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LETTER TO THE EDITORS

Sorption and Catalytic Properties of Natural Mordenite

The sorption properties of the natural zeolite, mordenite, suggest that the "windows" of the porous aluminosilicate framework probably consist of eight-membered rings with a free diameter no larger than 4.2 Å (*1*). The structure recently proposed by Meier, however, contains large channels which are parallel to the fiber axis of the crystal. These channels are accessible through 12-membered rings of oxygen atoms and they have a free (crystallographic) diameter of about 7 Å (*2*). Thus, the zeolite should sorb molecules at least as bulky as cyclohexane. Meier recognized the inconsistency of the structure with the sorption properties and suggested that the effective diameter of the channels was reduced to ~4 Å by stacking disorders.

We wish to report that the structure and sorption properties of natural (Nova Scotia) mordenite become compatible if the metal cations are removed by base exchange with acid, and, that the resulting "acid" zeolite has some remarkable catalytic properties.

Natural Nova Scotia mordenite was obtained in the form of pebbles from Ward's Scientific Establishment. It was ground and the portion passed through a 325-mesh sieve was studied. X-ray diffraction gave the expected pattern for the mineral along with evidence for a small amount of unidentified contaminant. The powder did not sorb cyclohexane. After digestion with 3 *N* hydrochloric acid, it had the composition: Na, 0.2%; Ca, 0.8%; Al_2O_3, 12%; SiO_2, 87%; X-ray diffraction showed that the material was still highly crystalline. The treated powder sorbed 5.6% of its weight of cyclohexane, and 13.2% of water. The dimensions of the channel given by Meier suggest that cyclohexane is likely to be sorbed as a one-dimensional fluid, i.e. as a single "string" of molecules. If one allows 6.6 Å of channel length per molecule, the calculated sorption at saturation is found to be 6.7 wt %, in reasonable agreement with the value found by experiment. It would seem that the accessibility of the large channels of powdered natural mordenite to large sorbate molecules is restricted by the lodgment of a fraction of the cations in these channels. The proposed "stacking disorders" probably are widely spaced, and play a minor role, if any, in modifying the sorption properties.

The acid-exchanged zeolite is a remarkably effective catalyst. Butane and cyclohexane are readily converted to isobutane and methylcyclopentane, respectively, at about 200°C with very slow deactivation of the catalyst. Neither of these reactions is effectively induced by silica-alumina cracking catalyst, except perhaps under drastically more severe reaction conditions (*3*) (see Table 1). Typical results from experiments in which cyclohexane-saturated helium, or *n*-butane vapor, are passed over the catalyst at 1 atm are described in Table 1. Other reactions catalyzed by the zeolite include the cracking of *n*-hexane at about 200°C to produce saturated fragments, and the conversion of benzene to toluene and ethylbenzene at about 400°C.

The mild conditions required to isomerize paraffins that contain no tertiary hydrogen (*4*), the ability to convert the stable benzene molecule, and the production of only

TABLE 1
Isomerization over Acid Mordenite

Feed	Contact time (sec)	Temp. (°C)	Time on stream (min)	% Conversion of feed	
				To isomer	To by-product
Cyclohexane	7	260	22	10.7	2.6
Cyclohexane	7	260	164	11.5	0.9
n-Butane	5	200	15	7.2	1.0
n-Butane[a]	600	481	—	2.8	7.2

[a] Data from experiment with amorphous silica-alumina shown for comparison; data taken from ref. 3.

saturated fragments by the low-temperature cracking of n-hexane, indicate that the acid-mordenite more closely resembles HCl-promoted $AlCl_3$ catalyst than amorphous silica-alumina. The extent to which the unusual behavior depends on the *number* of sites, as contrasted with the *kind* of sites, is now being studied.

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