water vapor in the regions 3500 – 4000 cm^{-1} and around 1595 cm^{-1} . The intensities of undercorrected bands increase within the first few centimeters of the fixed-bed, reaching a maximum peak at approximately 3 mm, and then decrease continuously thereafter (cf. Figure 4.23). The highest deviation at 3 mm corresponds to the region within the catalyst bed where the profile gradients are steepest, indicating the highest reaction rate. Analogously, overcompensated negative bands corresponding to CO_2 remain at 2349 cm^{-1} .

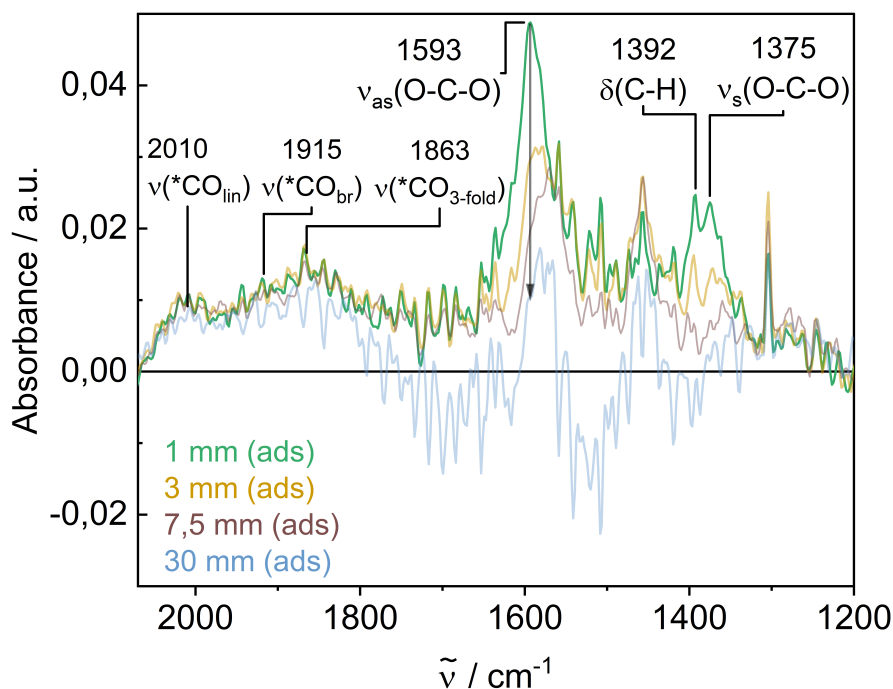


Fig. 4.25: Calculated absorbance spectra (A'_{ads}) highlighting the IR absorption of the surface adsorbates at measurement positions 1, 3, 7.5 and 30 mm within the catalyst bed of the CPR. Experimental conditions are provided in Table 4.1. Adapted from [81].

Despite some residual spectral interferences from the deformation vibrations (δ) of water vapor and CH_4 , which are centered at around 1595 cm^{-1} and 1306 cm^{-1} respectively, the signals of the adsorbed species on the catalyst surface remain clearly visible within the spectral range from 1200 to 2060 cm^{-1} . Figure 4.25 shows a magnification of this characteristic region using four different measurement positions at 1, 3, 7.5 and 30 mm in the catalyst bed as examples. The overlaid spectra indicate that the band intensities of the adsorbed carbonyl species between 2050 and 1700 cm^{-1} remain constant. In contrast, the band intensities of the formate species at 1375 , 1392 and 1593 cm^{-1} decrease steadily along the catalyst bed, indicating their progressive consumption.

In summary, the spectral information extracted from the calculated adsorbate profile (A'_{ads}) is consistent with the theoretical predictions outlined in Figure 3.8. The remaining spectral features correspond to the surface species on the catalyst, which vary along the catalyst bed on both the active metal (Ni) and on the support material ($\gamma\text{-Al}_2\text{O}_3$). The intensity of the IR absorption bands of the formate surface species decreases, indicating that the formate species is a kinetically relevant surface intermediate. In contrast, the intensities of

the carbonyl species remain constant along the catalyst bed without participating in the reaction.

4.4.6 Interpretation of evaluated IPO-DRIFTS Measurements

The comparison of Figures 4.14 and 4.25 indicates that the formate band intensities decrease along the catalyst bed in parallel with the decreasing CO₂ concentration. At the same time, no other adsorbate bands show significant changes in intensity. This observation suggests that formate species are quickly formed but consumed at a slower rate, allowing them to accumulate to concentrations that can be detected with DRIFTS. However, its bending (1393 cm⁻¹) and symmetric stretching (1375 cm⁻¹) vibration overlaps with the rovibrational band of water vapor (1595 cm⁻¹). Consequently, although the formate band intensities qualitatively decrease along the catalyst bed in parallel with the declining CO₂ concentration, their quantification remains imprecise for further analysis. In contrast, the bending vibration of formate at 1593 cm⁻¹ is significantly less affected by spectral interference due to the gap in the vibration band of water vapor, which is centered at 1595 cm⁻¹, and is therefore more applicable for a more detailed analysis. By normalizing the integrated band areas of the asymmetric stretching vibration at 1953 cm⁻¹ (green symbols), a comparison with the normalized mole fraction of CO₂ (orange symbols) reveals a close correlation between the two profiles, as shown in Figure 4.26. In contrast to the changing intensities of the formate surface species along the catalyst bed, the detected carbonyl adsorbates (*CO_{ads}) remain constant in the IPO DRIFTS profiles up to the exit of the catalyst bed (cf. Figure 4.25), allowing two possible interpretations. On the one hand, *CO_{ads} may act as a spectator species that is present due to dissociative CO₂ adsorption but does not participate in any kinetically relevant reaction pathway. On the other hand, CO₂ might adsorb on the surface of Ni nanoparticles to dissociate fast enough to *CO_{ads} at a characteristically high adsorption equilibrium constant to lead to an almost constant *CO_{ads} coverage within the investigated CO₂ conversion range. The rate-determining step could occur in the reaction sequence to CH₄ after the formation of *CO_{ads}, e.g., *CO_{ads} → *C_{ads} + *O_{ads} or *CO_{ads} + *H_{ads} → *HCO_{ads}. Both explanations result in an almost constant *CO_{ads} coverage across the examined CO₂ conversion range up to the end of the catalyst bed, as well as to a detectable constant *CO_{ads} signal.

By combining the experimental findings of this study with insights from the literature (Figure 2.9), a mechanistic interpretation of CO₂ methanation on a reduced Ni/γ-Al₂O₃ catalyst can be proposed, as illustrated in Figure 4.27. The dissociative adsorption of CO₂

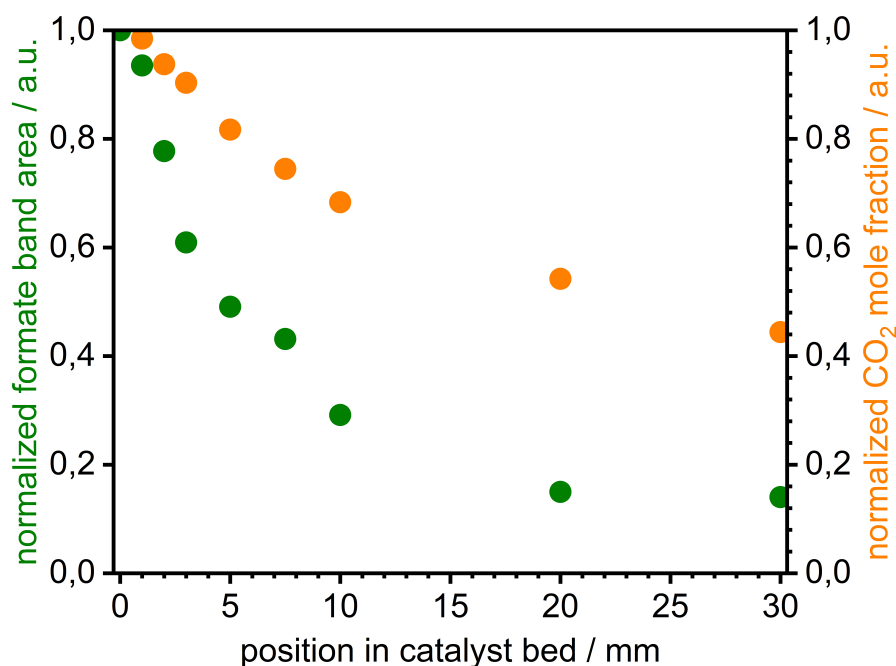


Fig. 4.26: Comparison of the integrated and normalized IR band areas of adsorbed formate (1595 cm^{-1} , green circle) with the normalized mole fraction profiles of CO_2 (orange circle) in the reactor. Adapted and modified from [81].

to form $^*\text{CO}_{\text{ads}}$ follows path (A), whereas the preferred associative reaction pathway follows path (B), beginning with the adsorption of CO_2 and H_2 . The acidic CO_2 is likely to interact preferentially with basic oxygen anions or hydroxyl groups on the alumina surface (cf. Section 2.5.5), forming bicarbonate or carbonate species [229]. In contrast, hydrogen dissociates on the metallic Ni nanoparticles, forming the basis for the hydrogenation of bicarbonate to formate through spillover effects [230]. Since neither carbonate nor bicarbonate species are detected in the IPO DRIFTS profiles, it can be inferred that the hydrogenation step proceeds rapidly and is potentially reversible. This is indicated by the emphasized bold equilibrium arrow, indicating a quasi-thermodynamic equilibrium between gaseous CO_2 and formate at the catalyst surface. The reaction pathway from formate to gaseous methane is not evident from the obtained adsorbate profile, nor does it reveal which additional intermediates may be involved. Nevertheless, formate must be hydrogenated to methane at a rate slower than it is produced, as indicated by a thin equilibrium arrow. Otherwise, the surface concentration would be too small to be detected spectroscopically. A plausible sequence of hydrogenation steps, postulated by Mebrahtu et al. [45] but not yet experimentally confirmed, is based on spillover effects and proceeds via the reaction pathway from bidentate formate ($^*\text{HCOO}_{\text{ads}}$)

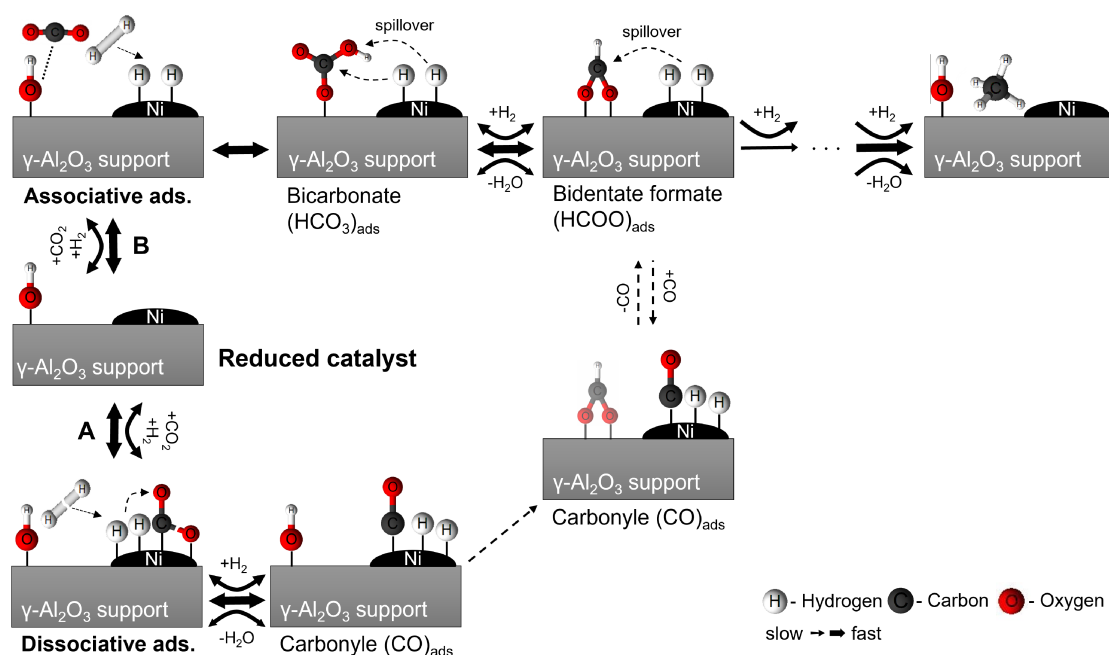


Fig. 4.27: Proposed reaction mechanism for the CO₂ methanation on a reduced Ni/γ-Al₂O₃ catalyst resulting from the structure–activity correlations of the IPO DRIFTS measurements. Formate, which is formed via the associative scheme, is proposed as the kinetically relevant surface intermediate. Adapted from [81].

to carboxyl (*CHOOH_{ads}), formaldehyde (*H₂CO_{ads}), methoxy (*H₃CO_{ads}), and finally to methane (CH₄). However, since no other adsorbed species apart from formate were detected spectroscopically, it can be concluded that all subsequent steps of formate hydrogenation proceed rapidly and are therefore of limited kinetic relevance.

5 Summary and Future Perspective

Solid catalysts are dynamic systems that respond to local reaction conditions in a catalytic reactor by changing their structure, surface adsorbates and reactivity. Detailed knowledge of these changes at the molecular and atomic scale is essential for improving and developing new solid catalysts. In laboratory practice, there are a variety of analytical methods (spectroscopy, microscopy, imaging) that use custom-designed *operando* spectroscopic cells to obtain catalytic information. These *operando* reaction cells are miniaturized catalytic reactors that are often either kinetically ill-defined or provide spectroscopic information of relatively low quality. Even in applications with well-designed *operando* spectroscopic cells, the experimenter must decide which reaction conditions to set for the measurements to simulate the process in the reactor, which proves difficult as the temperature, chemical composition and pressure vary widely inside a catalytic reactor. The attempt to integrate analytical methods directly into a catalytic reactor is also not technically feasible, as the typical industrial reactor is difficult to access analytically and is opaque to electromagnetic radiation due to its size and the nature of being a steel pressure tank.

In this work, a new measurement concept called Iso-Potential *Operando* Spectroscopy (IPOS) was introduced to demonstrate for the first time the dynamic changes in the surface chemistry of a catalytic fixed-bed in a reactor under iso-potential *operando* conditions using a spectroscopic method. The concept of IPOS is based on the separation of the functions of the 'catalytic reactor' and the 'spectroscopic cell'. However, if the catalyst in the spectroscopic cell is exposed to the same chemical potential $\mu(T, p, x)$ as the catalyst locally in the reactor, the catalyst in the spectroscopic cell hypothetically experiences the same structural changes, the same surface adsorbates and shows the same reactivity. To implement the concept, the reactor features a spatial sampling and temperature measurement technique that continuously feeds a small portion of the reaction mixture, sampled locally within the catalyst bed, into the spectroscopic cell ($\mu(x)$), which contains a small amount of the same catalyst. By replicating the locally measured reactor temperature ($\mu(T)$) and matching the pressure ($\mu(p)$) in the spectroscopic cell to that of the reactor, iso-potential conditions are established, thereby ensuring that the catalytic environment in the spectroscopic cell is

identical to that in the reactor ($\mu_{\text{reactor}} = \mu_{\text{cell}}$).

For the proof of concept of the IPOS concept, a laboratory-scale tubular reactor (profile reactor) in operation was coupled to a commercial DRIFTS cell (Harrick Scientific) to perform Iso-Potential *Operando* DRIFTS (IPO DRIFTS) measurements of surface adsorbate profiles along a catalytic fixed-bed. The test setup also included a gas dosing system (MFCs, Bronkhorst), a mass spectrometer (Pfeiffer Vacuum) for quantitative analysis of the gas-phase composition, and an IR spectrometer (Bruker) equipped with the DRIFTS cell. The compact profile reactor (CPR, Reacnostics GmbH) was equipped with a capillary sampling technique in which the capillary extends axially through the catalytic fixed-bed contained within the reactor tube. Gas samples were taken locally from the fixed-bed by moving the catalyst bed relative to the capillary and fed into a sampling line. To implement the IPO DRIFTS measurement concept, the experimental setup was designed to operate in different configurations, with the MS coupled directly to the sample line of the CPR or to the DRIFTS cell in between. The CO₂ methanation reaction, known as the Sabatier reaction, which has become increasingly important in recent decades, was chosen as a test reaction and investigated on a Ni/ γ -Al₂O₃ catalyst. For the analysis of the gas concentration by mass spectrometry using the internal standard method, Ar was added to the reaction mixture as an internal standard in a ratio of Ar : H₂ : CO₂ = 3 : 4 : 1. Due to certain limitations of the setup, e.g., a blank reactivity of the DRIFTS cell with the reaction mixture at temperatures above 350 °C, the operating conditions in the reactor were adapted to feasible reaction parameters (reaction temperature at 320 °C and reactor pressure at 1.1 bar, close to ambient pressure). The pressure drop across the fixed-bed in the CPR and the sampling system was negligible, resulting in nearly identical pressure in the DRIFTS cell, with an insignificant difference of about 100 mbar. The DRIFTS cell temperature was adjusted to match the local conditions measured in the CPR, thereby establishing iso-potential conditions in the DRIFTS cell. To minimize catalytic conversion and composition deviations between the CPR and the DRIFTS cell, the reactor flow rate was set to 120 ml min⁻¹ (STP) to maximize the sample flow, and the catalyst sample added to the cell was highly diluted in chemically inert CaF₂. Four separate and consecutive DRIFTS measurements were required to eliminate spectral interferences, such as gas phase absorptions, the bulk phase of the diluent, and unwanted contributions from adsorbed species on the surface of the diluent, to obtain IR absorption spectra of the adsorbates on the catalyst surface along the fixed-bed in the reactor. These included IPO DRIFTS measurements on the diluted catalyst (A), IPO DRIFTS measurements on the pure diluent

(C) and their respective reference measurements (B and D) using hydrogen as reference gas. The IR adsorbate profile of the species adsorbed on the catalyst surface was obtained by a double difference calculation of the recorded profile spectra $(A - B) - (C - D)$. The concentration profiles were measured in parallel with the DRIFTS profiles, which allowed for a correlation between the catalyst activity and the structural changes in response to locally varying reactor conditions.

During the IPO DRIFTS measurements, carbonyl ($^*\text{CO}_{\text{ads}}$) and formate ($^*\text{HCOO}_{\text{ads}}$) surface species were detected along the catalyst bed. The band intensity of the adsorbed CO remains constant regardless of its position in the catalyst bed, indicating that $^*\text{CO}_{\text{ads}}$ most likely acts as a spectator species without participating in the reaction. However, in the given experimental setting, it is not possible to precisely determine the function of $^*\text{CO}_{\text{ads}}$. Assuming it acts as an intermediate, the rate-determining step occurs later in the CH_4 formation pathway. A high adsorption equilibrium constant could ensure constant surface coverage across the investigated CO_2 conversion range, thus leading to a constant signal. In contrast, the band intensity of the formate surface species decreases as the CO_2 conversion increases, indicating that $^*\text{HCOO}_{\text{ads}}$ is a surface reaction intermediate that must be kinetically relevant. This observation is consistent with the associative reaction mechanism proposed in the literature, which involves formate as an intermediate. However, since neither carbonate, bicarbonate nor other adsorbate species that could be responsible for the formation of formate by hydrogenation could be identified in the IR spectra, the adsorption of CO_2 on the alumina surface and the reduction to formate is possibly fast and reversible. Moreover, this indicates that the hydrogenation of formate is a comparatively slower process compared to the preceding steps, as the formate species accumulate in a measurable concentration on the surface of the catalyst. This observation also appears to apply to all subsequent hydrogenation steps, as no spectroscopic evidence was found for carboxyl ($^*\text{CHOOH}_{\text{ads}}$), formaldehyde ($^*\text{H}_2\text{CO}_{\text{ads}}$) or methoxy ($^*\text{H}_3\text{CO}_{\text{ads}}$) surface species, which had been proposed as intermediates in the literature. However, this study and the cited references underline that the adsorption of CO_2 on alumina, the dissociative adsorption of hydrogen on the Ni nanoparticles and resulting spillover effects to the adsorbed CO_2 as well as the reduction of formate species, which seems to be the rate-determining step in methane formation, require further investigation in the future to optimize the development of more reactive and selective catalysts. Overall, applying the iso-potential operando DRIFTS measurement technique has proven to be a promising approach for verifying or disproving postulated reaction mechanisms by correlating the surface adsorbate profiles

with simultaneously measured concentration and temperature profiles along a catalytic fixed bed. These structure–activity correlations enable the discrimination between reaction intermediates and spectator species, providing a unique basis for predicting kinetic models.

In the future, kinetically well-designed iso-potential DRIFTS cells could further reduce the impact on the gas composition due to the blank reactivity of the DRIFTS cell and the additional catalyst conversion resulting from the amount of catalyst required for the IPO DRIFTS measurements. Beyond that, it would be feasible to integrate multiple sample compartments for simultaneous or quick consecutive measurements, thereby eliminating or shortening the time offset between two corresponding IPO DRIFTS measurement points and achieving significantly higher data quality. A similar method has already been developed by Drochner et al. [74] for an *in situ* cell in which the two sample crucibles are placed in the reaction atmosphere and can be alternately moved into the beam path via a gear mechanism. Reacnostics GmbH has seized and optimized this idea in the development of a new cell, equipped with two separate, kinetically well-defined reaction chambers. One chamber can be filled with the diluted catalyst, and the other with the pure diluent, enabling simultaneous IPO DRIFTS and reference measurements [231]. This approach will allow the collection of sufficient data in future experiments to support CAD simulations, validate reaction mechanisms, and develop accurate kinetic models.

In principle, the Iso-Potential *Operando* Spectroscopy (IPOS) concept is not limited to DRIFTS. It can be extended to other spectroscopic, imaging or microscopic techniques, such as Raman, UV-vis, EPR, NMR, XAS, XRD, or SEM and TEM to study the dynamics and reactivity of catalysts in catalytic reactors of any size and shape. If the spectroscopic cell is designed to meet the requirements of the analytical measurement method and can be adapted to the same reaction conditions as the catalytic reactor, iso-potential coupling is feasible, provided that the reactor allows spatial sampling. The transfer to industrial reactors, therefore, appears to be more of a technical than a fundamental challenge, for example, by installing a side-stream system in a reactor to couple an analytical reaction cell iso-potentially. IPOS holds significant potential as a powerful tool for advancing research in heterogeneous catalysis, both on a laboratory and industrial scale.

A Appendices

A.1 Chemical equilibrium of CO₂ methanation under experimental reaction conditions

For analytical investigations of a reaction system, it is essential that the system remains far from the equilibrium state, as the distance represents the driving force for the reaction. If a reaction is studied too close to its chemical equilibrium, the analytical results may affect the conclusions about its behavior. Thermodynamically limited reactions are those in which the equilibrium position is significantly shifted to the left toward the reactants, resulting in minimal conversion [75].

Tab. A.1: Stoichiometric table for the CO₂ methanation reaction under experimental reaction conditions specified in Table 4.1.

Species	Symbol	ν_i	$\dot{n}_{i,0}$ mmol min ⁻¹	$\dot{n}_{i,\text{eq}} = \dot{n}_{i,0} + \nu_i \dot{\xi}$ mmol min ⁻¹	$x_{i,\text{eq}} = \frac{\dot{n}_{i,\text{eq}}}{\dot{n}_{\text{eq}}}$
H ₂	A	-4	$\dot{n}_{A,0} = 2.452$	$\dot{n}_{A,0} - 4\dot{\xi}$	$\frac{\dot{n}_{A,0} - 4\dot{\xi}}{\dot{n}_{\text{eq}}}$
CO ₂	B	-1	$\dot{n}_{B,0} = 0.613$	$\dot{n}_{B,0} - \dot{\xi}$	$\frac{\dot{n}_{B,0} - \dot{\xi}}{\dot{n}_{\text{eq}}}$
CH ₄	C	1	0	$\dot{\xi}$	$\frac{\dot{\xi}}{\dot{n}_{\text{eq}}}$
H ₂ O	D	2	0	$2\dot{\xi}$	$\frac{2\dot{\xi}}{\dot{n}_{\text{eq}}}$
Ar	I	0	$\dot{n}_{I,0} = 1,839$	$\dot{n}_{I,0}$	$\frac{\dot{n}_{I,0}}{\dot{n}_{\text{eq}}}$
Σ		-2	$\dot{n}_0 = 4.905$	$\dot{n}_{\text{eq}} = \dot{n}_0 - 2\dot{\xi}$	

To examine the chemical equilibrium of the CO₂ methanation reaction, which can theoretically be achieved under the specified reactor conditions of 320 °C and 1.1 bar, the simple Sabatier reaction, involving the hydrogenation of CO₂ to CH₄ (cf. Eq. (2.20)), is considered. The reactant feed ratio was set to 3:4:1 (Ar:H₂:CO₂) with a total molar flow rate into the tube reactor of 4.905 mmol min⁻¹. The equilibrium constant (K) is calculated as a function of the reaction temperature, according to the calculation method outlined in Section 2.6.3 (cf. Equations (2.30) to (2.37)). From this, the extent of reaction is to be derived numerically using equation Eq. (2.33) based on the stoichiometry provided in Table 2.1. The equilibrium conversion of CO₂ can be correlated with the extent of reaction (cf. Eq. (4.1)) and plotted as a function of the reaction temperature in Figure A.1. This indicates a thermodynamic equilibrium conversion of over 90 % at a reaction temperature of 320 °C.

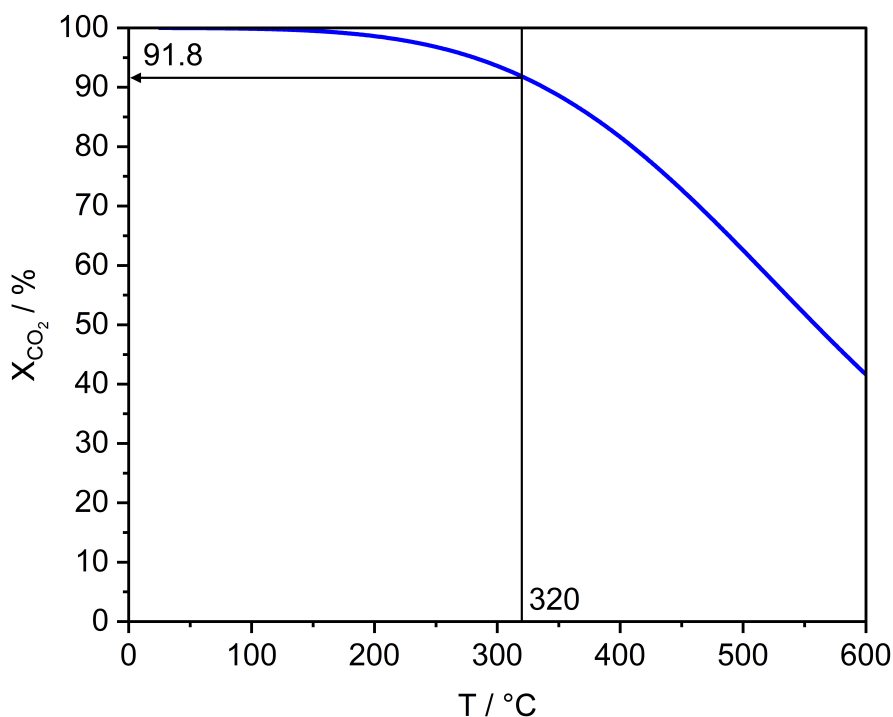


Fig. A.1: Equilibrium conversion of the CO₂ methanation reaction plotted against different reaction temperatures based on the experimental reaction conditions specified in Table 4.1.

A.2 Pressure drop in the CPR under experimental reaction conditions

A pressure drop in the catalyst fixed-bed can negatively affect the reactor operation, as the volumetric flow rate is limited and the reaction rate decreases. The larger the selected catalyst particle size, the less effect it has on the pressure drop [53]. By minimizing the pressure drop in the reactor, the reaction conditions of a plug-flow reactor are approximated, thereby creating ideal experimental conditions. Increasing the size of the catalyst particles to reduce the pressure drop is also only possible to a limited extent, as diffusion limitations can lead to a reduction in the catalytic performance [3]. The generally applied Ergun equation Eq. (A.1) can be used to calculate the pressure drop in a packed porous bed [232]. The first term on the left-hand side describes the pressure drop in laminar-dominated flow, while the turbulent-dominated flow is determined by the second term on the right-hand side [3].

$$\frac{\Delta p}{\Delta L} = 150 \frac{(1 - \epsilon_{\text{bed}})^2}{\epsilon_{\text{bed}}^3} \frac{\eta u_s}{d_{\text{cat}}^2} + 1,7 \frac{\rho u_s^2}{d_{\text{cat}}} \frac{(1 - \epsilon_{\text{bed}})}{\epsilon_{\text{bed}}^3} \quad (\text{A.1})$$

For simplicity, the density (ρ), viscosity (η) and superficial velocity (u_s), which actually change due to the reaction along the catalyst bed, are assumed to be those of the gas inlet mixture into the reactor at a reaction temperature of 320 °C and pressure of 1.1 bar. Since the reaction pressure is close to atmospheric pressure and the reaction gas mixture consists of non-associating species, the ideal gas law can be used to calculate the mixing density based on the average molar mass of the individual species ($\rho_{\text{mix}} = \frac{p (\sum x_i M_i)}{R T}$) [232]. The dynamic viscosity for multi-component systems can be derived from Wilke's mixing rule [232–234]:

$$\eta_{\text{mix}} = \sum_i \frac{x_i \eta_i}{\sum_j x_j \Phi_{i,j}} \quad (\text{A.2})$$

The Wilke's coefficients are a correlation between the individual species in the mixture ($\Phi_{\text{Ar,H}_2}$, $\Phi_{\text{H}_2,\text{Ar}}$, $\Phi_{\text{H}_2,\text{H}_2}$, $\Phi_{\text{H}_2,\text{CO}_2}$, etc.) using the viscosities (η_i) at the reaction conditions (calculated by a simple polynomial on the reaction temperature and pressure [162, 232])

and molecular weights (M_i) of the individual components [232–234]:

$$\Phi_{i,j} = \frac{\left[1 + \left(\frac{\eta_i}{\eta_j} \right)^{0,5} \left(\frac{M_j}{M_i} \right)^{0,25} \right]^2}{\sqrt{8 \left(1 + \frac{M_i}{M_j} \right)}} \quad (\text{A.3})$$

In the literature, a bed porosity of $\epsilon_{\text{bed}\infty} = 0,36 - 0,42$ is expected for infinitely extended, random-packed sphere beds [232], whereas for catalyst beds with a geometric relationship of $d_{\text{bed}}/d_{\text{cat}} > 10$, a void fraction of approximately 0.4 can be specified [3]. More precise information on the void fraction is provided by Sonntag's empirical relationship, assuming monodisperse spherical bulk solids [232, 235]:

$$\epsilon_{\text{bed}} = \epsilon_{\infty} + (1 - \epsilon_{\infty}) \frac{0,526}{d_{\text{bed}}/d_{\text{cat}}} \quad (\text{A.4})$$

With the particle diameter (d_{cat}) assumed to be the averaged sieve fraction of the catalyst (300 – 400 μm), the diameter of the catalyst bed corresponding to the tube reactor diameter ($d_{\text{bed}} = 4 \text{ mm}$), and the porosity of the infinitely expanded bed being $\epsilon_{\text{bed}\infty} = 0,39$, the void fraction of the catalytic fixed bed used in this work is 0.42.

Using the mass flux ($G = \rho_{\text{mix}} u_s = 144,21 \text{ g m}^{-2} \text{ s}^{-1}$) and the Reynolds number based on the catalyst particle size (cf. Eq. (A.6)), the Ergun equation (Eq. (A.1)) can be simplified to:

$$\Delta p = L_{\text{bed}} \frac{(1 - \epsilon_{\text{bed}})}{\epsilon_{\text{bed}}^3} \frac{G^2}{\rho d_{\text{cat}}} \left(150 \frac{(1 - \epsilon_{\text{bed}})}{Re_p} + 1,75 \right) \quad (\text{A.5})$$

$$Re_p = \frac{u_s \rho_{\text{mix}} d_{\text{cat}}}{\eta_{\text{mix}}} \quad (\text{A.6})$$

The Reynolds number is a dimensionless parameter that characterizes the flow conditions in a pipe. Dimensionless parameters are used to estimate mass transfer coefficients based on the material properties and geometry of the respective system [159]. Under the experimental reaction conditions specified in Table 4.1 and, for simplification, considering only the inlet reaction mixture without reaction change, a laminar flow with a minimum pressure drop of about 20 mbar dominated in the CPR. The parameters used for the evaluation are listed in Table A.2.

Tab. A.2: Parameters for the evaluation of the pressure drop through the catalytic fixed-bed in the CPR.

Parameter	CPR values	Unit
L_{bed}	0.03	m
A_{bed}	1.218×10^{-5}	m ²
$\bar{d}_{\text{cat}}$	0.35	mm
d_{bed}	4	mm
p_{reactor}	1.1	bar
u_s	0.301	m s ⁻¹
x_{Ar}	0.38	–
x_{H_2}	0.5	–
x_{CO_2}	0.13	–
M_{Ar}	39.948	g mol ⁻¹
M_{H_2}	2.016	g mol ⁻¹
M_{CO_2}	44.01	g mol ⁻¹
ρ_{mix}	0.479	kg m ⁻³
η_{Ar}	3.87×10^{-5}	Pa s
η_{H_2}	1.44×10^{-5}	Pa s
η_{CO_2}	2.76×10^{-5}	Pa s
η_{mix}	3.161×10^{-5}	Pa s
ϵ_{bed}	0.42	–
Re_p	1.5	–
Δp	20	mbar

A.3 Axial dispersion in the CPR under experimental reaction conditions

The transport process of the reaction mixture through the tubular reactor is determined by convection transport and molecular diffusion, with the extent of turbulence or mixing characterized by the axial dispersion coefficient (D_{ax}) [53]. For precise temperature–activity correlations in *operando* profile experiments, an approximated plug flow behavior in the fixed-bed tubular reactor is presupposed. Deviations from ideal plug flow occur, among other things, due to backmixing effects. Using the vessel dispersion number ($D_{ax}/u_s L$), these effects can be approximately correlated. As this dimensionless parameter approaches zero, its influence becomes negligible and insignificant compared to convective mass transport [236]. The reciprocal value is referred to as the reactor Peclet number (Pe_r) or Bodenstein number (Bo , cf. Eq. (A.7)), taking into account the catalyst bed length (L_{bed}) as the characteristic length. It indicates the ratio of the convective to the diffusive or dispersive rate of mass

transport [53]. In packed beds, the average flow velocity (v) results from the superficial velocity (u_s) divided by the bed porosity (ϵ_{bed}). Shortening the bed length increases the deviation from plug flow and promotes stronger axial mixing [237]. Levenspiel and Smith [238] describe the deviation from plug flow in their presented dispersion model and demonstrate, using residence time distributions, that an approximation to plug flow occurs for Bodenstein numbers of around 100 or higher [236]. For catalytic gas-solid reactions in fixed-bed reactors with laminar flow, the dispersion coefficient can be estimated using experimental correlations from the literature, for example, by Bischoff and Levenspiel [236]. For this purpose, the inverse of the fluid Peclet number ($1/Pe_f$, cf. Eq. (A.8)), which uses the catalyst particle diameter (d_{cat}) as the characteristic length [53], is related to the Reynolds number (Re_p , cf. Eq. (A.6)) and Schmidt number (Sc , cf. Eq. (A.9)).

$$Pe_r = Bo = \frac{v L}{D_{ax}} = \frac{u_s L_{\text{bed}}}{\epsilon_{\text{bed}} D_{ax}} = Pe_f \frac{L_{\text{bed}}}{d_{\text{cat}}} \quad (\text{A.7})$$

$$Pe_f = \frac{u_s d_{\text{cat}}}{\epsilon_{\text{bed}} D_{ax}} \quad (\text{A.8})$$

$$Sc = \frac{\nu}{D_{ij}} \quad (\text{A.9})$$

The Schmidt number is a dimensionless parameter that describes the ratio of momentum to mass diffusivity in a fluid and is used to characterize mass transfer processes. To determine the Schmidt number, the molecular diffusion coefficient (D_{ij}) is calculated using the Chapman-Enskog theory, which describes the transport phenomena in gases based on the kinetic theory of gases [239]:

$$D_{ij} = \frac{0,00266 T^{3/2}}{p M_{ij}^{1/2} \sigma_{AB}^2 \Omega_D} \quad (\text{A.10})$$

with

$$M_{ij} = 2 \left[\frac{1}{M_i} + \frac{1}{M_j} \right]^{-1} \quad (\text{A.11})$$

The temperature dependence of the diffusion collision integral ($\Omega_D(T^*)$), which determines how molecular interactions influence collision probabilities, can be determined using the

Lennard-Jones potential:

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635 T^*)} + \frac{1.03587}{\exp(1.52996 T^*)} + \frac{1.76474}{\exp(3.89411 T^*)} \quad (\text{A.12})$$

$$T^* = \frac{k_B}{\epsilon_{AB}} T_{\text{reactor}}$$

with

$$\epsilon_{AB} = \sqrt{(\epsilon_A \epsilon_B)} \quad (\text{A.13})$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

The characteristic Lennard-Jones energy (ϵ_A) and length (σ_A) indicate the strength of the attraction between two molecules at the optimum distance at which the interaction is strongest. Values for various gases are listed in the literature [239]. At low pressure, ideal behavior and a homogeneous mixture can be assumed, so that the binary diffusion coefficient (D_{ij}) is essentially independent of composition, and the Stefan-Maxwell equation can be simplified for multicomponent gas mixtures [239]:

$$D_{i,m} = \left(\sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{D_{ij}} \right)^{-1} \quad (\text{A.14})$$

With a calculated Schmidt number of less than 1 ($Sc = 0.72$, cf. Equations (A.9) to (A.12)) and a Reynolds number less than 10 ($Re_p = 1.5$, cf. Eq. (A.6)), an extent of dispersion of $1/P_{ef} \approx 0.5$ can be estimated [236]. The parameters used for the evaluation are listed in Tables A.2 and A.3 and, for simplicity, refer to the inlet reaction mixture without considering the reaction process in the catalyst bed. By rearranging the Eq. (A.8), an axial dispersion coefficient of $D_{ax} \approx 1.26 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ is obtained. Alternatively, the axial dispersion coefficient can also be approximately equated with the molecular diffusion coefficient of CO_2 ($D_{\text{CO}_2,m}$) in the multicomponent reaction mixture, as laminar flow is present under the given conditions and the particle Reynolds number is below 10 [240]. In this regime, backmixing is primarily dominated by molecular diffusion. Both approximations yield Bodenstein numbers above 100 (cf. Eq. (A.7)), indicating that axial dispersion is negligible and that ideal plug flow behavior can be assumed under the given conditions. As a rule of thumb, for laminar gas flow in reactor tubes through a catalytic fixed-bed, an ideal plug flow can be assumed if the Reynolds number is greater than 1 and $L_{\text{bed}}/d_{\text{cat}} > 50$ applies [156].

Tab. A.3: Parameters for the evaluation of the axial dispersion coefficient and the reactor Peclet number (Bodenstein number) to determine the axial dispersion in the CPR.

Parameter	CPR values	Unit
T_{reactor}	593.15	K
ν_{mix}	7.013×10^{-5}	$\text{m}^2 \text{s}^{-1}$
k_B	1.380649×10^{-23}	J K^{-1}
ϵ_{Ar}/k_B	93.3	K
$\epsilon_{\text{H}_2}/k_B$	59.7	K
$\epsilon_{\text{CO}_2}/k_B$	195.2	K
σ_{Ar}	3.542	Å
σ_{H_2}	2.827	Å
σ_{CO_2}	3.941	Å
$D_{\text{CO}_2,m}$	9.73×10^{-5}	$\text{m}^2 \text{s}^{-1}$
Sc	0.72	–
Pe_f (est. [236])	2	–
Pe_f' (calc. with $D_{\text{CO}_2,m}$)	2.59	–
D_{ax}	1.26×10^{-4}	$\text{m}^2 \text{s}^{-1}$
D_{ax}'	$D_{\text{CO}_2,m}$	$\text{m}^2 \text{s}^{-1}$
Bo	171	–
Bo'	222	–

A.4 External Mass Transfer Limitation in the CPR under experimental reaction conditions

When experimentally investigating heterogeneously catalyzed reactions, it is essential to ensure that the catalyst's behavior is not influenced by concentration gradients, which can limit the actual reaction kinetics due to external mass transport processes [241]. When the reaction mixture flows through the catalyst bed, a boundary layer forms around the surface of the catalyst particles, serving as an interface between the external surface of the particles and the surrounding fluid. The boundary layer thickness correlates with the bulk velocity. Since the reaction takes place exclusively on the external surface of the catalyst particles and not in the surrounding fluid, the flow velocity in the hydrodynamic boundary layer to the particle is decisive, so that the concentration of the diffusing reactants on the active catalyst surface corresponds to 99 % of the bulk concentration [53]. To obtain quick and easy estimates of whether the reaction rate is limited by interparticle mass transfer

A.4 External Mass Transfer Limitation in the CPR under experimental reaction conditions

phenomena, the Mears criterion can be used [53, 241]:

$$MR = \frac{-r_{\text{obs}}(\text{obs}) r_{\text{cat}} n}{k_m c_{i,b}} < 0.15 \quad (\text{A.15})$$

Where r_{obs} represents the most significant observed reaction rate per unit particle volume, ρ_b is the bulk density of the catalyst bed, r_{cat} is the radius of the catalyst particles, n is the reaction order, k_m is the mass transfer coefficient, and $c_{i,b}$ is the bulk reactant concentration. Even though the Mears criterion applies only to irreversible reactions, it still provides a good approximation, as shown in previous considerations of the measurements (cf. Section A.1) that indicate the chemical equilibrium lies far on the product side. With a calculated Mears criterion of less than 0.15, external mass transport effects can be neglected. It can be assumed that there is no concentration gradient between the bulk fluid and the external catalyst surface, and thus, no kinetic limitations on film diffusion exist. The derivation of the parameters and the results is listed and explained below.

Tab. A.4: Parameters for the evaluation of the Mears criterion to determine the intraparticle mass transfer limitation in the CPR.

Parameter	CPR values	Unit
V_{bed}	3.654×10^{-7}	m^3
Δm_{cat}	1.1×10^{-5}	$\text{kg}/\text{mm}_{\text{cat bed}}$
r_{obs}	-43.164	$\text{mol m}^{-3} \text{s}^{-1}$
r_{cat}	0.175	mm
n (est.)	2	–
$k_m(\text{CO}_2)$	0.37	m s^{-1}
$c_{\text{CO}_2,b}$	2.549	mol m^{-3}
MR	0.016	–

- The observed reaction rate is derived from the spatially resolved CO_2 concentration profile of the IPO DRIFTS measurements (cf. Figure 4.14a). The highest reaction rate is expected in the first 5 mm of the catalyst bed, which is due to the zone with the steepest gradients in molar flow rate and temperature. The observed reaction kinetics were estimated by applying linear regression to the interpolated catalyst mass per unit volume and the corresponding concentration profiles at the first four measurement positions (1, 2, 3 and 5 mm) in the catalyst bed.
- The reaction order is assumed to be 2 to ensure that the unknown actual reaction order is taken into account in the calculation.

- The mass transfer coefficient can be determined from the Sherwood number [52]:

$$k_m = \frac{Sh D_{ij}}{d_{cat}} \quad (\text{A.16})$$

The Sherwood number is a dimensionless parameter that describes the ratio of convective to molecular mass transfer and is usually presented in empirical correlations as a function of the Reynolds and Schmidt numbers. Several Sherwood correlations for various systems are available in the literature [242]. The most commonly used models are the Sherwood number correlations proposed by Frössling and Ranz-Marshall ($Sh = 2 + 0.6 Re_p^{\frac{1}{2}} Sc^{\frac{1}{3}}$) [243, 244], and by Wakao and Funazkri ($Sh = 2 + 1.1 Re_p^{0.6} Sc^{\frac{1}{3}}$) [245], which are based on film theory and assume that mass transport through the boundary layer occurs only by diffusion [242, 246]. The first correlation applies to the flow around individual spherical particles at low Reynolds numbers, and the second applies to laminar flow in tubular reactors for Reynolds numbers between $3 - 10^4$. The theoretical limits of both models occur at Reynolds numbers approaching zero. However, for the conditions described in this work, the Reynolds number was found to be small ($Re_p = 1.5$). A similar correlation proposed by Sherwood et al. [242]

$$Sh = 1,17 Re_p^{0,585} Sc^{\frac{1}{3}} \quad (\text{A.17})$$

seems more suitable for this application, as it provides a good approximation for laminar flows with Reynolds numbers between $1 - 3000$ and a bed porosity of $0.4 - 0.45$.

- The bulk reactant concentration is averaged from the CO_2 concentrations measured at the positions $1 - 5$ mm in the catalyst bed (cf. Figure 4.14a).

A.5 Intraparticle Mass Transfer Limitation in the CPR under experimental reaction conditions

The calculation of the Mears criterion (cf. Section A.4) indicates that mass transfer of the reactants from the bulk fluid through the boundary layer to the external surface of the catalyst particles occurs without film diffusion limitation. Since catalytically active sites are predominantly located on the internal surface of the pore network in solid catalysts, the reactants must diffuse into the interior of the porous particles. During pore diffusion, the chemical reaction takes place simultaneously at the active sites along the pore walls. The interplay between reaction rate and diffusion rate determines the development of concentration gradients within the catalyst particle. When pore diffusion is significantly

limiting, pronounced gradients can form, preventing full utilization of the particle interior [161]. This results in reduced catalyst efficiency and a decrease in the overall reaction rate. The effectiveness factor can be used to quantify internal diffusion limitations. It is defined as the ratio of the actual (observed) reaction rate – including potential transport limitations – to the intrinsic reaction rate that would be expected in the absence of concentration gradients if the pore surface were exposed to the same reactant concentration as the external catalyst surface [52]. Alternatively, the ratio of reaction to diffusion can be described by the Thiele modulus, a dimensionless parameter that characterizes this relationship. However, both moduli require knowledge of the intrinsic reaction kinetic. When the intrinsic reaction rate is unknown, internal diffusion limitations can be estimated using the Weisz-Prater criterion (N_{W-P}), which is based entirely on experimentally accessible or observable quantities and indicates negligible limitations if [53]:

$$N_{W-P} = \frac{-r_{obs} r_{cat}^2}{D_{eff} c_{ib}} \leq 0.3 \quad (A.18)$$

The Weisz modulus compares the observed reaction rate with the intraparticle diffusion rate to the active sites in the catalyst pores. It assumes negligible film diffusion and allows an estimation of whether pore diffusion limitations can be neglected for first-order reactions. If the calculated value is below 1, diffusion effects in the pore network are considered insignificant. For second-order reactions, however, the value should be below 0.3, as higher-order reactions are more sensitive to concentration changes and can therefore form more pronounced concentration gradients more quickly [52].

Since the pores in a catalyst particle typically do not form a straight, cylindrical structure, but rather a complex labyrinth network of variable pore sizes and voids, an effective diffusion coefficient (D_{eff}) has been defined in various pore structure models. It describes the average diffusion rate within a porous particle, taking into account geometric factors such as the porosity and tortuosity of the catalyst particle, as well as interactions along the actual diffusion path [53]:

$$D_{ij,eff} = \frac{\epsilon_{cat}}{\tau_{cat}} D_{ij} \quad D_{K,eff} = \frac{\epsilon_{cat}}{\tau_{cat}} D_{iK} \quad (A.19)$$

The particle porosity (ϵ_{cat}) describes the ratio of the void volume to the total volume of the pellet, while tortuosity (τ_{cat}) indicates the ratio of the actual path length traveled by a molecule to the direct, shortest connection between two points. Typical values for the particle porosity factor of support materials such as alumina are in the range between 0.55 – 0.72 and can be determined using the BET measurement method. The particle

tortuosity factor, on the other hand, requires specialized measurement methods, such as the dynamic method according to Wicke-Kallenbach. Typical values for supported metal catalysts range from 3 to 7 [247]. Since neither porosity nor tortuosity values were available for the calculations, literature values were used. The diffusion processes in solid catalysts are typically categorized into molecular diffusion (D_{ij}), driven by collisions between gas molecules, and Knudsen diffusion (D_{iK}), in which interactions between gas molecules and the pore walls dominate [52, 156]. Which mechanism predominates depends primarily on the ratio of the mean free path (λ) of the molecules to the pore diameter (d_{pore}), also known as the Knudsen number (Kn):

$$Kn = \frac{\lambda}{d_{\text{pore}}} \quad \text{with} \quad \lambda = \frac{k_B T_{\text{reactor}}}{\sqrt{2} \pi d_{\text{CO}_2}^2 p_{\text{reactor}}} \quad (\text{A.20})$$

The mean free path of the reaction molecules depends on the reactor temperature (T_{reactor}), the total pressure (p_{reactor}), and the effective collision cross section, which in turn is defined by the molecular diameter (d_{CO_2}). Considering the experimental reaction conditions in the CPR, the CO_2 diffusion flux through the pores yields a Knudsen number of 23 (Table A.5), which is significantly greater than 2. Values from BET measurements of pure alumina were used as pore diameters (d_{pore}) [190]. The high Knudsen number indicates that mass transport occurs predominantly in the Knudsen regime, characterized by frequent collisions between the gas molecules and the pore walls. Such values are typical for mesopores with diameters in the range of 2 – 50 nm, as commonly found in alumina-based catalysts. The effective diffusivity in particles for catalytic multicomponent gas-solid processes is primarily described using the Wilke and Stefan-Maxwell models (molecular diffusion), the dust-gas model (combined molecular and Knudsen diffusion), or its simplified Wilke-Bosanquet formulation [248]. The latter provides the following equation for the effective diffusion coefficient, considering the flux of CO_2 :

$$D_{\text{eff}} = \frac{1}{\frac{1}{D_{\text{CO}_2,m}} + \frac{1}{D_{\text{CO}_2,K}}} \frac{\epsilon_{\text{cat}}}{\tau_{\text{cat}}} \quad (\text{A.21})$$

The molecular diffusion coefficient is calculated according to Eq. (A.14) in Section A.3, and the Knudsen diffusion coefficient is determined by [249]:

$$D_{iK} = \frac{2}{3} \frac{r_{\text{cat}}}{M_i} \sqrt{\frac{8 RT}{\pi}} \quad (\text{A.22})$$

Applied to the Weisz-Prater criterion and the corresponding equations, the experimentally determined parameters listed in Tables A.2 to A.5 result in a value of $N_{W-P} = 2.4$, which indicates a moderate pore transport limitation and incomplete utilization of pore space. This can be attributed, first, to the very rapid reaction kinetics observed within the first 5 mm of the catalyst bed. The pronounced concentration gradient drives conversion mainly at the pore entrance, preventing reactants from penetrating the pore interior. Second, neither the tortuosity nor the porosity of the applied catalyst was experimentally determined, and the actual values may differ from the assumed ones, which can significantly affect the calculation of the Weisz-Prater criterion. Nevertheless, this work serves as a proof of concept for the proposed measurement method; therefore, the detailed investigation of reaction kinetics is not the primary focus, and a moderate pore transport limitation can be neglected.

Tab. A.5: Parameters for the evaluation of the Weisz-Prater criterion to determine the intraparticle mass transfer limitation in the CPR.

Parameter	CPR values	Unit
d_{CO_2}	3.3×10^{-10}	m
λ	1.54×10^{-7}	m
d_{pore}	6.62×10^{-9}	m
Kn	23	–
$D_{CO_2, K}$	1.18×10^{-6}	$m^2 s^{-1}$
ϵ_{cat}	0.55	–
τ_{cat}	3	–
D_{eff}	2.14×10^{-7}	$m^2 s^{-1}$
N_{W-P}	2.4	–

Abbreviations

Acronym	Description
BET	Brunauer-Emmett-Teller
CPR	Compact Profile Reactor
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
EPR	Electron Paramagnetic Resonance
eq	Equilibrium
ESM	Elemental Species Matrix
FIR	Far Infrared
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity
HOMO	Highest Occupied Molecular Orbital
ICP-OES	Optical Emission Spectroscopy with Inductively Coupled Plasma
ID	Inner Diameter
IPO DRIFTS	Iso-Potential <i>Operando</i> DRIFTS
IPOS	Iso-Potential <i>Operando</i> Spectroscopy
IR	Infrared
LIBS	Laser-Induced Breakdown Spectroscopy
LUMO	Lowest Unoccupied Molecular Orbital
MFC	Mass Flow Controller
MIR	Mid-Infrared
MO	Molecule Orbital
MR	Mears Criterion
MS	Mass Spectrometer
MSI	Metal Support Interaction
NG	Natural Gas

Abbreviations

Acronym	Description
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
OD	Outer Diameter
PtG	Power-to-Gas
P&ID	Piping and Instrumentation Diagram
rWGS	reverse Water-Gas Shift
SNG	Synthetic Natural Gas
SSITKA	Steady-State Iso-Topic Transient Kinetic Analysis
STEM	Scanning Transmission Electron Microscopy
STP	Standard Temperature and Pressure
TOF	Turnover Frequency
UV/Vis	Ultraviolet/Visible
WHSV	Weight Hourly Space Velocity
wt%	Weight Loading
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction

Greek letters

Letter	Unit	Description
N_{W-P}	–	Weisz-Prater criterion
Ω_D	–	Diffusion collision integral
$\Phi_{i,j}$	kg m^{-3}	Wilke's coefficient
δ	cm^{-1}	Deformation vibration
ξ	mol s^{-1}	Extent of reaction over time
ϵ_{bed}	–	Void fraction of the catalytic fixed bed (bed porosity)
ϵ_{cat}	–	Particle porosity factor (pore fraction)
ϵ_A	J	Characteristic Lennard-Jones energy of molecule A
ϵ	$\text{L mol}^{-1} \text{cm}^{-1}$	Decadic extinction coefficient)
η	Pa s	Dynamic viscosity of the fluid
λ	m	Mean free path of gas molecules
λ	nm	Wavelength
$\mu_i^\ominus$	J mol^{-1}	Chemical potential of species i in standard state
μ_i^*	J mol^{-1}	Chemical potential of pure species i
μ_i	J mol^{-1}	Chemical potential of species i
μ	kg	Reduced mass
ν_{as}	cm^{-1}	Asymmetric stretching vibration
ν_s	cm^{-1}	Symmetric stretching vibration
ν_i	–	Stoichiometric coefficient of species i
ν	$\text{m}^2 \text{s}^{-1}$	Kinematic viscosity of the fluid
ν	Hz	Vibrational frequency of adsorption
ρ_b	kg m^{-3}	Bulk density of the catalyst
ρ	kg m^{-3}	Fluid density
σ_A	Å	Characteristic Lennard-Jones length of molecule A
τ_{cat}	–	Particle tortuosity factor
$\tilde{\nu}$	cm^{-1}	Wavenumber

Greek letters

Letter	Unit	Description
ν	N_0	Vibrational quantum number
ξ	mol	Extent of reaction

Latin letters

Letter	Unit	Description
A_{bed}	m^2	Cross sectional area of the catalyst bed. CPR: considering the capillary
A	–	Absorbance
Bo	–	Bodenstein number
B	cm^{-1}	Rotational constant
D_{ax}	$\text{m}^2 \text{s}^{-1}$	Axial dispersion coefficient
D_{eff}	$\text{m}^2 \text{s}^{-1}$	Effective diffusion coefficient
$D_{i,m}$	$\text{m}^2 \text{s}^{-1}$	Molecular diffusion coefficient of species i in a multi-component gas mixture
D_{iK}	$\text{m}^2 \text{s}^{-1}$	Knudsen diffusion coefficient of a species i
D_{ij}	$\text{m}^2 \text{s}^{-1}$	Molecular (binary) diffusion coefficient of a species i and j
G	J	Gibbs energy or free enthalpy
G	$\text{kg m}^{-2} \text{s}^{-1}$	mass flux
I_0	lm m^{-3}	Intensity of the light at its source
I	lm m^{-3}	Intensity of light that reaches the detector
I	$\text{kg}^2 \text{m}$	Moment of inertia
J	$\mathbb{N}_0$	Rotational quantum number
K_x	–	(Special) equilibrium constant based on mole fractions
Kn	–	Knudsen number
K	–	(True) thermodynamic equilibrium constant
L_{bed}	m	Length of the catalytic fixed bed
L	m	Characteristic length
M_i	kg mol^{-1}	Molecular weight of a species i
M_{ij}	kg mol^{-1}	Molecular weight of a species i and j
Pe_f	–	Fluid Peclet number

Letter	Unit	Description
Pe_r	–	Reactor Peclet number
Re_p	–	Reynolds number based on particle size
R	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	Ideal gas constant
R	–	Reflectance
$S_{i,T}^{\ominus}$	J K^{-1}	Molar entropy of species i at reaction temperature (T)
Sc	–	Schmidt number
Sh	–	Sherwood number
S	J K^{-1}	Entropy
T_r	$^{\circ}\text{C}$	Local reactor temperature
T	$^{\circ}\text{C}$	Temperature of the reaction system
T	%	Transmittance
V_{bed}	m^3	Bulk volume of the catalyst bed considering the passing capillary
V	m^3	Volume
$\Delta_B G_{i,T}^{\ominus}$	J mol^{-1}	Standard free enthalpy of formation of species i at reaction temperature T
$\Delta_B H_{i,T}^{\ominus}$	kJ mol^{-1}	Molar standard enthalpy of formation of species i participating in reaction j at standard pressure ($p^{\ominus}$) and reaction temperature (T)
$\Delta_R G_{j,T}^{\ominus}$	J mol^{-1}	Standard Gibbs energy or standard free enthalpy of reaction j at reaction temperature T
$\Delta_R G_{j,T}$	J mol^{-1}	Gibbs energy or free enthalpy of reaction j at reaction temperature T
$\Delta_R H_{j,T}^{\ominus}$	kJ mol^{-1}	Standard reaction enthalpy of reaction j at standard pressure ($p^{\ominus}$) and reaction temperature (T)
$\Delta_R S_{j,T}^{\ominus}$	J K^{-1}	Standard reaction entropy of reaction j at standard pressure ($p^{\ominus}$) and reaction temperature (T)
a_i	–	Activity of species i in a gas mixture
$c_{i,b}$	mol m^{-3}	Bulk concentration of reactant i
$c_{p,i}$	$\text{kJ mol}^{-1} \text{ K}^{-1}$	Heat capacity of species i at temperature (T)
c	mol L	Molar concentration
c	$\sim 3 \times 10^{10} \text{ cm s}^{-1}$	Velocity of light
d_{bed}	m	Diameter of the catalytic fixed bed

Letter	Unit	Description
d_{cat}	m	Averaged diameter of the catalyst particles
d_{pore}	m	Averaged diameter of the catalyst pores
h	$6.626 \times 10^{-34} \text{ J s}$	Planck constant
k_B	$1.380649 \times 10^{-23} \text{ J K}^{-1}$	Boltzmann constant
k_m	m s^{-1}	Mass transfer coefficient
k	–	Molar absorption coefficient of the sample
k	N m^{-1}	Force constant of the bond
l	cm	Layer thickness (optical path)
n_i	mol	Amount of substance of a species i participating in reaction j
n	mol	Amount of substance
n	–	Reaction order
$p^\ominus$	1 bar	Pressure at standard state
p_i	bar	Partial pressure of species i in a reaction system
p_r	bar	Local reactor pressure
p	bar	Total pressure of the reaction system
r_0	Å	Bond length
r_{cat}	m	Radius of the catalyst particles
r_{obs}	$\text{mol kg}^{-1} \text{ s}$	Measured rate of reaction
S	–	Scattering coefficient of the sample
u_s	m s^{-1}	Superficial velocity over the entire cross section of the reactor tube
v	m s^{-1}	Flow velocity
x_i	–	Mole fraction of species i

List of Figures

2.1	Schematic overview of the IPO DRIFTS measurement technique: (I) Gas dosing system – set of Mass Flow Controllers (MFCs); (II) Spatial profile reactor – Compact profile Reactor (CPR); (III) Working principle of the spatially resolved capillary sampling technique; (IV) IR spectroscopy – DRIFTS cell; (V) Gas analytic – Mass Spectrometer (MS); (VI) Reference gas connection to the DRIFTS cell. Adopted and modified from [81]	16
2.2	(a) The characteristic IR absorption band of the symmetric bending vibration of water vapor ($\delta(\text{H—O—H})$) at 1595 cm^{-1} , exhibiting characteristic rovibrational fine structure with distinct P and R branches. (b) The IR absorption band of the asymmetric stretching vibration of methane at 3019 cm^{-1} , exhibiting quasi-rovibrational fine structure due to rotation–vibration coupling.	23
2.3	Illustration of the diffuse reflection of IR radiation from a catalyst surface, which interacts with the radiation and scatters it in multiple directions. . .	24
2.4	Simplified one-dimensional potential energy diagram for physisorption of a molecule at a catalyst surface, showing the attractive van der Waals force and the repulsive force due to Pauli repulsion [111].	28
2.5	Simplified one-dimensional potential energy diagram for the adsorption of a diatomic molecule approaching a surface: (a) Scheme of physisorption (blue) and dissociative chemisorption (orange) after Lennard-Jones [109]. (b) Scheme for the physisorption (blue), associative (green) and dissociative (orange) chemisorption on a catalytic metal surface [104].	30

2.6	Simplified Blyholder model of the CO chemisorption on a transition metal [123, 124]: a) Schematic illustration of σ -donation from the 5σ -MO of CO (HOMO) into the half-filled metal d-orbital (primarily the d_{z^2} orbital) of a transition metal atom (M), and π -back-donation from the occupied metal d-orbitals (d_{xz} , d_{yz}) into the two empty $2\pi^*$ -MO of CO (LUMO) [121]. b) Schematic electron configuration of the CO chemisorption to a transition metal. The 5σ -MO of CO, localized on carbon, lies close in energy to the metal Fermi level (E_f) within the d-band, which enables linear adsorption geometry [50].	33
2.7	(a) Standard reaction enthalpy (blue line) and standard Gibbs energy (red line) of the CO_2 methanation reaction as a function of certain reaction temperature range. (b) Logarithmized equilibrium constant as a function of the temperatures.	43
2.8	(a) Equilibrium conversion of the CO_2 methanation reaction as a function of temperature at different pressures. (b) Equilibrium composition of the gas mixture at varying reaction temperatures in relation to a stoichiometric feed ratio and standard reaction pressure.	44
2.9	Schematic description of the general CO_2 methanation reaction mechanism occurring on metal oxide supported catalysts. (A) Dissociative pathway: CO_2 dissociatively adsorbs as a carbonyl intermediate ($^*\text{CO}_{\text{ads}}$) on the metal particle and is hydrogenated to methane via carbon (A1) or oxygenate (A2). (B) Associative pathway: CO_2 associatively adsorbs as monodentate (B1) or bidentate (B2) formate intermediate ($^*\text{HCOO}_{\text{ads}}$) on the unreduced or reduced surface of the metal oxide support, respectively, and is hydrogenated to methane. Adopted from [81].	49
3.1	Illustration of the Compact Profile Reactor (CPR, A–B) and its sampling capillary technique (C), controlled and monitored via a control box (D). The inner components are labeled with numbers 1 – 9: ① reactor inlet ② reactor outlet ③ gas sampling for analytics ④ reactor tube ⑤ catalytic fixed-bed ⑥ quartz wool ⑦ sampling capillary ⑧ sampling orifice ⑨ thermocouple	56
3.2	CAD model (a) and flow chart (c) of the general setup of MFC modules and the implementation into a gas dosing table (b) containing different modules (A–C).	58

3.3	(a) A sequence of a mass spectrum during calibration of a methane-argon gas mixture. (b) Calibration line of the integrated peak area ratios of CH ₄ to the internal standard Ar.	60
3.4	(a) Setup of the IR spectrometer equipped with the components to obtain DRIFTS spectra. (b) Illustration of the DRIFTS chamber for a detailed overview. For explanation, the components are labeled with numbers 1 – 9: ① mirror collector assembly ② DRIFTS cell ③ mirrors ④ ZnSe-windows ⑤ MIR radiation ⑥ sample cup ⑦ gas inlet port ⑧ gas outlet port ⑨ water-cooling system ⑩ heating system ⑪ purge gas supply	61
3.5	Illustration of the iso-potential <i>operando</i> DRIFTS workflow. Adopted and modified from [81].	68
3.6	Schematic illustration of the bulk and surface state of a Ni/ γ -Al ₂ O ₃ catalyst in an iso-potential <i>operando</i> DRIFTS measurement during CO ₂ methanation. The DRIFTS cell is filled with a small amount of catalyst highly diluted in a diluent/‘white standard’ and exposed to the reaction mixture sampled locally from the reactor or to a reference gas. Temperature and pressure are adapted to the local reaction conditions (T_r , p_r) in the reactor. IR-absorptions, which can change when scanning through the reactor, are designated with x for the surface species, y for the gas phase and z for the bulk phases. IR-absorptions under reference conditions are denoted by 0. Instrument effects and absorptions in the beam path outside the DRIFTS cell are denoted by 1. (A) Iso-potential <i>operando</i> DRIFTS measurement, (B) reference measurement, (A'1) spectrum difference. Adopted and modified from [81].	70

3.7	The removal of IR absorption in the gas phase during an iso-potential <i>operando</i> DRIFTS measurement for CO ₂ methanation on a Ni/γ-Al ₂ O ₃ catalyst is illustrated schematically. The DRIFTS cell is filled with pure diluent/'white standard' and exposed to the reaction mixture sampled locally from the reactor along the fixed-bed, as well as to a reference gas separately. Temperature and pressure are adapted to the reaction conditions of the local measurement positions in the reactor (p_r , T_r). IR absorptions that can vary along the fixed bed on the catalyst are designated as x for surface species, y for the gas phase, and z for the bulk phases. IR absorptions under reference conditions are denoted as 0, while instrumental effects and absorptions in the beam path outside the DRIFTS cell are denoted as 1. (C) Iso-potential <i>operando</i> DRIFTS measurement, (D) reference measurement, (A'_2) spectrum difference. Adopted and modified from [81].	72
3.8	Surface adsorbates and bulk catalyst changes are extracted by calculating a subtraction spectrum (A'_{ads}) from the difference spectra ($A'_1 - A'_2$). The resulting absorbance spectrum contains the IR absorptions of adsorbates on both the catalyst and support surfaces (x), as well as the bulk absorptions of the catalyst and support (z) relative to the reference state. Adopted and modified from [81].	73
4.1	A simplified piping and instrumentation diagram of the experimental setup with the associated parts list.	77
4.2	Illustration of the DRIFTS cell prepared for IPO DRIFTS or reference measurements of a catalyst sample under a flowing reaction gas mixture or reference gas. The cell is filled with a small layer of a finely ground catalyst sample diluted in likewise finely ground CaF ₂ on top of a layer of pure CaF ₂	82
4.3	DRIFT spectra of a finely ground catalyst sample (Ni/γ-Al ₂ O ₃ catalyst) diluted in a likewise finely ground reference material/'white standard' (CaF ₂) under reaction conditions (Ar, H ₂ and CO ₂ feed with H ₂ : CO ₂ = 4 : 1, 6 mL min ⁻¹ flow rate, 320 °C set temperature). At a dilution ratio of 1:20 by mass (green spectrum), the surface adsorbate bands of carbonyl and formate are well resolved and clearly detectable, while an acceptably low CO ₂ conversion is observed, as evidenced by the small CH ₄ bands at 3019 cm ⁻¹ and 1306 cm ⁻¹ . Adopted and modified from [81].	83
4.4	Excerpt of mass spectrometry data of the reaction mixture sampled at the inlet and outlet of the catalytic fixed-bed in the CPR.	85

4.5	ICP-OES analysis of a freshly reduced Ni/ γ -Al ₂ O ₃ catalyst sample dissolved in aqua regia. The emitted plasma radiation was detected in the UV region characteristic of Ni (a) and quantified using a reference measurement with a standard solution (b).	87
4.6	Nitrogen adsorption-desorption isotherms of the freshly reduced Ni/ γ -Al ₂ O ₃ catalyst. The adsorption and desorption isotherms display a type IV hysteresis loop, characteristic of mesoporous materials.	88
4.7	STEM-EDS images of freshly reduced Ni/ γ -Al ₂ O ₃ catalyst particles spread on a holey carbon film using different detection modes to visualize the single catalyst phases: a) Secondary Electron (SE) detection, b) Dark Field (DF) imaging, c) Bright Field (BF) imaging. High-contrast overview images (bottom) show an average crystallite size of the framed nickel particles to be about 10 nm to 12 nm (below). Adopted from [81]	90
4.8	Hydrogen adsorption isotherms for nickel dispersed on alumina, measured using a calcined Ni/ γ -Al ₂ O ₃ catalyst sample freshly reduced under a hydrogen atmosphere. a) Total H ₂ chemisorption isotherm. b) H ₂ adsorption isotherm on alumina. c) H ₂ chemisorption isotherm on Ni. The reduction treatment was performed following the procedure in [196]. Adopted from [81].	92
4.9	Hydrogen adsorption isotherms for nickel dispersed on alumina, measured using a spent Ni/ γ -Al ₂ O ₃ catalyst sample treated under a hydrogen atmosphere. a) Total H ₂ chemisorption isotherm. b) H ₂ adsorption isotherm on alumina. c) H ₂ chemisorption isotherm on Ni. The reduction treatment was performed following the procedure in [196]. Adopted from [81].	93
4.10	X-ray diffraction patterns were carried out <i>ex situ</i> at three different measurement locations of the catalytic fixed-bed in a transmission mode over a 2θ range from 0 to 7° and converted to XRD images. The curves were averaged and represent the inlet, center, and outlet of the catalyst bed, revealing no significant differences between the positions. The measurements were performed at the beamline P21.1 at PETRA III (DESY, Hamburg). Adopted from [81].	95
4.11	HighScore Plus software was used to perform a qualitative phase assignment of the X-ray diffraction patterns by comparing them with reference patterns from the ICDD database. Adopted from [81].	95

4.12 Ex situ Raman spectroscopy was performed on the spent catalyst in the reactor tube to detect potential carbon deposits formed as by-products during the reaction. The spectra correspond to the inlet and outlet of the catalyst bed, with no significant carbon signals detected.	96
4.13 Ex situ LIBS analysis of spent catalyst particles extracted from the packed reactor tube after the reaction at the inlet (a) and outlet (b) of the fixed-bed.	98
4.14 Spatially resolved temperature and concentration profiles measured in the Compact Profile Reactor (CPR) during CO ₂ methanation over the Ni/ γ -Al ₂ O ₃ catalyst: (a) Molar flow rate profiles of the species. (b) Profiles of temperature, CO ₂ conversion, and CH ₄ selectivity. Experimental conditions are provided in Table 4.1. Adopted and modified from [81].	100
4.15 Comparison of spatially resolved CO ₂ conversion profiles measured with and without the DRIFTS cell connected in series to the CPR: DRIFTS cell filled with the catalyst sample diluted in CaF ₂ (blue points). DRIFTS cell filled solely with the reference material/'white standard' CaF ₂ (orange points). CPR operated alone, bypassing the DRIFTS cell (black points). Experimental conditions are provided in Table 4.1. Adopted and modified from [81].	103
4.16 Spatially resolved molar flow rate profiles from IPO DRIFTS measurements obtained downstream of the DRIFTS cell, which is connected in series with the CPR and filled with a) the diluent alone (C), and b) the diluted Ni/ γ -Al ₂ O ₃ catalyst sample (A). Experimental conditions are provided in Table 4.1. Adopted and modified from [81].	104
4.17 Absorbance spectra (A'_2) (cf. Figure 3.7, $C' - D'$), obtained from the difference between the IPO DRIFTS measurements (C') with the DRIFTS cell filled with the pure diluent/'white standard' exposed to the reaction mixture and the corresponding reference measurements (D') under H ₂ . (a) Waterfall plot of the referenced absorbance spectra as a function of the wavenumber and the measurement positions along the catalyst bed in the CPR. The vertical absorbance axis is split to visualize strong and weak bands. (b) Plot of absorbance as a function of wavenumber, illustrating the decrease in concentration of the observed gas phase species of the reaction mixture. Experimental conditions are provided in Table 4.1. Adapted and modified from [81].	106

- 4.18 **Absorbance spectra (A'_2) at measurement positions 1, 3 and 30 mm** (cf. Figure 3.7, $C' - D'$), obtained from the difference between the IPO DRIFTS measurements (C') with the DRIFTS cell filled with the pure diluent/'white standard' exposed to the reaction mixture and the corresponding reference measurements (D') under H_2 . Experimental conditions are provided in Table 4.1. Adapted from [81]. 108
- 4.19 Comparison of the integrated and normalized band areas of CO_2 (2349 cm^{-1} , green circle) and CH_4 (3019 cm^{-1} , green square) with the normalized mole fraction profiles of CO_2 (orange circle) and CH_4 (orange square) in the reactor. IR measurements were conducted following the workflow in Figure 3.5 (C), with the DRIFTS cell filled with the reference material/'white standard' (CaF_2), while mole fraction profiles were measured by MS according to the workflow in Figure 3.5 (X). Experimental conditions are provided in Table 4.1. Adapted and modified from [81]. 109
- 4.20 **Absorbance spectra (A'_1)** (cf. Figure 3.6, $A' - B'$), obtained from the difference between the IPO DRIFTS measurements (A') with the DRIFTS cell filled with the diluted catalyst sample exposed to the reaction mixture and the corresponding reference measurements (B') under H_2 . (a) Waterfall plot of the referenced absorbance spectra as a function of the wavenumber and the measurement positions along the catalyst bed in the CPR. (b) Plot of absorbance as a function of wavenumber, illustrating the decrease in concentration of both gas phase species in the reaction mixture and adsorbed species on the catalyst surface. The vertical absorbance axis is split to visualize strong and weak bands. Experimental conditions are provided in Table 4.1. Adapted from [81]. 111
- 4.21 Comparison of the integrated and normalized IR band areas of CO_2 (2349 cm^{-1} , green circles) and CH_4 (3019 cm^{-1} , green squares) with the normalized mole fraction profiles of CO_2 (orange circles) and CH_4 (orange squares) in the reactor. IR measurements were conducted following the workflow in Figure 3.5 (A), with the DRIFTS cell filled with the diluted catalyst sample. The mole fraction profile was obtained by mass spectrometry according to the workflow in Figure 3.5 (X). Experimental conditions are provided in Table 4.1. Adapted and modified from [81]. 112

4.22	Absorbance spectra (A'_1) at measurement positions 1, 3 and 30 mm (cf. Figure 3.6, $A' - B'$), obtained from the difference between the IPO DRIFTS measurements (A') with the DRIFTS cell filled with the diluted catalyst sample exposed to the reaction mixture and the corresponding reference measurements (B') under H_2 . Experimental conditions are provided in Table 4.1. Adapted from [81].	113
4.23	Calculated absorbance spectra (A'_{ads}) highlighting the IR absorption of the surface adsorbates along the catalyst bed in the CPR. (a) Waterfall plot of the absorbance spectra as a function of wavenumber and axial measurement position within the fixed bed. (b) Plot of absorbance as a function of wavenumber, illustrating the decrease in concentration of the observed surface adsorbates. Experimental conditions are provided in Table 4.1. Adapted from [81].	116
4.24	Referenced IR spectra recorded at 5 mm inside the catalyst bed, obtained by sampling the reaction mixture into the DRIFTS cell filled with the pure diluent CaF_2 (green spectrum) and with the diluted catalyst (orange spectrum). Experimental conditions are provided in Table 4.1. Adapted and modified from [81].	117
4.25	Calculated absorbance spectra (A'_{ads}) highlighting the IR absorption of the surface adsorbates at measurement positions 1, 3, 7.5 and 30 mm within the catalyst bed of the CPR. Experimental conditions are provided in Table 4.1. Adapted from [81].	118
4.26	Comparison of the integrated and normalized IR band areas of adsorbed formate (1595 cm^{-1} , green circle) with the normalized mole fraction profiles of CO_2 (orange circle) in the reactor. Adapted and modified from [81]. . . .	120
4.27	Proposed reaction mechanism for the CO_2 methanation on a reduced $Ni/\gamma-Al_2O_3$ catalyst resulting from the structure-activity correlations of the IPO DRIFTS measurements. Formate, which is formed via the associative scheme, is proposed as the kinetically relevant surface intermediate. Adapted from [81].	121
A.1	Equilibrium conversion of the CO_2 methanation reaction plotted against different reaction temperatures based on the experimental reaction conditions specified in Table 4.1.	128

List of Tables

2.1	Stoichiometric table for the CO ₂ methanation reaction	42
2.2	Values for the variables of the Shomate equation for calculating the integrated heat capacity, adopted from [162, 163]	43
3.1	List of chemicals used and their application for this work	52
3.2	Types and maximum flow rates of the MFCs (Bronkhorst™) used and the supplied gas species	59
4.1	Experimental parameter list of the iso-potential <i>operando</i> DRIFTS measurements. Adopted and modified from [81].	78
4.2	Clarification of the fragment ions observed with the mass spectrometer. . .	85
A.1	Stoichiometric table for the CO ₂ methanation reaction under experimental reaction conditions specified in Table 4.1.	127
A.2	Parameters for the evaluation of the pressure drop through the catalytic fixed-bed in the CPR.	131
A.3	Parameters for the evaluation of the axial dispersion coefficient and the reactor Peclet number (Bodenstein number) to determine the axial dispersion in the CPR.	134
A.4	Parameters for the evaluation of the Mears criterion to determine the intraparticle mass transfer limitation in the CPR.	135
A.5	Parameters for the evaluation of the Weisz-Prater criterion to determine the intraparticle mass transfer limitation in the CPR.	139

Bibliography

- [1] O. Deutschmann, H. Knözinger, K. Kochloefl, T. Turek, *Heterogeneous Catalysis and Solid Catalysts*, John Wiley & Sons, Ltd, 2009. doi:https://doi.org/10.1002/14356007.a05_313.pub2.
- [2] R. Schlögl, *Top Catal* 59 (2016) 772–786. doi:<https://doi.org/10.1007/s11244-016-0551-9>.
- [3] R. Horn, *Reaktoren für fluid-feststoff-reaktionen: Festbettreaktoren*, in: W. Reschetilowski, *Handbuch Chemische Reaktoren* (2020) 589–657.
- [4] G. Eigenberger, W. Ruppel, *Catalytic fixed-bed reactors*, in: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley Online Library, 2012. doi:https://doi.org/10.1002/14356007.b04_199.pub2.
- [5] M. A. Newton, *Chem. Soc. Rev.* 37 (12) (2008) 2644–2657. doi:<https://doi.org/10.1039/B707746G>.
- [6] B. M. Weckhuysen, *Angew. Chem. Int. Ed.* 48 (27) (2009) 4910–4943. doi:<https://doi.org/10.1002/anie.200900339>.
- [7] K. F. Kalz, R. Kraehnert, M. Dvoyashkin, R. Dittmeyer, R. Gläser, U. Krewer, K. Reuter, J.-D. Grunwaldt, *ChemCatChem* 9 (1) (2017) 17–29. doi:<https://doi.org/10.1002/cctc.201600996>.
- [8] R. Schlögl, *Angew. Chem. Int. Ed.* 54 (11) (2015) 3465–3520. doi:<https://doi.org/10.1002/anie.201410738>.
- [9] C. H. Bartholomew, R. J. Farrauto, *Fundamentals of industrial catalytic processes*, John Wiley & Sons, 2006.
- [10] M. Hunger, J. Weitkamp, *Angew. Chem. Int. Ed.* 40 (16) (2001) 2954–2971.
- [11] B. M. Weckhuysen, *Chem. Soc. Rev.* 39 (12) (2010) 4557–4559. doi:<https://doi.org/10.1039/C0CS90031A>.
- [12] U. Bentrup, *Chem. Soc. Rev.* 39 (12) (2010) 4718–4730. doi:<https://doi.org/10.1039/B919711G>.
- [13] M. A. Bañares, *Adv. Mater.* 23 (44) (2011) 5293–5301. doi:<https://doi.org/10.1002/adma.201101803>.

- [14] B. M. Weckhuysen, *Chem. Commun.* (2002) 97–110 doi:<https://doi.org/10.1039/B107686H>.
- [15] A. Chakrabarti, M. E. Ford, D. Gregory, R. Hu, C. J. Keturakis, S. Lwin, Y. Tang, Z. Yang, M. Zhu, M. A. Bañares, I. E. Wachs, *Catalysis Today* 283 (2017) 27–53. doi:<https://doi.org/10.1016/j.cattod.2016.12.012>.
- [16] F. Meunier, *Catalysis Today* 155 (3–4) (2010) 164–171. doi:<https://doi.org/10.1016/j.cattod.2009.11.017>.
- [17] H. Li, M. Rivallan, F. Thibault-Starzyk, A. Travert, F. C. Meunier, *Phys. Chem. Chem. Phys.* 15 (19) (2013) 7321–7327. doi:<https://doi.org/10.1039/C3CP50442E>.
- [18] H. Topsøe, *J. Catal.* 216 (1–2) (2003) 155–164. doi:[https://doi.org/10.1016/S0021-9517\(02\)00133-1](https://doi.org/10.1016/S0021-9517(02)00133-1).
- [19] M. A. Bañares, *Catalysis today* 100 (1–2) (2005) 71–77. doi:<https://doi.org/10.1016/j.cattod.2004.12.017>.
- [20] B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* 5 (20) (2003) 4351–4360. doi:<https://doi.org/10.1039/B309650P>.
- [21] F. C. Meunier, *Chem. Soc. Rev.* 39 (12) (2010) 4602–4614. doi:<https://doi.org/10.1039/B919705M>.
- [22] A. Urakawa, *Current opinion in chemical engineering* 12 (2016) 31–36. doi:<https://doi.org/10.1016/j.coche.2016.02.002>.
- [23] X. Li, X. Yang, J. Zhang, Y. Huang, B. Liu, *ACS Catalysis* 9 (3) (2019) 2521–2531. doi:<https://doi.org/10.1021/acscatal.8b04937>.
- [24] R. Horn, K. Williams, N. Degenstein, L. Schmidt, *J. Catal.* 242 (1) (2006) 92–102. doi:<https://doi.org/10.1016/j.jcat.2006.05.008>.
- [25] R. Horn, N. J. Degenstein, K. A. Williams, L. D. Schmidt, *Catal. Lett.* 110 (2006) 169–178. doi:<https://doi.org/10.1007/s10562-006-0117-8>.
- [26] M. Bosco, F. Vogel, *Catal. Today* 116 (3) (2006) 348–353. doi:<https://doi.org/10.1016/j.cattod.2006.05.064>.
- [27] J. Sá, D. L. A. Fernandes, F. Aiouache, A. Goguet, C. Hardacre, D. Lundie, W. Naeem, W. P. Partridge, C. Stere, *Analyst* 135 (9) (2010) 2260–2272. doi:<https://doi.org/10.1039/C0AN00303D>.
- [28] J. Kopyscinski, T. J. Schildhauer, F. Vogel, S. M. Biollaz, A. Wokaun, *J. Catal.* 271 (2) (2010) 262–279. doi:<https://doi.org/10.1016/j.jcat.2010.02.008>.
- [29] J. Touitou, K. Morgan, R. Burch, C. Hardacre, A. Goguet, *Catal. Sci. Technol.* 2 (9) (2012) 1811–1813. doi:<https://doi.org/10.1039/C2CY20141K>.

- [30] C. Stewart, E. K. Gibson, K. Morgan, G. Cibir, A. J. Dent, C. Hardacre, E. V. Kondratenko, V. A. Kondratenko, C. McManus, S. Rogers, et al., *ACS Catal.* 8 (9) (2018) 8255–8262. doi:<https://doi.org/10.1021/acscatal.8b01509>.
- [31] R. Horn, uS Patent 9,400,253 (2016).
- [32] R. Horn, O. Korup, uS Patent 10,746,661 (2020).
- [33] O. Korup, S. Mavlyankariev, M. Geske, C. F. Goldsmith, R. Horn, *Chemical Engineering and Processing: Process Intensification* 50 (10) (2011) 998–1009. doi:<https://doi.org/10.1016/j.cep.2011.05.024>.
- [34] M. Geske, O. Korup, R. Horn, *Catal. Sci. Technol.* 3 (1) (2013) 169–175. doi:<https://doi.org/10.1039/C2CY20489D>.
- [35] B. Wollak, D. Doronkin, D. Espinoza, T. Sheppard, O. Korup, M. Schmidt, S. Alizade-fanaloo, F. Rosowski, C. Schroer, J.-D. Grunwaldt, et al., *J. Catal.* 408 (2022) 372–387. doi:<https://doi.org/10.1016/j.jcat.2021.08.029>.
- [36] D. Espinoza, B. Wollak, T. L. Sheppard, A.-C. Dippel, M. Sturm, O. Gutowski, M. Schmidt, O. Korup, R. Horn, *ChemCatChem* 14 (24) (2022) e202200337. doi:<https://doi.org/10.1002/cctc.202200337>.
- [37] B. Wollak, D. Espinoza, A.-C. Dippel, M. Sturm, F. Vrljic, O. Gutowski, I. G. Nielsen, T. L. Sheppard, O. Korup, R. Horn, *J. Synchrotron Radiat.* 30 (3) (2023) 571–581. doi:<https://doi.org/10.1107/S1600577523001613>.
- [38] R. Horn, pCT/EP2020/079663 (2021).
- [39] J. Kopyscinski, T. J. Schildhauer, S. M. Biollaz, *Fuel* 89 (8) (2010) 1763–1783. doi:<https://doi.org/10.1016/j.fuel.2010.01.027>.
- [40] M. Götz, J. Lefebvre, F. Mörs, A. M. Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, *Renewable energy* 85 (2016) 1371–1390. doi:<https://doi.org/10.1016/j.renene.2015.07.066>.
- [41] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, *Fuel* 166 (2016) 276–296. doi:<https://doi.org/10.1016/j.fuel.2015.10.111>.
- [42] G. A. Mills, F. W. Steffgen, *Catalysis Reviews* 8 (1) (1974) 159–210. doi:<https://doi.org/10.1080/01614947408071860>.
- [43] W. Wei, G. Jinlong, *Front. Chem. Sci. Eng.* 5 (1) (2011) 2–10. doi:<https://doi.org/10.1007/s11705-010-0528-3>.
- [44] B. Miao, S. S. K. Ma, X. Wang, H. Su, S. H. Chan, *Catal. Sci. Technol.* 6 (12) (2016) 4048–4058. doi:<https://doi.org/10.1039/C6CY00478D>.
- [45] C. Mebrahtu, F. Krebs, S. Abate, S. Perathoner, G. Centi, R. Palkovits, *Stud. Surf. Sci.*

- Catal. 178 (2019) 85–103. doi:<https://doi.org/10.1016/B978-0-444-64127-4.00005-7>.
- [46] A. Solis-Garcia, J. C. Fierro-Gonzalez, *Journal of nanoscience and nanotechnology* 19 (6) (2019) 3110–3123. doi:<https://doi.org/10.1166/jnn.2019.16606>.
- [47] J. Ryczkowski, *Catalysis Today* 68 (4) (2001) 263–381. doi:[https://doi.org/10.1016/S0920-5861\(01\)00334-0](https://doi.org/10.1016/S0920-5861(01)00334-0).
- [48] IUPAC, catalyst (2025). doi:<https://doi.org/10.1351/goldbook.C00876>.
- [49] M. Appl, Ammonia, in: *Ullmann's encyclopedia of industrial chemistry*, in: *Ullmann's encyclopedia of industrial chemistry* (2011). doi:https://doi.org/10.1002/14356007.a02_143.pub3.
- [50] R. A. Van Santen, *Modern heterogeneous catalysis: an introduction*, John Wiley & Sons, 2017.
- [51] P. Sabatier, J.-B. Senderens, *CR Acad. Sci. Paris* 134 (1902) 514–516.
- [52] G. Ertl, *Handbook of heterogeneous catalysis*, VCH, 1997.
- [53] H. F. Scott, *Elements of chemical reaction engineering*, 5th Edition, Prentice Hall, 2016.
- [54] H. S. Taylor, *Proc. Roy. Soc. (London)* 108 (745) (1925) 105–111. doi:<https://doi.org/10.1098/rspa.1925.0061>.
- [55] O. Deutschmann, H. Knözinger, K. Kochloefl, T. Turek, *Heterogeneous Catalysis and Solid Catalysts, 2. Development and Types of Solid Catalysts*, John Wiley & Sons, Ltd, 2011. doi:https://doi.org/10.1002/14356007.o05_o02.
- [56] A. Hagemeyer, P. Strasser, A. F. Volpe Jr, *High-Throughput Screening in Chemical Catalysis: Technologies, Strategies and Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, 2004.
- [57] K. Morgan, J. Touitou, J.-S. Choi, C. Coney, C. Hardacre, J. A. Pihl, C. E. Stere, M.-Y. Kim, C. Stewart, A. Goguet, et al., *ACS Catal.* 6 (2) (2016) 1356–1381. doi:<https://doi.org/10.1021/acscatal.5b02602>.
- [58] A. Baiker, M. Bergougnan, *Can. J. Chem. Eng.* 63 (1) (1985) 138–145.
- [59] W. P. Partridge, J. M. Storey, S. A. Lewis, R. W. Smithwick, G. L. DeVault, M. J. Cunningham, N. W. Currier, T. M. Yonushonis, *SAE transactions* (2000) 2983–2991 doi:<https://www.jstor.org/stable/44746084>.
- [60] D. Dalle Nogare, N. Degenstein, R. Horn, P. Canu, L. Schmidt, *J. Catal.* 258 (1) (2008) 131–142. doi:<https://doi.org/10.1016/j.jcat.2008.06.006>.
- [61] R. Horn, K. Williams, N. Degenstein, A. Bitsch-Larsen, D. Dalle Nogare, S. Tupy,

- L. Schmidt, *Journal of Catalysis* 249 (2) (2007) 380–393. doi:<https://doi.org/10.1016/j.jcat.2007.05.011>.
- [62] R. Horn, K. A. Williams, N. J. Degenstein, L. D. Schmidt, *Chemical engineering science* 62 (5) (2007) 1298–1307. doi:<https://doi.org/10.1016/j.ces.2006.11.030>.
- [63] R. Horn, O. Korup, M. Geske, U. Zavyalova, I. Oprea, R. Schlögl, *Review of Scientific Instruments* 81 (6) (2010) 064102. doi:<https://doi.org/10.1063/1.3428727>.
- [64] J. Touitou, R. Burch, C. Hardacre, C. McManus, K. Morgan, J. Sá, A. Goguet, *Analyst* 138 (10) (2013) 2858–2862. doi:<https://doi.org/10.1039/C3AN00250K>.
- [65] F. Wolke, Y. Hu, M. Schmidt, O. Korup, R. Horn, E. Reichelt, M. Jahn, A. Michaelis, *Catalysis communications* 158 (2021) 106335. doi:<https://doi.org/10.1016/j.catcom.2021.106335>.
- [66] A. Aquino, O. Korup, R. Horn, *Industrial & engineering chemistry research* 62 (7) (2023) 3098–3115. doi:<https://doi.org/10.1021/acs.iecr.2c03373>.
- [67] L. Lukashuk, K. Foettinger, *Johnson Matthey Technology Review* 62 (3) (2018) 316–331. doi:<https://doi.org/10.1595/205651318X15234323420569>.
- [68] A. Dixon, O. Deutschmann, *Spatially Resolved Operando Measurements in Heterogeneous Catalytic Reactors*, Vol. 50, Academic Press, 2017.
- [69] X. Shi, X. Lin, R. Luo, S. Wu, L. Li, Z.-J. Zhao, J. Gong, *JACS Au* 1 (12) (2021) 2100–2120. doi:<https://doi.org/10.1021/jacsau.1c00355>.
- [70] F. Zaera, *Chem. Soc. Rev.* 43 (22) (2014) 7624–7663. doi:<https://doi.org/10.1039/C3CS60374A>.
- [71] F. Meunier, A. Goguet, S. Shekhtman, D. Rooney, H. Daly, *Applied Catalysis A: General* 340 (2) (2008) 196–202. doi:<https://doi.org/10.1016/j.apcata.2008.02.034>.
- [72] N. E. Tsakoumis, A. P. York, D. Chen, M. Rønning, *Catal. Sci. Technol.* 5 (11) (2015) 4859–4883. doi:<https://doi.org/10.1039/C5CY00269A>.
- [73] I. E. Wachs, M. A. Bañares, *Springer Handbook of Advanced Catalyst Characterization*, Springer Nature, 2023.
- [74] A. Drochner, M. Fehlings, K. Krauß, H. Vogel, *Chem. Eng. Technol.* 23 (4) (2000) 319–322. doi:[https://doi.org/10.1002/\(SICI\)1521-4125\(200004\)23:4<319::AID-CEAT319>3.0.CO;2-4](https://doi.org/10.1002/(SICI)1521-4125(200004)23:4<319::AID-CEAT319>3.0.CO;2-4).
- [75] P. W. Atkins, *Physikalische Chemie*, 3rd Edition, John Wiley & Sons, 2001.
- [76] W. J. Moore, *Grundlagen der physikalischen Chemie*, Walter de Gruyter, 1990.
- [77] J. B. Ott, J. Boerio-Goates, *Chemical thermodynamics: principles and applications*, London, UK, San Diego: Academic Press, 2000. doi:<http://www.sciencedirect.com/science/book/9780125309905>.

- [78] M. Schrader, *Prinzipien und Anwendungen der Physikalischen Chemie*, 2nd Edition, Berlin, Heidelberg: Springer Berlin Heidelberg, 2024.
- [79] L.-Q. Chen, *Thermodynamic equilibrium and stability of materials*, Singapore: Springer Singapore, 2022.
- [80] R. G. Mortimer, *Physical chemistry*, 2nd Edition, San Diego: Harcourt/Academic Press, 2000. doi:<http://www.sciencedirect.com/science/book/9780125083454>.
- [81] S. Sichert, S.-F. Stahl, O. Korup, R. Horn, *ACS Catalysis* 14 (2024) 8676–8693. doi:<https://doi.org/10.1021/acscatal.4c00536>.
- [82] J. W. Niemantsverdriet, *Spectroscopy in catalysis: an introduction*, John Wiley & Sons, 2007.
- [83] G. Gauglitz, D. S. Moore, et al., *Handbook of spectroscopy*, 2nd Edition, Vol. 4, Wiley-Vch Weinheim, Germany, 2014.
- [84] C. Lamberti, A. Zecchina, E. Groppo, S. Bordiga, *Chem. Soc. Rev.* 39 (12) (2010) 4951–5001. doi:[10.1039/C0CS00117A](https://doi.org/10.1039/C0CS00117A).
- [85] H. Günzler, H.-U. Gremlich, *IR-Spektroskopie: Eine Einführung*, 4th Edition, Wiley-VCH Verlag GmbH & Co. KGaA, 2003.
- [86] P. R. Griffiths, J. A. de Haseth, *Fourier Transform Infrared Spectrometry*, 2nd Edition, John Wiley & Sons, 2007.
- [87] B. H. Stuart, *Infrared spectroscopy: fundamentals and applications*, John Wiley & Sons, 2004.
- [88] H. Günzler, A. Williams, *Handbook of analytical techniques*, Evolution 1 (2001).
- [89] T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, Vol. 1, National Bureau of Standards, 1972.
- [90] J. Linnett, *Transactions of the Faraday Society* 41 (1945) 223–232.
- [91] W. J. Moore, D. O. Hummel, *Physikalische Chemie*, Walter de Gruyter, 2019.
- [92] C. N. Banwell, E. M. McCash, *Molekülspektroskopie: ein Grundkurs*, Oldenbourg Wissenschaftsverlag, 1999.
- [93] M. Elstner, *Physikalische Chemie II: Quantenmechanik und Spektroskopie*, Springer, 2020.
- [94] J. M. Hollas, *Modern spectroscopy*, John Wiley & Sons, 2004.
- [95] R. K. Hanson, R. M. Spearrin, C. S. Goldenstein, *Spectroscopy and optical diagnostics for gases*, Vol. 1, Springer, 2016.
- [96] Y. Ozaki, C. Huck, S. Tsuchikawa, S. B. Engelsen, *Near-infrared spectroscopy: theory, spectral analysis, instrumentation, and applications*, Springer Nature Singapore Pte Ltd., 2021.

-
- [97] G. Kortüm, W. Braun, G. Herzog, *Angew. Chem. Int. Ed.* 2 (7) (1963) 333–341. doi:<https://doi.org/10.1002/anie.196303331>.
- [98] M. P. Fuller, P. R. Griffiths, *Analytical chemistry* 50 (13) (1978) 1906–1910.
- [99] F. Meunier, *React. Chem. Eng.* 1 (2) (2016) 134–141. doi:<https://doi.org/10.1039/C5RE00018A>.
- [100] J. Sirita, S. Phanichphant, F. C. Meunier, *Anal. Chem.* 79 (10) (2007) 3912–3918. doi:<https://doi.org/10.1021/ac0702802>.
- [101] H. S. Fogler, *Essentials of Chemical Reaction Engineering: Essenti Chemica Reactio Engi*, Pearson Education, 2010.
- [102] R. I. Masel, *Principles of adsorption and reaction on solid surfaces*, Vol. 3, John Wiley & Sons, 1996.
- [103] J. Wisniak, *Educación química* 21 (1) (2010) 60–69. doi:[https://doi.org/10.1016/S0187-893X\(18\)30074-0](https://doi.org/10.1016/S0187-893X(18)30074-0).
- [104] I. Chorkendorff, J. W. Niemantsverdriet, *Concepts of modern catalysis and kinetics*, John Wiley & Sons, 2003.
- [105] H. S. Taylor, *Journal of the American Chemical Society* 53 (2) (1931) 578–597. doi:<https://doi.org/10.1021/ja01353a022>.
- [106] D. Y. Murzin, *Engineering catalysis*, Walter de Gruyter GmbH & Co KG, 2020.
- [107] H. Ibach, *Physics of surfaces and interfaces*, Vol. 12, Springer, 2006.
- [108] T. Fauster, L. Hammer, K. Heinz, M. A. Schneider, *Surface Physics: Fundamentals and Methods*, Walter de Gruyter GmbH & Co KG, 2020.
- [109] R. Prins, A. Wang, X. Li, F. Sapountzi, *Introduction to Heterogeneous Catalysis*, Vol. 1, World Scientific, 2016.
- [110] J. Lennard-Jones, *Trans. Faraday Soc.* 28 (1932) 333–359. doi:<https://doi.org/10.1039/TF9322800333>.
- [111] M. D. Lechner, *Einführung in die Quantenchemie*, Springer, 2017.
- [112] I. Langmuir, *Journal of the American Chemical Society* 34 (7) (1912) 860–877. doi:<https://doi.org/10.1021/ja02208a003>.
- [113] J. R. H. Ross, *Heterogeneous catalysis: Fundamentals and applications*, Elsevier, 2012.
- [114] K. Hauffe, S. R. Morrison, *Adsorption: eine Einführung in die Probleme der Adsorption*, Walter de Gruyter, 2011.
- [115] F. Huber, J. Berwanger, S. Polesya, S. Mankovsky, H. Ebert, F. J. Giessibl, *Science* 366 (6462) (2019) 235–238. doi:[10.1126/science.aay3444](https://doi.org/10.1126/science.aay3444).
- [116] W. Reschetilowski, *Einführung in die heterogene Katalyse*, Springer-Verlag, 2015.

- [117] M. Gajdoš, A. Eichler, J. Hafner, *J. Phys.: Condens. Matter* 16 (8) (2004) 1141. doi:10.1088/0953-8984/16/8/001.
- [118] B. Hammer, J. K. Nørskov, *Adv. Catal.* 45 (2000) 71–129. doi:https://doi.org/10.1016/S0360-0564(02)45013-4.
- [119] G. Blyholder, *J. Phys. Chem.* 68 (10) (1964) 2772–2777. doi:https://doi.org/10.1021/j100792a006.
- [120] G. Broden, T. Rhodin, C. Brucker, R. Benbow, Z. Hurych, *Surf. Sci.* 59 (2) (1976) 593–611. doi:https://doi.org/10.1016/0039-6028(76)90038-8.
- [121] S. S. Sung, R. Hoffmann, *J. Am. Chem. Soc.* 107 (3) (1985) 578–584. doi:https://doi.org/10.1021/ja00289a009.
- [122] H. Steinrück, M. D'evalyn, R. Madix, *Surface science* 172 (3) (1986) L561–L567. doi:https://doi.org/10.1016/0039-6028(86)90496-6.
- [123] B. L. Mojet, S. D. Ebbesen, L. Lefferts, *Chem. Soc. Rev.* 39 (12) (2010) 4643–4655. doi:https://doi.org/10.1039/C0CS00014K.
- [124] A. Föhlisch, M. Nyberg, P. Bennich, L. Triguero, J. Hasselström, O. Karis, L. Pettersson, A. Nilsson, *J. Chem. Phys.* 112 (4) (2000) 1946–1958. doi:https://doi.org/10.1063/1.480773.
- [125] L. Little, C. H. Amberg, *Can. J. Chem.* 40 (10) (1962) 1997–2006. doi:https://doi.org/10.1139/v62-306.
- [126] N. Sheppard, C. De La Cruz, *Catalysis today* 70 (1–3) (2001) 3–13. doi:https://doi.org/10.1016/S0920-5861(01)00403-5.
- [127] C. Olsen, R. Masel, *Surface Science* 201 (3) (1988) 444–460. doi:https://doi.org/10.1016/0039-6028(88)90496-7.
- [128] R. Eischens, S. Francis, W. Pliskin, *J. Phys. Chem.* 60 (2) (1956) 194–201. doi:https://doi.org/10.1021/j150536a015.
- [129] H. Steininger, S. Lehwald, H. Ibach, *Surface Science* 123 (2–3) (1982) 264–282. doi:https://doi.org/10.1016/0039-6028(82)90328-4.
- [130] P. Hollins, *Surface Science Reports* 16 (2) (1992) 51–94. doi:https://doi.org/10.1016/0167-5729(92)90008-Y.
- [131] S. Kattel, P. Liu, J. G. Chen, *J. Am. Chem. Soc.* 139 (29) (2017) 9739–9754. doi:https://doi.org/10.1021/jacs.7b05362.
- [132] Y. Guo, S. Mei, K. Yuan, D.-J. Wang, H.-C. Liu, C.-H. Yan, Y.-W. Zhang, *ACS Catal.* 8 (7) (2018) 6203–6215. doi:https://doi.org/10.1021/acscatal.7b04469.
- [133] T. W. van Deelen, C. Hernández Mejía, K. P. de Jong, *Nat. Catal.* 2 (11) (2019) 955–970. doi:https://doi.org/10.1038/s41929-019-0364-x.

- [134] W. C. Conner Jr, J. L. Falconer, *Chem. Rev.* 95 (3) (1995) 759–788.
- [135] R. Prins, *Chem. Rev.* 112 (5) (2012) 2714–2738. doi:<https://doi.org/10.1021/cr200346z>.
- [136] H. Shen, H. Li, Z. Yang, C. Li, *GEE* 7 (6) (2022) 1161–1198. doi:<https://doi.org/10.1016/j.gee.2022.01.013>.
- [137] P. A. Thiel, T. E. Madey, *Surf. Sci. Rep.* 7 (6–8) (1987) 211–385. doi:[https://doi.org/10.1016/0167-5729\(87\)90001-X](https://doi.org/10.1016/0167-5729(87)90001-X).
- [138] B. C. Brodie, *Proc. R. Soc. Lond.* 21 (139–147) (1873) 245–247. doi:<https://doi.org/10.1098/rsp1.1872.0052>.
- [139] C. Vogt, M. Monai, G. J. Kramer, B. M. Weckhuysen, *Nat. Catal.* 2 (3) (2019) 188–197. doi:<https://doi.org/10.1038/s41929-019-0244-4>.
- [140] Statistical review of world energy 2023, accessed: 2023-11-01.
URL <https://www.energyinst.org/statistical-review>
- [141] I. E. Agency, *World energy outlook 2023* (2023).
URL <https://www.iea.org/reports/world-energy-outlook-2023>
- [142] M. Bailera, P. Lisbona, L. M. Romeo, S. Espatolero, *Renew. Sust. Energ. Rev.* 69 (2017) 292–312. doi:<https://doi.org/10.1016/j.rser.2016.11.130>.
- [143] J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* 118 (2) (2018) 434–504. doi:<https://doi.org/10.1021/acs.chemrev.7b00435>.
- [144] J. Ashok, S. Pati, P. Hongmanorom, Z. Tianxi, C. Junmei, S. Kawi, *Catalysis Today* 356 (2020) 471–489. doi:<https://doi.org/10.1016/j.cattod.2020.07.023>.
- [145] W. J. Lee, C. Li, H. Prajitno, J. Yoo, J. Patel, Y. Yang, S. Lim, *Catal. Today* 368 (2021) 2–19. doi:<https://doi.org/10.1016/j.cattod.2020.02.017>.
- [146] M. Sterner, M. Specht, *Energies* 14 (20) (2021) 6594. doi:<https://doi.org/10.3390/en14206594>.
- [147] H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, et al., *Chemical reviews* 101 (4) (2001) 953–996. doi:<https://doi.org/10.1021/cr000018s>.
- [148] G. Centi, E. A. Quadrelli, S. Perathoner, *Energy Environ. Sci.* 6 (6) (2013) 1711–1731. doi:<https://doi.org/10.1039/C3EE00056G>.
- [149] R. Schlögl, *Chemical energy storage*, 2nd Edition, de Gruyter Berlin, 2022.
- [150] M. Thema, F. Bauer, M. Sterner, *Renewable and Sustainable Energy Reviews* 112 (2019) 775–787. doi:<https://doi.org/10.1016/j.rser.2019.06.030>.

- [151] L. Li, W. Zeng, M. Song, X. Wu, G. Li, C. Hu, *Catalysts* 12 (2) (2022) 244. doi:<https://doi.org/10.3390/catal12020244>.
- [152] J. Gao, Y. Wang, Y. Ping, D. Hu, G. Xu, F. Gu, F. Su, *RSC Adv.* 2 (6) (2012) 2358–2368. doi:<https://doi.org/10.1039/C2RA00632D>.
- [153] J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, *RSC Adv.* 5 (29) (2015) 22759–22776. doi:<https://doi.org/10.1039/C4RA16114A>.
- [154] K. Ghaib, K. Nitz, F.-Z. Ben-Fares, *ChemBioEng Reviews* 3 (6) (2016) 266–275. doi:<https://doi.org/10.1002/cben.201600022>.
- [155] K. Hertwig, L. Martens, *Chemische Verfahrenstechnik: Berechnung, Auslegung und Betrieb chemischer Reaktoren*, 2nd Edition, Oldenbourg Wissenschaftsverlag Verlag, 2012.
- [156] G. Emig, E. Klemm, H. Freund, K.-D. Hungenberg, *Chemische Reaktionstechnik*, 6th Edition, Springer, 2017.
- [157] M. Baerns, *Technische chemie*, 2nd Edition, John Wiley & Sons, 2013.
- [158] A. Behr, D. W. Agar, J. Jörissen, A. J. Vorholt, *Einführung in die technische Chemie*, Vol. 120, Springer, 2010.
- [159] G. Emig, E. Klemm, *Technische Chemie: Einführung in die chemische Reaktionstechnik*, Springer-Verlag, 2006.
- [160] M. Doble, *Perry's chemical engineers' handbook*, McGraw-Hill, New York, US (2007).
- [161] R. Güttel, T. Turek, *Chemische Reaktionstechnik*, Springer, 2021.
- [162] P. Linstrom, W. Mallard, *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, accessed: 2023-07-05. doi:<https://doi.org/10.18434/T4D303>.
- [163] M. W. Chase, *J. Phys. Chem. Ref. Data* (1998) 1529–1564.
- [164] T. Yarbaş, N. Ayas, *Int. J. Hydrogen Energy* 49 (2024) 1134–1144. doi:<https://doi.org/10.1016/j.ijhydene.2023.06.223>.
- [165] F. Fischer, H. Tropsch, P. Diltthey, *Brennst. Chem* 6 (1925) 265–271.
- [166] M. Vannice, *Catal. Rev.* 14 (1) (1976) 153–191. doi:<https://doi.org/10.1080/03602457608073410>.
- [167] M. Younas, L. Loong Kong, M. J. Bashir, H. Nadeem, A. Shehzad, S. Sethupathi, *Energy Fuels* 30 (11) (2016) 8815–8831. doi:<https://doi.org/10.1021/acs.energyfuels.6b01723>.
- [168] G. D. Weatherbee, C. H. Bartholomew, *Journal of Catalysis* 87 (2) (1984) 352–362. doi:[https://doi.org/10.1016/0021-9517\(84\)90196-9](https://doi.org/10.1016/0021-9517(84)90196-9).

- [169] G. Garbarino, D. Bellotti, P. Riani, L. Magistri, G. Busca, *International journal of hydrogen energy* 40 (30) (2015) 9171–9182. doi:<https://doi.org/10.1016/j.ijhydene.2015.05.059>.
- [170] A. Beuls, C. Swalus, M. Jacquemin, G. Heyen, A. Karelovic, P. Ruiz, *Applied Catalysis B: Environmental* 113 (2012) 2–10. doi:<https://doi.org/10.1016/j.apcatb.2011.02.033>.
- [171] C. H. Bartholomew, *Appl. Catal. A Gen.* 212 (1–2) (2001) 17–60. doi:[https://doi.org/10.1016/S0926-860X\(00\)00843-7](https://doi.org/10.1016/S0926-860X(00)00843-7).
- [172] E. de Smit, B. M. Weckhuysen, *Chemical Society Reviews* 37 (12) (2008) 2758–2781. doi:<https://doi.org/10.1039/B805427D>.
- [173] J. Kirchner, Z. Baysal, S. Kureti, *ChemCatChem* 12 (4) (2020) 981–988. doi:<https://doi.org/10.1002/cctc.201901956>.
- [174] T. Franken, A. Heel, *J. CO₂ Util.* 39 (2020) 101175. doi:<https://doi.org/10.1016/j.jcou.2020.101175>.
- [175] P. Frontera, A. Macario, M. Ferraro, P. Antonucci, *Catalysts* 7 (2) (2017) 59. doi:<https://doi.org/10.3390/catal7020059>.
- [176] B. Mutz, H. W. Carvalho, S. Mangold, W. Kleist, J.-D. Grunwaldt, *J. Catal.* 327 (2015) 48–53. doi:<https://doi.org/10.1016/j.jcat.2015.04.006>.
- [177] G. Garbarino, P. Riani, L. Magistri, G. Busca, *International journal of hydrogen energy* 39 (22) (2014) 11557–11565. doi:<https://doi.org/10.1016/j.ijhydene.2014.05.111>.
- [178] S. Ewald, M. Kolbeck, T. Kratky, M. Wolf, O. Hinrichsen, *Applied Catalysis A: General* 570 (2019) 376–386. doi:<https://doi.org/10.1016/j.apcata.2018.10.033>.
- [179] L. Shen, J. Xu, M. Zhu, Y.-F. Han, *ACS Catal.* 10 (24) (2020) 14581–14591. doi:<https://doi.org/10.1021/acscatal.0c03471>.
- [180] M. Aziz, A. Jalil, S. Triwahyono, A. Ahmad, *Green Chem.* 17 (5) (2015) 2647–2663. doi:<https://doi.org/10.1039/C5GC00119F>.
- [181] W. Li, H. Wang, X. Jiang, J. Zhu, Z. Liu, X. Guo, C. Song, *RSC Adv.* 8 (14) (2018) 7651–7669.
- [182] C. Vogt, B. M. Weckhuysen, *Nat. Rev. Chem.* 6 (2) (2022) 89–111. doi:<https://doi.org/10.1038/s41570-021-00340-y>.
- [183] C. Vogt, F. Meirer, M. Monai, E. Groeneveld, D. Ferri, R. A. van Santen, M. Nachtegaal, R. R. Unocic, A. I. Frenkel, B. M. Weckhuysen, *Nat. Commun.* 12 (1) (2021) 7096. doi:<https://doi.org/10.1038/s41467-021-27474-3>.
- [184] C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C. J. Kiely, P. H. Berben,

- F. Meirer, B. M. Weckhuysen, *Nat. Catal.* 1 (2) (2018) 127–134. doi:<https://doi.org/10.1038/s41929-017-0016-y>.
- [185] Z. Hao, J. Shen, S. Lin, X. Han, X. Chang, J. Liu, M. Li, X. Ma, *Appl. Catal. B* 286 (2021) 119922. doi:<https://doi.org/10.1016/j.apcatb.2021.119922>.
- [186] G. Spanò, M. Ferri, R. Cheula, M. Monai, B. M. Weckhuysen, M. Maestri, *ACS Catal.* 15 (10) (2025) 8194–8203. doi:<https://doi.org/10.1021/acscatal.4c08084>.
- [187] E. Sterk, A. Nieuwelink, M. Monai, J. Louwen, E. Vogt, I. Filot, B. Weckhuysen, *JACS Au* 2 (12) (2022) 2714–2730. doi:<https://doi.org/10.1021/jacsau.2c00430>.
- [188] C. H. Tan, S. Nomanbhay, A. H. Shamsuddin, Y.-K. Park, H. Hernández-Cocoletzi, P. L. Show, *Front. Energy Res.* 9 (2022) 795423. doi:<https://doi.org/10.3389/fenrg.2021.795423>.
- [189] T. Klinger, Synthesis of a nickel catalyst for the methanation of carbondioxide by impregnation, Bachelor Thesis, Hamburg University of Technology, 2021.
- [190] S. Seiß, Synthesis and characterization of a supported nickel catalyst for the methanation of CO₂, Master Thesis, Hamburg University of Technology, 2021.
- [191] I. Chen, S. Y. Lin, D. W. Shiue, *Ind. Eng. Chem. Res.* 27 (6) (1988) 926–929. doi:<https://doi.org/10.1021/ie00078a005>.
- [192] Spheres and extrudates, accessed: 2023-07-05.
URL <https://www.sasolgermany.de>
- [193] G. A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems, *Chemical Reviews* 65 (2) (1965) 177–198. doi:<https://doi.org/10.1006/jcis.1996.0242>.
- [194] K. M. Hardiman, C.-H. Hsu, T. T. Ying, A. A. Adesina, *J. Mol. Catal. A. Chem.* 239 (1-2) (2005) 41–48. doi:<https://doi.org/10.1016/j.molcata.2005.05.030>.
- [195] I. Chen, D. W. Shiue, *Ind. Eng. Chem. Res.* 27 (3) (1988) 429–434. doi:<https://doi.org/10.1021/ie00075a011>.
- [196] Din 66136-2: Determination of the degree of dispersion of metals using chemisorption – part 2: Volumetric method (Jan. 2007).
- [197] T. Degen, M. Sadki, E. Bron, U. König, G. Nénert, *Powder Diffraction* 29 (S2) (2014) S13–S18. doi:[10.1017/S0885715614000840](https://doi.org/10.1017/S0885715614000840).
- [198] T. Armaroli, T. Bécue, S. Gautier, *Oil & Gas Science and Technology* 59 (2) (2004) 215–237. doi:<https://doi.org/10.2516/ogst:2004016>.
- [199] C. Mondelli, V. Dal Santo, A. Trovarelli, M. Boaro, A. Fusi, R. Psaro, S. Recchia, *Catal. Today* 113 (1-2) (2006) 81–86. doi:<https://doi.org/10.1016/j.cattod.2005.11.014>.

- [200] Din iso 9277:2010 determination of the specific surface area of solids by gas adsorption – bet method (Jan. 2014).
- [201] K. S. Sing, *Pure & Appl. Chem.* 57 (4) (1985) 603–619. doi:<https://doi.org/10.1351/pac198557040603>.
- [202] Din 66136-2: Determination of the dispersion degree of metals using gas chemisorption – part 1: Principles (Feb. 2017).
- [203] J. Kieffer, V. Valls, N. Blanc, C. Hennig, *Journal of Synchrotron Radiation* 27 (2) (2020) 558–566. doi:[10.1107/S1600577520000776](https://doi.org/10.1107/S1600577520000776).
- [204] O. Korup, R. Schlögl, R. Horn, *Catal. today* 181 (1) (2012) 177–183. doi:<https://doi.org/10.1016/j.cattod.2011.04.051>.
- [205] B. Mutz, P. Sprenger, W. Wang, D. Wang, W. Kleist, J.-D. Grunwaldt, *Applied Catalysis A: General* 556 (2018) 160–171. doi:<https://doi.org/10.1016/j.apcata.2018.01.026>.
- [206] H. Rajavelu, N. J. Vasa, S. Seshadri, *Applied Spectroscopy* 75 (7) (2021) 893–900. doi:<https://opg.optica.org/as/abstract.cfm?URI=as-75-7-893>.
- [207] D. A. Cremers, L. J. Radziemski, *Handbook of laser-induced breakdown spectroscopy*, John Wiley & Sons, 2013.
- [208] S. Musazzi, U. Perini, *Laser-induced breakdown spectroscopy*, Springer, 2014.
- [209] A. Wolf, A. Jess, C. Kern, *Chem. Eng. Technol.* 39 (6) (2016) 1040–1048. doi:<https://doi.org/10.1002/ceat.201500548>.
- [210] T. Hecht, *Physikalische Grundlagen der IR-Spektroskopie*, Springer, 2019.
- [211] H. A. Al-Abadleh, V. Grassian, *Langmuir* 19 (2) (2003) 341–347. doi:<https://doi.org/10.1021/la026208a>.
- [212] C. Morterra, G. Magnacca, *Catal. Today* 27 (3-4) (1996) 497–532. doi:[https://doi.org/10.1016/0920-5861\(95\)00163-8](https://doi.org/10.1016/0920-5861(95)00163-8).
- [213] K. Hadjiivanov, *Adv. Catal.* 57 (2014) 99–318. doi:<https://doi.org/10.1016/B978-0-12-800127-1.00002-3>.
- [214] F. Solymosi, A. Erdöhelyi, T. Bánsági, *J. Catal.* 68 (2) (1981) 371–382. doi:[https://doi.org/10.1016/0021-9517\(81\)90106-8](https://doi.org/10.1016/0021-9517(81)90106-8).
- [215] M. R. Prairie, A. Renken, J. G. Highfield, K. R. Thampi, M. Grätzel, *J. Catal.* 129 (1) (1991) 130–144.
- [216] M. Marwood, R. Doepper, A. Renken, *Appl. Catal. A-Gen.* 151 (1) (1997) 223–246. doi:[https://doi.org/10.1016/S0926-860X\(96\)00267-0](https://doi.org/10.1016/S0926-860X(96)00267-0).
- [217] S. Eckle, H.-G. Anfang, R. J. Behm, *J. Phys. Chem. C* 115 (4) (2011) 1361–1367. doi:<https://doi.org/10.1021/jp108106t>.

- [218] G. Busca, V. Lorenzelli, *Mater. Chem.* 7 (1) (1982) 89–126. doi:[https://doi.org/10.1016/0390-6035\(82\)90059-1](https://doi.org/10.1016/0390-6035(82)90059-1).
- [219] A. Cárdenas-Arenas, A. Quindimil, A. Davó-Quiñonero, E. Bailón-García, D. Lozano-Castello, U. De-La-Torre, B. Pereda-Ayo, J. A. González-Marcos, J. R. González-Velasco, A. Bueno-López, *Appl. Catal. B: Environ.* 265 (2020) 118538. doi:<https://doi.org/10.1016/j.apcatb.2019.118538>.
- [220] C. Schild, A. Wokaun, R. A. Koeppel, A. Baiker, *J. Phys. Chem.* 95 (16) (1991) 6341–6346. doi:<https://doi.org/10.1021/j100169a049>.
- [221] P. U. Aldana, F. Ocampo, K. Kobl, B. Louis, F. Thibault-Starzyk, M. Daturi, P. Bazin, S. Thomas, A. Roger, *Catalysis Today* 215 (2013) 201–207. doi:<https://doi.org/10.1016/j.cattod.2013.02.019>.
- [222] X. Wang, Y. Hong, H. Shi, J. Szanyi, *J. Catal.* 343 (2016) 185–195. doi:<https://doi.org/10.1016/j.jcat.2016.02.001>.
- [223] H. Muroyama, Y. Tsuda, T. Asakoshi, H. Masitah, T. Okanishi, T. Matsui, K. Eguchi, *J. Catal.* 343 (2016) 178–184. doi:<https://doi.org/10.1016/j.jcat.2016.07.018>.
- [224] S.-i. Fujita, M. Nakamura, T. Doi, N. Takezawa, *Appl. Catal. A-Gen.* 104 (1) (1993) 87–100. doi:[https://doi.org/10.1016/0926-860X\(93\)80212-9](https://doi.org/10.1016/0926-860X(93)80212-9).
- [225] A. Erdőhelyi, M. Pásztor, F. Solymosi, *J. Catal.* 98 (1) (1986) 166–177. doi:[https://doi.org/10.1016/0021-9517\(86\)90306-4](https://doi.org/10.1016/0021-9517(86)90306-4).
- [226] R. Eischens, W. Pliskin, *Adv. Catal.* 10 (1958) 1–56. doi:[https://doi.org/10.1016/S0360-0564\(08\)60403-4](https://doi.org/10.1016/S0360-0564(08)60403-4).
- [227] X. Wang, H. Shi, J. H. Kwak, J. Szanyi, *ACS Catal.* 5 (11) (2015) 6337–6349. doi:<https://doi.org/10.1021/acscatal.5b01464>.
- [228] M. Agnelli, H. Swaan, C. Marquez-Alvarez, G. Martin, C. Mirodatos, *J. Catal.* 175 (1) (1998) 117–128. doi:<https://doi.org/10.1006/jcat.1998.1978>.
- [229] Q. Pan, J. Peng, T. Sun, S. Wang, S. Wang, *Catal. Commun.* 45 (2014) 74–78. doi:<https://doi.org/10.1016/j.catcom.2013.10.034>.
- [230] S. Tada, R. Kikuchi, *Catal. Sci. Technol.* 5 (6) (2015) 3061–3070. doi:[10.1039/C5CY00150A](https://doi.org/10.1039/C5CY00150A).
- [231] Reacnostics gmbh: μ -drifts cell Accessed: 2025-04-21.
URL <https://www.reacnostics.com/>
- [232] P. Stephan, S. Kabelac, M. Kind, D. Mewes, K. Schaber, T. Wetzel, *VDI-Wärmeatlas*, 12th Edition, Springer-Verlag, 2019.

-
- [233] C. R. Wilke, *J. Chem. Phys.* 18 (4) (1950) 517–519. doi:<https://doi.org/10.1063/1.1747673>.
- [234] T. A. Davidson, *A simple and accurate method for calculating viscosity of gaseous mixtures*, Vol. 9456, US Department of the Interior, Bureau of Mines, 1993.
- [235] G. Sonntag, *CIT* 32 (5) (1960) 317–329. doi:<https://doi.org/10.1002/cite.330320502>.
- [236] O. Levenspiel, *Chemical reaction engineering*, John Wiley & sons, 1998.
- [237] F. Kapteijn, J. A. Moulijn, *Laboratory Catalytic Reactors: Aspects of Catalyst Testing*, Wiley-VCH Weinheim, 1997.
- [238] O. Levenspiel, W. Smith, *Chemical Engineering Science* 6 (4-5) (1957) 227–235. doi:[https://doi.org/10.1016/0009-2509\(57\)85021-0](https://doi.org/10.1016/0009-2509(57)85021-0).
- [239] B. E. Poling, J. M. Prausnitz, J. P. O'connell, et al., *The properties of gases and liquids*, 5th Edition, McGraw-hill New York, 2001.
- [240] M. Jakubith, *Grundoperationen und chemische Reaktionstechnik*, John Wiley & sons, 1998.
- [241] D. E. Mears, *Ind. Eng. Chem. Process Des. Dev.* 10 (4) (1971) 541–547. doi:<https://doi.org/10.1021/i260040a020>.
- [242] F. Montagnaro, *Energies* 17 (17) (2024) 4342. doi:<https://doi.org/10.3390/en17174342>.
- [243] N. Froessling, *Gerlands Beitr. Geophys.* 52 (1938) 107—216.
- [244] W. Ranz, W.E.; Marshall, *Chem. Eng. Prog.* 48 (1952) 141–146.
- [245] N. Wakao, T. Funazkri, *Chemical Engineering Science* 33 (10) (1978) 1375–1384. doi:[https://doi.org/10.1016/0009-2509\(78\)85120-3](https://doi.org/10.1016/0009-2509(78)85120-3).
- [246] M. G. Nugraha, R. Andersson, B. Andersson, *Chemical Engineering Science* 249 (2022) 117292. doi:<https://doi.org/10.1016/j.ces.2021.117292>.
- [247] W. Reschetilowski, *Handbuch Chemische Reaktoren*, Springer, 2020.
- [248] J. Solsvik, H. A. Jakobsen, *Transport in porous media* 93 (1) (2012) 99–126. doi:<https://doi.org/10.1007/s11242-012-9946-7>.
- [249] G. F. Froment, K. B. Bischoff, J. De Wilde, *Chemical reactor analysis and design*, 3rd Edition, Wiley New York, 2011.
- [250] M. Baumhauer, U. Bulmann, A.-K. Watolla, *KI-Tools in Studium und Lehre: Handreichung der TU Hamburg*, 2nd Edition, Technische Universität Hamburg, 2024. doi:<https://doi.org/10.15480/882.13337>.

Tools

- Microsoft PowerPoint was used for image and figure preparation.
- OriginPro 2025 was used for data visualization and graph generation.
- MATLAB R2020b was used for numerical calculations and data analysis.
- Microsoft Excel was used for supplementary calculations.
- OPUS 6 was used for spectral data analysis.
- ACD/3D Viewer was used for drawing and visualization of chemical structures.
- For linguistic editing and stylistic refinement [250], the tools Grammarly and ChatGPT were used selectively; full responsibility for the scientific content, interpretations, and conclusions rests solely with the author.