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LETTERS TO THE EDITORS

On the Origin of an External Surface Barrier to Sorption in Microporous Solids: Reply to F. Vigné-Maeder

Vigné-Maeder (*1*) has recently questioned the origin of the external surface barrier to sorption in microporous solids as discussed by us in terms of surface curvature effect (*2, 3*). Her conclusion is that the energy barrier does not originate in the curvature at the pore rim but in the heterogeneity of the surface and that the model proposed by us therefore fails in this respect. Before presenting our results which give more insight into our proposal and that of Vigné-Maeder, we wish to remind the reader that we did not exclude the effect of surface atomic corrugation, in particular for spherical atoms or molecules (see page 61 in Ref. (*2*)). Physically, the notions of convexity and concavity also hold at the atomic level.

In the framework of van der Waals interactions, the present calculations were performed using a procedure similar to that used by Vigné-Maeder, with a Lennard–Jones-type expression for the potential (*4*). Iso-interaction energy contours were computed for both Ne and Xi interacting with the external and internal surfaces of a mordenite slab obtained by a cut of the crystal along the (001) planes at z values ±11.28 Å ($1.5 \times c$, c being the unit cell parameter along z). In our case, periodicity along the x and y directions was introduced by the minimal image condition (*5*). Two cases were considered, one in which only the surface oxygen atoms were taken into account, and the other by additional consideration of the Si T (tetrahedrally coordinated) atoms in the pore walls.

Figure 1 shows iso-interaction potential energy maps for the Ne and Xe atoms in mordenite in the (100) plane at $x = 0$, with and without the presence of the underlying Si atoms. Note that the repulsive iso-energy contours are not shown to visualize the framework. These maps reproduce well the results of Vigné-Maeder and indicate, as we predicted earlier (*2*), the preferential location of the sorbed atoms in the most confined environments, i.e., the side-pockets of the mordenite channels (the "nesting" effect). Interestingly, the presence of underlying Si atoms does not noticeably alter the iso-interaction potential energy profiles, which supports the assumption made by Vigné-Maeder who only considered oxygen atoms. To some extent, slightly lower energies are observed principally at the external surface, as seen from a comparison of Figs. 1A and 1B, and of Figs. 1C and 1D. It is also clear from these iso-energy contours that an atom approaching the surface will preferentially glide toward the hollow sorption sites of low sorption energy found on the external surface.

It is possible to evaluate from such energy maps the change in interaction energy for a Ne or a Xe atom moving along the lowest energy pathway connecting the most stable position on the external surface to the most stable position on the mordenite internal surface side pockets. Figures 2A and 2B show the energy change along such trajectories. Energy barriers due to the convexity (of topographic and atomic origins) at the pore rim are observed in both cases and are not very sensitive, as expected from the above remark, to the presence of Si. In both cases, the barriers correspond to about 43 to 47% of the absolute sorption energy on the external surface which agrees well with the 50% value predicted by the continuum model (*2–3*). The barrier profile may be considered as rather smooth, as the

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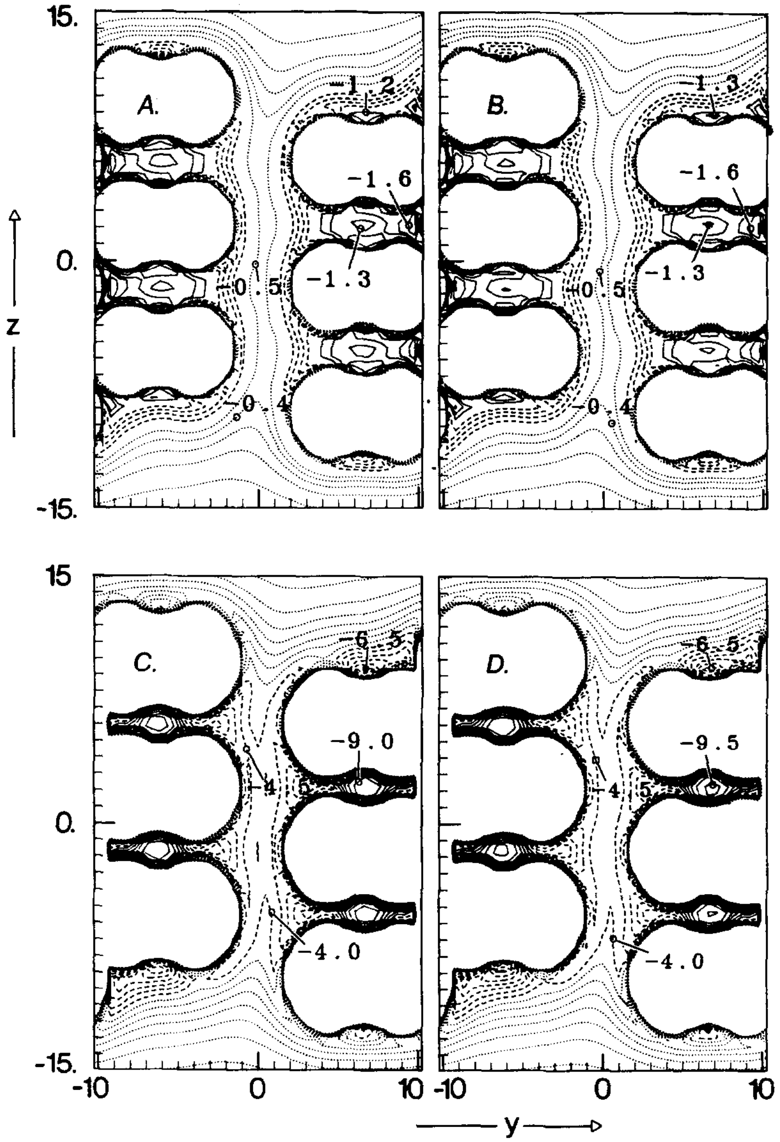

FIG. 1. Iso-interaction energy contour maps for a Ne or a Xe atom in mordenite (MOR) in the (100) plane at $x = 0$ ($-10.2 \leq y \leq 10.2$; $-15 \leq z \leq 15$ Å). A slab is obtained by cutting the crystal along the (001) planes of z values ±11.28 Å ($1.5 \times c$). Energies are given in kilocalories per mole at 0.1 and 0.5 kcal mol^{-1} intervals for Ne and Xe, respectively: (—) −1.7 to −1.1 kcal mol^{-1} for Ne and −10 to −7 kcal mol^{-1} for Xe; (---) −1.0 to −0.6 kcal mol^{-1} for Ne and −6.5 to −4 kcal mol^{-1} for Xe; (....) −0.5 to 0 kcal mol^{-1} for Ne and −3.5 to 0 kcal mol^{-1} for Xi. (A) Ne in MOR (O only), (B) Ne in MOR (O and Si), (C) Xe in MOR (O only), (D) Xe in MOR (O and Si).

molecule turns around the pore rim, with superimposed features originating from surface corrugation effects as pointed out by Vigné-Maeder.

Finally it is interesting to note that the sorption energy minima in the side pockets are at −1.53 and −9.5 kcal mol^{-1} for Ne and Xe, respectively. These values compare relatively well with those predicted by our simple continuum model (*2*, *6*), i.e., −1.01 and −7.65 kcal mol^{-1}.

Thus our conclusions are that:

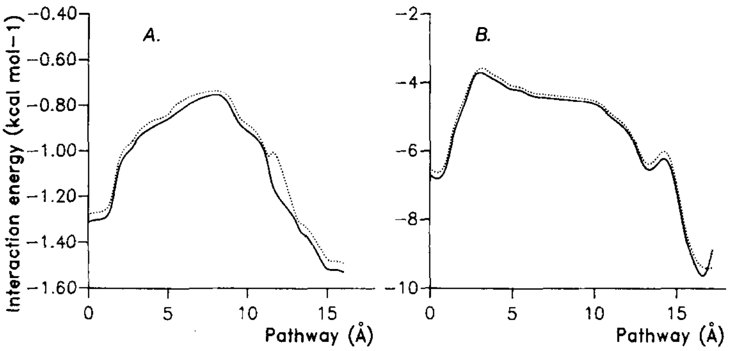

FIG. 2. Interaction energy for an atom of (A) Ne and (B) Xe moving along the minimum energy pathway leading from the most stable position on the external surface to the most stable position in the mordenite side pockets. (....) O only; (—) O and Si.

(i) the convexity at the pore rim is affected by both the framework topography (surface curvature) and the atomic corrugation of the surface;

(ii) the energy barrier opposing the penetration of a (spherical) atom into the pores is indeed about half the sorption energy of the molecule on the external surface as predicted earlier by Derouane *et al.* (*2–3*);

(iii) framework atoms (cations) of low polarizability, which are further screened by the surface oxygen atoms and are buried in the zeolite pore walls, have little effect on van der Waals-type molecule–zeolite interactions.

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