COMMENTS

On the Sticking Probability of Aromatic Molecules on Zeolites. Comment on "STICKING PROBABILITY ON ZEOLITES"

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Zeolites and crystalline microporous solids are critical materials for selective sorption and catalysis, as the similar size of the pores and the reacting/sorbing molecules allows controlling the access to the pores. Branched hydrocarbons and substituted aromatic molecules, for example, are being separated with zeolitic sorbents and catalytically converted in large scale technical processes using the principles of shape selectivity.

While the similar size of the minimum kinetic diameter of these molecules can be used to control the selectivity, the steric constraints also decrease the rate of access of molecules having minimum kinetic diameters smaller than the effective opening of the micropores. Such kinetic hindrance lowers the potential rate of separation or the productivity of shape selective catalysts. To improve material properties and to minimize the retardation of the equilibration, the elementary steps of sorption and diffusion have been addressed theoretically and experimentally.[1,2] These studies have shown that the direct access of molecules to the micropores is highly improbable. Thus, a sequential mechanism can be postulated consisting of (i) the collision and sorption of the molecules with the outer particle surface, (ii) random mobility at the outer surface similar to a two-dimensional gas, (iii) the entering into the micropores, and (iv) diffusion to sorption sites inside the pores.

The diffusion inside the pores is experimentally and theoretically described in great detail,[3−7] but the preceding steps are still under vivid discussion. Recently, we have reported that the transport of (alkyl-substituted) benzene molecules (benzene, toluene, *p*- and *o*-xylene) proceeds via physisorption in a weakly bound state at the external surface of the sorbent, allowing high two-dimensional mobility on the surface. In consequence, it was concluded that the transport to SiOH and SiOHAl groups on the zeolite surface and inside the pores occurs in parallel.[8] Within this context, we have also reported that the sticking probabilities of these molecules on the surface of micropore free amorphous SiO_2 are in the order of $10^{-6}-10^{-7}$. This experimental number has been challenged recently by Simon et al., suggesting that such low numbers might have been determined under diffusion-limited conditions.[9] To show that the measurements have been performed under conditions free of disturbing artifacts such as local exothermicity caused by the adsorption process or external diffusion limitations, we readdress here the boundary conditions of the sticking probability for the sorption process.

The sticking probability is defined as the ratio of the overall rate of adsorption to the collision rate of the sorbing molecule.[10]
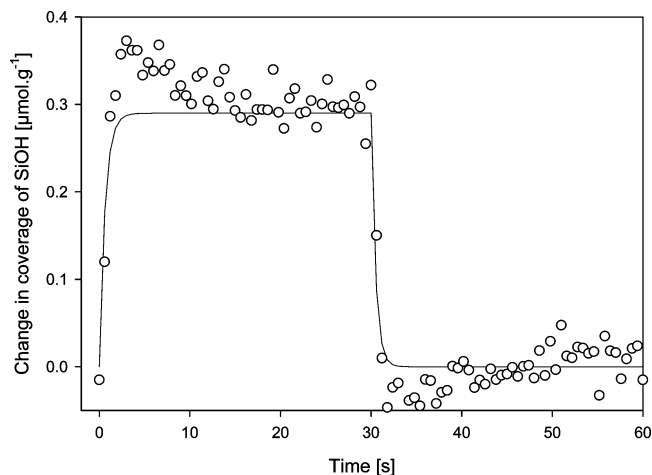
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Figure 1. Changes in the coverage of the SiOH groups of H/ZSM-5 with *o*-xylene during a pressure step of $6.0 \times 10^{-2} \pm 2.5 \times 10^{-3}$ mbar at 403 K.

In the experiments discussed here, the change in the surface composition was followed during a pressure modulation of $\pm 2.5 \times 10^{-3}$ mbar around the equilibrium pressure of 6.0×10^{-2} mbar of the aromatic molecules by rapid scan IR spectroscopy.[8] The changes in the coverage of the SiOH groups (silanol groups) and SiOHAl groups (Brønsted acidic bridging hydroxy groups) were obtained by integration of the bands at 3745 and 3610 cm^{-1}, respectively, in a series of time resolved spectra. As an example, the changes in the surface concentration of *o*-xylene on the SiOH groups of H/ZSM-5 are shown in Figure 1. The rate of adsorption (r_{ads}) can be written as

$$r_{ads} = \alpha \frac{\langle u \rangle}{4} n$$

with

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}}$$

$$n = \frac{N}{V} = \frac{p}{RT} N_A$$

in which α denotes the sticking probability, $\langle u \rangle$ the mean gas velocity, n the number of molecules per volume, T the temperature, p the pressure, N the total number of molecules, N_A Avogadro's number, V the volume, and M the molecular mass. The rate of desorption is given by

$$r_{des} = k c_{sites} \theta$$

with k denoting the rate constant, c_{sites} the concentration of sites, and θ the coverage of the sites. The concentration of molecules on the surface (i.e., $c_{sites}\theta$) was determined from the density of SiOH groups (determined by ¹H MAS NMR) and the decrease in the intensity of the corresponding band at 3745 cm^{-1} after adsorption of the molecules. (It has been independently measured that the molar extinction coefficient for the band of the

SiOH groups is constant during sorption of benzene at 403 K up to pressures of 0.1 mbar at 403 K). The adsorption−desorption equilibrium is established before the pressure modulation occurs (i.e., $r_{ads} = r_{des}$). Thus, initially only the rate of adsorption changes at the pressure step, as r_{ads} directly depends on the pressure, while the change in r_{des} follows as the coverage changes. From the change in r_{ads} (calculated from the initial slope of the change in coverage of the SiOH groups) and the collision frequency at the outer side of the particle, the average sticking probability can be derived within the small variations in pressure and surface coverage

$$\Delta r_{ads} = \alpha \frac{\langle u \rangle p_2}{4\,RT} N_A - \alpha \frac{\langle u \rangle p_1}{4\,RT} N_A$$

from which follows

$$\alpha = \frac{\Delta r_{ads}}{\dfrac{\langle u \rangle N_A}{4\,RT}(p_2 - p_1)}$$

For the amorphous SiO_2 sample (Aerosil 200), the surface area (200 m²/g) and the concentration of SiOH groups (0.54 mmol/g) were directly determined using nitrogen sorption and ^{1}H MAS NMR spectroscopy, respectively. From the experimental data presented in ref 8, sticking probabilities in the order of 10^{-7} were obtained for the amorphous SiO_2 sample (i.e., xylene isomers $\alpha = 7.5 \times 10^{-6}$, toluene $\alpha = 2.5 \times 10^{-6}$, benzene $\alpha = 1.7 \times 10^{-6}$). Using preliminary experiments, we have estimated a similar sticking probability for benzene on a ZSM-5 sample.[11]

For zeolite samples, additional assumptions had to be made in order to calculate the sticking probability: (i) the area of pore openings has to be subtracted from the external surface area (if physisorption would also occur over the pore opening, the surface area would be about 10% higher), (ii) the distribution of the SiOH groups on the different crystallographic surface orientations was assumed to be homogeneous, and (iii) if the molecules can enter into the micropores, sorption and diffusion into the volume of the zeolite particle have to be taken into account. We have shown previously that the sorption kinetics can only be explained by assuming that molecules are first bound in a weak and highly mobile sorbed state at the surface without direct contact to hydroxy groups, followed by a fast surface diffusion process to the SiOH and SiOHAl groups. A significant population of this preadsorbed state was, however, not observed (e.g., by following the intensity of the benzene ring deformation or C−H stretching vibrations). As a result of the two pathways, we can only determine the sticking probability for *o*-xylene, which does not enter into the pores of the H/ZSM-5 zeolite under the experimental conditions, while for the other molecules the two transport channels (to the SiOH and SiOHAl groups) result in significantly slower uptake rates on the SiOH groups (i.e., *p*-xylene $k = 0.5$ s⁻¹, *o*-xylene $k = 1.82$ s⁻¹) and in a lower increase in coverage after the pressure step (i.e., *p*-xylene $\Delta c_{OH} = 0.32$ μmol/g, *o*-xylene $\Delta c_{OH} = 0.38$ μmol/g). Under these assumptions, the sticking probability for the sorption of *o*-xylene on the H/ZSM-5 sample is approximately 5×10^{-7}.

This number is in strong contrast to the estimates of Simon et al.,[9] who suggested that the sticking probability of *n*-alkanes is close to 1. Their conclusion is based on the fact that in the zeolitic host−guest system considered (notably ethane in NaX) molecular propagation through a bed of crystals is adequately represented by a Gaussian function whose mean square width ("the mean square displacement") increases in proportion to the
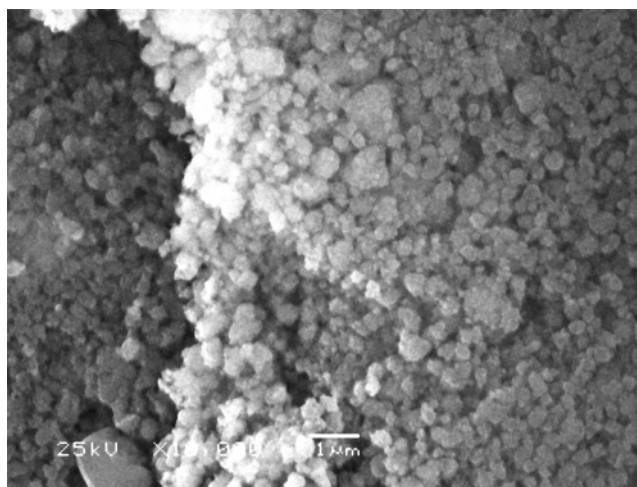

Figure 2. SEM of the surface of a wafer used for IR spectroscopy.

observation time. This is the behavior required by Fick's second law so that—with respect to long-range diffusion—the bed of zeolite crystallites may be considered as a quasi-continuum, whose diffusivity is referred to as the long-range diffusivity. As a necessary and sufficient supposition of this observation, molecular collisions from the gas phase with the outer surface of the crystallites have to lead to a continuation of the molecular trajectory within the zeolite crystals with a probability of much larger than 10^{-7}. Otherwise, the probability distribution of molecular displacements would have to consist of a superposition of a broad and narrow distribution, corresponding to those molecules which have been repeatedly rejected from the outer surface and those remaining in the intracrystalline space, rather than of a single Gaussian. A semiquantitative estimate based on this consideration leads to sticking probabilities most probably in the range between 0.5 and 1. This number was supported by molecular dynamics calculations of *n*-butane on Silicalite-1, which also resulted in a sticking probability between 0.8 and 0.4 (depending on the loading). Finally, the authors concluded that the low sticking probabilities reported by the experiments published in ref 8 are most probably due to transport limitations of the molecules through the bed of zeolite particles (i.e., external mass transfer).

To verify the absence of such limitations, we have now compared the interparticle space in the powder sample and in the wafer used for the IR experiments. The scanning electron microscopy (SEM) picture of a H/ZSM-5 wafer pressed at 1 t/cm² is shown in Figure 2. The interparticle space between the individual ZSM-5 crystals (size 0.1−0.2 μm) is in the order of 0.05−0.1 μm. Consequently, the diffusion of the molecules can be described as Knudsen diffusion with a diffusion coefficient for benzene in the order of 2×10^{-5} m²·s⁻¹. In contrast, the diffusion coefficient for benzene inside the pores of the material prepared as a wafer is in the order of 10^{-14} m²·s⁻¹, estimated from the change of the coverage of SiOHAl groups by applying the square root law. The intraparticle diffusion coefficients can be calculated by[6]

$$D_{long\text{-}range} = p_{inter} D_{inter}$$

with p_{inter} and D_{inter} denoting the fraction of molecules in the intercrystalline space and their diffusivity. From the gravimetric sorption isotherms, p_{inter} was determined to be 4.7×10^{-5} m²·s⁻¹ for benzene at a partial pressure of 6.0×10^{-2} mbar and 403 K.

As expected, the diffusion inside the pores is significantly slower than that in the interparticle space. As the diffusion

coefficient for benzene inside the pores of the material prepared as a wafer is in the order typically observed on this material in powder form, for example, by the frequency response method, it is clearly shown that the sample preparation does not induce additional transport limitations. It should also be noted that the Brunauer−Emmett−Teller (BET) surface area of the sample in powder form and pressed as a wafer was nearly identical (387 and 381 m^2/g for the sample in powder and pressed form, respectively). Additionally, in the presence of mass transfer limitations in the void space between the zeolite particles, the uptake rates of the substituted benzene molecules on the SiOH and SiOHAl groups should be nearly identical, as external diffusion would be the rate-determining step.

Having given evidence that the results reported by us here and in the earlier publication are not diffusion limited, the question as to why the two approaches applied suggest sticking coefficients which are order of magnitudes apart remains. On one hand, the paper of Simon et al.[9] describes the diffusion of *n*-alkanes, which have a significantly smaller kinetic diameter compared to benzene (i.e., 0.42 nm vs 0.55 nm) and, therefore, will diffuse faster into the pores as the reorientation from the gas phase geometry to the optimum orientation for the pore entering will be entropically less demanding.[12] On the other hand, our work describes the sticking probability for the collision of a molecule on the external surface, while in ref 9 the rate of the transport into the pores is used to determine α. The mean gas velocity of the benzene molecules under the conditions studied is in the order 280 m·s^{-1}, and for a particle size of 10 μm, the molecules will encounter 10^{12} collisions while moving around the crystals. Therefore, even at a sticking probability of 10^{-7}, a sufficient number of molecules will be adsorbed within a regime with a root-mean-square displacement ($\langle x(t)^2\rangle^{1/2}$) of 100 μm during the PFG-NMR experiment. For the molecular dynamics simulations, the second argument used in ref 9, the ratio between the kinetic diameter of the molecule and the pore diameter is decisive for the rate molecules will enter into the pore. Using nonflexible molecules and pores, Skoulidas et al.[2] have shown that the rate of molecules entering the pores will approach zero, if both radii are the same. This is the borderline case for molecules such as benzene in ZSM-5, while for *n*-alkanes on ZSM-5 an increase of about 4 to 5 orders of magnitude was predicted. Thus, we conclude that the differences reported in both publications are due to the different size and geometry of the molecules used. However, there remains some discrepancy, as the difference between the estimated values from PFG measurements and the measurements reported here amounts to about 5 to 6 orders of magnitude. With the arguments used above, we would tentatively attribute this to problems with the estimation of the values.

At the end, we wish to give a rationalization as to why the sticking coefficient has to be that low, given the mechanism of adsorption established. If a molecule adsorbs via a physisorbed precursor state, which allows the free translation, but partially hinders rotation and vibration, the probability that a molecule stays at the surface after a collision can be described by

$$\alpha = \frac{q_{rot}^{\#}q_{vib}^{\#}}{q_{rot}^{gas}q_{vib}^{gas}}$$

where q_{rot}^{gas}, $q_{rot}^{\#}$, q_{vib}^{gas}, and $q_{vib}^{\#}$ are the rotational and vibrational partition functions of the molecule in the gas phase and in the adsorbed precursor state.[13] Let us assume that in the weakly sorbed state only the rotation of the molecules will be partially hindered. The rotation partition function of a molecule is given by

$$q_{rot} = \frac{1}{\sigma}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2}\sqrt{\pi I_x I_y I_z}$$

with σ being the molecule symmetry number, k_B the Boltzmann constant, h the Planck constant, and I_x, I_y, and I_z the moment of inertia along the three Cartesian coordinates. The corresponding entropy per degree of freedom for the rotation (S_{rot}) can be calculated from the rotation partition function by

$$S_{rot} = R\left(\ln q_{rot} + \frac{3}{2}\right)$$

Substitution of the entropy of rotation into the equation for the sticking probability leads to

$$\alpha = e^{-[(S_{rot}-S_{rot}^{\#})/R]} = e^{-(\Delta S_{rot}/R)}$$

At 403 K, the entropy of rotation of benzene for each degree of freedom is 90 J·mol^{-1}·K^{-1}, which results in sticking probabilities of 1.9×10^{-5}, 3.7×10^{-10}, and 7.2×10^{-15} when one, two, or three degrees of freedom for rotation are lost in the adsorbed state. This shows the general principle that sorption is more likely, if the molecule retains its rotational (and vibrational) degrees of freedom, that is, at minimum entropy loss compared to the gas phase. The sticking probabilities for benzene, toluene, and xylene on SiO$_2$ and on ZSM-5 in the order of 10^{-7} indicate that the molecules cannot rotate feely in the adsorbed state. At least one degree of freedom for rotation is lost compared to the gas phase, and a second mode seems to be strongly hindered. Further measurement and simulations will be necessary to fully understand the consequences of the low sticking probability on the sorption and transport process.

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