

The Calcined Faujasite Series

A Reply to Kerr, Olson, and Dempsey

In their letter, Kerr *et al.* (1) (KOD) take issue with a number of statements made in an earlier paper by Ambs and Flank (2) (AF). We believe that most of the differences between KOD and AF are due to semantics or misunderstanding.

In the AF paper, the term "ultrastable" faujasite was applied only to the material prepared by the intermediate calcination procedure of McDaniel and Maher (3) (MM). KOD apply the term also to the product of a single "deep bed" calcination of ammonium-exchanged faujasite, as described by Kerr (4). This product is claimed to be the same as that prepared by the MM procedure. Such a claim may well be true for particular specimens. However, as KOD admit, these preparative procedures are not free of uncontrolled variables such as the water vapor pressure in the deep bed procedure and, equivalently, the bed geometry in the intermediate calcination procedure, as well as others, e.g., the silica to alumina ratio, particle size, and the detailed thermal history of the sample. KOD refer to limiting cases, and thus indicate a recognition of the fact that these variables, at least, can give rise to continuously variable series of products.

Thus, the exact product formed is somewhat indeterminate, and reproducibility depends upon very careful control of experimental technique. In other words, the terms that have been used seem to refer to materials with rather imprecisely defined structures and properties.

Since it has not been firmly established that "ultrastable" faujasite contains octahedral Al, nor that the less imperfect "HY" does not contain it to some degree (perhaps as much as 5% occupancy), it seems pointless to argue further as to whether one should emphasize differences or similarities between materials differing mainly in the degree of lattice imperfection, or what may

essentially correspond to the same thing here, the occupancy of the octahedral sites by Al ions. We would agree, of course, that the extreme members of such a series are different to some degree, as we stated in the AF paper.

We suggest that hypotheses based on limited data in a series cannot always be generalized and may be, in some instances, quite misleading. The complex interactions involved in this system, when fine details are examined, make it necessary to look beyond simple interpretations for a more complete understanding of the relationships involved. A review of the available data emphasizes the many variables that exert influences, large and small, on the results obtained. It is apparent that extremes in behavior as well as all conceivable shadings in between can be found.

We would, therefore, be quite reluctant about trying to give names to different segments of a continuum, or to describe by a single designation the broad range of properties covered by all but one or both end members of the series, the remaining closely related member or members being described by another designation. We would be especially reluctant if, by so doing, we would ignore the intermediate regions or the artificial nature of such definitions. We prefer not to obscure the relationships which we recognize do in fact exist.

We also find it difficult to accept the implication that cationic Al does not migrate to a site with undisturbed anionic framework charge, as opposed to a site depleted in charge due to the hydrolysis of an Al from the framework. It would seem that the electrostatic driving force for this would be quite strong, especially at elevated temperatures.

It should be further noted that it has not been *shown* that the structures proposed in KOD's letter are distinct, and it does not

follow that if there are some chemical composition differences they are "hence structurally different," especially when one allows for the possibility of structural substitution. The reaction equations cited have been proposed but not clearly established or independently supported. The implication of confirmed and proven points in the KOD statement is thus somewhat over-emphasized.

With regard to some of the details cited, we agree that KOD Ref. (2) did not explicitly propose involvement of water in NaY collapse, but we must point out that hydroxyl groups are present in sodium faujasite and can be seen by TG and, sometimes, also by IR (5) and via Bronsted acid activity (6). There is some indication that self-steaming of NaY samples may have an effect on stability, and that this effect may interact with other variables.

Private discussion with Dr. Kerr established the fact that the samples of KOD Ref. (4), like those of AF, were not calcined before DTA evaluation, but this was not clear from an examination of Table II of Kerr's paper, which combined data obtained on differently prepared samples into one table but lacked explicit further details. The correction is, of course, valid.

It would have been better if the samples were more clearly distinguished as was done in the AF experimental section. Those samples receiving a final calcination were separately noted in AF Fig. 2 and were shown on a separate curve.

On the last point cited by KOD, the crystal used by Olson and Dempsey (7) obviously had some degree of degradation. The exact amount, while uncertain, was probably not too large, but had to be finite because the thermal activation of the crystal would be diffusion-limited and some of the difficultly removable water would be removed only at elevated temperatures. It was impossible to chemically determine the exact degree of exchange for the single crystal. It would thus be an exaggeration to claim that tetracoordinate

aluminum was solely present. The composition of the crystal was only grossly estimated, and we felt it may have been possible to detect some cations, although at the time of writing, we were not sure of the exact circumstances involved in the work. In the absence of better evidence, we cannot dispute KOD's statement of lack of conflict. It is clear, however, that perhaps 5% occupancy of octahedral sites by Al would be undetectable in Olson and Dempsey's work.

Finally, we note that we discussed the fate of the aluminum generally, and not the detailed mechanism by which it met its fate. We feel that our proposed general mechanism for aluminosilicate degradation is adequate to explain the data we have seen, and to organize them on a consistent and logical basis. It is not complete, of course, and we await further proposals along these lines that will advance our understanding of an admittedly complex situation.

REFERENCES

1. KERR, G. T., OLSON, D. H., AND DEMPSEY, E., *J. Catal.* **18**, 236 (1970).
2. AMBS, W. J., AND FLANK, W. H., *J. Catal.* **14**, 118 (1969).
3. MCDANIEL, C. V., AND MAHER, P. K., *Conf. Mol. Sieves*, Soc. Chem. Ind., London, April, 1967.
4. KERR, G. T., *J. Catal.* **15**, 200 (1969).
5. CARTER, J. L., LUCCHESI, P. J., AND YATES, D. J. C., *J. Phys. Chem.* **68**, 1385 (1964); ANGELL, C. L., AND SHAFFER, P. C., *J. Phys. Chem.* **69**, 3463 (1965).
6. BARTLEY, B. H., HABGOOD, H. W., AND GEORGE, Z. M., *J. Phys. Chem.* **72**, 1689 (1968).
7. OLSON, D. H., AND DEMPSEY, E., *J. Catal.* **13**, 221 (1969).

W. J. AMBS
W. H. FLANK

Houdry Laboratories
Air Products & Chemicals, Inc.
Linwood, Pennsylvania 19061
Received May 1, 1970