Orientation of Hydrocarbon Chains in Molecular Sieve 5A: Additional Evidence for Effects of Surface Curvature[1]

Derouane *et al.* have proposed (*1–4*) an elegant model for the van der Waals interaction of an adsorbed molecule with a curved surface of an adsorbent pore. This interaction acquires significance, particularly when we consider adsorption and catalysis in zeolites. According to this model, a molecule adsorbed in the pore will orient in such a fashion as to lie closest to the walls of the zeolite cage and achieve the best possible fit between its size (and shape) and the intrazeolite environment. It also envisages a concept of "creep" diffusion or motion of chain molecules effected by local deformation of molecular segments. The authors have applied these concepts of surface curvature effect to explain a number of physical and chemical phenomena in zeolite systems. During our studies on the adsorption, desorption, and kinetics of linear paraffins on molecular sieve 5A (*5, 6*), we have arrived at the same conclusions with respect to the orientation of paraffin chains. We observed (*5*) that when molecular sieve 5A saturated with normal alkanes was subjected to temperature-programmed desorption two desorption phases resulted if the number of carbon atoms in the alkane chain was less than 10. Higher *n*-alkanes gave rise to an additional high-temperature phase whose magnitude increased with an increase in the carbon chain length. The first two phases were attributed to the desorption of alkane molecules filling the internal cavities and the interparticle space. We ascribed the third phase to those molecules which were too long to be accommodated in a single cavity but extended into the adjacent cavities through the eight-ring windows. The additional energy due to the in-

teraction of the hydrocarbon segment with the close-fitting windows will enable the hydrocarbon chain to acquire this orientation rather than be contained within a single cavity in a coiled fashion. This leads to the question whether the molecular segment within the cavity assumes a linear or curved orientation. It is known (*7, 8*) that the interaction energy of $-CH_2-$ group is higher when the hydrocarbon is close to the wall than when it is in the center of the cavity. This fact should favor the former position. However, the conclusive evidence for this effect has been provided by our thermal desorption data. Had the alkane molecule been oriented linearly along the central axis (11.4 Å) of the zeolite A super cage, *n*-octane molecule (13.2 Å) should also have given rise to the high-temperature desorption phase. But this phase begins to appear only with *n*-decane (15.6 Å) which has the minimum chain length required when the molecule acquires an orientation "sticking" to the curved "walls" of the cage with the "head" and "tail" methyl groups located at the center of the eight-ring windows. One expects that such an orientation will not be possible if the chain is less flexible as in the case when the molecule contains groups such as $-C≡C-$ which hinder the free rotation of the molecular segments. Indeed, we have recently observed that during thermal desorption of olefins and dienes from 5A, even shorter molecules such as 1,5-hexadiene and 1-octene give rise to the third desorption phase (*9*). Such an interplay between the alkyl chain length and the zeolite cage dimensions were first noted by Gorring (*10*) who observed a "window of high transmittance" for C_{11} and C_{12} *n*-paraffin molecules in zeolite KT. This author invoked the concept of the alkyl chain in the

zeolite cage extending beyond the eight-membered cage aperture to explain the high diffusivity of these paraffin molecules.

It is known that diffusion of alkanes in 5A is influenced by preadsorbed polar molecules. We have observed (6) that the presence of 0.8 mol/cavity of water molecule suppressed the apparent diffusion coefficient (D/r^2) from 0.7 to 0.4 × 10^{-4} s^{-1}. The molecular sieve 5A studied is the predominantly calcium-exchanged form of zeolite [$Ca_4Na_4(SiO_2)_{12}(AlO_2)_{12}$]. As a consequence of the exchange of the eight sodium ions by four calcium ions the cationic sites at the apertures become vacant. Hence the adsorbed water molecules (which hydrate the zeolite cations) will not occupy cationic sites at the entrance to the supercage (11). Consequently, a satisfactory explanation of the influence of 0.8 mol/cavity of water on diffusivity could not be offered in terms of the partial blocking of the aperture by adsorbed water molecule. The creep diffusion model proposed by Derouane et al. (1–4) provides a valid explanation for this observation. The water molecule adsorbed near the calcium ion at the S1 position outside the sodalite cage would offer resistance to the creep motion of the alkane molecules. In fact, these water molecules would function as "molecular speed breakers" suppressing the mobility of the carbon chain within the cavity.

In conclusion, the surface curvature model has provided a firm theoretical basis for several of the unique experimental observations in molecular sieve adsorption and catalysis.

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