

NOTE

Adsorption and diffusion in zeolites: The pitfall of isotypic crystal structures

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Molecular simulations have become an important tool to study and predict the properties of adsorbed molecules in zeolites. Beside the force field [1], the crystal structure of the zeolite represents another important input to the simulations. All-silica structures are investigated most often where crystallographic studies provide the atoms' positions in the unit cell (procedure *i*). If experimental data on the purely siliceous structure is yet not available, either the database of the International Zeolite Association (IZA) can be accessed which, for every framework type, offers predictions of the siliceous structure based on theoretical considerations (*ii*), or an experimental structure which is not purely siliceous can be converted by, for example, substituting the aluminium atoms of an aluminosilicate by silicon atoms (*iii*). A PFG NMR study by Hedin *et al.* [2] has indicated that the self-diffusion coefficient of propylene in different LTA-type zeolites may be quite sensitive to compositional but also structural changes [2]. To definitively rule out the influence of composition, we have performed Monte Carlo simulations of methane in different zeolite structures of the same framework type (procedure *i*, *ii* and *iii*) in order to assess the influence of the zeolite structure on the thermodynamics and mass transport of guest molecules.

Henry coefficients, H , and transition-state theory self-diffusion coefficients at zero loading, D are calculated for methane, modeled as a united atom [3], in siliceous structures of the frameworks LTA, SAS and ITE (300 K). Apart from the IZA structures [4], the zeolites investigated here include the all-silica structures, as experimentally determined by Corma *et al.* (LTA), Wragg *et al.* (SAS) and Cambor *et al.* (ITE) [5–7], as well as an aluminosilicate (LTA by Pluth and Smith) and a magnesioaluminophosphate (SAS by Patinec *et al.*) [8, 9]. The latter two are converted to purely siliceous structures according to procedure *iii* mentioned above.

The chosen framework types belong to the group of cage-type zeolites [10]. Their pore structure includes broad regions (cages) and very narrow regions (windows) which, together, form large entropic diffusion barriers to methane molecules. The windows are in fact so small that a methane molecule just fits into them (kinetic diameter of a methane bead: $\sigma_{\text{CH}_4}^{\text{LJ}} = 3.72 \text{ \AA}$; diameter of the windows, determined as the largest hard sphere that fits: $d \approx 4 \text{ \AA}$, compare Table 1).

It is important to mention that, in our simulations, we use a rigid zeolite model. Including

flexibility may quantitatively change our results, in particular for the here studied cage-type zeolites. More details on the effects of zeolite flexibility can be found in Ref 11.

The influence of the crystal structure on adsorption is moderate, see Table 1. Henry coefficients differ by -32% (LTA Pluth and Smith) and +23% (ITE Cambor *et al.*) from the corresponding H_{IZA} of a given framework type. Seemingly, a larger Henry coefficient can be correlated with a smaller unit cell and thus cage because the average potential in the zeolite cage becomes denser but more attractive in consequence of decreasing cage size, see also Fig. 1.

The impact of structure variations on the diffusivity is much stronger than on adsorption. In particular, the differences between the diffusion coefficients obtained with the IZA structures and with the “true” all-silica crystals are large; the latter ones are smaller by factors of 2.9, 15.3 and 161 for LTA, SAS and ITE, respectively. Interestingly, an analysis of the free-energy and potential-energy profiles reveals that, irrespective the framework type, the entropic diffusion barriers observed in different structures, i.e. $-\Delta S/k_B = (\Delta F - \Delta U)/(k_B T)$, hardly vary. Significant changes manifest only for the potential-energy barrier. This might be rationalized by the following arguments.

The differences between the structures stem largely from subtle variations in the unit-cell size. So, neither the area in the window region that is accessible for a hopping molecule nor the volume of the cages change significantly. The ratio of these two factors does, however, determine the entropic barrier. By contrast, the potential energy in this region is, due to the tight fit of the molecule, very sensitive to small variations. Thus a hardly noticeable decrease in accessible area (smaller unit cell) leads to an unproportional increase in the potential energy in the window (more repulsive). Together with the observation that the average cage potential decreases with decreasing cage size (more attractive) leads to a potential barrier that increases with decreasing cage size. Finally, note that the effects described here are also observed at finite loadings, see Supplementary Material, where we, furthermore, describe our methodology in more detail.

In summary, we have investigated the influence of the crystal structure on adsorption and diffusion of methane in cage-type zeolites. In contrast to the Henry coefficient, the self-diffusion coefficient can, in fact, be extremely sensitive to very small structural differences supporting experimental observations [2]. Since we feel that these subtleties may have been underestimated in the past and in order to enhance the reproducibility of future simulation

studies we suggest to always provide the actual crystal structure files used in simulation studies, for example in the Supplementary Material.

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Supplementary Online Material

Supplementary material associated with this note can be found, free of charge, in the online version.

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Table 1. Methane henry coefficients and TST self-diffusivities at zero loading.

Crystal structure	$a^\alpha \times b^\alpha \times c^\alpha$	d^α	H^β	D^γ
LTA				
IZA ^δ [4]	11.919×11.919×11.919	4.14	4.18	78.08 _{4.30}
Corma <i>et al.</i> ^δ [5]	11.867×11.867×11.867	4.00	4.45	27.39 _{1.60}
Pluth and Smith ^δ [8]	24.555×24.555×24.555	4.00	2.85	112.91 _{4.05}
SAS				
IZA [4]	14.349×14.349×10.398	4.21	6.87	118.06 _{5.70}
Wragg <i>et al.</i> [6]	14.104×14.104×10.188	4.02	9.29	7.72 _{0.83}
Patinec <i>et al.</i> [9]	14.322×14.322×10.424	4.16	6.94	160.84 _{12.23}
ITE				
IZA [4]	20.753× 9.804×20.009	4.15	56.75	155.72 _{0.89}
Camblor <i>et al.</i> [7]	20.622× 9.724×19.623	3.79	69.99	0.97 _{0.09}

Notes: $^\alpha$ 10^{-10} m, $^\beta$ 10^{-3} mol Pa⁻¹ m⁻³, $^\gamma$ 10^{-12} m² s⁻¹ (errors as subscripts). ^δ The unit cell of the 4A zeolite by Pluth and Smith accommodates 2×2×2 cages whereas the structures by the IZA and by Corma *et al.* each accommodate a single cage.

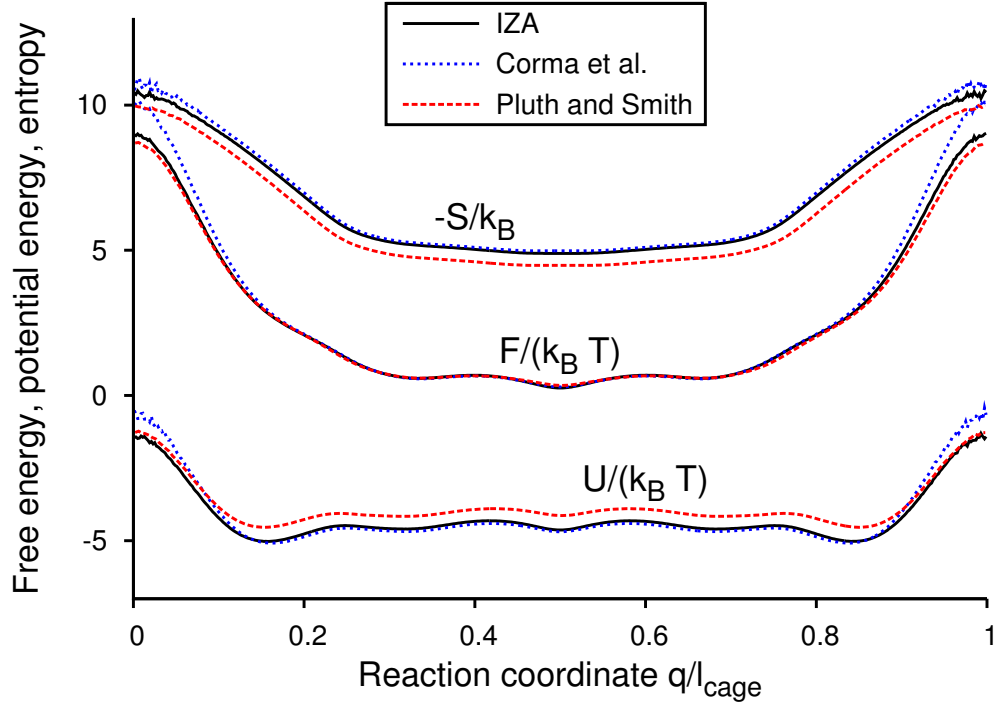


Figure 1. Free-energy, potential-energy and entropy profile of methane diffusing in different LTA structures.