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A Tentative Model of Y Zeolites to Explain Their Acid Behavior

In an earlier note in this Journal (*1*) it was proposed that the acidity variation in Al deficient zeolite HY (*2*) is dependent upon the number of square faces of sodalite cages carrying two Al ions. In a comment on Ref. (*1*) Barthomeuf (*3*) suggested that the scheme would have to be refined to explain the acid properties of non-Al deficient samples. The object of this paper is to propose a model for Y zeolite that will encompass all of the results of Beaumont and Barthomeuf.

The main point to be explained relates to the situation that, while the proposal of Ref. (*1*) provides, apparently, for 24 strong acid sites/unit cell and 32 weak ones, experiment (*2*) indicates the presence of about 40 strong sites and 16 weak ones.

To resolve the discrepancy a refinement of the point of view of Ref. (*1*) is required, although the basic premise, that *the acidity variation depends upon the number of sodalite cage square faces carrying two Al ions* is retained. The model is based upon ordered structures that are centro symmetric through the centers of hexagonal prisms (*5*).

According to the work of Olson and Dempsey (*4*), the part of the zeolite structure of primary importance for proton location is the hexagonal prism. Dissection of sodalite cages as in Ref. (*1*) does not explicitly take account of the hexagonal prisms. In Ref. (*4*) evidence is given to suggest that in a HY zeolite protons occupy sites on a hexagonal prism as shown in Fig. 1 [see Fig. 1 of Ref. (*4*)]. The Al ions in Fig. 1 are distributed as in Ref. (*5*) so as to preserve the center of symmetry. As in Ref. (*4*) it is suggested that the ir band at 3640 cm^{-1} arises from protons H_1 lying outside the hexagonal prism in the zeolite large cavity, while the band at 3540 cm^{-1} arises from protons H_2 lying inside the hexagonal prism.

Referring now to the work of Ward and Hansford (*6*), on exchanging H^+ for Na^+ in Y zeolite the band at 3640 cm^{-1} grows, virtually exclusively, while the first 30 or so sodium ions are exchanged. While the last 26 or so sodiums are exchanged the band at 3540 cm^{-1} grows almost exclusively. The interpretation by Dempsey and Olson (*7*) suggests that the work of Ward and Hansford demonstrates mainly that, on exchanging H^+ for Na^+, the last 26 sodium ions, that in the dehydrated zeolite occupy sites I and I′ within the sodalite cage, hexagonal prism complex [identified by Eulenberger *et al.* (*8*)], remain there, through rehydration and exchange, until the 30 sodium ions occupying the sites II in the large cavity are removed.

Applying the foregoing to the work of Beaumont and Barthomeuf (*2*) it would seem that as exchange of sodium for hydrogen proceeds the first 16 protons are of H_1 type and produce weak acidity, the next 14 or so protons are also of H_1 type and produce strong acidity, while the final 26 or so protons are mainly of H_2 type, and also produce strong acidity.

The first point to be made is that if two types of proton, occupying the same crystallographic position (H_1), produce different chemical behaviors, we must seek a rather subtle structural distinction between the environments of the two types of proton, that is eliminated when we compare

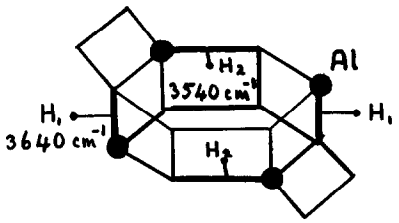

FIG. 1. Hexagonal prism of HY zeolite showing location of the protons and the corresponding infrared frequencies.

the second (strong) H_1 group and the final (strong) H_2 group—that *are* crystallographically distinct.

The second point is that the model devised to explain the exchange behavior must also be adaptable to explain the production of weak and strong acid sites on removal of Al ions from the zeolite framework by EDTA treatment.

Figure 2 shows a dissection of a sodalite cage into square faces as in Ref. (*1*) but now the figure refers to the material with Si/Al = 2:1. It also includes (broken lines) the hexagonal prism square faces contiguous with each sodalite cage square face. The chain-dotted lines across each hexagonal prism square denote that only half of each of these squares is to be considered to be related to the sodalite cage under examination. For the Si/Al = 2:1 material there are two α sodalite cage squares (carrying two Al ions) and four β squares (carrying one Al ion). Also indicated in Fig. 2 are the proton positions consistent with Ref. (*4*). Figure 3 should clarify the basis on which Fig. 2 is drawn.

In Fig. 2 attention is drawn to the fact that the Al ions in the α faces each have two close Al neighbors. As in Ref. (*1*) it is suggested that protons associated with these Al ions will represent weak acid sites but *the presence of two rather than one close Al neighbor is emphasized as being critical.* For the material with Si/Al = 2:1 it is predicted that there will be 4 weak acid sites/sodalite cage or 32/unit cell.

In order, from the model of Fig. 2, to form the material with Si/Al = 2.43:1 it is

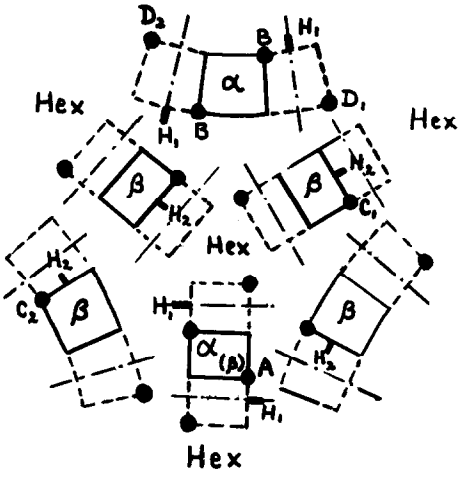

FIG. 2. Square faces of a sodalite cage of a 2:1 HY zeolite showing: (--) the contiguous hexagonal prism square faces, the aluminum ion locations (●) and the proton locations. Faces carrying two Al ions are designated α, those carrying one Al ion β. Hex indicates that the adjacent squares combine to form a hexagonal prism. The view is normal to one of the hexagonal prisms.

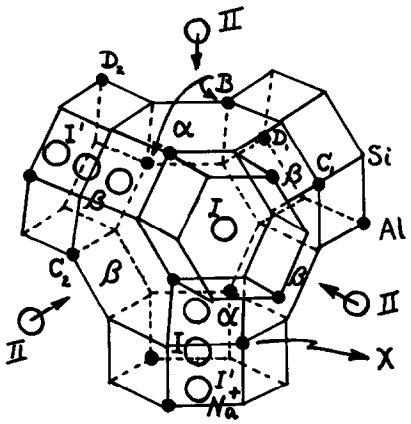

FIG. 3. Single sodalite cage (1/8 of unit cell) of NaY zeolite with completed hexagonal prisms. For clarity the hexagonal prism facing forward is drawn smaller than the others, and it does not have its full complement of cations. Similarly the upper right hexagonal prism has none of its associated cations. All hexagonal prisms should resemble the lower or the upper left one. The site II cations have also been displaced away from their associated faces. Sodium ions (○); aluminum ions (●). The lettering corresponds to that on Fig. 2.

necessary to replace one Al by a Si. Contrary to the suggestion in Ref. (*1*) that the Al should be removed from a β face (producing a square face empty of Al ions) it is now suggested that the Al will go from one of the α faces—say from site A. This converts the relevant face to a β face, removes a potential weak acid site and (since the criterion of two close Al neighbors now fails for the remaining Al ion on the face) converts a potential weak acid site into a potential strong one. Thus in the Si/Al = 2.43:1 material we start out with only 2 potential weak acid sites/sodalite cage, or 16/unit cell. As Beaumont and Barthomeuf show (*2*), with progressive exchange of H^+ for Na^+, the character of these sites will appear.

If this picture is correct, taken along with the work of Refs. (*4,6,8*), it is implied that in the Si/Al = 2.43:1 material there will be, per sodalite cage, 16 potential weak acid sites based on protons of H_1 type, 8 potential strong acid sites of H_1 type, and about 6–8 potential strong acid sites that should be of H_2 type, but that, in the light of ir evidence (and because, up to about 54% exchange, these sites are blocked by sodium ions) are of H_1 type. Since the symmetry of each Al ion site is such that it can accommodate either an H_1 or an H_2 proton type, it must be assumed that the need to accommodate additional protons beyond 24, while H_2 sites are blocked by Na^+ ions, forces a departure from the symmetry proposed by Olsen and Dempsey (*4*) despite the fact that this may cause protons to be close neighbors on the edges of hexagonal prisms—perhaps until, with higher exchange, H_2 sites become cleared, at which point a rearrangement of pseudo-H_1 sites to H_2 sites may take place progressively with further exchange.

Applying the model to the work of Beaumont and Barthomeuf (*2*) on the progressive removal of Al from zeolite Y simple energetic considerations would suggest that the first Al to be removed would be one of the two in the single α face of the 2.43:1 material—labeled B in Fig. 2. Unfortunately removal of either *one* of these Al ions (8/unit cell) would immediately eliminate directly or indirectly (using the criterion of two close Al neighbors for a weak acid site) *all* of the weak acid sites. Beaumont and Barthomeuf found that *two* Al ions (16/unit cell) have to be removed to obtain a material with only strong acidity. In developing the model, then, to embrace the experimental evidence on Al removal, we are forced to the statement that EDTA treatment removes not a B Al ion but first one and then the other of the Al ions labeled C_1 and C_2 from β faces. Because of the centrosymmetric nature of the model the removal of the C ions will simultaneously cause the removal of ions D_1 and D_2 from neighboring sodalite cages converting first one and then the second weak acid site to a strong acid site. It seems plausible that the high concentration of site I and I′ sodium ions found by Eulenberger *et al.* (*8*), that remain in the small pore system until site II sodiums have been exchanged, may make it easier to remove the D aluminums before the B aluminums.

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