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Simulating the Adsorption of Alkanes in Zeolites

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The configurational-bias Monte Carlo technique is applied to simulate the adsorption of long chain alkanes in zeolites. This simulation technique is several orders of magnitude more efficient than conventional methods that can be used to simulate the adsorption of long chain alkanes. The calculated heats of adsorption are found to be in excellent agreement with experimental data. The results show a surprising chain length dependence of the heats of adsorption. This dependence has a simple molecular explanation in terms of preferential siting of the long chain alkanes.

Zeolites are crystalline inorganic polymers that form a three-dimensional network of micropores. These pores are accessible to various guest molecules. The large internal surface, the thermal stability, and the presence of acid sites make zeolites an important class of catalytic materials for petrochemical applications. For a rational use of zeolites, it is essential to have a detailed knowledge of the behavior of the adsorbed molecules inside the pores of the zeolites. Unfortunately, such information is very difficult to obtain, particularly for long chain hydrocarbon molecules.

Catalytic conversion inside the pores of a zeolite can be seen schematically as a three-step process: (i) the adsorption and diffusion of the reactants, (ii) the catalytic conversion, and (iii) the diffusion and desorption of products from the zeolite. The overall activity and selectivity of a particular reaction is the result of a delicate balance of these three processes. Much experimental and theoretical effort is directed toward obtaining a detailed understanding of each of these steps at a molecular level (*1*). The high selectivity of zeolites implies that the behavior of the adsorbed molecules is system-specific. It is therefore essential to be able to study the behavior of the adsorbed molecules of interest under reaction conditions.

Computer simulations, used with molecular dynamics or Monte Carlo techniques, are an attractive alternative to experiments because these methods can, in principle, provide information for conditions under which experiments are not feasible. Indeed, over the last few years there has been considerable progress in simulating adsorption in zeolites [for a recent review, see (*2*)]. In practice, however, computer simulations have been limited to atoms or small molecular guest molecules and could not be extended to molecules of catalytic relevance. These limitations are discussed by June *et al.* (*3*); in this work, molecular dynamics was used to study the behavior of butane and hexane in the zeolite silicalite. June *et al.* observed that the diffusion of these alkanes is very slow and the rate of diffusion decreases with increasing chain length. Therefore, long simulations are required to obtain reliable results.

The Monte Carlo technique is not limited by the slow diffusion of the molecules, because moves can be made to arbitrary positions in the zeolite. For chain molecules, however, this is not the case because the probability of finding a position without overlap between hydrocarbon and zeolite decreases exponentially with chain length. Recently, we have developed a method, configurational-bias Monte Carlo, to simulate chain molecules (*4*, *5*). We demonstrate here that this approach can be used to study the behavior of long chain hydrocarbons in zeolites and allows us to address the much debated question of the preferential adsorption of the *n*-alkanes in the different channels of silicalite.

We used the configurational-bias Monte Carlo technique to study the adsorption of *n*-butane to *n*-dodecane in silicalite. In contrast to the conventional Monte Carlo technique, in the configurational-bias Monte Carlo technique a molecule is not inserted at random but is grown atom by atom such that overlap with the zeolite atoms is avoided (Fig. 1). This growing process introduces a bias that is removed by adjusting the acceptance rules (*4*–*7*). A simulation is performed in cycles, and each cycle consists of a number of randomly selected moves: displacement of particles, rotation of particles, partial regrowing of a molecule, and regrowing of a molecule at a randomly selected position. For the latter two moves, the configurational-bias Monte Carlo technique is used with a total simulation consisting of at least 10^6 cycles. The alkanes are described with the model of (*8*). This model yields an accurate description of their phase behavior. Following Kiselev and co-workers (*9*), we assume that the zeolite lattice is rigid and that the zeolite-alkane interactions are dominated by dispersive interactions. Lattice vibrations can have a pronounced effect on the diffusion because these vibrations may lower the diffusional barriers. Because these barriers hardly contribute to the equilibrium distribution, we expect that the effect of lattice vibrations on the equilibrium properties is small. The details of the model are given in Table 1.

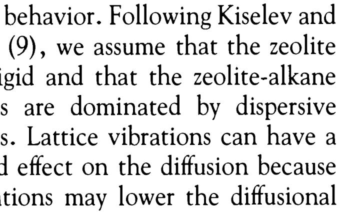

Fig. 1. Schematic drawing of the growing of an alkane in a zeolite in a configurational-bias Monte Carlo move. The black circles represent the atoms of the zeolite, and the white circles represent the atoms of the alkane. Seven atoms have been grown successfully, and an attempt is made to insert the eighth. The arrows indicate seven trial positions for which the energy u_i is calculated. Out of these seven positions one is selected with a probability $p_i = \exp(-u_i/k_BT)/w_{\mathrm{new}}(\ell)$ with $w_{\mathrm{new}}(\ell) = \Sigma_j \exp(-u_j/k_BT)$, where T is the temperature and k_B is Boltzmann's constant. Similarly, for the old configuration we calculate $w_{\mathrm{old}}(\ell) = \Sigma_j \exp(-u_j/k_BT)$. This is repeated until the entire chain of length m has been grown. It can be proven (*5*) that the bias of the growing is removed by the replacement of $\exp(-\Delta U/k_BT)$ by $\Pi_{\ell=1}^{m} w_{\mathrm{new}}(\ell)/\Pi_{\ell=1}^{m} w_{\mathrm{old}}(\ell)$ in the acceptance rule. Comparison with molecular dynamics shows that configurational-bias Monte Carlo is two orders of magnitude more efficient for butane and up to 12 orders of magnitude more efficient for dodecane.

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In Fig. 2, the calculated heats of adsorption are compared with experimental data. Dubinin *et al.* (*10*) showed, using data of C_2 to C_5, that the heat of adsorption increases 10 kJ/mol per CH_2 group. Our calculations give 11 kJ/mol per CH_2 group. Interestingly, we observe a change in slope for the longer alkanes. For octane and longer linear alkanes, we estimate 13 kJ/mol per CH_2 group.

Figure 3 shows a schematic picture of the silicalite structure. Silicalite has two types of channels, straight and "zigzag," which cross at the intersection. Knowledge of the distribution of the alkanes over the various channels is required to understand adsorption and diffusion in silicalite. At this point it is important to note that we focus on silicalite (which does not contain acid sites); for zeolites containing acid sites, the distribution may be different. At present, there is no consensus in the literature on the distribution of alkanes. To interpret experimental adsorption isotherms, Jacobs *et al.* (*11*) assumed that for C_3 through C_5 there is no preferential adsorption, that C_6 through C_8 favor the straight channels, and that for C_9 through C_{10} the zigzag channels are the preferred sites. Caro *et al.* (*12*) found the diffusion of short alkanes to be consistent with a model in which the alkanes preferentially adsorb in the intersections. Richards and Rees (*13*) explained adsorption isotherms, assuming that the longer alkanes prefer the zigzag channels. Thamm (*14*) concluded that his microcalorimetry experiments were consistent with a model without any preferential adsorption. Similarly, computer simulation studies have not yielded a consistent picture. Titiloye *et al.* (*15*) concluded from energy minimization studies that the alkanes prefer the intersections. Molecular dynamics simulations by June *et al.* (*3*) showed that C_4 and C_6 are equally likely to be found in the zigzag and straight channels, whereas the simulations of C_3 by Nicholas *et al.* (*16*) showed a preferential adsorption in the zigzag channels.

The distribution of the alkanes over the channels as a function of carbon number, n_C, as calculated from our simulations is shown in Table 2. For the short alkanes, the probability of being in the zigzag channel is nearly equal to the probability of being in the straight channel. This finding is consistent with the results of June *et al.* (*3*). For the larger alkanes ($>C_8$), the straight channel is favored above the zigzag channel. In Fig. 4 the probability distribution of butane (Fig. 4, top) is compared with that of dodecane (Fig. 4, bottom). Whereas the plots of butane show an equal density of points in the straight and zigzag channels, dodecane has a significantly lower probability of being in the zigzag channels. In a sense, silicalite becomes more and

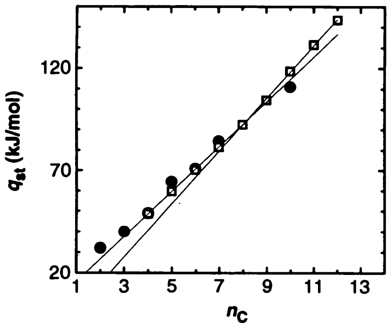

Fig. 2. The heats of adsorption of the alkanes in silicalite. For butane and hexane, our simulation results (denoted by hollow squares) are in excellent agreement with the molecular dynamics simulations of June *et al.* (*3*). The solid lines are linear fits to the data, which give a slope of 11 kJ/mol per carbon atom for C_4 to C_8 and 13 kJ/mol per carbon atom for C_8 to C_{12}. The experimental data (denoted by filled circles) are compiled from (*10, 14, 19–22*).

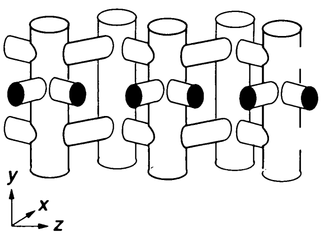

Fig. 3. Schematic drawing of the pore structure of silicalite.

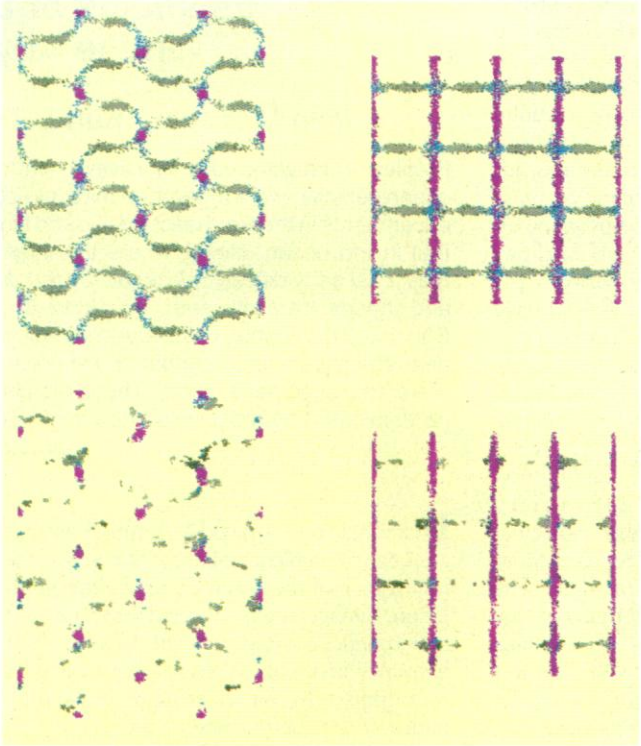

Fig. 4. Distributions of butane (**top**) and dodecane (**bottom**) over the various channels of silicalite. At regular intervals during the simulations, the end to end vector of the alkane molecule is calculated, and, depending on its orientation, a color is selected: blue for the intersection, gray for the zigzag channel, and magenta for the straight channel; a dot in the selected color is drawn at the position of the center of mass of the molecule. The density of the dots is a measure of the probability of finding an alkane in a particular section of the zeolite. The left figures are projections on the *x–z* plane, and the right figures are projections on the *y–z* plane (see Fig. 3).

Table 1. Details of the *n*-alkane–zeolite model. The alkane model is based on the united-atom description; that is, methyl and methylene groups are considered as a single interaction center. The pseudo-atoms in a given chain are assumed to be connected by rigid bonds (d_{CC} = 1.54 Å). The nonbonded interactions are described by Lennard-Jones potentials (top), which are truncated at 13.8 Å. The usual tail corrections are used to estimate the interactions beyond the cutoff. The parameters for the unlike interactions have been calculated with $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. The intramolecular interactions include bond bending (middle) and torsion (bottom). Because the Si atoms are much smaller than the O atoms, the contributions of the Si atoms can be taken into account implicitly in the effective potential of the O atoms (*9*). The alkane-zeolite interactions are similar to the ones used by June *et al.* (*3*).

Potential function	Parameters
$U_{LJ}(r_{ij}) = 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6]$	$\sigma_{CH_3} = \sigma_{CH_2} = 3.93$ Å; $\epsilon_{CH_3} = 114.0$ K; $\epsilon_{CH_2} = 47.0$ K $\epsilon_{CH_3,O} = \sigma_{CH_2,O} = 3.364$ Å; $\epsilon_{CH_2,O} = \epsilon_{CH_2,O} = 84.0$ K
$U_{bending}(\theta_i) = 1/2\ k_\theta\ (\theta_i - \theta_{eq})^2$	$k_\theta = 62\,500$ K rad^{-2}; $\theta_{eq} = 114°$
$U_{torsion}(\phi_i) = a_1\ (1 + \cos\phi_i) + a_2[1 - \cos(2\ \phi_i)] + a_3\ [1 + \cos(3\ \phi_i)]$	$a_1 = 355.03$ K; $a_2 = -68.19$ K; $a_3 = 791.32$ K

Table 2. Distribution of alkanes over the various channels [zigzag (z-z), straight (str.), and intersection (int.)] of silicalite at 298 K.

n_C	z-z	str.	int.
C_4	0.50	0.42	0.08
C_5	0.49	0.44	0.07
C_6	0.45	0.49	0.06
C_7	0.41	0.54	0.05
C_8	0.36	0.59	0.05
C_9	0.31	0.65	0.04
C_{10}	0.18	0.78	0.03
C_{11}	0.18	0.79	0.04
C_{12}	0.20	0.77	0.03

more "unidimensional" with increasing length of the hydrocarbon. Because the energetics of hydrocarbon adsorption in the two types of channels are different, this preferential adsorption influences the heats of adsorption and causes the change in slope of the heats of adsorption as a function of carbon number (see Fig. 2).

Many practical applications require knowledge of the adsorption isotherm, which gives the number of molecules adsorbed in a zeolite. Simulations of these adsorption isotherms can be performed in the grand canonical ensemble, which allows for the exchange of molecules between the zeolite and reservoir. Such simulations have been performed for small molecules (*17*), and use of the configurational-bias Monte Carlo technique would make it possible to simulate the adsorption isotherms of long chain alkanes under realistic conditions.

The calculation of the heat of adsorption of decane took approximately 20 hours on a workstation (*18*). A comparable molecular dynamics simulation would require thousands of years of supercomputer time. The saving in time is due to the fact that with the configurational-bias technique we can take advantage of special Monte Carlo moves that are impossible in nature but very efficient on a computer. In this respect it is interesting that experimentally the equilibration of decane in silicalite took 2 weeks (*19*). The price we had to pay for being able to perform these simulations is that we could not get direct information on the dynamics of the guest molecules. However, our method can provide the free energy of an alkane molecule as a function of its position along the channel. This free energy corrugation can subsequently be used in conjunction with transition state theory to investigate diffusion. This would be a very interesting direction for future work.

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Estimates of Diapycnal Mixing in the Abyssal Ocean

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Profiles of diapycnal eddy diffusivity to a maximum depth of 4000 meters were derived from ocean velocity and temperature microstructure data obtained in conjunction with separate experiments in the Northeast Pacific and Northeast Atlantic oceans. These profiles indicate that in the ocean interior where the internal wave field is at background intensity, the diapycnal eddy diffusivity is small (on the order of 0.1×10^{-4} meters squared per second) and independent of depth, in apparent contradiction with large-scale budget studies. Enhanced dissipation is observed in regions of elevated internal wave energy, particularly near steeply sloping boundaries (where the eddy diffusivity estimates exceed 1×10^{-4} meters squared per second). These results suggest that basin-averaged mixing rates may be dominated by processes occurring near the ocean boundaries.

Diapycnal flow in the ocean interior, with its attendant turbulent mixing, represents the return limb of the ocean thermohaline circulation. Surface waters advected into regions of atmospheric cooling at high latitudes lose buoyancy and sink to abyssal depths and in turn displace lighter waters upward. Maintenance of the thermocline in the face of this upward advection of cold water is believed to be accomplished by downward (more precisely, diapycnal) diffusion of heat (*1*, *2*). The intensity of the meridional overturning circulation and the diapycnal mixing in the abyss, as well as the mechanisms responsible for the mixing, represents a fundamental oceanographic question.

A seeming paradox has developed between indirect estimates of the turbulent eddy diffusivity (*K*) from advection-diffusion models and from budgeting studies (*2*, *3*) and diffusivity estimates deduced from microstructure measurements (*4*). The microstructure-based estimates are typically an order of magnitude less than those inferred indirectly. However, few direct comparisons have been possible because the indirect schemes have been applied principally to the deep ocean, whereas most of the microstructure measurements have come from the upper 1 km of the ocean. One exception is the work of Moum and Osborn (*5*), who reported estimates of *K* derived from 11 velocity microstructure profiles to a maximum depth of 2240 m in the Northwest Pacific (three of which extended deeper than 1655 m). Their data suggested that eddy diffusivity increased with depth; extrapolation of Moum and Osborn's profile to abyssal depths yielded a diffusivity on the order of 1×10^{-4} m^2 s^{-1}, the canonical value obtained from vertical advective-diffusive models (*2*). We describe a somewhat larger set of 22 ocean microstructure (and fine-scale velocity) profiles extending to a depth of 3000 m (four of which are to 3800 to 4000 m).

From March to April of 1991 and 1992, vertical profiles of velocity and temperature microstructure were obtained with the free-

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