

LETTER TO THE EDITORS

On the Origin of an External Surface Barrier to Sorption
in Microporous Solids

To explain the large difference between the diffusion coefficients obtained with macroscopic sorption techniques (gravimetry) or microscopic ones (NMR, neutron scattering) some authors have postulated the existence of an energy barrier at the external surface of the zeolite. This energy barrier could originate in the partial blockage of the pore apertures possibly due to the presence of amorphous deposits or structural defects. More recently, Derouane *et al.* (1) proposed an additional explanation for the existence of a transport resistance at the pore opening of zeolites. Modeling the pore opening as a hemispherical crater in the flat surface and considering attractive forces of van der Waals type, they speculated on the existence of an energy barrier at the pore entry originating in the convex curvature of the pore rim.

In this Letter we provide evidence that a direct calculation of the interaction energy, performed in the same context (attractive forces of van der Waals type and spherical molecules), does not lead to the existence of any energy barrier related to a convex curvature effect. If any barrier exists, it would be associated with specific structural properties of the external surface.

The basic idea of Derouane *et al.* is that the van der Waals energy W of a molecule adsorbed on a surface depends on the surface curvature: $W(\text{concave}) > W(\text{flat}) > W(\text{convex})$. This qualitative concept is deduced from a model where the solid is represented as an isotropic dielectric continuum with spherical or cylindrical cavities and the adsorbed molecule as a polarizable point. This model allows the evaluation of the ratio of the adsorption energy on a curved surface and on a flat one.

In order to stay inside the framework of the van der Waals forces, we considered the interaction of an atom of rare gas with several zeolites and we used a potential expression of Lennard-Jones type (2),

$$V = \sum_i (-Cr_i^{-6} + Br_i^{-12}),$$

where i denotes the oxygen atoms of the zeolite and r_i is the distance of i from the rare gas atom; the oxygen atoms corresponding to r_i larger than 14 Å were not taken into account. As the energy barrier is predicted to be higher for large molecules, we report in Fig. 1 potential maps corresponding to one Xe atom interacting with mordenite. The surface is obtained by a clear cut of the crystal (along the plane parallel to [001] and of z value 1.06c) considering only the resulting surface oxygen atoms. Obviously the surface built up in this way represents an oversimplification of a real surface, where structure defects and hydrogen atoms could be expected. However, what we need here is to represent the atomic structure of a "flat" external surface, independently from the chemical nature of the surface atoms.

Figure 1b shows the potential distribution on the mirror plane of a main channel and its side pockets. It must be pointed out that the areas corresponding to negative potentials do not describe the void space of the cavities but represent only the space accessible to the center of mass of the adsorbate atom (X, Y, Z in Fig. 1 refer to the coordinates of the center of mass). The obliquely hatched areas represent regions of very high potential from which the Xe atom is completely excluded. In agreement with the Derouane concept of "nesting," the in-

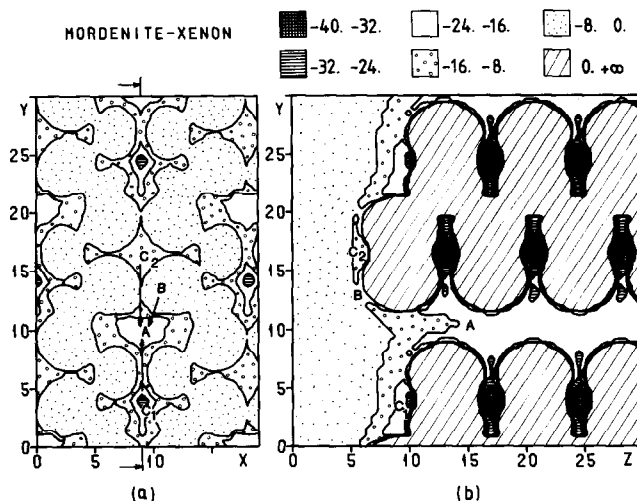


FIG. 1. Potential map for a Xe atom in mordenite. The crystal is cut along the crystallographic plane [001] of z value $1.06c = 8 \text{ \AA}$. Energies in kilojoules per mole. Distances in angstroms. (a) Map of the minimal potential values for the Xe atom adsorbed on the external surface. (b) Potential map in the plane [200].

teraction energy turns out to be deeper in the pockets (-40 to -32 kJ/mol) where the size of the molecule approaches the void volume than in the larger main channel (-24 to -16 kJ/mol). Figure 1a represents the map of the minimal potential value that can be reached by the Xe atom approaching the outer surface of the crystal. The channel opening appears as a white area (denoted A) while the outer surface itself is characterized by different energetic domains referred to as B, C₁, or C₂. The B domain, corresponding to weak potential values (-8 to 0 kJ/mol), coincides with prominent surface oxygen atoms. Deeper potential values (-32 to -24 , or -16 to -8 kJ/mol), denoted C₁ or C₂ areas, describe hollows surrounded by surface oxygen atoms in the outer surface of the crystal.

The probability for a Xe atom to enter directly a pore of the crystal turns out to be very small, so that the Xe atom will rather adsorb on the outer surface in a first step and will further move in the potential well reported in Fig. 1a before entering the pore or desorbing ultimately. The question is to

determine whether it must overcome an energy barrier to penetrate the pore or not. It is clear that a Xe atom coming from a type B energy domain will see its energy continuously decreasing without any barrier until it finally succeeds in entering the pore (path B \rightarrow A in Fig. 1). However, if it comes from a type C domain, it will have to overcome an energy barrier to ultimately penetrate the pore opening (barrier of ~ 17 kJ/mol for the path C₁ \rightarrow A and ~ 8 kJ/mol for C₂ \rightarrow A). It must be pointed out that this energy barrier does not originate in the curvature at the opening, but in the heterogeneity of the surface.

Neglect of the external surface relief is probably the reason for the failure of the model of Derouane *et al.* concerning the origin of the surface barrier. Actually the surface curvature is no more convex at the pore opening than on the atoms composing the external surface of the zeolite crystal.

REFERENCES

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*Institut de Recherches sur la Catalyse
2 avenue Albert Einstein
69626 Villeurbanne Cédex, France*

F. VIGNÉ-MAEDER

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