Influence of Defects on the External Crystal Surface on Molecular Uptake into MFI-Type Zeolites

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The interference microscopy technique, which was recently introduced in our laboratory, is applied to study transient intracrystalline concentration profiles in ZSM-5 crystals during adsorption and desorption of isobutane. Two different zeolite samples were used, viz., samples of etched and of nonetched ZSM-5 crystals. Etching has been carried out to remove the outer layer of the crystal surface, which may contain large amounts of defects and impurities. Studying the transient concentration profiles in both samples provides unique information on the influence of surface defects on molecular uptake. It is shown that, depending on their type, the defects of the crystal surface can either increase or decrease the rate of adsorption/desorption. The former effect is associated with adsorption/desorption through cracks in the crystal surface. The latter has its origin in the blockage or structural changes of the external crystal surface, leading to the appearance of surface transport barriers. Owing to the ability of interference microscopy to gain direct insight into the influence of surface defects on molecular uptake, this technique gives more accurate information on the transport diffusivities in zeolite crystals than the classical uptake methods.

1. Introduction

Zeolites represent an important class of microporous materials, which are widely used in large-scale industrial separations and catalysis. Optimization of industrial applications of zeolites requires an understanding of the transport of guest molecules and of its role in controlling molecular uptake. Intracrystalline transport in zeolites has been the subject of a large number of recent theoretical and experimental studies.[1−5] In comparison, the influence of the external surface of zeolite crystals on uptake has been much less thoroughly investigated. An application of computer simulations to study mass transfer through crystal surfaces has been hindered by the difficulty of obtaining detailed knowledge of the surface structure of real-life zeolite crystals. Despite this deficiency, in recent years computer simulations have provided important insights on the influence of surface structure on molecular uptake.[6−9] In particular, it was shown that, for molecules with characteristic diameters comparable with the size of the pore openings, a small change in the latter could easily cause an order-of-magnitude change in the mass transfer rate.[6−8] It is therefore clear that structural changes in the surface layer with a thickness in the nanometer range may lead to the appearance of significant transport barriers for mass transfer. As a result, the permeability of these barriers may even determine the rate of molecular uptake. Recent development and improvement of the experimental techniques, such as atomic force microscopy and high-resolution electron microscopy,[10−12] which are capable of probing zeolite crystal surfaces, open the possibility to incorporate the knowledge of the real zeolite surface into computer simulations.

Similarly to the situation with the computer modeling of mass transfer through the crystal surface, the lack of suitable experimental methods has hindered experimental studies of the role of the external crystal surface in molecular uptake. Probably the most significant

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finding in this area is related to the observations of transport barriers on the external surface of zeolite crystals.[13−15] Although these observations have been made for a large number of different zeolite/adsorbate systems, they were mainly based on indirect results, such as the results of the analysis of adsorption/desorption curves obtained by classical uptake and zero-length column (ZLC) methods. A somewhat more direct approach to studying the role of the crystal surface in molecular uptake has become available only recently with the introduction of the interference microscopy technique in our laboratory. This technique is capable of monitoring intracrystalline concentration profiles for a selected zeolite crystal during molecular adsorption or desorption with an unprecedented spatial resolution. In the present work we demonstrate that the analysis of the profiles allows detailed elucidation of the role of surface defects in adsorption/desorption.[16−21] In particular, it will be shown that different types of defects may lead either to the occurrence of transport resistances on a crystal surface or to an enhancement of the adsorption/desorption rate due to the existence of cracks on the surface. MFI-type zeolites have been chosen as model systems for this work.

A better understanding of the role of the surface of zeolite crystals in mass transfer is extremely important in view of the persistent discrepancies between the values of intracrystalline diffusivities obtained by various experimental techniques.[1,5] The discrepancies are especially large between the diffusivities measured by the microscopic techniques, i.e., by such techniques as pulsed field gradient (PFG) NMR and quasi-elastic neutron scattering (QENS), which are capable of probing much smaller molecular displacements than the size of individual crystals, and by the classical uptake techniques, which measure overall adsorption/desorption. The apparent diffusivities determined by the classical methods will obviously be reduced if surface resistance to mass transfer is significant.

2. Materials and Methods

Materials. Two calcined samples of zeolite ZSM-5 with a Si/Al ratio around 40 and a mean crystal size of $50 \times 50 \times 140\ \mu m^3$ were used for the measurements. The samples were prepared from the same as-synthesized zeolite ZSM-5 following two different procedures:[22] while the first sample (i.e., the nonetched sample) was prepared by the calcination of the as-synthesized zeolite without any additional treatment, the second sample (i.e., the etched sample) was first subjected to the etching in an aqueous solution of HF with acetone, and only then calcined. Following the procedure suggested by Wloch (ref 22), the etching was carried out to remove the outer layers, which may contain various defects and impurities, from the zeolite crystal surface. The details of the sample preparations are described in ref 22. Isobutane (Aldrich, 99%) was used as an adsorbate.

Interference Microscopy Measurements. Interference microscopy is the only technique which allows monitoring intracrystalline concentration profiles of guests in microporous crystals with high spatial resolution. The detailed description of this technique may be found in refs 16−19. Briefly, the interference microscopy method is based on the change of the refractive index of porous crystals due to adsorption or desorption of guest molecules. The magnitude of the changes of the local refractive index during adsorption/desorption is expected to be proportional to that of the changes in the local adsorbate concentration. Using the assumption of such proportionality, direct monitoring of the dynamics of the integrals of the local concentration in the direction of light propagation becomes possible. The concentration integrals are recorded with a spatial resolution of $\sim 0.5 \times 0.5\ \mu m^2$.

For the measurements and the zeolite activation the zeolite sample (usually several dozens of crystals) was introduced into the specially made optical cell connected to the vacuum system. Prior to the measurements, the sample was activated by keeping it under high vacuum at 200 °C for over 12 h. The measurements of the concentration integrals during adsorption or desorption of isobutane were performed with a selected zeolite crystal at room temperature (25 C). By performing the measurements with several crystals, for each type of measurement it was verified that the results are reproducible. The adsorption (desorption) was initiated by a rapid (~20 s) change of the isobutane pressure in the cell from 0 to 10 mbar (from 10 to 0 mbar). After this initial change, the pressure in the cell was kept constant over the whole duration of the measurements. With each crystal the measurements were performed for two different crystal orientations with respect to the direction of observation. The change of crystal orientation was achieved by the cell vibrations generated by softly tapping the cell wall. Reliable performance of this procedure requires some practice to avoid displacing and therefore losing the chosen crystal among the others in the cell.

3. Results and Discussion

Internal Structure of the Crystals. Figures 1a,b and 2a,b show the images of typical ZSM-5 crystals from the nonetched and etched samples, respectively, for the two different crystal orientations. These images reveal the crystal shape and the hourglass structure, which are typical for the MFI-type crystals consisting of several constituents.[12,23−25] The nonlinear shape of the lines of the interference patterns (Figure 2a,b), which were produced by using the shearing mechanism of the interference microscope, further supports the assumption that these crystals are agglomerates of several components.[18,26] Similar interference patterns were observed in every crystal studied.

At present, the nature of the components and the reasons for their appearance in MFI-type crystals are not entirely clear. In most studies the existence of such components has been attributed to regular intergrowth effects.[23−25] This has led to the assumption that the

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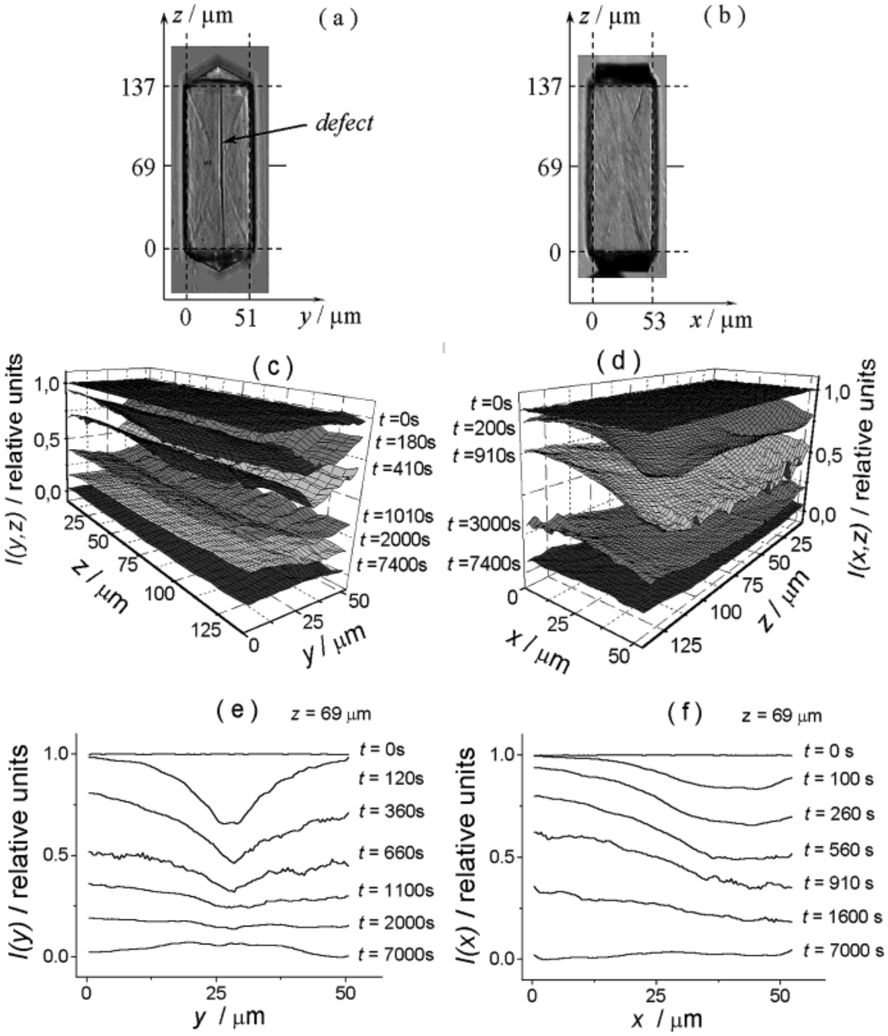

Figure 1. Microscopic images of the crystal and intracrystalline concentration profiles of isobutane recorded by interference microscopy during the desorption of isobutane in nonetched ZSM-5 crystals. The observation direction was perpendicular to the (*z*, *y*) plane in parts a, c, and e and perpendicular to the (*z*, *x*) plane in parts b, d, and f. The desorption was initiated by a rapid change of the isobutane pressure in the cell from 10 to 0 mbar. The concentration integrals $I = 1.0$ correspond to those measured under equilibrium with an isobutane pressure of 10 mbar. The *t* values shown in parts c−f indicate the time intervals after the start of desorption.

crystallographic directions are different for different constituents in the crystals. At the same time, recent results of an investigation by atomic force microscopy suggest that the difference between different constituents is related only to variations in the concentration of silanol groups.[12] Evaluating the atomic force microscopy data, the authors of ref 12 argue that the crystallographic directions of all constituents are the same.

In recent papers we have reported the results of interference microscopy studies of the influence of the internal structure of silicalite-1 crystals on the uptake of isobutane.[18,26] In particular, it was shown that the intersections between different constituents serve as mild barriers for intracrystalline transport. Comparison of the shapes of the measured profiles with those obtained by dynamic Monte Carlo (MC) simulations has allowed us to rule out, for the studied crystals, the possibility of a rapid uptake of isobutane through the internal intersections directly from the gas phase surrounding the crystals. The shape of the simulated profiles was found to be not particularly sensitive to the crystallographic orientations of the different constituents, which were also considered in ref 12. Hence, our conclusion about the role of the internal intersections in the molecular uptake can be assumed to be valid also for the case when the crystallographic orientations of all constituents are the same. This conclusion is in agreement with the results of ref 12, which suggest that the intersections are crystal regions with a high concentration of defects. These defects may be responsible for the mild transport barriers on the intersections, which were revealed in our previous studies.[18,26]

Defects on the External Surface of the Crystals. In addition to the hourglass structure, the crystal images in Figures 1a and 2a reveal linelike defects, which run along the *z* direction through the central part of the crystals. These features were observed in the majority of the studied crystals from both samples. It is important to note that in each particular crystal such a defect was usually detected only on a single crystal face (i.e., either on the (*z*, *x*) or on the (*z*, *y*) face). The role of this defect in the adsorption/desorption of isobutane has been clarified by the studies of the intracrystalline concentration profiles.

Intracrystalline Concentration Profiles. Figures 1c−f and 2c−f show the evolution of the intracrystalline

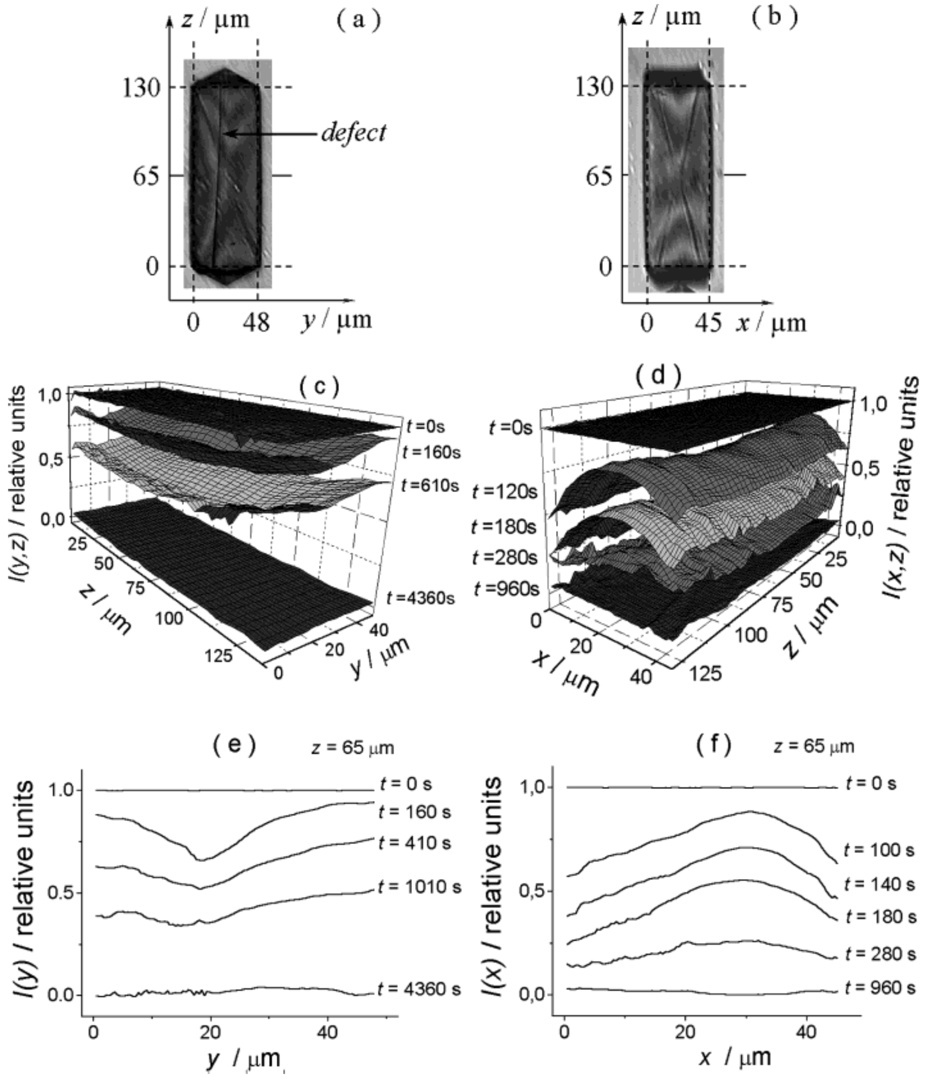

Figure 2. Same as Figure 1 for the etched ZSM-5 crystals.

concentration profiles in the course of isobutane desorption. While the c and d sections of the figures present 2-dimensional concentration profiles, sections e and f show profiles along the *x* or *y* direction in the central part of the crystals. The profiles in sections c and e reveal anomalous desorption patterns: in the middle part of the crystals the desorption proceeds faster than near the crystal edges. Comparison of the profiles in sections c and e of Figures 1 and 2 with the corresponding crystal images shows that the areas of fastest desorption are located around the above-discussed line-like defects. These defects obviously represent cracks, which protrude deeply into the crystal volume. The existence of these defects opens an additional route for isobutane adsorption/desorption, i.e., the adsorption/desorption from/to the gas phase through the crack surface. Two experimental findings suggest that the cracks penetrate approximately to the middle part of the crystal. The first one is the observation of the nonsymmetric profiles after the 90° change of the crystal orientation with respect to the face with the defect (Figures 1d,f and 2d,f). In particular, the profiles in Figures 1f and 2f show that the mean rates of desorption in the left (small *x* values) and in the right (large *x* values) parts of the crystals are different. Faster desorption occurs in the crystal parts containing the face where the crack was observed. The second finding is the fact that no cracks were observed on the crystal face opposite the one revealing the defect. Hence, the cracks obviously do not penetrate the whole width (depth) of the crystals. Instead, they stop somewhere in the middle part, halfway through the crystal.

The overall shape of the concentration profiles obtained for the crystals from the nonetched sample (Figure 1) is in striking contrast with the shape, which can be expected for desorption through the outer surface of the crystal assuming that the intracrystalline diffusion is the rate-determining process.[18,26] Indeed, we have not observed any pronounced concentration decrease near the crystal edges in the transient concentration profiles, which is to be expected in the latter case. This result suggests the existence of strong transport barriers on the crystal surface (excluding the surface of the cracks), which mainly determine the rate of adsorption/desorption. Experimental data suggesting the existence of transport barriers on the external surface of ZSM-5 crystals have been reported in a number of papers. It was shown in ref 14 that the fitting of the experimental uptake curves for *p*-ethyltoluene in ZSM-5 by the theoretical model requires the introduction of surface barriers. In another work, the coking of mesitylene in the sample of HZSM-5 was shown to create surface resistances.[13] Mesitylene molecules are too large to be adsorbed into the zeolite. Hence, the coking must have taken place on the crystal surface, resulting in the formation of surface barriers. Finally, a significant increase in the rate of the *n*-hexane uptake in the etched ZSM-5 sample in comparison to the nonetched one,[22] as observed in previous studies with crystals from the same synthesis, clearly signals the presence of surface transport barriers in the nonetched sample. The formation of these barriers can be attributed to the partial blockage of pore entrances by deposits from a saturated reaction mixture during the final stage of the synthesis.[22]

The concentration profiles along the *x* and *y* directions, which were recorded in the etched crystals during the adsorption (desorption) of isobutane, reveal increasing (decreasing) concentration integrals with decreasing distance from the crystal edges. Parts d and f of Figure 2 show examples of such profiles measured during desorption. The shape of the profiles in Figure 2d,f indicates that the influence of surface barriers on the rate of desorption has diminished and, consequently, the role of intracrystalline diffusion in desorption has increased in comparison with that of the nonetched sample. Comparison between the time scales of the profiles in Figures 1d,f and 2d,f indicates that as a result of the etching also the overall desorption rate has become larger. This observation is in qualitative agreement with the results obtained previously for the uptake of *n*-hexane.[22]

Measurement of the intracrystalline concentration profiles in crystals from the etched sample has shown that the strength of surface barriers in any particular crystal often increases with increasing number of adsorption/desorption cycles which were carried out with this crystal. The strengthening of the barriers has manifested itself in (i) flatter concentration profiles measured during adsorption/desorption and (ii) smaller overall rates of adsorption/desorption. Figure 2 provides an example of such observations. The flatter shape of the profiles near the crystal edges and the slower rate of the changes of the profiles during isobutane desorption for the (*z*, *y*) crystal orientation, in comparison with the (*z*, *x*) crystal orientation, clearly indicate the presence of stronger surface barriers for measurements with the former orientation. This is related to the fact that the measurements with the (*z*, *y*) orientation were performed after measurements with the (*z*, *x*) orientation. The strengthening of the surface barriers during the adsorption/desorption measurements may be related to the immobilization of adsorbate molecules (i.e., of isobutane and/or of impurities present in isobutane) on strong adsorption sites in a layer close to the crystal surface. Such immobilization may create additional steric hindrance for the nonimmobilized molecules leaving or entering the pore mouths. A similar strengthening of surface barriers in MFI-type crystals with increasing exposure time to adsorbate (mesitylene) has been reported in ref 13.

Fitting of the Experimental Concentration Profiles by the Results of MC Simulations. Figure 3 provides a comparison between the experimental profiles, which were recorded under the same conditions and with the same crystal as those in Figure 2f, and the corresponding profiles obtained by dynamic MC simulations. These simulations have been performed for the MFI-type crystals, which consist of the six constituents as discussed elsewhere.[12,18,24,26] To simplify the simulations, the surface of the crystals has been assumed to be free of transport barriers and cracks. This assumption was shown to be valid for the silicalite-1 crystals studied earlier.[18,26]

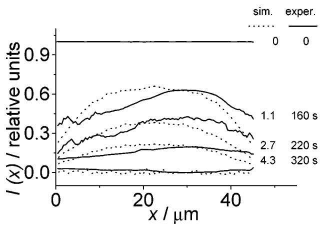

Figure 3. Intracrystalline concentration profiles of isobutane along the *x* direction for the ZSM-5 crystal shown in Figure 2a,b at different times after the start of desorption. The observation direction was perpendicular to the (*z*, *x*) plane, *z* = 65 μm. The concentration integrals *I*(*x*) were measured by interference microscopy (full lines) and were also obtained by dynamic MC simulations (dotted lines) assuming that there are no transport barriers and no cracks on the crystal surface. For the simulated profiles the time unit is 10^3 elementary diffusion steps. The details of the simulations are presented in ref 26.

It is seen in Figure 3 that, in general, the measured profiles are much flatter than the simulated profiles. This can obviously be explained by the influence of transport barriers on the external surface of the crystals experimentally studied. Also, the measured profiles reveal the shape, which is much less symmetric with respect to the middle part of the crystal in comparison with the perfectly symmetric one obtained by the simulations.

This suggests that desorption occurs through the crack surface (Figure 2a), in addition to desorption through the external crystal surface. Comparison of the measured and the simulated profiles allows an estimate of the intracrystalline diffusivity of isobutane.[26] Assuming equivalency between the profile measured after 160 s and the simulated profile after 1.1×10^3 elementary steps in Figure 3, the time of the elementary diffusion step used in the simulation can be estimated as $\tau = 160/1100 = 0.15$ s. It has to be noted that the value of τ would be slightly different if for the estimate the corresponding simulated and the measured profiles in Figure 3 for larger times were used. Since we have disregarded the surface defects in the simulations, this difference is not unexpected. Disregarding surface defects leads not only to the unperfect match between the shapes of the simulated and the measured profiles, but also to differences in the kinetics of desorption between the simulation and experiment. Comparison of the crystal dimensions in the (*x*, *y*) plane (45×45 μm^2) with that of the simulation lattice (60×60 (units of the elementary diffusion steps)^2) yields a value of $l = 45/60 = 0.75$ μm for the length of the elementary diffusion step in the simulations. The mean diffusivity can be estimated as[26]

$$D = \frac{1}{3}\frac{l^2}{6\tau}[1.0 + 0.36 + 0.11] \tag{1}$$

where the expression in the brackets and the factor 1/3 in the right part of the equation are introduced to take into account the diffusion anisotropy in the MFI-type zeolites. The channel system of the MFY-type zeolites consists of straight and zigzag channels.[27] The first two numbers in the brackets give the relative probabilities of the elementary diffusion step in the MC simulations along the directions of these channels. The ratio of these probabilities was assumed to be equal to the ratio of the corresponding diffusivities calculated for the straight and zigzag channels using transition-state theory.[28] The diffusion along the third direction, which coincides with the z direction in Figures 1 and 2, may take place only by a constant interchange of diffusing molecules between the straight and zigzag channels.[1] This results in a quite low diffusivity and, consequently, in a low probability for the elementary diffusion step used in the simulations for this direction. The latter probability is given by the third number in the brackets in eq 1. Using eq 1, we have obtained the value 0.3×10^{-12} m^2 s^{-1}. This value should only be considered as a lower limit for the mean diffusion coefficient of isobutane because the surface resistances were not taken into account in the simulations. In this relation also the influence of the crack in the crystal surface (Figure 2a) needs to be discussed. In contrast to the surface barriers, the crack leads to an acceleration of the adsorption rate, as discussed above. However, judging from the relatively small difference between the profiles in Figure 3 for the crystal parts with and without the crack (i.e., for the large and small values of x in Figure 3), its influence on the profiles is not significant. This influence was neglected for the purpose of our estimate. For the intracrystalline diffusivity of isobutane in silicalite-1 we have previously obtained a value of 1×10^{-12} m^2 s^{-1}, using interference microscopy data.[26] This value, as well as the isobutane diffusivities, which were measured in MFI-type crystals by techniques other than interference microscopy, are in good agreement with our present estimate of the lower limit for the diffusion coefficient of isobutane.[29−32]

Heat Effects during Interference Microscopy Measurements. When measuring transport diffusivities in zeolites, one has to consider the so-called heat effects.[1] These effects are related to the release (consumption) of heat due to adsorption (desorption) of guest molecules in zeolite crystals. As a result, the zeolite temperature may be expected to change. It is usually assumed that in a bed of loosely packed zeolite crystals the rate of the heat transfer between different zeolite crystals or between zeolite crystals and their surroundings is much smaller than that inside zeolite crystals. Under such conditions heat effects lead to a temperature change, which can be expected to be the same for different parts of any particular zeolite crystal due to fast intracrystalline heat transfer. There are two main consequences of such a temperature change for the kinetics of the adsorption/desorption process. First, the transient change of the zeolite temperature leads to a transient change of the equilibrium intracrystalline concentration of adsorbate. Second, the temperature increase or decrease can be expected to change the intracrystalline diffusivity of adsorbate molecules. Both phenomena would affect the adsorption/desorption kinetics. However, for the desorption from zeolite crystals into a vacuum usually only the second factor needs to be considered because the equilibrium intracrystalline concentration of adsorbate under vacuum remains close to zero and is practically unaffected by relatively small temperature changes due to heat effects. A simple estimate of the heat transfer rate for the system considered in the present study (see Appendix A) shows that the rate of radiation heat transfer is large enough to ensure essentially isothermal conditions. The same conclusion has been made more generally in refs 33 and 34 for the conditions of typical interference microscopy studies.

4. Concluding Remarks

In this paper we report the results of an interference microscopy study of the influence of defects on the external surface of ZSM-5 crystals on molecular adsorption/desorption. Interference microscopy was recently introduced in our laboratory for the investigation of intracrystalline concentration profiles during adsorption and desorption of adsorbates in zeolite crystals. Monitoring intracrystalline concentration profiles opens a new, direct way to study the role of surface defects in molecular uptake. Depending on their type, the defects on the crystal surface were shown to be able to increase or to decrease the rate of adsorption/desorption. The former is associated with the existence of an additional adsorption/desorption pathway, namely, with the adsorption/desorption through cracks in the crystal surface. The latter has its origin in the blockage or structural changes of the external crystal surface, leading to the appearance of surface barriers.

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Appendix A: Analysis of Heat Effects

Adiabatic Temperature Change. The maximum possible temperature change may be estimated from a straightforward heat balance, assuming no heat transfer to or from the surroundings.

From the equilibrium data for isobutane/silicalite-1[35] at around 300 K and 10 mbar, the loading is about 0.54

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mol/kg and the heat of adsorption is about 47.5 kJ/mol. Assuming an approximate value of 10^3 J/(kg K) for the heat capacity,[36] we obtain a value of about 26 K for the adiabatic temperature change for desorption to a vacuum. The actual temperature change will be substantially smaller than this for two reasons: (i) The zeolite crystals are in contact with the relatively massive cell wall, which will serve as a heat sink, thereby increasing substantially the "effective" thermal capacity. (ii) Heat will be exchanged with the surroundings by radiation and convection (although under vacuum the latter contribution will be minimal).

Heat Dissipation Rate. To estimate the rate of heat dissipation, we consider only the effect of radiation in accordance with the Stefan–Boltzmann law

$$\frac{\partial Q}{\partial t} = \epsilon\sigma A({T_0}^4 - T^4) \tag{A1}$$

where T and T_0 represent, respectively, the temperatures of the crystal and the surroundings, $\sigma = 5.6703 \times 10^{-8}$ W/(m^2 K^4) (Stefan–Boltzmann constant), ϵ is the emissivity (~0.8), and A is the external area of the crystal. Since $T \approx T_0$, the differential heat balance therefore yields

$$V\rho C_p \frac{\partial T}{\partial t} = \epsilon\sigma A({T_0}^4 - T^4) \approx 4\epsilon\sigma A {T_0}^3 (T_0 - T) \tag{A2}$$

where V, ρ, and C_p denote, respectively, the volume, density, and heat capacity of the crystal. With the initial condition $T(t) = T(0)$ at $t = 0$ (initial temperature change $T_0 - T(0)$) the solution is

$$\ln \frac{T_0 - T(t)}{T_0 - T(0)} = -\frac{t}{\tau}, \tag{A3}$$

where $\tau = V\rho C_p/4\epsilon\sigma A {T_0}^3$ is the time constant. Assuming $\epsilon = 0.8$, $A = 0.3 \times 10^{-7}$ m^2,[37] $T_0 = 297$ K, $V = 0.4 \times 10^{-12}$ m^3,[37] $\rho = 1.7 \times 10^3$ kg/m^3,[27] and $C_p = 10^3$ J/(kg K),[36] eq A3 yields $\tau = 4.6$ s, showing that the temperature difference will fall to a tenth of the initial value in about 10 s. Since the characteristic times for adsorption/desorption are thousands of seconds, we can safely assume that the intrusion of heat effects will be negligible.

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(36) Breck, D. W. *Zeolites Molecular Sieves—Structure, Chemistry and Use*; Wiley: New York, 1974.

(37) The crystal size was assumed to be 50 × 50 × 140 μm^3.