

Diffusion of Long *n*-Alkanes in Silicalite. A Comparison between Neutron Scattering Experiments and Hierarchical Simulation Results

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New quasi-elastic neutron scattering (QENS) data are presented for the self-diffusion of normal alkanes up to hexadecane in the zeolite silicalite at low occupancy. Measured diffusivities at 300 K are higher than in Na-ZSM-5 and agree with the predictions of molecular dynamics and a hierarchical transition-state theory/Brownian dynamics conducted on the same systems. Activation energies for diffusion are around 5 kJ/mol for C₁–C₆ but rise with carbon number for C₈–C₁₆ to approximately 15 kJ/mol for C₁₆. An explanation is suggested by the hierarchical simulation, which finds that C₁–C₆ tend to reside entirely within the interiors of single channel segments and diffuse through jumps across energetically less favorable channel intersections, while longer molecules straddle channel intersections and must undergo conformational rearrangements in order to diffuse. The agreement between QENS and simulations reflects that the two methods probe motion over the same small (nm) length scales. Self-diffusivities measured by pulsed field gradient nuclear magnetic resonance (PFG-NMR) in the same systems are appreciably lower. This is because PFG-NMR probes motion over significantly longer (μm) length scales and is therefore more sensitive to defects in the silicalite crystals.

Introduction

A number of significant industrial processes, such as fluid catalytic cracking, hydrocarbon separation, and catalytic dewaxing, operate on streams containing long hydrocarbon molecules and employ zeolites as sorbents or catalysts. The diffusion rates of the hydrocarbon molecules in the zeolite pores are critical to the performance of these processes, e.g., to the degree of separation achieved or to the extent to which zeolite crystals are utilized in catalytic reactions (effectiveness factor). Of the various zeolites employed in the petrochemical industry, the intermediate-pore MFI family is particularly important from the point of view of applications.

The diffusion of *n*-alkanes in MFI zeolites is also of great fundamental interest. A long-standing question has been whether diffusivity in these systems exhibits a non-monotonic dependence on chain length ("window effect"), as reported for the smaller-pore CHA and ERI families. The actual magnitude of diffusion coefficients of *n*-alkanes in MFI zeolites has been a point of controversy, with early "macroscopic" measurements yielding values which are by 3 orders of magnitude lower than those from more recent "microscopic" measurements, such as QENS and PFG-NMR and from molecular simulations (ref 1, Chapter 14). The effect of counterions on transport rates in MFI zeolites is another issue which requires quantitative understanding.

Various experimental and theoretical methods have been used to characterize the mobility of alkanes in MFI-type zeolites (ref 1, Chapter 14). The structure type code MFI refers to ZSM-5 and to its Al-free polymorph, silicalite. Silicalite, which has no

compensating cations, is an ideal system for molecular simulations. This structure contains straight channels (S) interconnected by sinusoidal or zigzag channels (Z), each made of ten-membered oxygen rings, so that the free diameters are about 5.5 Å. The two channels come together at intersections (I) of approximate diameter of 9 Å. The diffusion of long linear alkanes in silicalite was first studied theoretically with a hierarchical simulation method based on Brownian motion and transition-state theory.² MD simulations performed at infinite dilution with a rigid framework yielded very large diffusivities with an oscillatory dependence on chain length.³ More recent MD simulations do not confirm this trend and predict that the diffusivities decrease steadily from methane to *n*-octane.⁴ The influence of the flexibility of the lattice was also studied in the latter work: self-diffusion is higher in a flexible than in a rigid silicalite model for the lowest loadings and the shortest alkanes (methane and *n*-butane), while for *n*-hexane and *n*-octane, diffusivities in the flexible and rigid zeolite models are practically identical.⁴

The diffusivities of chains up to C₁₄ have been measured in the past by QENS in Na-ZSM-5 zeolite.⁵ For *n*-alkanes up to C₆, a good agreement with the hierarchical simulation results was observed, but a deviation was found beyond C₈.⁵ More recent QENS measurements performed on *n*-octane in silicalite gave larger diffusivities than in Na-ZSM-5.⁶ The QENS measurements, combined with MD simulations, pointed out the influence on diffusion of the extraframework cations, especially for the longer alkanes.⁶ The aim of this Letter is to check if the discrepancies between QENS and the hierarchical simulation results for long *n*-alkanes, about 1 order of magnitude, can be narrowed down by measuring again the QENS diffusivities of the longer chains in silicalite.

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Experimental Section

The new QENS experiments were performed at the Institut Laue-Langevin, Grenoble, France, using the IN16 spectrometer. Spectra were recorded at different scattering angles, corresponding to wavevector transfers, Q , ranging from 0.19 to 1.4 \AA^{-1} . The energy resolution, measured with a vanadium standard or with the dehydrated zeolite, had a Gaussian line shape with a fwhm of about 1 \mu eV , depending on Q . The energy transfer was analyzed in a window of $\pm 14 \text{ \mu eV}$. The silicalite sample was activated by heating to 773 K under oxygen flow and pumped to 10^{-4} Pa at the same temperature. After cooling, the n -alkanes were adsorbed onto the activated zeolite. Hydrogenated compounds were used in order to obtain self-diffusivities (the large neutron cross-section of hydrogen is essentially incoherent). The alkane concentrations were chosen to have the same neutron transmission as the n -hexane sample, whose loading was 2 molecules per unit cell (u.c.), i.e., there were about 28 hydrogen atoms per u.c. This corresponds to 1.56 C_8 , 1.3 C_{10} , 1.08 C_{12} , 0.93 C_{14} , and 0.82 C_{16} per u.c. Self-diffusivity is expected to be a weak function of occupancy at these loadings, which are low compared to saturation and should therefore lead to infrequent encounters between different sorbate molecules in the pores. It has been reported that the diffusivity of C_8 in Na-ZSM-5 decreases by only 25% when the loading increases from 0.9 to 2.2 molecules per u.c.⁵ Note that saturation in the isotherms of C_6 at 300 K occurs at around eight molecules per u.c. (see Table 14.1, p 472 of ref 1). Given that measurements have been carried out at the same (small) fractional occupancy of the intracrystalline pore space, it is meaningful to compare diffusivities across all systems. Any attempt to correct for occupancy dependence would lead to higher uncertainty in the results. The samples were transferred inside a glovebox into cylindrical aluminum containers. A cell containing the same amount of dehydrated zeolite (transmission: 98%) was also prepared, and its signal was subtracted from the spectra recorded with the loaded samples.

Results and Discussion

As in the case of n -octane,⁶ the diffusion coefficients for the longer n -alkanes were found to be larger in silicalite than in Na-ZSM-5. A comparison is made in Figure 1 for n -decane at 300 K, same scattering angle, and comparable loadings. The broadening, hence the diffusivity, is larger in Figure 1b than in Figure 1a. The QENS spectra were first fitted individually with a Lorentzian function, corresponding to the diffusion motion, convoluted with the instrumental resolution. All the spectra were then fitted simultaneously with an isotropic jump diffusion model previously described.⁵ The values for the self-diffusivities derived by QENS at 300 K in Na-ZSM-5 and silicalite are reported in Table 1. The ratio of the diffusivities in silicalite, compared with Na-ZSM-5, appears to increase with increasing chain length. This is in agreement with MD simulations,⁶ and confirms that the sodium cations are situated in the channels.

A comparison between the self-diffusivities D derived from different techniques at 300 K is made in Figure 2. The agreement between QENS and the hierarchical simulation is now much better than in the previous study,⁵ which reported QENS results from Na-ZSM-5 rather than silicalite. For C_{10} , the difference is less than a factor of 2, which is negligible, considering the experimental errors on the QENS values (30% from C_8 to C_{12} and 50% for C_{14} and C_{16}) and the error associated with the coarse-graining procedures invoked in the simulations. That predictions from the hierarchical simulations are somewhat higher than QENS measurements in silicalite is expected, given

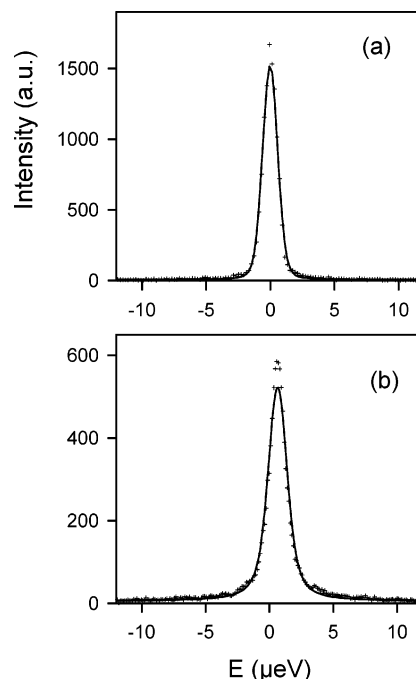


Figure 1. Comparison of the QENS spectra obtained at 300 K for n -decane in (a) Na-ZSM-5, 1.8 molecule per u.c.; (b) silicalite, 1.3 molecule per u.c. ($Q = 0.29 \text{ \AA}^{-1}$).

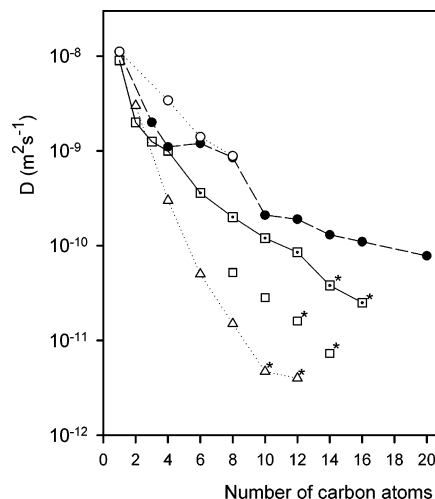


Figure 2. Self-diffusion coefficients, obtained at 300 K by different techniques, for n -alkanes in silicalite: (○) MD simulations,⁴ (●) hierarchical simulations,² (□) QENS in Na-ZSM-5,⁵ (□*) QENS in silicalite, and (△) PFG NMR.¹⁰ Asterisked symbols correspond to extrapolation to 300 K.

TABLE 1: Comparison of the Averaged Self-Diffusivities for Long n -Alkanes in Na-ZSM-5 and Silicalite, Obtained by QENS at 300 K^a

	$D(\text{Na-ZSM-5})$	$D(\text{silicalite})$	$D(\text{silicalite})/D(\text{Na-ZSM-5})$
C_8	5.2×10^{-11}	2.0×10^{-10}	3.8
C_{10}	2.8×10^{-11}	1.2×10^{-10}	4.2
C_{12}	$1.6 \times 10^{-11} \text{ }^b$	8.5×10^{-11}	5.3
C_{14}	$7.3 \times 10^{-12} \text{ }^b$	$3.8 \times 10^{-11} \text{ }^b$	5.2
C_{16}		$2.5 \times 10^{-11} \text{ }^b$	

^a Diffusivities are in $\text{m}^2 \text{ s}^{-1}$. ^b Values were obtained after extrapolating to 300 K.

that simulations refer to the infinite dilution limit, while measurements have been carried out at an equivalent occupancy of two C_6 molecules per u.c. (see above). The discrepancy between QENS/simulations and PFG-NMR increases with

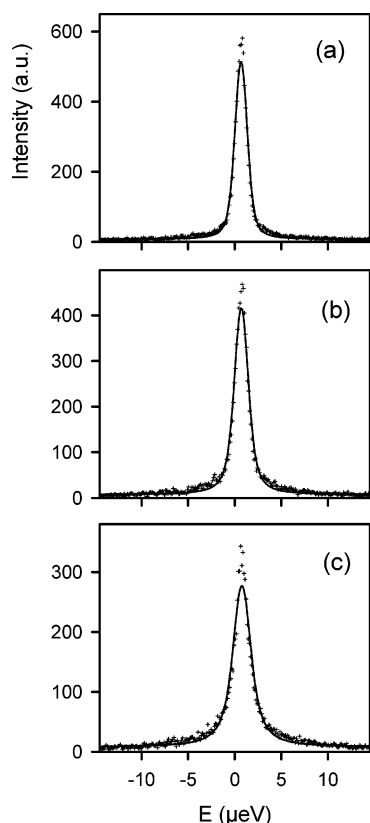


Figure 3. Comparison between experimental (+) and calculated (full line) QENS spectra obtained for *n*-dodecane in silicalite at (a) 300 K, (b) 350 K, and (c) 400 K ($Q = 0.29 \text{ \AA}^{-1}$).

increasing chain length. Ethane diffusivities from QENS and from PFG-NMR are within experimental error of each other, while for C_8 – C_{14} hydrocarbons, PFG-NMR diffusivities are clearly lower. The discrepancy between QENS/simulations and PFG-NMR at high chain length is attributable to defects in the silicalite structure.¹⁰ PFG-NMR, which monitors molecular displacements on the order of micrometers, is much more sensitive to such defects than QENS, which has an effective length scale of nanometers. For other zeolites, there is generally a much better agreement between QENS and PFG-NMR.^{7,8} This highlights the specificity of MFI-type crystals. It appears that this zeolite cannot be synthesized without internal transport barriers.

For each molecule, QENS measurements were carried out at three different temperatures (Figure 3) so that activation energies E_a for diffusion could be obtained. These are plotted in Figure 4, where they are compared with the hierarchical simulation method. Again, the agreement between the two methods is remarkable: the activation energy of *n*-alkanes shorter than C_6 – C_8 is small and constant ($\approx 5 \text{ kJ/mol}$), while it increases for the longer chains. Whether a plateau is reached at C_{20} , as predicted from the simulations, could be tested in the future by neutron spin-echo measurements, since this technique allows probing much slower motions.⁹

The detailed simulation work of Maginn et al.^{11,2} provides an explanation for the chain-length dependence of D and E_a of hydrocarbons in silicalite. Channel interiors (Z, S) are energetically more favorable than the more open channel intersections (I), because they allow methylene and methyl segments to maximize their dispersive interactions with the zeolite framework. Chain configurations have been categorized in terms of the sequence of environments (S, Z, I) through which they pass; following ref 11, we will call such a sequence a “coarse-grained conformation”. The shorter alkanes C_4 and C_6 can reside entirely

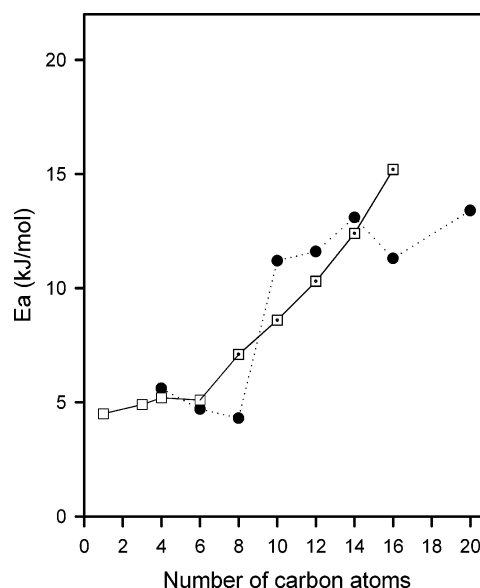


Figure 4. Comparison of the activation energies for diffusion derived for *n*-alkanes in silicalite from (●) hierarchical simulations,² (□) QENS in ZSM-5,⁵ and (□) QENS in silicalite.

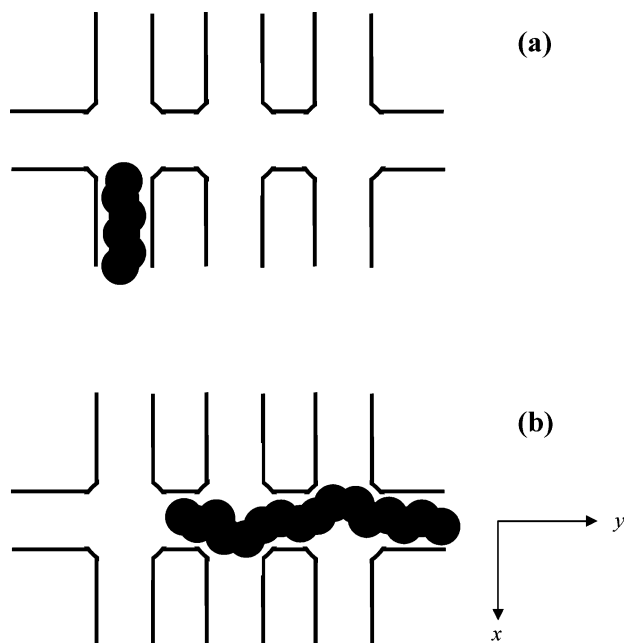


Figure 5. Schematics of (a) a hexane molecule sorbed in a Z coarse-grained conformation and (b) an *n*-hexadecane molecule sorbed in a SISIS coarse-grained conformation within silicalite.

within a channel interior, with the Z coarse-grained conformation being the most probable for both species at 300 K. On the contrary, C_8 and longer alkanes have to straddle and/or poke into a channel intersection. At 300 K, the most probable coarse-grained conformation is SIS for C_8 , C_{10} , and C_{12} ; SISI for C_{14} ; and SISIS for C_{16} and C_{20} . (See Tables 4–6 of ref 11). For C_4 and C_6 , the rate-limiting step for diffusion at low occupancy is essentially a jump across the less favorable I region, which is roughly 5 kJ/mol higher in energy than S or Z.^{2,12} On the contrary, visual inspection of simulation configurations reveals that longer chains, which span channel intersections, tend to adhere to the walls of the I regions they traverse, to maintain their favorable dispersive interactions with the zeolite framework (see Figure 5). To accomplish this, one or more of the torsion angles of the chains have to distort away from the trans state adopted exclusively within the channels. These torsional

“defects” must slide along a chain to allow translational motion within the channels. Thus, translational diffusion of longer chains is necessarily accompanied by some conformational change. The observed activation energy (Figure 4) is indeed commensurate with the energy barrier for trans–gauche isomerization of a skeletal bond, which is around 12 kJ/mol in normal alkanes. The hypothesis that higher activation energies for diffusion of alkanes longer than C₈ are associated with conformational change of bonds located in the intersection regions can be tested quantitatively by accumulating torsion angle distributions and analyzing conformational transitions in the three different environments of the pore system.

Conclusions

In this work, we have presented new QENS data for the self-diffusion of alkanes up to C₁₆ in silicalite. No evidence of a “window effect” is observed in these systems. The measured diffusivities and activation energies are in very good agreement with a previous hierarchical simulation study.^{2,11} Starting from detailed atomistic calculations in a rigid framework, the latter study analyzed diffusion in terms of activated passages of chain ends between channel interiors and channel intersection regions and Brownian motion of chain ends within the channels. An explanation has been proposed for the chain-length dependence of the activation energy in terms of the siting and conformational distributions predicted by the simulation study. For MFI-type zeolites, one expects a good agreement between molecular simulations and QENS, because the two techniques are probing similar time and space scales. The discrepancy observed with PFG-NMR data is an indirect indication of transport barriers caused by defects within the crystals. Further work on alkane diffusion in silicalite could concentrate on (a) diffusivity measurements for alkanes longer than C₁₆ via the neutron spin-echo method; (b) further elucidation, through analysis of

simulation trajectories, of the coupling between conformational rearrangements in intersection regions and translational diffusion proposed herein to explain the chain length dependence of the activation energy (Figure 4); and (c) systematic measurements of the self-diffusivity of the same alkane in a variety of silicalite samples where defect concentration is varied in a controlled way, e.g., by the fluoride synthesis method.

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