Mathematical Modeling of Diffusive Potentials Within Carbon Molecular Sieves

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Molecular sieve materials are used in largescale industrial processes for gas separation. These materials have pores of molecular dimensions that give rise to selective adsorption; the selectivity is a result of the different rates of activated diffusion into the pore structure. It is believed that the diffusing molecule experiences a net repulsive interaction upon entering very narrow pores and thus must pass over an energy barrier to gain admittance to the adsorption volume. The differences in magnitude of these energy barriers for various species gives rise to different diffusion rates and thus eauses separation.

A fundamentally important parameter in the study of molecular sieves for separations processes is the critical pore dimension (cpd) below which diffusion for a particular species becomes activated. At the cpd, the minimum potential for diffusion is zero. Previous attempts at calculating the cpd from interaction potentials have been limited to simple gases (He, Ar, Ne, Kr) (l). In this paper, the cpd's and diffusion activation energies are calculated for a number of nonspherical molecules in carbon molecular sieves.

An aperture-cavity pore system exists in carbon molecular sieves (2). Thus, diffusion through the pore structure is rate-limited by passage through slit-shaped apertures. For nonspherical molecules, diffusion involves some loss of rotational freedom. This phenomena is explicitly included in the model presented below.

The model applied here was described by Steele (3) for the interaction of gases with solid surfaces. It is based on the summation of the atomatom interactions over the entire solid; the interaction is described by Lennard-Jones (12-6) functions with parameters given by applying the Lorentz-Berthelot (L-B) combining rules. Steele applied this approach to the interaction of N₂ with the basal plane of graphite (4). The interaction function for polyatomic species is the sum of the atomatom interactions of each atom in the adsorbate with the surface. The potential function is simplified by expressing it as a Fourier series and taking the first two terms. Details are given elsewhere (3). The interaction potential for a linear molecule is

$$\mathbf{i}(\tau, \beta, \alpha, \gamma) = \sum_{i=1}^{n} \mathbf{w}_{0}(z_{i}) + \mathbf{i} = \mathbf{1}_{n}$$
$$\sum_{i=1}^{n} \mathbf{w}_{1}(\mathbf{g}z_{i}) f(\tau, \gamma, \alpha) \qquad (1)$$

where τ is the length of the position vector of the molecular center-of-symmetry relative to the surface unit cell; a is the in-plane orientation angle between the projection of the molecular axis onto the surface and the surface lattice vector; γ is the polar angle between the position vector to the center of symmetry and the surface unit cell; β is the angle between the molecular axis and the normal to the surface; g is the length of the smallest nonzero reciprocal lattice vector for the graphite basal plane, and z_i is the distance of the ith atom from the surface. The terms w_0 , w_1 , and f in eqn (1) are described elsewhere (5). The first term on the r.h.s. of eqn (1) determines the gross changes in the interaction potential as the molecule moves away from the surface. The second term determines the change in potential as the molecule moves within the unit cell.

This approach allowed us to characterize the diffusion of CO, CO_2 , N_2 , O_2 , Ar and He along the pore centerline of slit-shaped pores whose walls are composed of basal planes. The parameters for the (L-B) combining rules are provided elsewhere (5). First, changes in potential upon insertion of a molecule in the pore were determined by considering only the w_o terms and superimposing the potential from each wall. The pore width at which the minimum potential energy becomes zero was taken as the cpd. Finally, the energy barrier for diffusion in the 121> and 101> crystallographic directions were computed by calculating the w₁ terms within a pore with the cpd.

Results and Discussion

The validity of the above model was predicated on the ability to predict the heat of adsorption at zero coverage on the graphite basal plane. Comparison of the calculated and experimentally estimated heats of adsorption for the various species agree to within 0.15 kcal/mol. The cpd were computed by summing the potential from each wall for a series of pore widths. Slit widths which gave zero interaction energy are given in Table 1. The preferred orientation of the linear molecules is parallel to the pore wall. The order of effective molecular size for unactivated entrance into the pores He < C0, $C0_2 < 0_2 < H_2 < N_2 < Ar$.

Table 1. Summary of Calculated Critical Pore Dimensions

Gas	<u>Slit Width, A</u>
CO	5.41
H ₂	5.48
co ₂	5.42
°2	5.44
N ₂	5.72
Ar	5.75
Не	5.08

The order of effective molecular size shows that CO_2 should be smaller, and therefore more accessible to pores than N_2 . This is precisely what is observed experimentally (1,6). To date, estimates based on gas-phase kinetic diameters or minimum dimensions have predicted results in direct contradiction to experimental findings (6,7). To the authors' knowledge this is the first time that the anomaly between experiment and theory has been resolved.

Experimental data on O_2 and N_2 adsorption rates on carbons show that O_2 can penetrate the pore structure more easily than N_2 (6,8). The present model shows that O_2 is smaller than N_2 by about 0.3 A, about twice that predicted from minimum dimension estimates. This is reflected in a difference in activation energy of 5.6 kcal/mol for diffusion through a 5.44 A pore.

The diffusion barrier for movement within the aperture can be estimated by examining the w_1 terms of eqn (1). This barrier is due to changes in potential as the molecule moves across the surface unit cell. Diffusional barriers were calculated in the 1121> and 1101> directions. Linear molecules have some rotational freedom in the basal plane and, thus, the diffusion barrier is dependent on the α -angle, at each position. Maximum and minimum diffusion barriers have been calculated for passage of each species through an aperture of the cpd (see Table 2).

Two barriers to diffusion through apertures exists. First, the molecule must enter the aperture from a large cavity and then must diffuse within the aperture; either barrier may be rate limiting. For example, for CO_2 and N_2 diffusing through a 5.42 A pore, the mean diffusion barrier within the pore is 1.5 kcal/mol, i.e., once they enter the pore both CO_2 and N_2 diffuse at similar rates. The energy barrier for pore entry for CO_2 is zero whereas for N_2 it is 5.8 kcal/mol. Thus, the rate limiting process for N_2 diffusion is aperture entry.

Hydrogen has been shown to have a slightly

Table 2. Energy Barrier to Diffusion in the <1101> <1121> Directions

		1121			1101	
Gas	Max		min	max		min
со	1.86		0.38	1.44		1.19
^N 2	2.83		0.68	2.05		2.04
°2	1.93		0.14	2.41		2.39
co2	9.19		1.16	3.82		3.06
^н 2		1.65			0.41	
Ar		2.67			0.67	
He		0.93			0.23	

larger cpd than CO_2 . The barrier for aperture entry for H₂ into a 5.42 A aperture is 0.5 kcal/mol and is zero for CO_2 . However, the barrier for diffusion within this aperture is only 0.5 kcal/mol for H₂ compared to 1.5 kcal/mol for CO_2 . Therefore, even though it is slightly more difficult for H₂ to enter the aperture, it will diffuse much faster once it is within the aperture.

The cpd can only be used as a first approximation to estimate the separation efficiency of a molecular sieve. The rate of diffusion within the pores as well as the cpd must be taken into account when determining the accessibility of a species to the pore structure.

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