Concerted Diffusion of Molecular Clusters in a Molecular Sieve

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We show that attractive interactions between molecules adsorbed in molecular sieves play a vital role in the mechanisms and rates of intracrystalline diffusion. Over a wide temperature range, the single-file diffusion of CF_4, SF_6, and CCl_4 in $AlPO_4$-5 is dominated by the diffusion of molecular clusters. SF_6 and CCl_4 clusters diffuse by concerted mechanisms involving all of the cluster's molecules simultaneously. The activation energies, E_a, for these mechanisms are strongly size dependent and are lower than E_a for monomer diffusion. [S0031-9007(97)04486-4]

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Molecular sieves are microporous, crystalline materials used in many applications involving separations, catalysis, and shape-selective chemistry. In these applications, the mechanisms and rates of intracrystalline adsorbate diffusion are of fundamental importance [1,2]. One regime that has received considerable recent attention occurs when adsorbed molecules are sufficiently large that, although they can diffuse along a pore, they cannot pass other adsorbed molecules in a pore [3–7]. This type of diffusion is known as single-file diffusion [3–6]. One striking feature of single-file diffusion is that the mean-squared displacement of a tracer particle is proportional to $t^{1/2}$ at long times [3–6,8]. The existence of single-file diffusion was first predicted over twenty years ago [8], but has only recently been experimentally demonstrated [3–5].

A number of models are available that predict transport rates and other relevant features of adsorbates during single-file diffusion [4,6,8–10]. The most important simplifying assumptions in these models are that the only interactions between adsorbed molecules are short-ranged hard-core repulsions and that the motions of adsorbates at any loading can be described in terms of the motions executed by an isolated adsorbate. In this Letter, we examine the diffusion mechanisms of three species that undergo single-file diffusion in the molecular sieve $AlPO_4$-5: CF_4, SF_6, and CCl_4. The nonintersecting quasicylindrical pores of $AlPO_4$-5 have made this material a useful prototype for understanding the role of adsorbate size on intracrystalline diffusion [3–7,11]. We show below that the attractive van der Waals interactions that exist between molecules of these three species can have an enormous impact on their diffusion. In particular, the concerted diffusion of molecular clusters can be the dominant diffusion mechanism for molecular transport in these systems. One significant implication of this result is that single-particle models of single-file diffusion [4,8–10] cannot accurately describe particle mobilities during single-file diffusion, so new theoretical descriptions must be sought.

To examine adsorbed CF_4, SF_6, and CCl_4 in $AlPO_4$-5, we have derived Kiselev-type potentials for these systems [6,7,12]. These potentials represent the adsorbates by Lennard-Jones particles [13], hold the $AlPO_4$-5 lattice rigid, and represent the adsorbate-lattice interactions by Lennard-Jones interactions between adsorbates and lattice O atoms with appropriately chosen parameters [6,7,12]. Potentials of this type have been used in a range of studies of adsorbate motion in molecular sieves (see, e.g., Refs. [6,14]). CF_4, SF_6, and CCl_4 all perform single-file diffusion in $AlPO_4$-5 [7]. For each of these species, the potential energy surface of an isolated adsorbed molecule consists of energetic minima (binding sites) spaced $a = 4.24$ Å, apart along the pore [6]. Potential energy barriers exist between binding sites so, at sufficiently low temperatures, isolated molecules diffuse by activated hopping between binding sites.

To assess the role of adsorbate-adsorbate interactions during single-file diffusion, we have examined the diffusion and dissociation mechanisms of clusters of adsorbed molecules. The typical displacements of large molecules perpendicular to the pore direction in $AlPO_4$-5 are small relative to typical molecular spacings along the pore [6]. Hence, we use a one-dimensional (1D) model in which lateral displacements are neglected and the position of the ith molecule is defined to be x_i. The corrugated potential due to the lattice is assumed to be sinusoidal [4], and we only include adsorbate-adsorbate interactions between neighboring molecules. Hence, the potential energy of a cluster of n molecules with $\mathbf{x} = (x_1, \dots, x_n)$ is

$$U(\mathbf{x}) = \sum_{i=1}^{n} \frac{E_a}{2} \sin\left(\frac{2\pi x_i}{a}\right) + \sum_{i=1}^{n-1} U_{\mathrm{LJ}}(|x_{i+1} - x_i|)\,. \tag{1}$$

E_a is the diffusion activation energy of an isolated molecule (from the full potential) and U_{LJ} is the Lennard-Jones potential for the adsorbed species (with hard-sphere radius σ) [13]. All of the results presented below use Eq. (1), although the generality of our results for the full potential is discussed. If U_{LJ} in Eq. (1) is replaced with a harmonic potential, Eq. (1) becomes the Frenkel-Kontorova (FK) model [15,16], which has been widely used to model dislocations in solids. Equation (1), unlike the FK model, can be used to describe cluster dissociation (see below).

The minima of Eq. (1) can be found with standard numerical optimization methods. Cluster motion can be accurately described by minimum-energy paths (MEPs) between local minima, at least at low temperatures. To find MEPs, we use an extension of a method developed by Elber and co-workers [17,18]. A discretized path between two local minima, $[\mathbf{x}^k]_{k=1,\ldots,M}$ is said to be a MEP if

$$\sum_{k=2}^{M-1} [|\nabla U(\mathbf{x}^k) - (\nabla U(\mathbf{x}^k) \cdot \hat{\mathbf{s}}^k)\hat{\mathbf{s}}^k| + \alpha|\mathbf{x}^{k-1} + \mathbf{x}^{k+1} - 2\mathbf{x}^k|] = 0. \qquad (2)$$

Here, $\mathbf{x}^k = (x_1^k, \ldots, x_n^k)$ is a cluster configuration and $\hat{\mathbf{s}}^k$ is a unit vector along the local path [17,18]. The first group of terms ensures that the path is a steepest descent path on the nD potential energy surface [17,18]. The second group of terms ensures that points on the path are equally spaced. Using appropriate values of $\alpha > 0$ prevents the bunching of points on trial paths that can occur when $\alpha = 0$. To find a MEP, a trial path is chosen connecting two local minima, and a gradient flow algorithm is used that converges to a path satisfying Eq. (2).

We first consider the properties of a pair of SF_6 molecules adsorbed in $AlPO_4$-5. In this case, our MEP results can be verified by a direct examination of the 2D potential. The adsorbate interaction is minimized when $|x_2 - x_1| = 2^{1/6}\sigma = 6.185$ Å [13], a distance 45.9% larger than the distance between single-particle binding sites. When Eq. (1) is minimized, the molecules of a SF_6 dimer are 6.049 Å apart with energy 127.5 K lower than two isolated adsorbed molecules. The diffusion and dissociation mechanisms available to this dimer are more complex than would be suspected from typical lattice gas (LG) descriptions [9,10] because of the strong mismatch between the lattice and intermolecular spacings. A diffusion mechanism that can be described by LG models [9,10] is a stepwise mechanism, where one molecule hops and is subsequently joined by the other. The MEP for the SF_6 dimer diffusion mechanism analogous to stepwise motion is illustrated in Fig. 1(a). The incommensurate minimum-energy state of the dimer can be seen at the beginning and end of the path. The total, static-energy barrier for this path (that is, the energy difference between the minimum-energy state and the highest of the local energy maxima along the MEP) is 202.1 K. It is interesting to note that there is a distinct but energetically equivalent MEP that shifts the dimer twice as far along the pore. The MEP for dimer dissociation consists of the first three frames of Fig. 1(a) followed by one of the molecules hopping away from the other along the pore. The total energy barrier to dissociation is 217.6 K; much higher than in models without attractive interactions [9,10]. This process cannot be described by the FK model [15,16]. These results suggest that over a wide temperature range, stepwise diffusion of SF_6 dimers occurs at a similar or faster rate than dimer dissociation and is much slower than the hopping of isolated SF_6 molecules, which has an energy barrier of 90.1 K.

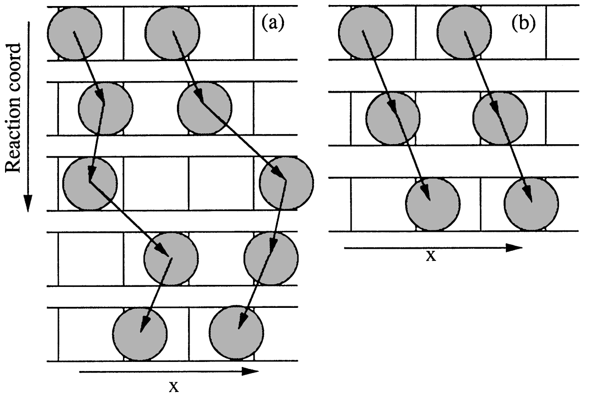

FIG. 1. Illustrations of SF_6 dimer diffusion by (a) stepwise motion and (b) concerted diffusion. Vertical lines show the transition states between binding sites of isolated molecules.

Any model of dimer motion that only included stepwise diffusion and dissociation would give a completely inaccurate description of the true dimer motion. SF_6 dimer motion is dominated by a concerted diffusion mechanism that cannot be approximated by stepwise motions of single molecules. This mechanism is shown in Fig. 1(b); the two molecules move together along the pore with only small deviations in their spacing. The energy barrier for this mechanism is only 21.5 K (cf., 90.1 K for monomer diffusion and 202.1 K for stepwise dimer diffusion). This low barrier arises from the mismatch between the molecular and lattice spacings; as one molecule moves through a region where the lattice potential is increasing, the lattice potential of the other molecule decreases. We have verified that this mechanism also exists if the 6D dimer potential discussed above is used. It can be seen from the energy barriers alone that the concerted diffusion of SF_6 dimers will be significantly faster than monomer diffusion, stepwise dimer diffusion, or dimer dissociation over a wide temperature range. This observation is the first example of the central result of this Letter: *The single-file diffusion of molecules in molecular sieves can be dominated by concerted motions of molecular clusters*. Adsorbate diffusion by concerted motions is well known in the diffusion of atomic adsorbates and clusters on crystal surfaces [16,19,20] and is strongly analogous to the motion of dislocations in solids [15]. Our results are the first indication that this phenomenon occurs during diffusion in molecular sieves.

The existence of concerted diffusion mechanisms with low activation energies is not restricted to SF_6 dimers in $AlPO_4$-5. We have examined the motion of SF_6 and CCl_4 clusters containing up to 24 molecules. In every case, the lowest energy barrier for cluster motion is when clusters move in a concerted fashion. These motions are well approximated by rigid body translations of clusters with adsorbates uniformly separated by $2^{1/6}\sigma$. The activation energies for these concerted motions are shown in Fig. 2. One striking feature of Fig. 2 is that, for both SF_6 and CCl_4, the highest cluster diffusion activation energy occurs for monomers ($n = 1$). Thus, at every temperature where isolated molecules are mobile in these systems, clusters of *all* sizes are also mobile.

The curves in Fig. 2 can be understood in terms of the mismatch between the molecular and lattice spacings. For example, a number of "magic" cluster sizes [16] with very low activation energies appear in Fig. 2. Approximating clusters by the rigid body mentioned above, magic clusters with even n should appear when every molecule in the cluster can be paired with another molecule that is completely out of phase with respect to the periodic lattice potential. This occurs when cluster pairs are $k + 1/2$ lattice spacings apart for some integer k. In this case, the paired contributions of the lattice potential to the total potential make no net contribution to the diffusion activation energy. Hence, magic clusters should appear when $n \simeq (2k + 1)/M$, where n is an even integer, k is an integer, and $M = 2^{1/6}\sigma/a$ is the dimensionless mismatch. For SF_6 (CCl_4), $M = 1.459$ (1.557). This criterion predicts magic clusters with even n when $n = 2, 24, 50, 72, \ldots$ $(2, 16, 34, 52, 70, \ldots)$ for SF_6 (CCl_4), in good agreement with Fig. 2. Furthermore, clusters with one more or fewer molecules than these magic sizes have activation energies comparable to a monomer, because there is one molecule in the cluster whose oscillatory lattice potential cannot be canceled. The existence of magic cluster sizes with odd n (for example, $n = 11$ for CCl_4) can be understood with similar arguments.

While activation energies allow a great deal of insight into cluster diffusion mechanisms, additional information is necessary to determine the rate of cluster motion. One useful approximation to cluster diffusion rates is based on harmonic transition-state theory (TST) [21]. With this approximation, the tracer diffusivity of a cluster is $D = \nu_{\mathrm{TST}} a^2 \exp(-E_a/kT)/2$, where E_a is the activation energy and ν_{TST} is the ratio of the real normal mode frequencies at the minimum energy state and transition state [21]. Harmonic TST is valid for $T \ll E_a$. The TST predictions for the tracer diffusivities of SF_6 clusters are shown in Fig. 3. The results for CCl_4 are qualitatively similar. In general, ν_{TST} decreases as the cluster mass is increased (with some exceptions, for example, $\nu_{\mathrm{TST}}^{n=3} < \nu_{\mathrm{TST}}^{n=4}$). This behavior combines with the highly size-dependent cluster activation energies to make the size dependence of D a complicated function of temperature. The most significant feature of Fig. 3 is that, when harmonic TST is valid, clusters with $n = 2$ or 4 diffuse faster than monomers. At very low temperatures, the monomer diffusion rate is slower than or comparable to the diffusivity of all the clusters shown in Fig. 3.

One implication of our findings for experimental studies is that the diffusion rates of molecules in pores with finite concentrations may be faster than those of isolated, individual molecules. Indeed, in recent experimental studies [4], anomalously high diffusion rates were inferred from single-file mobilities at finite concentrations. Our results indicate that the concerted diffusion of molecular clusters could contribute to these trends. It is important to note, however, that our discussion above deals exclusively with isolated molecular clusters. A more challenging but experimentally relevant issue is the evolution of pores containing many clusters. For SF_6 and CCl_4 clusters it is always energetically favorable for two clusters to coalesce into a single, larger cluster. Cluster coalescence in these systems is an activated process (due to the corrugation of the substrate potential) with energy barriers similar to the barriers for cluster diffusion. Thus, coalescence will be an important effect for pores containing multiple clusters. This phenomenon is entirely analogous to the coalescence and growth of clusters on crystal surfaces via cluster diffusion [16,22].

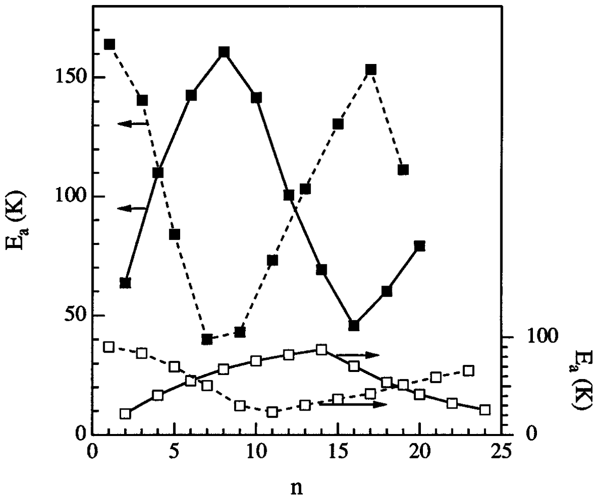

FIG. 2. The activation energy, E_a, for concerted diffusion of SF_6 and CCl_4 clusters (open and filled symbols, respectively) containing n molecules. The vertical axis for SF_6 (CCl_4) is shown on the right (left). The data with odd (even) n are connected with dashed (solid) curves to guide the eye.

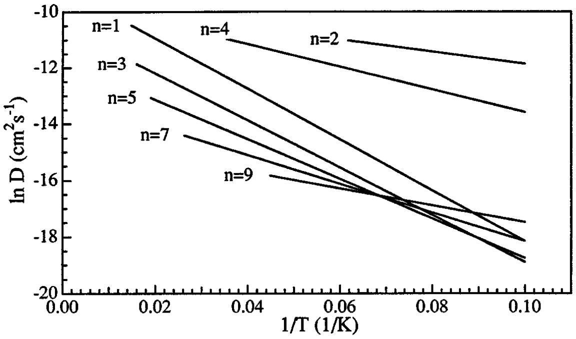

FIG. 3. The diffusion coefficients of SF_6 clusters with $n = 1$, 2, 3, 4, 5, 7, and 9 predicted by harmonic TST. For each cluster, data is shown for $T \leq 0.75 E_a$ K.

In addition to coalescing with other clusters, adsorbed clusters can dissociate. We have calculated MEPs for the separation of SF_6 clusters into cluster pairs. As with diffusion, concerted motions play an extremely important role in cluster dissociation. Events that involve the motion of multimolecule fragments proceed by quasirigid body motions very similar to those seen for concerted diffusion. In general, the multiple MEPs for dissociation have very similar energy barriers. For example, a cluster with $n = 6$ can fragment into clusters with $n = 5$ and 1, 4 and 2, or 3 and 3 with activation energies of 217, 213, and 228 K, respectively. All of the SF_6 clusters we have examined have cluster dissociation barriers of 200–230 K.

The discussion above allows a qualitative description of pores containing many clusters to be given. In the most practically relevant temperature regime, which occurs at temperatures high enough that cluster dissociation occurs, the cluster size distribution results from a dynamic equilibrium between coalescence and dissociation. The transport rates of individual molecules will be determined by the distribution of cluster sizes. An important future challenge will be to predict cluster diffusion rates accurately in this temperature regime (the TST method used above is not valid) and to develop methods that allow the prediction of equilibrium cluster properties.

The single-file diffusion of CF_4 is more complex than SF_6 or CCl_4. CF_4 tetramer provide an interesting example of the rich features of this system. Although $M = 1.244$, CF_4 tetramer are not magic clusters; the simple criterion above cannot describe these clusters because it assumes that the minimum-energy state has molecules spaced uniformly $2^{1/6}\sigma$ apart. In fact, the minimum-energy state consists of two CF_4 pairs separated by a vacant site (see Fig. 4). The energetically preferred cluster diffusion mechanism involves the vacancy hopping through the cluster. The energy barrier for this process (71.8 K) is much less than the monomer diffusion barrier (134 K [7]). CF_4 dimers (trimers) also perform stepwise diffusion with $E_a = 170.6$ (125.3) K. As for SF_6 and CCl_4, CF_4 clusters diffuse with activation energies considerably lower than the barriers to cluster fragmentation.

In conclusion, interadsorbate attractions are an extremely important feature in the mobility of particles during single-file diffusion in molecular sieves. In all of the cases we examined, the energy barriers for fragmentation of molecular clusters are considerably higher than the monomer diffusion barrier. Thus, molecular clusters are stable or metastable over a wide temperature range where isolated monomers are mobile. The barriers for cluster diffusion are often much lower than the monomer diffusion barrier, so cluster diffusion will occur whenever monomer diffusion occurs. Our findings indicate that cluster diffusion could underlie the unusually high rates measured for single-file diffusion in recent NMR studies [4] and that future theoretical efforts should focus on accurately describing this phenomenon.

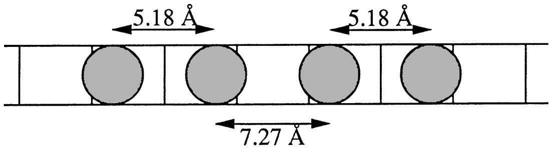

FIG. 4. The minimum-energy state of a CF_4 quadramer.

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