

# Novel Model Explaining Toluene Diffusion in HZSM-5 after Surface Modification

Shourong Zheng, Hiroaki Tanaka, Andreas Jentys,\* and Johannes A. Lercher

*Institut für Technische Chemie II, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching, Germany*

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The diffusivities of toluene in HZSM-5 zeolites before and after silylation by chemical liquid deposition of tetraethoxysilane were studied using the frequency response method. Silylation did not lead to variations in the equilibrium amount of toluene adsorbed in the zeolite. Two diffusion processes are identified in both materials and tentatively assigned to the diffusion of toluene in the straight and sinusoidal channels of the zeolites. The difference in toluene diffusivities is associated with the tortuosity of the diffusion pathways in the sinusoidal channels and connected transport barriers. Toluene diffusivities in both channels depend on the toluene loading. This is attributed to variations in the strength of the bonding induced by varying degrees of the interaction of toluene with the acid sites of the zeolite. Silylation of the zeolite leads to a decrease in toluene diffusivities in the straight and sinusoidal channels of the zeolites. In addition, the relative importance of transport in the sinusoidal channels increases after the modification, while the total uptake remains unaffected. In contrast to earlier interpretations invoking narrowing pores, the effect of surface modification could be associated for the first time with arbitrary blocking of pore entrances, thus enhancing the tortuosity of possible diffusion pathways.

## Introduction

Zeolites based on the MFI structure such as HZSM-5 have attracted great interest, because of their pronounced para selectivity in isomerization, disproportionation, and alkylation reactions of methyl- and ethyl-substituted benzenes.<sup>1–3</sup> Because the diffusivities of products and reactants, which have minimum kinetic diameters similar to the minimum pore openings of ZSM-5, are crucial parameters for controlling the shape selectivity, numerous papers addressing sorption and transport of aromatic molecules such as benzene, toluene, and xylenes in ZSM-5 zeolites have been published.<sup>4,5</sup> A wide variety of experimental techniques and theoretical approaches to study diffusion processes including pulsed-field-gradient NMR (PFG NMR),<sup>4,5</sup> quasielastic neutron scattering (QENS),<sup>6,7</sup> tracer exchange,<sup>8</sup> zero-length column,<sup>9,10</sup> uptake-rate measurement followed by FT-IR<sup>11,12</sup> and gravimetry,<sup>13,14</sup> the frequency response (FR) method,<sup>15,16</sup> and simulation<sup>17,18</sup> were applied to this problem. Typically, the self-diffusivity is determined with PFG NMR and QENS, while uptake measurements are used to observe transport diffusivity. Conceptually, the difference between them is that transport diffusivity is determined under nonequilibrium conditions, while self-diffusivity is obtained under equilibrium conditions. Transport diffusivity can be related to the intracrystalline diffusivity by applying the Darken equation.<sup>19</sup> Significant discrepancies, however, have been reported for the same diffusion processes determined by different techniques.<sup>4</sup>

Typically, as-synthesized HZSM-5 zeolites show only a minor shape selectivity in reactions of substituted benzene molecules, which is generally attributed to the presence of unselective acid sites located on the external surface and in the pore mouth region of the zeolites as well as to slightly too large pore openings of HZSM-5 zeolites.<sup>20,21</sup> To achieve enhanced para selectivity, postsynthesis modification of zeolites is necessary. The deposition of an inert silica layer on the external surface of zeolites applying chemical vapor deposition (CVD)<sup>22–24</sup> or chemical

liquid deposition (CLD)<sup>25,26</sup> has been shown to be one of the most effective approaches to tailor the external surface of zeolites in order to obtain stable and shape-selective catalysts. This type of modification leads to a combination of two beneficial effects, i.e., a passivation of the acid sites located on the external surface and in the pore mouth region, and modification of this pore entrance.

In principle, silylation effects of HZSM-5 zeolites can be assessed by studying the diffusion of molecules with kinetic diameters comparable to the size of the pores. A successful narrowing of pore openings of zeolites will result in a significant hindrance for the diffusion of aromatic molecules with relatively larger diameters, such as *o*-xylene.<sup>27</sup> The influence of the modification of the external surface on the diffusivities of aromatic molecules with relatively small diameters, such as benzene, toluene, and *p*-xylene, has been seldom addressed in detail.<sup>28</sup>

In this contribution, the sorption and diffusion of toluene in HZSM-5, modified by chemical liquid deposition of tetraethoxysilane (TEOS), was studied by the frequency response method. The influence of silylation on the diffusivities of toluene was related to the structural properties of the zeolites before and after silylation in order to explain the enhanced shape selectivity of the modified zeolite.

## Experimental Section

**Materials.** HZSM-5 zeolite with a silica–alumina ratio of 45 and a particle size of 3  $\mu\text{m}$  was used as the parent material. The modification was carried out applying chemical liquid deposition of TEOS according to the following procedure. First, 2 g of zeolite was suspended in 50 mL of hexane and heated to reflux under stirring. Then, 0.3 mL of TEOS (equal to 4 wt %  $\text{SiO}_2$ ) was added into the mixture and the mixture was kept under reflux conditions for 1 h. Hexane was removed by evaporation, and the sample was calcined at 773 K in dry air

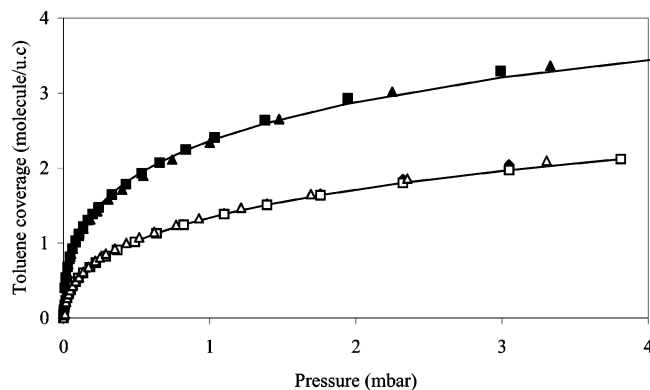
for 4 h. The parent and modified zeolites are referred to as HZ and HZM, respectively. The effects of the modification on the concentration of the acid site distribution in the zeolite were described previously.<sup>29</sup>

**Adsorption of Toluene.** The adsorption isotherms and the differential heats of adsorption of toluene in the zeolite samples were measured in a modified SETARAM TG-DSC 111 instrument. Approximately 15 mg of sample was pressed into wafers, broken into small platelets, and charged into the quartz crucible used in the TG-DSC system. The sample was activated by heating to 823 K with an increment of 10 K/min for 1 h in a vacuum ( $p < 10^{-6}$  mbar). After activation, the temperature of the sample was stabilized at 373 or 403 K. Toluene was introduced into the closed system in small doses and allowed to equilibrate with the zeolite until further pressure decrease and mass increase were not observed. The toluene pulses were repeated until toluene pressure reached 14 mbar. The increase in the mass of the sample and the heat flux during the adsorption process were collected simultaneously.

**Diffusion Measurements by the Frequency Response Method.** The diffusivities of toluene in the parent and silylated zeolites were measured using the frequency response method.<sup>16,30</sup> Approximately 30 mg of zeolite was carefully dispersed on several layers of glass wool in a quartz tube to avoid the bed-depth effects.<sup>31</sup> The sample was activated at 823 K under vacuum (pressure below  $10^{-7}$  mbar) for 1 h. Toluene with partial pressures between 0.05 and 1.5 mbar was introduced into the system at 373 or 403 K. After the sorption equilibrium was established, the volume of the system was modulated by magnetically driven plate sealed with bellows, which resulted in a square-wave perturbation of the volume ( $\pm 1\%$ ) in a frequency range between 0.001 and 1 Hz.<sup>32</sup> The response of the pressure to the volume perturbation was recorded with a Baratron pressure transducer (MKS 16A11TCC).

The measurement of diffusion coefficients by the frequency response method is based on a perturbation of the sorption equilibrium by a modulation of the pressure resulting from the periodic change (square wave) of the volume of the closed chamber.<sup>15</sup> When a periodic volume modulation is applied to an ideal gas in a closed system, the pressure of the gas varies at the same frequency and with the same function (e.g., sine wave, square wave) as the volume perturbation. In the presence of a microporous solid (sorbing the molecules), the change in the pressure leads to a variation in the amount adsorbed. Delays in establishing the adsorption/desorption equilibrium are related to mass transport effects assuming that the adsorption process itself is not the rate-determining step in the equilibration kinetics. More specifically, the pressure changes during periodic variations of the pressure result from two effects: (i) During the periodic pressure variation, the solid adsorbs (or desorbs) molecules from the gas phase leading to a lower amplitude in the pressure compared to the empty cell. (ii) The diffusion of the sorbate molecules in (or out) of the micropores delays the time necessary to achieve the new pressure equilibrium, which leads to a phase difference between the pressure responses of the empty system and the system containing the sorbent. It should be emphasized that the effects measured under such circumstances always might include all possible transfer steps, i.e., the transport of the molecules from the gas phase to the surface of the molecular sieve, the pore entering process, and the diffusion into the channels.<sup>33</sup>

The characteristic parameters of the frequency response experiment, i.e., the phase lag and amplitude, are obtained experimentally from the pressure response during the volume



**Figure 1.** Isotherms of (■, □) HZ and (▲, △) HZM at 373 K (filled symbols) and 403 K (open symbols).

perturbations at different frequencies using Fourier transformation.<sup>34</sup> Typically, the characteristic functions of the frequency response method are described by the following equations:

$$\text{in phase: } (P_B/P_Z) \cos \Phi_{Z-B} - 1 = K\delta_c \quad (1)$$

$$\text{out of phase: } (P_B/P_Z) \sin \Phi_{Z-B} = K\delta_s \quad (2)$$

$$\delta_c = (1/\eta)[(\sinh \eta + \sin \eta)/(\cosh \eta + \cos \eta)] \quad (3)$$

$$\delta_s = (1/\eta)[(\sinh \eta - \sin \eta)/(\cosh \eta - \cos \eta)] \quad (4)$$

$$\eta = (\omega L^2/2D)^{1/2} \quad (5)$$

$\Phi_{Z-B}$  is the difference between the phase lags in the presence and absence of the zeolite,  $P_B$  and  $P_Z$  are the relative amplitudes of the pressure during the volume change in the absence and in the presence of the zeolite,  $\omega$  is the angular frequency of the volume modulation,  $D$  is the diffusion coefficient, and  $L$  is the diameter of zeolite crystals.  $\delta_c$  and  $\delta_s$ , which are functions of the diffusion coefficient, are known as the in-phase and out-of-phase characteristic functions, respectively.  $K$  is a constant related to the gradient of the sorption isotherm at the equilibrium pressure  $p_e$ .<sup>15</sup>

$$K = (RT_0/V_e)(dQ_e/dp_e) \quad (6)$$

where  $T_0$  is the temperature,  $V_e$  is the system volume,  $Q_e$  is the equilibrium amount sorbed, and  $p_e$  is the equilibrium partial pressure. The in-phase and out-of-phase functions obtained from the experimental measurements over the frequency range studied were fitted to obtain the diffusion coefficients using a model with two individual diffusion processes under isothermal conditions given in eqs 7 and 8.<sup>35</sup>

$$\text{in phase: } (P_B/P_Z) \cos \Phi_{Z-B} - 1 = K_H\delta_{c,H} + K_L\delta_{c,L} \quad (7)$$

$$\text{out of phase: } (P_B/P_Z) \sin \Phi_{Z-B} = K_H\delta_{s,H} + K_L\delta_{s,L} \quad (8)$$

where the indices H and L denote the fast and slow diffusion processes, respectively. In principle, the diffusion process with the maximum out-of-phase characteristic function at higher frequency is indicative of a higher diffusion coefficient.

## Results

The sorption isotherms of toluene in the parent and silylated zeolites, shown in Figure 1, could be well described by the Langmuir–Freundlich model:<sup>13</sup>

$$Q = \frac{Q_0 b p^m}{1 + b p^m} \quad (9)$$

where  $Q$  denotes the amount of toluene adsorbed at a pressure  $p$ ;  $Q_0$  is the maximum amount of toluene adsorbed. The constants  $Q_0$ ,  $b$ , and  $m$  obtained by fitting the experimental data are listed in Table 1.

The intracrystalline diffusion coefficients of toluene in the parent and silylated zeolites at different toluene loadings were obtained by correcting the transport diffusion coefficients, determined by the frequency response method, using the Darken equation:<sup>19</sup>

$$D_0 = D \frac{\partial \ln Q}{\partial \ln p} \quad (10)$$

where  $D_0$  denotes the intracrystalline diffusion coefficient of toluene,  $D$  is the transport diffusion coefficient, and  $Q$  is the amount of toluene adsorbed at a partial pressure  $p$ .

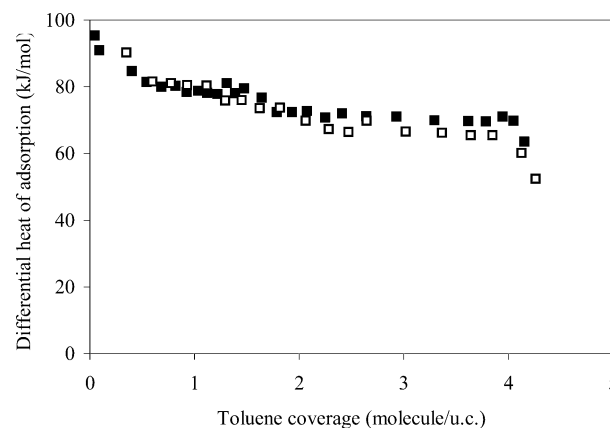
The differential heats of adsorption as a function of the toluene coverage determined at 373 K for the parent and silylated zeolites are compared in Figure 2. For both samples the heats of adsorption showed a similar dependence on the coverage of toluene. In the region of toluene loadings below 0.5 molecules per unit cell (mol./u.c.), the differential heats of adsorption decreased from 100 to 80 kJ/mol. At toluene loadings between 0.5 and 1.6 and between 2 and 4 mol./u.c., constant heats of adsorption of 80 and 70 kJ/mol, respectively, were observed for both zeolite samples, while at toluene loadings above 4 mol./u.c. a sharp decrease in the heats of adsorption was observed.

The characteristic functions of the frequency response experiment during toluene adsorption with an equilibrium partial pressure of 0.6 mbar in the parent and silylated zeolites are shown in Figures 3 and 4. Acceptable fitting of the experimental data was only possible assuming two contributions to the overall transport process; hence two maxima of the out-of-phase characteristic function were observed.<sup>36</sup>

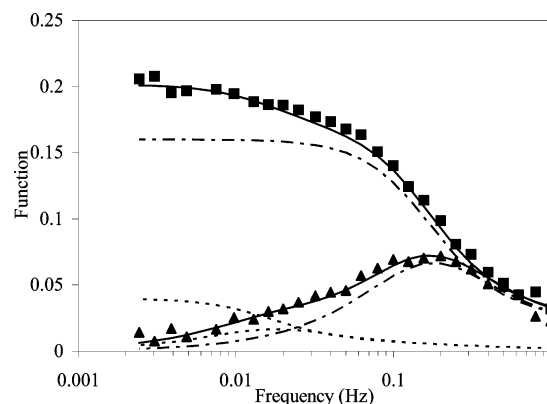
The amount of molecules diffusing through the pores of the sample during the pressure modulation in the frequency response experiments is characterized by  $K$ . For the toluene diffusion studied at a partial pressure of 0.6 mbar, the  $K$  values for the diffusion process with high ( $K_H$ ) and low diffusivity ( $K_L$ ) were 0.32 and 0.11 for HZ and 0.225 and 0.225 for HZM, respectively. This indicates that for the parent material a larger number of molecules were involved in the transport process with the higher diffusivity, while after the modification an equal number of molecules were involved in both diffusion processes. The dependencies of the intracrystalline diffusion coefficients for the two diffusion processes  $D_H$  and  $D_L$  at 373 and 403 K on the toluene loading are shown in Figure 5 for HZ and in Figure 6 for HZM. Silylation led to a decrease in the diffusivities by a factor of 4 for  $D_H$  and 2 for  $D_L$  at all temperatures. In both samples the intracrystalline diffusivity determined at 373 and 403 K increased with increasing toluene loading in the zeolites and remained approximately constant at toluene loadings higher than 2 and 1.2 mol./u.c., respectively, while the ratios of  $K_H$  to  $K_L$  were independent of toluene loading for both zeolites.

## Discussion

**Toluene Adsorption in the Zeolites.** For toluene adsorption in ZSM-5 type zeolites three possible locations were reported: (i) intersections between the straight and sinusoidal channels, (ii) straight channels, and (iii) sinusoidal channels. For both



**Figure 2.** Heats of adsorption of toluene in HZ (□) and HZM (■) at 373 K.

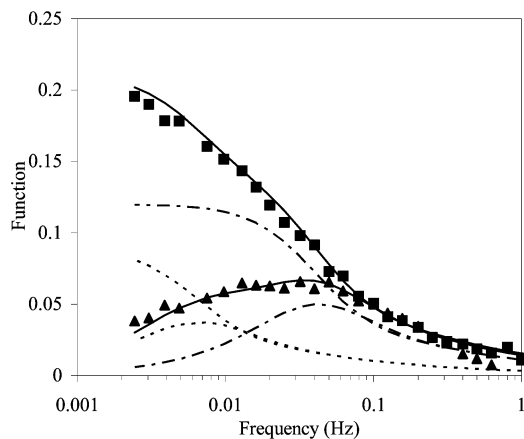


**Figure 3.** FR spectra of toluene diffusion in HZ at 373 K and toluene pressure of 0.6 mbar. Experimental data of (■) in-phase and (▲) out-of-phase characteristic functions. Theoretical fitting using (—) two-process model, (···) slow diffusion process, and (— · —) fast diffusion process.

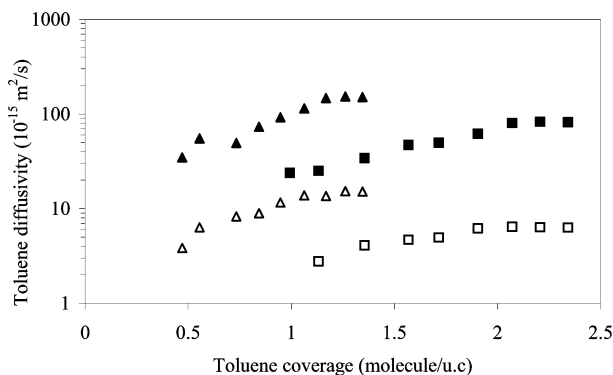
**TABLE 1: Parameters of Isotherms**

	HZ		HZM	
	373 K	403 K	373 K	403 K
$Q_0$	13.6	6.5	13.3	6.3
$b$	0.21	0.26	0.22	0.30
$m$	0.38	0.47	0.39	0.51

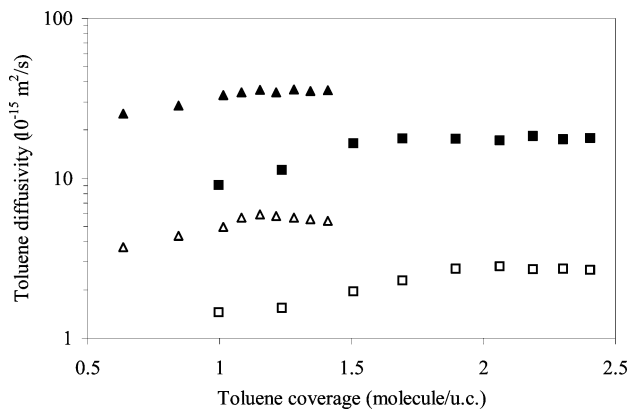
zeolite samples the heat of adsorption sharply decreased from 100 to 80 kJ/mol at loadings below 0.5 mol./u.c., revealing the presence of a minor fraction of strongly (probably Lewis) acidic sorption sites. These sites are most likely related to extraframework Al oxide species.<sup>37</sup> Equally, for both zeolite samples the heats of adsorption at toluene loadings below 1.6 mol./u.c. were 10 kJ/mol higher compared to toluene loadings between 2 and 4 mol./u.c. The concentration of Brønsted acid sites in these samples is 1.6 sites per unit cell.<sup>29</sup> Therefore, the additional contribution of 10 kJ/mol observed in the heat of adsorption at low loadings can be directly related to the hydrogen bonding interaction of toluene with the SiOHAl groups, which were in good agreement with the results of Thamm.<sup>38</sup> Toluene molecules preferentially occupy the intersections of the zeolite channels<sup>39</sup> at toluene loadings below 2 mol./u.c. and interact with the bridging hydroxyl groups via hydrogen bonding interaction at toluene loadings below 1.6 mol./u.c., which also implies that most of the acid sites are located in the intersections of the zeolites. Also, at toluene loadings between 2 and 4 mol./u.c. constant heats of adsorption were observed, which indicates that in this range toluene molecules are adsorbed at intersections



**Figure 4.** FR spectra of toluene diffusion in HZM at 373 K and toluene pressure of 0.6 mbar. Experimental data of (■) in-phase and (▲) out-of-phase characteristic functions. Theoretical fitting using (—) two-process model, (···) slow diffusion process, and (— · —) fast diffusion process.



**Figure 5.** Dependence of diffusivities of toluene in HZ on molecule loading at (■, □) 373 and (▲, △) 403 K. Filled symbols denote the fast diffusion process and open symbols the slow diffusion process.



**Figure 6.** Dependence of diffusivities of toluene in HZM on molecule loading at (■, □) 373 and (▲, △) 403 K. Filled symbols denote the fast diffusion process and open symbols the slow diffusion process.

without further apparent contribution of the direct interaction with the bridging hydroxyl groups (Brønsted acid sites) to the heat of adsorption. The number of intersections per unit cell in ZSM-5 type zeolites is 4, and therefore, at toluene loadings above 4 mol./u.c. all available sorption sites at intersections were occupied, which is reflected in a sharp decrease in the heats of adsorption.

The dimensions of the straight channels, the sinusoidal channels, and the intersections are  $5.6 \times 5.3$ ,  $5.5 \times 5.1$ , and  $8.9$  Å, respectively.<sup>5</sup> As the kinetic diameter of toluene molecules ( $5.8$  Å) is close to the dimensions of the straight or

sinusoidal channels, the repulsive forces between toluene molecules and the pore walls are more dominant compared to positions in the intersections. Simulation results<sup>40,41</sup> also showed that the potential energy of toluene molecules located in the straight or sinusoidal channels is higher compared to that in the intersections of HZSM-5 zeolite.

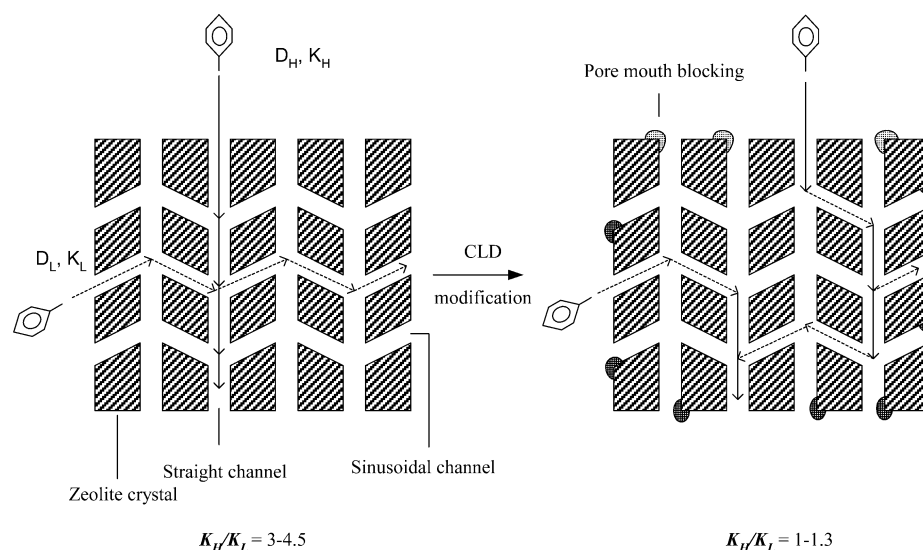
**Toluene Diffusion in the Zeolites.** Two independent processes for toluene diffusion in ZSM-5 were observed by Rees et al.<sup>42</sup> and were explained by toluene diffusion in the straight and sinusoidal channels of ZSM-5. Alternatively, the diffusion of toluene molecules with the methyl group oriented in front or to the back was proposed for the two processes.<sup>42</sup> However, the diffusivities of toluene usually observed are only 2–3 times higher compared to those of benzene,<sup>43</sup> which cannot show an orientation effect.<sup>44,45</sup> On the basis of the large difference between the diffusivities of the two processes (about 10 times for the parent material), we favor the assignment of the two diffusion processes to toluene diffusion in the straight and sinusoidal channels. For toluene diffusion in HZ at 373 K, the corrected diffusion coefficient for the fast process is  $8 \times 10^{-14}$  m<sup>2</sup>/s, which is in agreement with the results reported in the literature,<sup>43,46</sup> while for the slow diffusion process the corrected diffusion coefficient was  $6.5 \times 10^{-15}$  m<sup>2</sup>/s. Note that both diffusion coefficients were not dependent on the toluene loading at loadings above 2 mol./u.c.

In principle, toluene can access the adsorption sites at the intersections of the zeolite by diffusing through the straight or the sinusoidal channels. As the diameter of sinusoidal channels is slightly smaller than that of the straight channels, a lower diffusivity for toluene in the sinusoidal channels compared to the straight channels is expected. However, the difference between the diffusion coefficients of the two processes is about an order of magnitude, which appears to be too large to result solely from the difference in the pore diameter. Therefore, we like to speculate that the difference in the diffusion coefficients results from the tortuosity when using the sinusoidal channels for transport. During utilization of the sinusoidal channels by diffusing toluene molecules, the molecules have to change their direction in each intersection. This necessary reorientation is equivalent to a low transition entropy in the pathway of this transport process, which should consequently lead to lower diffusivities in the sinusoidal channels compared to the straight channels of the zeolite.

It is interesting to note that for the dependence of the diffusivity on the loading of toluene different trends were reported in the literature. Choudhary et al.<sup>47</sup> and Tsikoyiannis<sup>48</sup> observed, in accordance with the results reported here, increasing diffusivities with the loading in the pores. However, a constant<sup>14</sup> and a decreasing diffusivity<sup>42</sup> with increasing toluene concentration were also observed. In the range of toluene loadings studied by the frequency response method, the toluene diffusivities increased in both materials and remained constant at toluene loadings above 2 mol./u.c. This trend can be described with a type III diffusion process assuming the decreased mobility of diffusion molecules is due to the strong interaction with the adsorption sites of zeolite.<sup>49,50</sup>

Based on the diffusion following a random walk model, toluene molecules move inside the pores by jumps between adsorption sites.<sup>51</sup> Consequently, the residence time of toluene molecules adsorbed on intersections of the zeolite with Brønsted acid sites will be longer compared to sorption sites at intersections without Brønsted acid sites due to the additional sorption energy of 10 kJ/mol resulting from the hydrogen bonding of toluene with the SiOHAl groups. In agreement with the heats



**SCHEME 1: Influence of CLD Modification on Toluene Diffusion in the Zeolites**

of adsorption measured for both samples, the diffusivity increases with the loading as long as Brønsted acid sites are available for adsorption (coverage lower than 2 mol./u.c. at 373 K). At toluene loadings above 2 mol./u.c., all Brønsted acid sites are occupied by toluene and, therefore, a higher diffusivity was observed, which did not depend on the toluene loading of the sample. In agreement with other authors,<sup>52,53</sup> we would like to speculate that the presence of Brønsted acid sites retards the toluene diffusion. In addition, Hufton et al.<sup>54</sup> also observed lower diffusivities of isobutene in silicalite at coverage below one molecule per seven channel intersections due to the presence of defect sites acting as strong adsorption sites. Note that the diffusivities of toluene observed at 403 K remain constant at lower toluene loadings (1.2 mol./u.c.) compared to that at 373 K for the parent and silylated zeolites (see Figures 5 and 6). This indicates that the influence of the direct interaction of the bridging hydroxyl groups with toluene molecules on the diffusivity decreases with increasing temperature. Note that Masuda et al.<sup>55</sup> also observed the same diffusivities of aromatic molecules in HZSM-5 and in silicalite (i.e., nonacidic ZSM-5) at high temperatures, although at lower temperatures markedly lower diffusivities were observed in HZSM-5 compared to silicalite.

Due to its large kinetic diameter of 10.3 Å TEOS was concluded to modify only the external surface of ZSM-5<sup>29</sup> by a reaction of TEOS with the bridging hydroxyl groups located in the pore mouth region and silanol groups located on the external surface of the crystals. Brønsted acid sites accessible for TEOS molecules are effectively passivated by the deposition of an amorphous oxide layer. In addition, silylation is claimed to lead to narrowing or blocking of the pore entrance,<sup>27</sup> which may directly influence the transport of the molecules to sites inside the pores. Two independent diffusion processes, assigned to the transport utilizing only straight channels (described by  $K_H$  and  $D_H$ ) and also sinusoidal channels (described by  $K_L$  and  $D_L$ ), were observed in this study. After silylation, toluene diffusivities in both channels decreased. Moreover, the ratio between the diffusivities describing the transport process of toluene through the zeolites (i.e., into the pores, through the channels, and out of the pores) in the straight and sinusoidal channels (i.e.,  $D_H/D_L$ ) decreased from 10 to 6 after the modification. In addition, after silylation the ratio  $K_H/K_L$ , which is indicative for the amount of molecules involved in the diffusion process, decreased from 3 and 4.5 to 1 and 1.3 at 373

and 403 K, respectively. Note that  $K$  is proportional to the gradient of the sorption isotherm (see eq 6) and indicates the change in the number of molecules adsorbed ( $dQ$ ) during the pressure step ( $dp$ ) in the frequency response experiment. Therefore, the increase in the ratio  $K_H/K_L$  clearly points out that after the silylation a larger fraction of molecules diffused in ZSM-5 utilizing the sinusoidal channels compared to the parent material.

In general, the modification of HZSM-5 by TEOS could lead either to a narrowing or to a complete blocking of the pore openings. Note that this is not an absolute measure as the degree of pore blocking depends on the kinetic diameter of the molecules diffusing into the channels of the zeolite. For a given amount of TEOS deposited on HZSM-5, molecules with a small kinetic diameter (e.g., alkanes) might still enter the zeolite pores through the modified pore openings, but the narrowed aperture leads to a lower diffusivity. However, for the same material the pores might be too narrow for molecules with a slightly larger kinetic diameter (e.g., toluene) and, therefore, blockage of the pore openings would be detected for this substrate. For the transport of toluene into the modified HZSM-5 zeolite, a decrease in the diffusivities for the transport through the straight and sinusoidal channels and a lower amount of toluene molecules entering through the straight channels compared to the sinusoidal channels were observed.

The lower diffusivities after the modification point either to a narrowing of the pores or to a partial blocking of the pores. The first situation can be straightforwardly explained by the dependence of the diffusion coefficient on the pore diameter,<sup>56</sup> which reflects the hindered mobility of molecules diffusing inside the channels of a molecule sieve in the configurational regime. However, in the case of a partial blocking of the pores the diffusivity would be lowered in proportion to the fraction of blocked pore entrances. For the parent and modified zeolites identical sorption isotherms of toluene were observed (see Figure 1), which indicates that the toluene uptakes under equilibrium conditions are not affected by the modification. We have previously shown that the modification resulted in a deposition of  $\text{SiO}_2$  on the outer surface, while the interior pores of the material were not affected.<sup>27</sup> Consequently, in both materials the same number of molecules is transported between the gas phase and the sorption sites (at the intersections) during the pressure modulation in the frequency response experiments. A fraction of pore entrances is blocked after the modification;

however, the average length of the diffusion path from the remaining accessible pore entrances to the sorption sites inside the zeolite particle increases compared to that in the unmodified zeolite. A schematic comparison of the diffusion pathways in the parent and modified zeolites is given in Scheme 1. On the basis of this model we propose that the average length and tortuosity of the diffusion pathway are increased. Note that we observed a 10 times higher diffusion coefficient for toluene using only the straight channels compared to molecules using also the sinusoidal channels for the parent material. The increased tortuosity of the diffusion path inside the modified material will, therefore, lead to a lower diffusivity of toluene compared to the parent material and to a higher fraction of molecules utilizing also the sinusoidal channel for transport. Thus, the modification of the outer surface by blocking a fraction of the pore openings for aromatic molecules will impede the sole use of a large fraction of straight channels for transporting aromatic molecules. Therefore, the length and tortuosity of the diffusion pathway of the molecules are increased, which is reflected by the increased contribution of  $K_L$  relative to  $K_H$ . Note that these effects lead to a slower transport process inside the pores of the modified zeolite, although the silylation only modifies the external surface and blocks pore openings. The silylation does not affect the toluene sorption isotherm. Therefore, an identical number of molecules have to enter through the pores and the sum of  $K_H$  and  $K_L$  remains the same for both materials.

On the basis of the decrease in  $D_H$  by 4 times after the modification, we speculate that about 75% of the pore entrances are blocked after the modification. This is in perfect agreement with the decrease in the concentration of SiOHAl groups located on the external surface and in the pore mouth region by 73% after the modification.<sup>29</sup> It should be emphasized, however, that the change in the ratio between  $K_H$  and  $K_L$  does not indicate a preferential blocking of the straight channels and that the model proposed suggests instead that arbitrary patches of pores are blocked for both channel systems.

The model agrees perfectly with the enhanced para selectivity of the modified HZSM-5 catalysts for toluene disproportionation,<sup>27,57</sup> as catalysts with a larger primary crystal size, which also results in increased length of intraparticle diffusion pathways, show enhanced shape selectivity and only a minor decrease of activity.

## Conclusions

The diffusivities of toluene in HZSM-5 zeolites before and after silylation by chemical liquid deposition of tetraethoxysilane were studied using the frequency response method. Two diffusion processes were identified for both materials. The faster process was assigned to the transport of toluene in the straight channels; the slower process was assigned to the transport utilizing also the sinusoidal channels of the zeolite. The main reason for the differences in the diffusivity is, therefore, related to the tortuosity of the diffusion pathways of the sinusoidal channels. The diffusivities in both channels were found to be a function of the toluene loading and related to the interaction of toluene with the acid sites of the zeolite. Silylation of the zeolite leads to a decrease in toluene diffusivities via both pathways through arbitrary blocking of pore openings. This conclusion is well supported by the fact that the amount of toluene molecules accessing the sorption sites using also the sinusoidal channels increases after the modification, while the total uptake remains unaffected. The decrease in the amount of toluene diffusion in the straight channels of the silylated zeolite resulted from a partial blocking of about 75% of the pore openings after the silylation.

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## References and Notes

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