JOURNAL OF CATALYSIS 49, 115–119 (1977)

Aluminum Ion Distributions in Zeolites

In a recent letter to the Editors of this Journal Mikovsky and Marshall (MM) (*1*) develop a modified method of quantifying the suggestion [Dempsey (*2*, *3*)] that the geometrical distribution of the available aluminum ions over the square faces of the sodalite cages of the H-zeolite structure gives rise to the two distinct levels of acid strength observed by Beaumont and Barthomeuf (*4*). This Note forms a comment upon Ref. (*1*).

The essence of the proposals of MM lies (a) in abandoning, or, at least, weakening, the suggestion that the aluminum ions in the zeolite framework are ordered; (b) in an application of the fact that each aluminum ion lies in three zeolite square faces: these points are not independent of each other. To proceed from (a) MM must first investigate the aluminum ion distribution in a selected Y-zeolite over a suitably large section of the crystal. For this section they select an unspecified repeating unit that turns out to be the unit cell. (Perhaps a series of repeating units of various sizes should be investigated to show that the solution reached by MM is unconstrained by the unit chosen.) By going beyond the crystallographic basis (the fundamental repeating symmetry unit of the structure) MM must consider, explicitly, all first neighbors of each aluminum ion in their chosen unit. (A first neighbor aluminum ion is an aluminum ion lying at the minimum possible distance from any specified aluminum ion—by Löwenstein's rule, the diagonal of a 'square' face.)

On the other hand, the author's point of view, stated explicitly in Refs. (*2*, *3*), is that aluminum ions (in the structures considered by the author) are ordered in the crystallographic basis of the faujasite fcc diamond structure. This, in turn (since the basis is centrosymmetric), permits consideration of the arrangement of, and the neighbors of, ions in a single representative sodalite cage of the structure, and, for the present problem, permits descriptions in terms of the square faces of this sodalite cage. Justification for this point of view, first proposed in Ref. (*5*), comes from Refs. (*6*, *7*) and, hopefully, from the remainder of this paper.

It should not be inferred from the foregoing that any criticism of the approach of MM is implied; as explained below, for the zeolite composition selected by MM for study, their approach, or a modification of it, is probably essential for a resolution of the question of aluminum ordering that seems to lie at the heart of the acidity problem. It is hoped to describe this modification in a later paper.

In Ref. (*3*) it was suggested that, although, owing to the symmetries involved, the individual sodalite cage squares could be used for discussion, the critical aspect of the situation described is the presence of two, rather than one, first neighboring aluminum ion for each aluminum ion in the sodalite cage. Although it was not stated explicitly, brief consideration of Fig. 2, Ref. (*3*), or Fig. 1 below, will make it clear that, while each α-face contains two aluminum ions, each with two close aluminum neighbors, each β-face contains one aluminum ion with, *at most*, one close aluminum neighbor; the α-face

ISSN 0021-9517

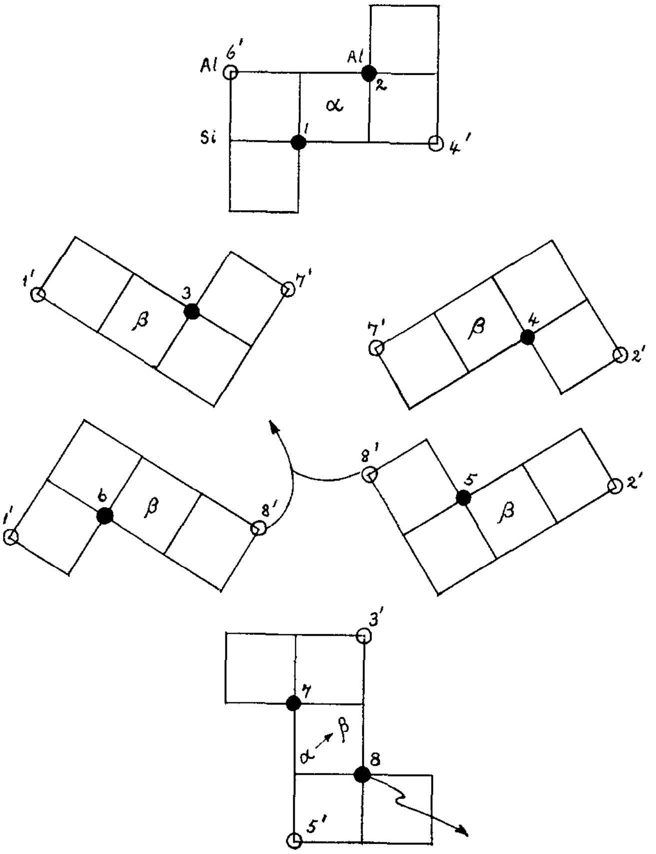

FIG. 1. Exploded view of Si/Al = 2:1 sodalite cage based on square faces of the cage and showing contiguous faces. Al ions represented by numbered (●, ○). Unmarked corners are Si ions. Prime numbers are equivalent (through an inversion center) to unmarked ones. Position 8 (and 8′) has Al replaced by Si to form Si/Al = 2.43:1 material.

sites are taken to form Beaumont and Barthomeuf's weak acid sites, and the β-face sites their strong acid sites. In attributing to the author the assumption that strong sites are formed only by aluminum ions with no first aluminum neighbors, MM are in error; this view was modified in Ref. (*3*). Thus, using MM's notation, and taking n_s to represent strong sites and n_w weak sites,

$$n_s = n_0 + n_1,$$
$$n_w = n_2 + (n_3).$$

[In the models considered in Refs. (*2* and *3*), $n_3 = 0$.] Justification for this view comes from Refs. (*3*, *4*)—and also from the paper of MM.

Referring to Fig. 3 of MM the n_0 and n_1 peaks arise within 25°C of each other on the temperature scale, and the distributions overlap considerably. This suggests, qualitatively, that n_0 and n_1 sites are rather similar to each other, and that they are more similar to each other than n_2 sites are to n_1 sites (~60°C separation) or n_3 sites are to n_2 sites (~70°C separation). Furthermore, as drawn, MM's Fig. 2 bears little resemblance to Beaumont and Barthomeuf's important Fig. 2 (*4*)—which first prompted the conjectures of Ref. (*2*). By adding the n_1 line and the n_0 line in MM's Fig. 2, and placing the n_2 and n_3 lines to correspond to a sequence of aluminum removal, however, a fair approximation to

TABLE 1

Si/Al	I			II			III			IV			Total Al ions
	Remov. seq.	N_w	N_s $n_1 + n_0$	Remov. seq.	N_w	N_s $n_1 + n_0$	Remov. seq.	N_w	N_s $n_1 + n_0$	Remov. seq.	N_w	N_s $n_1 + n_0$	
2	0	32	32										64
2.43	8	16	32 + 8	8	16	32 + 8	4	24	32	4	24	32	56
3	4	8	32 + 8	2	0	32 + 16	6	16	32	8	8	32 + 8	48
3.8	6	0	32 + 8	etc.			3	8	32	1	0	16 + 24	40
etc.	etc.						5	0	32	etc.			32
							etc.						

the form of Beaumont and Barthomeuf's figure is obtained—see Fig. 2 below.

For completeness, Table 1 shows four possible sequences of aluminum ion removal from the 2.43:1 Si/Al material of Refs. (*2–4*). Note particularly that each sequence starts from the 2:1 ratio, and that progression from the 2:1 to the 2.43 material is assumed to involve a difference in synthesis rather than (as for the remainder of the sequence) aluminum removal from already synthesized crystals. The removal sequence identifies ions i and their equivalents i' in adjacent sodalite cages (according to the labeling of Fig. 1); all other numbers relate to a unit cell.

The results of Beaumont and Barthomeuf suggest that the first sequence typifies the difference between a 2:1 and a 2.43:1 material, as synthesized, and the sequence of aluminum removal, by EDTA treatment, starting from the 2.43:1 material.

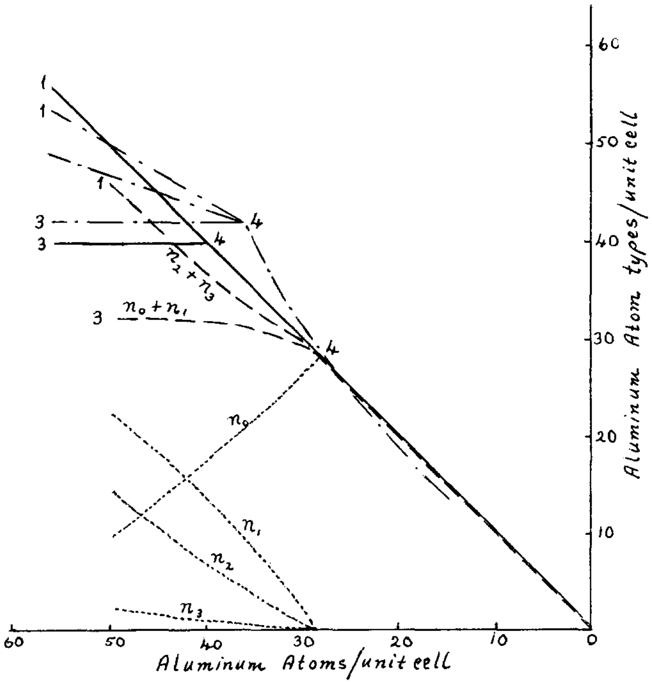

FIG. 2. (— -) Experimental data of Beaumont and Barthomeuf; (- - -) data of MM; (— —) data of MM replotted; (—) model of this paper [and of Ref. (*3*)]. For any one set of curves, line 1–4 represents weak acid sites, in the sense used by Beaumont and Barthomeuf, and lines 3–4–origin represent strong acid sites.

The treatment of faujasite type zeolites pursued by the author during the last decade or so, is based upon a view of the materials as being essentially ionic. Ionic materials, typically, may be considered to be constructed of identical small crystal units, each having zero net charge and zero dipole moment. In the case of the faujasite structure the centrosymmetric nature, mentioned above, of the faujasite crystallographic basis makes it an appropriate ionic building unit; and use of this unit leads to zeolite models having the following restricted range of compositions:

$$\text{Si/Al} = 96/96,\ 104/88,\ 112/80,\ 120/72,\ 128/64,\ 136/56,\ 144/48,\ \text{etc.} \qquad \text{(A)}$$

Perhaps fortuitously the material investigated by Beaumont and Barthomeuf corresponds to the sixth composition ratio of this series; although its structure, on an atomic scale, may well deviate from the ionic ideal. The material used by MM, on the other hand, with 50 aluminum ions/unit cell, does not fit into the series so that, (a) any unit used to build an ionic model of *identical* repeating units must be larger than the crystallographic basis; (b) the possibilities for a degree of random distribution of aluminum ions are increased.

If, however, we relax the requirement for identical repeating units, while retaining the crystallographic basis as our repeating unit, we may postulate that a zeolite sample having 50 aluminum ions/unit cell may be a mixture of appropriate proportions (1:3) of crystals having Si/Al = 2.43 and 3. Alternatively, one may postulate that the composition of individual growing crystals shifts (as aluminum is consumed from the synthesis gel) from the 2.43 ratio to the 3:1 ratio. This would require individual crystals to be ordered in two different regimes on either side of a shell of ordering discontinuity within the crystal—a somewhat improbable concept that would minimize crystal entropy.

On the other hand since there does seem to be strong justification for the assumption of ordering of aluminum and silicon ions in zeolite structures, as evidenced by the work of Dempsey *et al.* (*6*) [see also the important comment by Kühl on the paper by Smith in the proceedings of the Second International Zeolite Conference (*8*)], one might propose that the materials of sequence (A) form a distinct class different from materials of intermediate composition. In this connection it would be interesting to carry out calculations of the type described by MM in which the ordered arrangement of ions corresponding to the nearest ratio of sequence (A) is observed, and adding or removing only a few (up to 4/unit cell) aluminum ions, at random (in a first approximation), to achieve intermediate compositions such as that with 50 aluminum ions.

Clearly a detailed experimental study of the synthesis of faujasites of varying composition, and of the kinetics of aluminum removal, would be of great theoretical, and, perhaps, even practical, interest. (Related catalytic studies should also be carried out.) Study of the stability of zeolites as a function of composition (perhaps using microcalorimetry) and of the stability of zeolites of sequence (A) following a variety of thermal treatments would also be extremely interesting.[1] Possibly there may exist ordered and disordered versions of the same materials in the compositions of sequence (A). It must be remembered, of course, that order/dis-

---

[1] That such investigations may have important potential practical application is evidenced by the work of Kerr and Chester (*9*) at Mobil R and D Corporation Laboratories that produced very high silica forms of Y-zeolite. This work followed a suggestion by the author (*9*), in early 1971, that appropriate thermal treatment might provide a means of overcoming the long standing problem of the progressive, and eventually catastrophic, structural degradation of normal Y-zeolite that usually occurs on removal of aluminum beyond about 30% of the base material aluminum content.

order phenomena conventionally lie in the category of second order phase changes with lambda specific heat transitions as a function of temperature, and, ideally, zero associated latent heats.

REFERENCES

1. Mikovsky, R. J., and Marshall, J. F., *J. Catal.* **44**, 170 (1976).
2. Dempsey, E., *J. Catal.* **33**, 497 (1974).
3. Dempsey, E., *J. Catal.* **39**, 155 (1975).
4. Beaumont, R., and Barthomeuf, D., *J. Catal.* **27**, 45 (1972).
5. Dempsey, E., *in* "Molecular Sieves," p. 293. Soc. of Chem. Ind., 1969.
6. Dempsey, E., Kühl, G. H., and Olson, D. H., *J. Phys. Chem.* **73**, 387 (1969).
7. Dempsey, E., *J. Phys. Chem.* **73**, 3660 (1969).
8. Kühl, G. H., see Smith, J. V., *Advan. Chem. Ser.* **101**, 171 (1971).
9. Dempsey, E., Chester, A. W., and Kerr, G. T., unpublished data, 1971.

E. Dempsey

64, Pewley Way
Guildford, Surrey, England

Received January 24, 1977