Influence of the Acid Sites on the Intracrystalline Diffusion of Hexanes and Their Mixtures within MFI-Zeolites

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The intracrystalline diffusivities and component loadings of mixtures of *n*-hexane and 2-methylpentane within silicalite-1 (crystal size 150 μm) and HZSM-5 (140 μm) have been measured at 433 K as a function of the *n*-hexane/2-methylpentane ratio in the gas phase (at constant total hydrocarbon pressure of 6.6 kPa) using the Positron Emission Profiling technique. Strong preferential adsorption of the linear alkane over the branched one has been observed in HZSM-5, while in silicalite only a slightly higher adsorption of *n*-hexane was observed. The diffusivities of both components in the mixtures decrease with increasing 2-methylpentane content and have been found to be approximately two times lower in HZSM-5 than those in silicalite. When the concentration of the branched hexane in the adsorbed phase becomes close to 3 molecules per unit cell, the influence of the acid sites on the diffusion of linear hexane diminishes compared to the influence of the blockage of the zeolite network with the slowly moving 2-methylpentane. The apparent activation energies of the diffusion for *n*-hexane and 2-methylpentane have been measured at temperatures between 393 K and 533 K under similar conditions. For *n*-hexane, these values were found to be very close in silicalite and ZSM-5: 18.5 ± 1.5 kJ/mol and 22 ± 2 kJ/mol, respectively. For 2-methylpentane the activation energies were found to be very high: 66 ± 6 kJ/mol and 72 ± 3 kJ/mol, respectively.

1. Introduction

Diffusion and adsorption of hydrocarbons in MFI-type zeolites are of great interest for already several decades. The main reason is that the MFI-zeolite catalysts are widely used in the industrial hydrocarbon conversion processes because of their high activity and selectivity. But the catalyst performance is strongly influenced by the diffusion of the reactant mixture.

A number of experimental and theoretical works has been done on the adsorption and diffusion of single components within zeolites,[1] and it has been accepted that the behavior of a component in multicomponent mixtures cannot be predicted from the behavior of a single component.[2–4] Under reaction conditions diffusion proceeds under the presence of other molecules (reactant/product), therefore, the investigation of the adsorption and diffusion of multicomponent mixtures is of vital importance.

Several experimental and theoretical studies have been dedicated to the investigation of binary mixtures of hydrocarbons[2,4,5] in silicalite-1, which is all-silica MFI-type zeolite without acid sites. However, the diffusion under reaction conditions takes place inside the catalyst containing Brønsted sites, which also might affect molecular transport of the reactant mixture components. So far, no studies on multicomponent mixtures have been made to establish a possible influence of the acid sites on the diffusion of binary mixture components.

However, there are some studies, which compare the diffusivities of single components in silicalite and HZSM-5.[6–8] Zikanova et al.[6] using a constant volume method observed that at temperatures between 303 and 423 K diffusion of benzene in HZSM-5 is twice as slow as in silicalite. These results are in a good agreement with those obtained by a frequency-response method:[8] at temperatures of 375–415 K the diffusivity of benzene was 2–3 times lower in the presence of acid sites than in silicalite. Later, Masuda et al.[7] studied the diffusion of aromatics (benzene, toluene, para-xylene) in MFI-type zeolites with different amount of acid sites at 423–723 K. They concluded that at low temperatures, the diffusivities decrease with increasing amount of acid sites and the activation energy of diffusion is close to the adsorption enthalpy value.

Here, we use the Positron Emission Profiling (PEP) technique. PEP is an in situ technique which allows simultaneous measurement of the diffusion and adsorption of single compounds or multicomponent mixtures.

In our experiments, we studied the adsorption and diffusion of *n*-hexane and 2-methylpentane and their mixtures in two MFI-type zeolites: silicalite and HZSM-5. Silicalite and HZSM-5 are the zeolites with the same framework structure, consisting of straight and zigzag channels with the intersections between them. Silicalite is a highly siliceous zeolite, which means that it does not contain any acid sites while HZSM-5 does. *n*-Hexane and 2-methylpentane represent the reactant/product system for the hydroisomerization reaction of *n*-hexane. This reaction is catalyzed by the noble metal (Pt) loaded zeolite, containing acid sites.

The main purpose of this study was to compare the behavior of linear and isohexanes and their binary mixtures in silicalite

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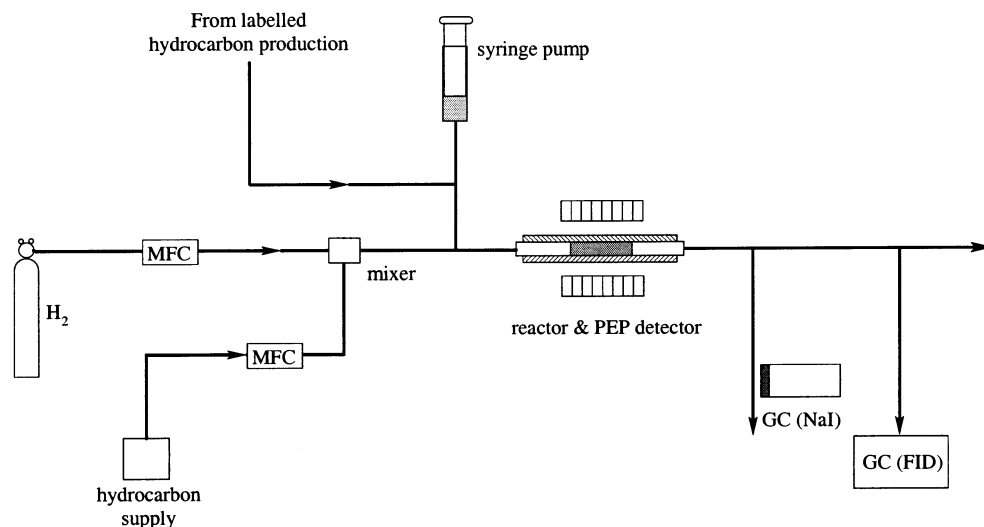‡ Accelerator Laboratory, Schuit Institute of Catalysis, Eindhoven University of Technology.

Figure 1. Scheme of the Positron Emission Profiling setup.

and HZSM-5. The experiments have been performed at 393 K and 533 K to prevent the occurrence of any reaction, which has been checked by chromatographic analysis of the outlet mixture composition. To exclude macropore diffusion, large crystals (150 μm of silicalite and 140 μm of HZSM-5) have been used without pelletizing.

2. Experimental Section

2.1 Experimental Setup. The PEP technique is a radio-chemical method using β^+-emitting isotopes. In our case ^{11}C-labeled hydrocarbons are used. The isotope ^{11}C is produced via irradiation of a nitrogen target with 12 MeV protons from the 30 MeV AVF Cyclotron of Eindhoven University of Technology.

Further, [11]CO is transferred to the setup for the radiolabeled hydrocarbon (*n*-hexane, 2-methylpentane) production via homo-logation reaction. Detailed information can be found in ref 9. After the separation of the reaction products, the hydrocarbon of interest (*n*-hexane or 2-methylpentane in our case) is collected into the syringe (Figure 1) and introduced into the fixed bed reactor, containing zeolite (silicalite or HZSM-5).

The radioactive nuclei decay with a half-life time of 20.4 min, emitting a positron. The positrons annihilate with electrons from the surrounding matter, yielding pairs of γ-photons. Nine pairs of detector banks for the detection of the γ-photons are mounted above and below the reactor. Because the photons are emitted in exactly opposite directions, the position of the decay is determined by coincident detection of a pair of photons along the cylindrical axis of the reactor. In this way, a space and time-resolved profile of the injected radiolabeled alkanes can be obtained (Figure 2) with a time resolution of 1 s and a spatial resolution of 3 mm. A detailed description of the detection system can be found in ref 10.

In the tracer-exchange PEP experiments (TEX-PEP), ^{11}C-labeled hydrocarbons are continuously introduced in a flow of nonlabeled molecules, passing through the catalytic reactor. The exchange process between ^{11}C labeled and nonlabeled molecules can be monitored. When the equilibrium between radiolabeled molecules in the gas and adsorbed phase has been reached, the flow of radiolabeled hydrocarbons is switched off, and the reexchange process takes place. The reexchange part of the TEX-PEP profiles is used to get needed information such as the constant of adsorption and diffusivity of the given hydro-carbon. The detailed description of the TEX-PEP experiments has been published earlier.[11]
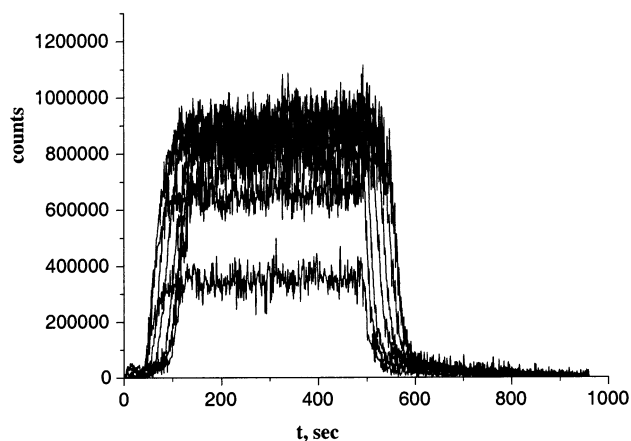

Figure 2. Experimental data: TEX-PEP profiles for 8 positions, *n*-hexane in silicalite, $T = 413$ K.

The constant flow of nonlabeled hydrocarbons in hydrogen as a carrier gas was fed into the PEP-reactor. The mixture composition has been set using a Bronkhorst CEM system. The *n*-hexane and 2-methylpentane used in the experiments have been obtained from Aldrich (99.9% purity) and were used as received.

The experiments to determine the component maximum loading were performed using a Balzers Quadrupole mass-spectrometer system QMG-420. The zeolite sample was exposed to the hydrocarbon/hydrogen stream at 433 K until the equi-librium between the gas and adsorbed phase has been reached. The corresponding masses were monitored with the mass-spectrometer (2 for hydrogen and 69 for the hydrocarbon). After the equilibration, the flow of the hydrocarbon was switched off, and desorption started. The amount of the hydrocarbon desorbed was measured. The loading has been taken as a saturation one when further increase in the partial pressure of the hydrocarbon did not result in the increase of the adsorbed concentration.

2.2 Zeolite Samples. The silicalite-1 sample used has been kindly supplied by Shell Research and Technology Center, Amsterdam. Scanning electron microscopy showed that it consisted of regular coffin-shaped crystals with an average size of $150 \times 50 \times 30$ μm.

HZSM-5 has been kindly provided by Dr. L. Gora from Delft University. The average crystal size was determined with scanning electron microscopy and turned out to be $140 \times 30 \times 30$ μm. Si/Al ratio was 40 in the initial gel composition, yielding

Intracrystalline Diffusion of Hexanes

J. Phys. Chem. B, Vol. 106, No. 37, 2002 **9561**

the concentration of the Brønsted sites $[H^+] = 7.5 \times 10^{-6}$ mol/g $\pm 2.5 \times 10^{-6}$ mol/g. This concentration has been determined by temperature-programmed isopropylamine decomposition.[12] This is possible because it is known that one molecule of isopropylamine is decomposed per Brønsted site, thus, the acid site concentration is equal to the amount of isopropylamine decomposed per gram of zeolite. The bed porosity was determined to be $\epsilon = 0.44$.

Prior to experiments zeolites have been activated in a hydrogen stream for 2 h at 723K.

3. Modeling

A typical TEX-PEP profile (response from the PEP-detector in time) is presented on Figure 2. To interpret the data provided by the TEX-PEP experiments, an appropriate mathematical model is used to describe the reexchange process in the zeolite reactor bed. A detailed description of the model and more information about its application can be found in ref 2. Below, we will briefly describe the modeling of the experiments.

In the model used, it is assumed that the transport of molecules occurs via convection and axial diffusion in the bed, adsorption/desorption at the crystal surface and diffusion inside the pores of the crystals. Zeolite crystals are considered to have spherical shape with radius $R = 25$ μm, defined as the radius of the sphere having the same external surface area-to-volume ratio as the coffin shaped zeolite crystals.

Mass transfer through the bed, resulting from diffusion, convection and mass transfer to the zeolite crystals, can be described by following equation

$$\frac{\partial c_{gas}}{\partial t} = D_{ax}\frac{\partial^2 c_{gas}}{\partial z^2} - v_{int}\frac{\partial c_{gas}}{\partial z} + \frac{3(1-\epsilon)}{R\epsilon}N_c \quad (1)$$

In this equation c_{gas} is a gas-phase concentration in the catalyst bed, D_{ax} is the axial diffusion coefficient, calculated from the molecular diffusion coefficient of the component, v_{int} the interstitial velocity, which is defined as

$$v_{int} = \frac{v_{sup}}{\epsilon} \quad (2)$$

in which v_{sup} is the gas flow velocity in the empty reactor. R, D_{ax}, v_{int}, and ϵ are fixed parameters, which can be determined or estimated.

The term N_c stands for the mass flux through the boundary of the zeolite crystal and is determined by diffusion to the crystal boundary because diffusion in the zeolite micropores is assumed to be the rate-limiting step for the adsorption/desorption at the crystal boundary

$$N_c = -D_c\frac{\partial c_x}{\partial x}\Big|_{x=R} \quad (3)$$

where c_x is an adsorbed concentration inside the particle, D_c is the intracrystalline diffusivity. Diffusion through the laminar fluid film surrounding the particles can be neglected, as this process is much faster than diffusion inside the zeolite crystal. Mass transport in the pores of the zeolite crystal is only determined by diffusion

$$\frac{\partial c_x}{\partial t} = D_c\left[\frac{\partial^2 c_x}{\partial x^2} + \frac{2}{x}\frac{\partial c_x}{\partial x}\right] \quad (4)$$

In this equation x is the radial coordinate in the crystal. The
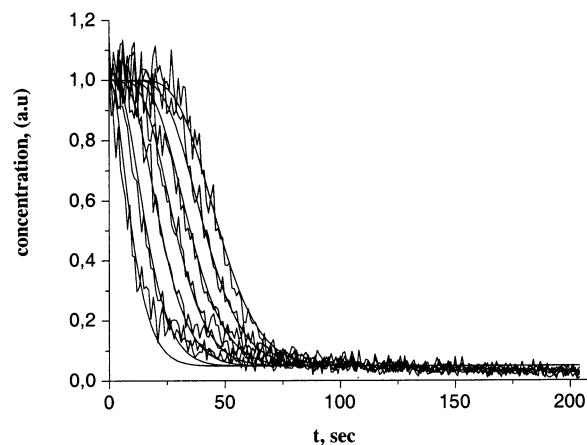

Figure 3. Experimental data fitted by the model: n-hexane in silicalite, $T = 413$ K.

random orientation of the crystals inside the reactor allows to consider the micropore diffusion as an isotropic process,[2] even though the diffusion in silicalite is known to be anisotropic.[13–15]

The boundary condition at the center of the particle is obtained from the symmetry reasons

$$\frac{\partial c_x}{\partial x}\Big|_{x=0} = 0 \quad (5)$$

The adsorbed concentration at the crystal boundary is proportional to the gas-phase concentration

$$c_x(R, z, t) = K_a \times c_{gas}(z, t) \quad (6)$$

where z is the coordinate along the catalyst bed, and K_a is the adsorption equilibrium constant.

At the beginning of the tracer reexchange process the system is in equilibrium, so the initial conditions are

$$c_{gas}(z, t) = c_0 \quad (7)$$

$$c_x(x, z, t) = K_a \times c_0 \quad (8)$$

c_0 is the injected initial tracer concentration.

The equations described above are solved using the numerical method of lines.[16] Solving the model yields values for the concentration at each bed and crystal gridpoint. As the PEP detector measures the total concentration of labeled molecules in a certain section of the catalyst bed, volume averaging must be applied to simulate the response. Fitting the modeled concentration profiles to the measured ones yields a value of the unknown parameters such as the adsorption constant K_a and intracrystalline diffusivity D_c. An example fit of the experimental data is shown in Figure 3.

4. Results and Discussion

In this section the results on the binary mixtures concerning adsorption and diffusion in silicalite and HZSM-5 are presented. Comparison between these zeolites provides information about the effect of the component interactions with the acid sites.

The single component diffusion and adsorption in these two zeolites are discussed in order to determine the influence of the Brønsted sites on n-hexane and 2-methylpentane separately.

4.1 Adsorption and Diffusion of 2-Methylpentane/n-Hexane Mixtures in HZSM-5 and Silicalite. Diffusivities and loadings of n-hexane and 2-methylpentane in their mixtures with different ratios between the components (total hydrocarbon
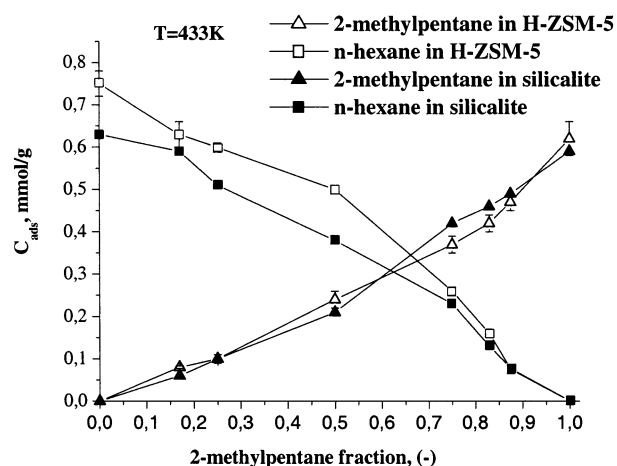
Figure 4. Loadings of mixture components in both MFI-type zeolites as a function of 2-methylpentane fraction in the gas phase.

TABLE 1: Loadings of Single Components in Silicalite and HZSM-5 at 433 K

	n-hexane (mmol/g)		2-methylpentane (mmol/g)	
zeolite	6.6 kPa	c^{max}	6.6 kPa	c^{max}
HZSM-5	0.75	1.1 ± 0.2	0.62	0.74 ± 0.04
silicalite	0.63	1.2 ± 0.2	0.59	0.75 ± 0.02

pressure has been kept constant p = 6.6 kPa) have been measured in silicalite and HZSM-5 at 433K.

4.1.1 Adsorption. The loadings of the components in silicalite and HZSM-5 are shown in Figure 4. The adsorbed concentration of n-hexane in HZSM-5 is higher than in silicalite. This result should be expected from the presence of the acid sites, since the enthalpy of n-hexane adsorption in HZSM-5 was reported to be higher than in silicalite.[17]

F. Eder,[17] who studied adsorption of 2-methylpentane and n-hexane in MFI-type zeolites, found that in HZSM-5 there are 2 molecules of n-hexane adsorbed per acid site, while isoalkane molecules are unable to form an adsorption complex of two molecules with the acid site. Indeed, in our study, 2-methylpentane loadings in mixtures in HZSM-5 are very close to those in silicalite (Figure 4).

The loading of n-hexane in mixtures is somewhat higher than it might be as if it were proportional to its partial pressure (Figure 4). On the contrary, the 2-methylpentane loading is lower. This indicates stronger preferential adsorption of n-hexane over isohexane in their mixtures in HZSM-5 than in silicalite.

In the earlier experimental and CBMC simulation studies[2,18] of n-hexane/isohexane mixtures in silicalite, a slight preferential adsorption of linear alkane over the branched one has been observed. CBMC simulations[18] have shown that n-hexane can be situated everywhere inside silicalite micropores, whereas for isohexane, it is more suitable to be located in the channel intersection because of entropy reasons. Consequently, 2-methylpentane is being pushed out from silicalite by n-hexane. In fact, in HZSM-5 the situation for n-hexane appears to be even more favorable, because 2 molecules of n-hexane can be adsorbed on the acid site under the same pressure conditions.[17] As a result, the linear alkane has a higher packing efficiency.

Table 1 shows the adsorbed concentrations of pure components at the partial pressure used. In silicalite, the amount of n-hexane is just slightly higher than the one of isohexane, whereas in HZSM-5 due to the interactions with the acid sites the linear alkane is obviously better adsorbed than 2-methyl-pentane.

The maximum loadings of each component have been measured using a mass-spectrometer (section 2). The values found for the alkanes in both zeolites confirm our assumption (Table 1). n-Hexane, indeed, has a sorption capacity approximately equal to 7 molecules per unit cell, which is in a fair agreement with other studies[17,19,20] whereas 2-methylpentane maximum loading is close to 4 molecules per unit cell, which is equal to the amount of the channel intersections per unit cell of MFI-type zeolites. As it was mentioned before, for isoalkanes, the intersections of the zigzag and straight channels are the most sterically and energetically suitable locations. To obtain loadings higher than 4 molecules per unit cell, the isoalkanes must find the energetically less favorable positions, most probably in the channels. This requires very high pressures.[18]

The experimental study of the single component adsorption of n-butane and isobutane with the volumetric method in silicalite and HZSM-5 leads to similar conclusions.[21] Valion et al.[21] found that, under identical conditions the n-butane loading was 1.5−2.0 times higher than that of isobutane in the temperature range 273−413 K. In HZSM-5, the complete saturation with butanes was reached at lower pressures because of the stronger interactions with the acid sites. For n-butane, the maximum loading measured was about 8 molecules per unit cell, whereas for isobutane, the inflection in the isotherm was observed at adsorption of 4 molecules per unit cell.

Therefore, we conclude that in HZSM-5 zeolite, interaction with the acid sites results in the preferential adsorption of linear hexane over the branched one in their mixtures because of the n-hexane higher packing efficiency and its ability to form a bimolecular complex with the acid site.

4.1.2 Diffusion. Figure 5 shows the diffusivities of the components in the zeolites as a function of the 2-methylpentane fraction in the gas phase. The diffusivities of both hydrocarbons linearly decrease with increasing content of the branched hexane in both MFI-type zeolites (Figures 5 and 6).

In HZSM-5, the diffusion of alkanes is approximately two times slower than in silicalite. Obviously, the presence of the acid sites is affecting molecular transport via stronger interactions with the n-hexane molecules. A similar effect of Brønsted sites on the single component diffusion of aromatics was observed in MFI-type zeolites with different concentration of acid sites.[6−8] The frequency response technique gives similar results for n-butane and isobutane diffusion in silicalite and HZSM-5:[21] the diffusivity of both components was approximately twice as low in the zeolite containing acid sites, with the diffusion of isobutane being significantly slower compared to n-butane.

In the present study of binary mixtures, the diffusivity of the fast component (n-hexane) in HZSM-5 is influenced by two factors: the presence of slow 2-methylpentane molecules and by the interaction with acid sites. As long as the concentration of the branched hexane does not exceed a critical value, the effect of the Brønsted sites is dominating.

A behavior similar to that of n-hexane is observed for 2-methylpentane (Figure 6). Indeed, with increasing 2-methyl-pentane gas phase concentration (which means the increasing loading inside zeolite pores), its diffusivity decreases in both zeolites. In HZSM-5, the diffusivity of 2-methylpentane is also approximately two times lower than in silicalite at any fraction of 2-methylpentane. Therefore, the presence of the Brønsted sites noticeably decreases the diffusivities of both hexanes, probably because of stronger interactions between the diffusants and the acid sites, which causes the increased holding time at the adsorption site.
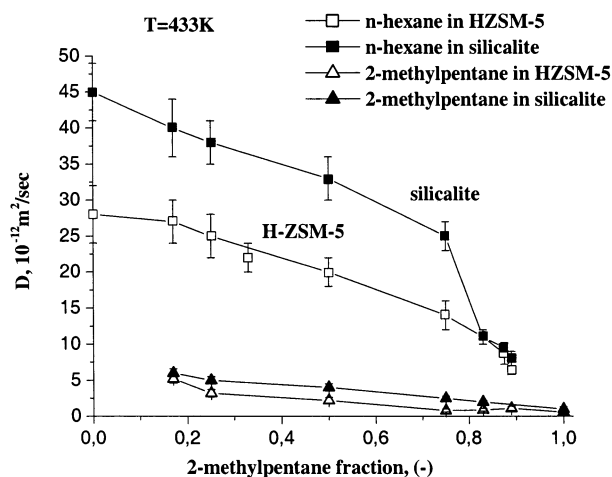
Intracrystalline Diffusion of Hexanes

J. Phys. Chem. B, Vol. 106, No. 37, 2002 **9563**

Figure 5. Diffusivities of mixture components in both MFI-type zeolites as a function of 2-methylpentane fraction in the gas phase.
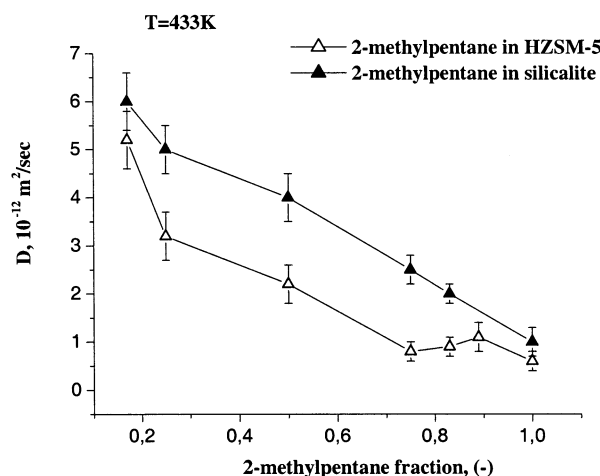

Figure 6. Diffusivities of 2-methylpentane only in mixtures in both MFI-type zeolites as a function of 2-methylpentane fraction (enlarged picture from Figure 5).

As soon as the concentration of 2-methylpentane in the gas-phase reaches a certain value (about 80% of the total concentration under the conditions of our study), the influence of the acid sites on the *n*-hexane diffusivity is not dominant anymore in comparison with the pore occupation with slow moving 2-methylpentane.

Figure 7 shows the dependence of the diffusivities of both components versus the concentration of adsorbed 2-methylpentane in terms of molecules per unit cell. The diffusivities of *n*-hexane in silicalite and HZSM-5 become equal when the concentration of 2-methylpentane reaches approximately 2.7 molecules per unit cell.

In the case of 2-methylpentane itself, the diffusivity in silicalite becomes very close to the value in HZSM-5 when the loading reaches approximately 2.75 molecules per unit cell (Figure 7).

In an earlier investigation of binary mixtures of linear and monobranched hexanes in silicalite,[2] we have shown that the zeolite pore network blockage occurs when the concentration of the branched alkane (2-methylpentane) exceeds 2.7 molecules per unit cell. From Monte Carlo simulations,[18] it is known that monobranched molecules such as 2-methylpentane or 3-methylpentane, due to their structure, prefer to occupy the intersections between straight and zigzag channels in MFI-type zeolites. From the crystallographic zeolite structure[22] it is known that the silicalite (or HZSM-5) unit cell contain four intersections.
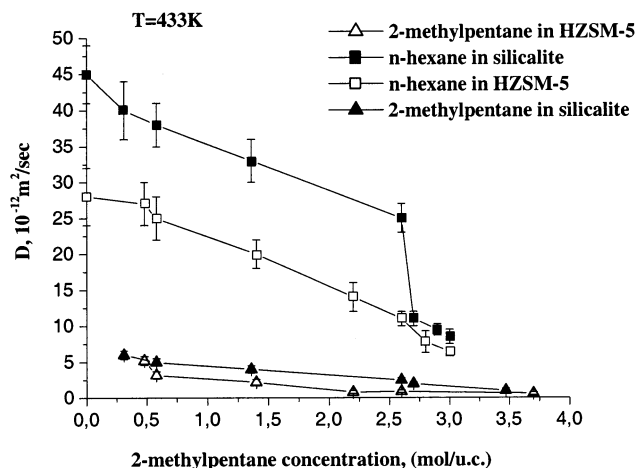

Figure 7. Diffusivities of mixture components in both MFI-type zeolites as a function of 2-methylpentane loading.

Therefore, the diffusivity of *n*-hexane in silicalite sharply decreases when approximately three of four intersections are occupied by slow 2-methylpentane. (We are grateful to the Reviewer who informed us that percolation theory would predict that to happen when ~3.1 molecules are trapped in the intersections. This agrees with our observations within the experimental accuracy.)

From Figure 7, it is clear that when the 2-methylpentane loading increases further, the *n*-hexane diffusivity in silicalite becomes close to that in HZSM-5 and continues to decrease. Probably, the reason is that the influence of adsorbed 2-methylpentane, whose diffusivity is 10 times lower, on *n*-hexane is stronger than the influence of the acid sites, which causes the only two-times decrease in the diffusivity. Indeed, in silicalite *n*-hexane molecules move very fast compared to those in HZSM-5, but as soon as 2-methylpentane molecules appear the diffusion of linear alkane slows down, and at the moment when a significant part of the intersections is blocked by isohexane, *n*-hexane molecules are trapped inside zigzag or straight channels. As a result, *n*-hexane molecules cannot freely diffuse between the channels. Because the diffusion of 2-methylpentane is significantly slower, the diffusivity of *n*-hexane in silicalite drops till the same value as in HZSM-5. A further decrease in the diffusivities with increasing isohexane fraction in both zeolites is caused by the pore network blockage with 2-methylpentane molecules.

Our observations are confirmed by a recent experimental study of diffusion in silicalite of binary mixtures of alkanes (*n*-heptane, *n*-octane) and aromatics (ortho- and meta-xylenes).[4] Masuda et al.[4] found the same effect of a slower component (aromatics) to decrease the diffusion of the fast component (alkane) via pore connection blockage.

They have also measured that the diffusion of the slow component is not affected,[4] which is in agreement with studies of methane-xenon mixtures.[23] On the contrary, our study shows the decrease in the diffusivities of 2-methylpentane in both MFI-type zeolites with increasing loading (Figure 5). Most probably, this effect has not been observed in the other studies because at the similar temperatures the hydrocarbon pressure used was low (13.3 Pa in[4]), whereas in our experiments (6.6 kPa) the loading was high enough to obtain more than half of the intersections blocked by 2-methylpentane.

Thus, from the experiments performed on the binary mixtures of 2-methylpentane/*n*-hexane in HZSM-5 and silicalite, we can conclude that in HZSM-5 both components experience the
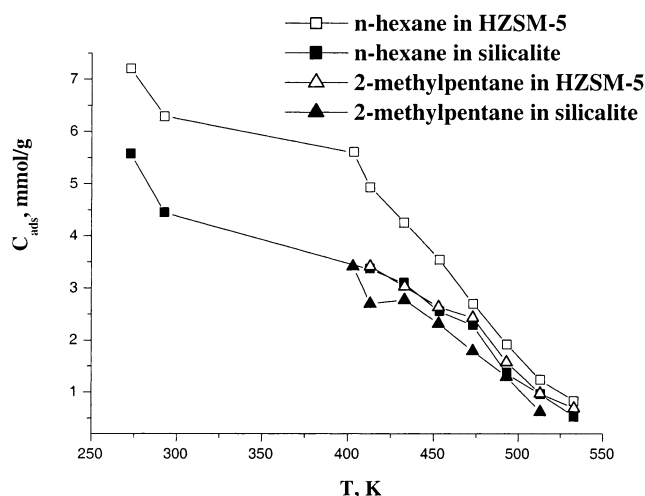
Figure 8. Loadings of hexanes measured at different temperatures in silicalite and HZSM-5.

TABLE 2: Diffusion Parameters for *n*-Hexane

	E_a, kJ/mol	
zeolite	TEX-PEP	literature
silicalite	18.5 ± 1.5	$16-19$
HZSM-5	22.0 ± 2.0	$20-24$

influence of two factors: interactions with the acid sites, and the concentration of 2-methylpentane. Interaction with the acid sites causes preferential adsorption of *n*-hexane over 2-methylpentane and a decrease in the diffusion of both components by a factor of 2. Increased loading of slow 2-methylpentane diminishes the influence of the acid sites in HZSM-5, so that the diffusivity of *n*-hexane in HZSM-5 becomes equal to that in silicalite and decreases almost until the value of 2-methylpentane.

4.2 Adsorptive and Diffusive Properties of Single Components in HZSM-5 and Silicalite. From the experiments with mixtures, we concluded that there is an influence of the interaction with the acid sites on both components. Therefore, the experiments with the single components have been performed in order to determine possible differences in the diffusion parameters such as the activation energy between silicalite and HZSM-5. The loadings of *n*-hexane and 2-methylpentane in these two zeolites have also been measured at temperatures between 373 K and 533 K with an interval of 20 degrees. The hydrocarbon pressure was taken identical to that in the binary mixture experiments (6.6 kPa). The values of the apparent activation energies have been obtained.

4.2.1 n-Hexane. Figure 8 shows the loadings of *n*-hexane in both zeolites at the temperature range used. Under similar conditions, the adsorbed concentration of *n*-hexane is higher than that of 2-methylpentane, especially at lower temperatures. As has been discussed in section 4.1.1, the interaction with the Brønsted sites results in higher enthalpy of adsorption and allows to form a bimolecular complex with the acid site. This leads, under similar conditions, to a higher loadings of *n*-hexane in HZSM-5 than in silicalite.

From the temperature dependence of the diffusivity of *n*-hexane in both zeolites, the activation energies have been calculated (Table 2). Arrhenius plots are shown in Figure 9. The data obtained in this work are compared with values found in the literature.

The results show that the values of the activation energy measured with the TEX-PEP technique are very close for both
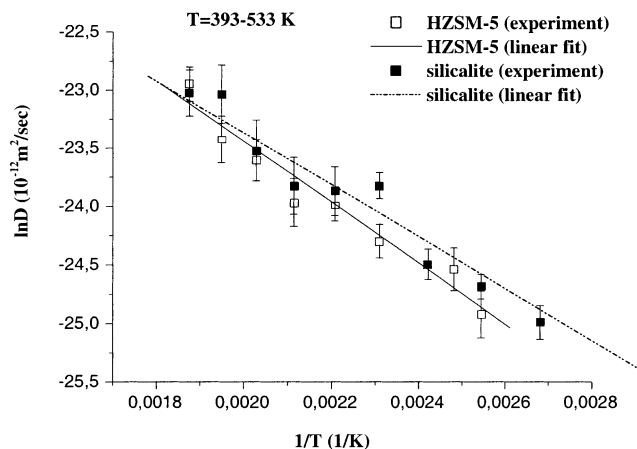

Figure 9. Arrhenius plots for diffusivities of *n*-hexane in silicalite and HZSM-5.

zeolites. Because of the limited accuracy of the TEX-PEP technique, it is difficult to establish a certain value as a difference in the activation energies of *n*-hexane in HZSM-5 and silicalite (Table 2). The experiments performed with the mixtures at 433K (section 4.1.2), ensure us that the difference between the activation energies of *n*-hexane diffusion in HZSM-5 and silicalite provides a two times decrease in the diffusivity of *n*-hexane at 433K in the presence of the acid sites.

Valion et al.[21] have measured the activation energy of diffusion for *n*-butane in silicalite and HZSM-5 with the frequency-response method. They found values of 10.7 and 13.1 kJ/mol respectively, which resulted in approximately a double decrease in the *n*-butane diffusivity in the presence of the Brønsted sites. This confirms our observations that there is an effect of the interactions with the acid sites on the activation energy of alkane diffusion in MFI-type zeolites, but the contribution is not very significant.

Our data on the activation energy of *n*-hexane are in a good agreement with the values provided by other techniques (Table 2). The activation energy of *n*-hexane diffusion in HZSM-5 equal to 24 kJ/mol has been obtained by the frequency response method.[24] The constant volume method provided 20 kJ/mol,[25] which is identical to the activation energy of diffusion for *n*-hexane of 20 ± 2 kJ/mol measured in this work.

The value of the activation energy for silicalite, provided by TEX-PEP, is confirmed by other methods, such as the ZLC-method and the Square wave method,[26,27] (Table 2). Techniques such as membrane permeation and TEOM (tapered element oscillating microbalance), provided a somewhat higher value of the activation energy of *n*-hexane: 34.7 kJ/mol[28] and 38 kJ/mol,[29] respectively. In the membrane permeation technique very high loadings up to 8 molecules per unit cell were used, which can explain the discrepancy with other techniques. The value provided by Zhu et al.[29] is the corrected activation energy. The diffusivities were measured at different conditions (partial pressures) and the loadings were up to 5.25 molecules per unit cell, so the corrected diffusivities were an order of magnitude lower than those measured in this work. On the contrary, PFG NMR[30] provided a significantly lower activation energy of 7 ± 2 kJ/mol with the diffusivities significantly higher than reported here. This is a well recognized problem of the discrepancies between the macro- and microscopic measurements. The authors of a novel macroscopic ultrahigh vacuum technique Multitrack[31] claimed that one of the reasons for lower values of the diffusivities measured by macroscopic methods is the diffusion resistance caused by the presence of a carrier gas. The

Intracrystalline Diffusion of Hexanes

J. Phys. Chem. B, Vol. 106, No. 37, 2002 **9565**

TABLE 3: Diffusion Parameters for 2-Methylpentane

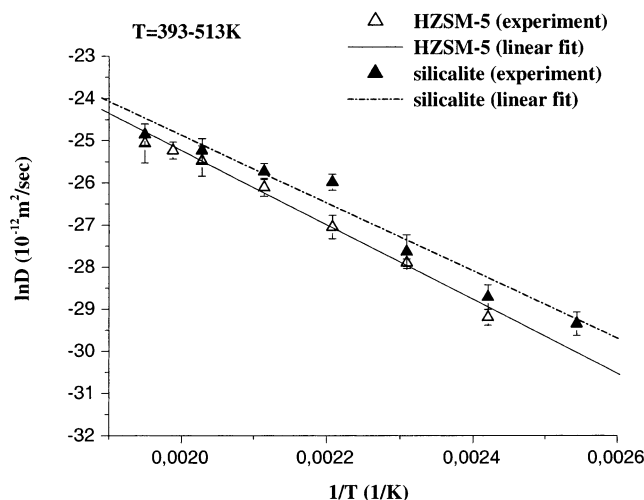| zeolite	E_a, kJ/mol		D(m^2/sec), $T = 423$ K			
	TEX-PEP	literature	grav.[32]	grav.[33]	TAP[34]	PEP
silicalite	66 ± 6	46, [32]	2×10^{-12}			1.1×10^{-12}
HZSM-5	72 ± 3	24, [34]; 36, [33]		9×10^{-13}	1×10^{-12}	4×10^{-13}

Figure 10. Arrhenius plots for diffusivities of 2-methylpentane in silicalite and HZSM-5.

diffusivities obtained by the frequency response (FR) technique[14] are also essentially higher than those from TEX-PEP. The FR method is able to distinguish the diffusion in straight and sinusoidal channels, yielding the corresponding corrected (according to the Darken equation) diffusion coefficients. In TEX-PEP experiments, mean diffusivities are measured. In the modeling of the experimental data, some approximations are made (see section 3): the zeolite is considered to be of a spherical shape and the micropore diffusion is described as an isotropic process, therefore, the mean intracrystalline diffusion coefficient is determined from the experiments.[2] Despite the discrepancies described above, the activation energy of *n*-hexane diffusion in the straight channels of silicalite (21.7 ± 2) derived from FR experiments[14] is close to the apparent activation energy reported here.

One would expect an increase in the activation energy of diffusion in the presence of the acid sites. Because of the interactions of alkanes with the Brønsted sites the molecules have to overcome a certain energy barrier to detach from the acid site and hop to the next one. A comparison between the data obtained by different techniques for silicalite and HZSM-5 supports this presumption, but the difference in the values is not that significant that this can be established with an absolute certainty with the aid of the techniques available.

4.2.2 2-Methylpentane. Arrhenius plots for the diffusion of 2-methylpentane in silicalite and HZSM-5 are presented in Figure 10. In silicalite, the diffusivities have been measured at 393−513 K and in HZSM-5 at 413−533 K, because of experimental limitations.

It turned out that, at elevated temperatures, the signal-to-noise ratio in the measurement is too low, because the adsorbed concentration of 2-methylpentane is low, especially on silicalite. Thus, we were not able to measure the diffusivity and the loading of 2-methylpentane in silicalite at 533 K. This is also the reason for the increased experimental error.

Activation energy values that are being referred to for 2-methylpentane in silicalite and HZSM-5 are both significantly higher than those for *n*-hexane, which results in an order of

magnitude difference in the diffusion coefficients for these compounds. This in agreement with the earlier studies of linear and mono- and di-branched alkanes in MFI-type zeolites.[32,33] The commonly accepted explanation for the high activation energies of diffusion for the isoalkanes in MFI-type zeolites is that due to its higher critical diameter, isoalkanes experience a steric hindrance to their diffusion.

Similar to *n*-hexane, we find the best estimated value for the apparent activation energy of 2-methylpentane diffusion in HZSM-5 to be higher than in silicalite (Table 3). This is in agreement with the findings of the frequency-response technique for isobutane diffusion[21] in MFI-type zeolites. The activation energy of isobutane was measured to be 1.2 kJ/mol higher in HZSM-5. The PEP technique does not allow us to be that accurate in this case, but in combination with the data on mixture experiments (section 4.1.2) it is possible to claim that the alkane interactions with the Brønsted sites result in the increase in the activation energy of diffusion.

The values of the activation energy for 2-methylpentane in both zeolites, measured here are significantly higher than those measured by other techniques (Table 3). Gravimetric measurements[32] provide an activation energy of 46 kJ/mol on silicalite, which is even higher than on HZSM-5 measured by Xiao and Wei[33] with the same method ($E_a = 36$ kJ/mol) and by Keipert and Baerns[34] with a transient technique ($E_a = 24$ kJ/mol).

The discrepancies between the values of the activation energies provided by different authors can be attributed to the different alkane partial pressures used in the experiments. There are some theoretical and experimental studies, which indicate a significant concentration dependence of intracrystalline diffusion.[32,33,35−37] Coppens et al.[37] have shown with Monte Carlo simulations for ZSM-5 zeolite that the diffusivity can drop by a factor of 10 when the occupancy is close to the saturation. In this work, we performed our experiments under hydrocarbon partial pressure of 6.6 kPa, which is higher than typically used in the gravimetric and volumetric measurements.

Figure 8 shows the loadings of 2-methylpentane and *n*-hexane in both zeolites in the temperature interval used to determine the activation energy of diffusion. The loading of 2-methylpentane in our experiments reaches 0.5−3.5 molecules per unit cell with the loadings in HZSM-5 slightly higher than in silicalite at the same temperatures. The maximum loadings of 2-methylpentane in silicalite and HZSM-5 were measured to be 0.75 $\pm$ 0.02 mmol/g and 0.75 $\pm$ 0.04 mmol/g respectively, which is approximately equal to 4.2 molecules per unit cell (Table 1). Under the partial pressure and temperatures used, the loadings of the zeolites were up to 80% of the saturation, which is higher compared to other techniques. Indeed, in the transient experiments with the TAP reactor[34] a pulse of a very small amount of molecules is made on the zero-occupancy zeolite, so the influence of the loading on diffusion can be excluded. It is also important to note that the experimental conditions (partial pressure) used in the gravimetric experiments[32,33] to determine the diffusion parameters such as activation energy are not specified. Therefore, it is actually not very correct to compare these values (Table 3), obtained under different conditions.

Unfortunately, it is not possible to make a definite conclusion from the literature data about the relation between the influence

of the acid sites and the activation energy of 2-methylpentane diffusion. Our experimental data indicate that in HZSM-5 the best estimated value of the diffusion activation energy for 2-methylpentane is slightly higher than that in silicalite, but because of the higher experimental error for 2-methylpentane experiments in silicalite, we cannot unambiguously conclude this.

5. Conclusions

The diffusion and adsorption of linear/branched hexane mixtures and single components in silicalite and HZSM-5 have been studied with the PEP technique. Comparison between these zeolites leads to the following conclusions:

1. The interaction with the acid sites causes a decrease in the diffusivities of both alkanes. The values of the activation energy of diffusion for both alkanes were found to be slightly higher in HZSM-5.

2. In HZSM-5 the diffusivity of *n*-hexane in the mixtures with 2-methylpentane is influenced by two factors: (a) interaction with the acid sites which decreases the diffusivity; (b) the presence of 2-methylpentane, which has a ten-times lower diffusivity. As soon as the loading of isohexane exceeds 2.7 molecules per unit cell, the effect of the Brønsted sites on the diffusion becomes negligible, so that the diffusivities in silicalite and HZSM-5 are equal and decrease further with increasing 2-methylpentane content.

3. Interaction with the acid sites causes a preferential adsorption of the linear hexane over the branched one from their mixtures, probably because of the ability of *n*-hexane to form a bimolecular complex with one acid site and its higher packing efficiency. On the contrary, 2-methylpentane loadings in mixtures in silicalite and HZSM-5 are very close because it is supposed that they can only occupy the channel intersections.

References and Notes

(1) Kärger, J.; Ruthven, D. M. *Diffusion in Zeolites and other Microporous Solids*; John Wiley & Sons: New York, 1992.

(2) Schuring, D.; Koriabkina, A. O.; de Jong, A. M.; Smit, B.; van Santen, R. A. *J. Phys. Chem. B* **2001**, *105*(32), 7690−7698.

(3) Krishna, R.; Vlught, T. J. H.; Smit, B. *Chem. Eng. Sci.* **1999**, *54*, 1751−1757.

(4) Masuda, T.; Fujikata, Y.; Ikeda, H.; Hashimoto, K. *Micropor. Mater.* **2000**, *38*, 323−332.

(5) Paschek, D.; Krishna, R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3185−3191.

(6) Zikanova, A.; Bülow, M.; Schlodder, H. *Zeolites* **1987**, *7*, 115−118.

(7) Masuda, T.; Fujikata, Y.; Nishida, K.; Hashimoto, K. *Micropor. Mater.* **1998**, *23*, 157−167.

(8) Shen, D.; Rees, L. V. C. *Zeolites* **1991**, *11*, 666−671.

(9) Cunningham, R. H.; Mangnus, A. V. G.; van Grondelle, J.; van Santen, R. A. *J. Mol. Catal. A: Chem.* **1996**, *107*, 153−158.

(10) Mangnus, A. V. G.; van IJzendoorn, L. J.; de Goeij, J. J. M.; Cunningham, R. H.; van Santen, R. A.; de Voigt, M. J. A. *Nucl. Instr. Methods B* **1995**, *99*, 649−652.

(11) Schumacher, R. R.; Anderson, B. G.; Noordhoek, N. J.; de Gauw, F. J. M.; de Jong, A. M.; de Voigt, M. J. A.; van Santen, R. A. *Micropor. Mater.* **2000**, *35*−*36*, 315−326.

(12) Juskellis, M. V.; Slanga, J. P.; Roberrie, T. G.; Peters, A. W. *J. Catal.* **1992**, *138*, 391−394.

(13) Hong, U.; Kärger, J.; Kramer, R.; Pfeifer, H.; Seiffert, G.; Müller, U.; Unger, K. K.; Lück, H.-B.; Ito, T. *Zeolites* **1991**, *11*, 816.

(14) Song, L.; Rees, L. V. C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*(4), 649−657.

(15) Geier, O.; Vasenkov, S.; Lehmann, E.; Kärger, J.; Schemmert, U.; Rakoszy, R. A.; Weitkamp, J. *J. Phys. Chem. B* **2001**, *105*, 10 217−10 222.

(16) Schiesser, W. E. *The Numerical Method of Lines*; Academic Press: San Diego, 1991.

(17) Eder, F. *Thermodynamics and Siting of Alkane Sorption in Molecular Sieves*; Twente: University of Twente, Ph.D. Thesis, 1996.

(18) Vlugt, T. J.; Krishna, R.; Smit, B. *J. Phys. Chem. B* **1999**, *103*, 1102−1118.

(19) Wu, P.; Debebe, A.; Ma, Y. *Zeolites* **1983**, *3*, 118.

(20) Anderson, J.; Foger, K.; Mole, T.; Rajadhyaksha, R.; Sanders, J. *J. Catal.* **1979**, *58*, 114.

(21) Valyon, J.; Onyestyk, Gy.; Rees, L. V. C. In *Proceedings of 2nd Pac. Basin. Conference* **2000**, 482−486.

(22) Baerlocher, Ch.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types* 2001, Elsevier.

(23) Jost, S.; Bar, N.-K.; Fritzshe, S.; Haberlandt, R.; Kärger, J. In *The Proceedings of 12th International Zeolite Conference*; 1999, 149−152.

(24) Bülow, M.; Schodder, H.; Rees, L. V. C.; Caro, J.; Richards, R. In *The Proceedings of 7th International Zeolite Conference* 1986, Tokyo.

(25) Hashimoto, K.; Masuda, T.; Murakami, N. In *Zeolite Chemistry and Catalysis*; Jacobs, P. A., Jaeger, N. I., Kubelkova, L., Wichterlova, B., Eds.; Elsevier Science Ltd.: New York, 1991; pp 477−484.

(26) van den Begin, N.; Rees, L. V. C. Caro, J.; Bülow, M. *Zeolites* **1989**, *9*, 287.

(27) Eic, M.; Ruthven, D. M. *Stud. Surf. Sci.* **1989**, *49*, 897.

(28) Millot, B.; Methivier, A.; Jobic, H.; Moueddeb, H.; Dalmon, J. A. *Micropor. Mater.* **2000**, *38*, 85−95.

(29) Zhu, W.; Kapteijn, F.; Moulijn, J. A. *Micropor. Mater.* **2001**, *47*, 157−171.

(30) Hienk, W.; Kärger, J.; Pfeifer, H.; Datema, K. P.; Nowak, A. K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3505.

(31) Nijhuis, T. A.; van den Broeke, L. J. P.; ven de Graaf, J. M.; Kapteijn, F.; Makkee, M.; Moulijn, J. A. *Chem. Eng. Sci.* **1997**, *52*(19), 3401−3404.

(32) Cavalcante, C. L.; Ruthven, D. M. *Ind. Eng. Chem. Res.* **1995**, *34*, 185.

(33) Xiao, J.; Wei, J. *Chem. Eng. Sci.* **1992**, *47*, 1143.

(34) Keipert, O. P.; Baerns, M. *Chem. Eng. Sci.* **1998**, *53*, 3623.

(35) Chen, N. Y.; Degnan, T.; Smith, C. *Molecular Transport and Reaction in Zeolites*; John Wiley & Sons: New York, 1994.

(36) Coppens, M.-O.; Bell, A. T.; Chakraborty, A. K. *Chem. Eng. Sci.* **1999**, *54*, 3455−3463.

(37) Coppens, M.-O.; Bell, A. T.; Chakraborty, A. K. *Chem. Eng. Sci.* **1998**, *53*, 2053−2061.