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LETTER TO THE EDITORS

Acid Strength and Aluminum Site Reactivity of Y Zeolites

Referring to the very interesting paper by Beaumont and Barthomeuf (*1*) in which two distinct types of acidity are found in X and Y zeolites upon successively greater extractions of aluminum from the crystal framework, certain key statements may be isolated. The authors start with a material of Si/Al = 17/7.

On p. 47 ". . . the lowest number of sodium ions, 56 − 40 = 16, that must be exchanged by protons to give a zeolite with a strong acidity. Therefore 30% of the total number of sodium cations neutralizes the weakest acidity and 70% interacts with the stronger one."

On p. 47 "Zeolites containing less than 35 aluminum atoms per unit cell are only strongly acidic."

On p. 49 ". . . the more dealuminated samples using acetylacetone still contain 38 atoms per unit cell. That is, no more than about 30% of the aluminum atoms are removed. Even hot solutions of acetylacetone cannot pass this limit. In this way only the most easily removable part of the aluminum is extracted . . . the extraction begins to remove the aluminum atoms selectively giving the lowest acidities. The aluminum atoms associated with the strong acidity are extracted only after there is no more aluminum of the first type."

The general implication, as pointed out by the authors of Ref. (*1*), is that "the chemical properties of the aluminum of the faujasite lattice are not homogeneous and that they characterise two major types of aluminum and evaluate their number." The authors state ". . . the scattering of the acid strength of the Y zeolites is linked to a fundamental property of the aluminum sites, i.e., to a fundamental property of their structure."

Later the authors of Ref. (*1*) point out that various investigators have shown that the ultrastable Y material has 38 aluminum atoms, a number that Beaumont and Barthomeuf link to their limit of 38 aluminum atoms that cannot be extracted using acetylacetone.

"All of the results suggest that 35–40 aluminum atoms are strongly linked (bound) in the lattice; the other aluminum atoms, up to 56, (i.e., the remaining 21–16 aluminum atoms) consist of differently and more weakly bonded atoms. Their removal from the framework gives rise to new material (ultrastable Y)."

The authors also state that neither diffusion phenomena nor changes in accessibility of the several extraction agents can explain why the strong acid sites are selectively involved only after the removal of 30–35% of the aluminum (or sodium cations).

To provide an explanation of these results—at least in principle—consider the following simple electrostatic argument.

The truncated octahedron that forms a sodalite cage may be dissected in a variety of ways: *either* into four hexagons, associated with site I cation positions (i.e., associated with hexagonal prisms in the complete crystal structure), *or* into four hexagons associated with site II cation positions, (i.e., associated with the zeolite supercage), *or* into six square faces normally associated with site III cation positions. Possible distributions of the aluminum

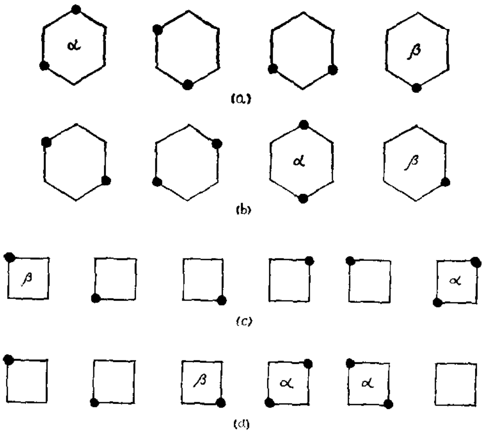

FIG. 1. Distribution of aluminum atoms (black points) over faces of a sodalite cage in different dissections: (a) dissection to site I hexagonal faces; (b) dissection to site II hexagonal faces; (c), (d) alternative aluminum atom distributions over dissection to square faces. All for Si/Al = 2.43.

atoms (or ions—assuming the aluminum to carry the net unit negative charge of the AlO_4 group) over these faces, to correspond to the Si/Al ratio of Beaumont and Barthomeuf, are shown in Fig. 1a–d.

The arrangement of the aluminum atoms on hexagons in Fig. 1 has been chosen in accordance with the ordered aluminum arrangement discussed in various papers (*2–4*); but this arrangement is not essential to the argument. It is sufficient to observe (accepting Löwenstein's rule) that two aluminum atoms in a hexagon are separated by a minimum distance of $3^{1/2}a$, (where "a" is the Si–O–Si separation) whereas in a square they are separated by a distance of $2^{1/2}a$, which is about 18% less than the minimum hexagon separation. Clearly if we are to invoke electrostatic arguments, it is appropriate to consider distributions on *square faces,* although the argument obviously applies generally. Building the square faces into a sodalite cage will, of course, produce the situation that each aluminum is influenced by all other aluminum atoms in the cage and in adjacent cages and not only by the possible presence of another aluminum atom in the face (and in the dissection) being considered. Again, in a first approximation, and in principle, the simple argument presented below is valid.

If we refer to faces of the truncated octahedron, of whichever shape, that are doubly occupied by aluminum atoms, as "α" faces, and those that are singly occupied as "β" faces it is clear that the aluminum atoms of β faces (being somewhat further removed from another aluminum atom than those in α faces) will be more strongly bound *into the zeolite structure* than will *either* of the aluminum atoms in α faces. Similarly the protons associated with the aluminum atoms of β faces will have properties different from those associated with the aluminum atoms of α faces. We suggest that the former (β face) protons are the *initial* strongly acidic sites of Beaumont and Barthomeuf.

On attempting to remove aluminum from the crystal structure, the aluminum atoms of α faces will be more vulnerable electrostatically (i.e., less strongly bound) than those of β faces (on account of the mutual repulsion between the aluminum atoms). One cannot predict which aluminum atom of an approximately equivalent α face pair will be removed; but the aluminum atom *remaining* after chemical attack will be more *strongly bound into the crystal than it was* formerly. Since it will now approximate to the aluminum atom of a β face (especially if a silicon atom diffuses from elsewhere to fill the aluminum vacancy) we may assume that a *new* strongly acidic site is created from a previously weak one, by the removal of the aluminum atom. (i.e., created at the proton of the *remaining* aluminum in the α face). Thus we propose that the aluminum atoms are not in an a priori way distinct in the crystal (except for those in β faces at the outset) and neither, therefore, are the acid sites.

Eventually we reach a point, in progressive aluminum removal, where *all* faces are at most singly occupied by aluminum atoms. We have removed all of the easily removable aluminum atoms, although precisely which ones, of α face pairs, these will be, would require examination of the crystal structure along the lines of Ref. (*2*). The structure is now hypothesized to be at its optimum stability (probably with aluminum vacancies healed by silicon atoms), and is the ultrastable material.

To go further in aluminum removal will require more drastic chemical treatment than hitherto, and the crystal structure will probably degrade progressively, unless the vacancies are healed as they are produced; in which case the structural stability should further increase, asymptotically, towards a limiting value.

Consider the numbers involved. For hexagonal faces some three aluminum atoms per sodalite cage will be easily removed, i.e., 24/unit cell, which, according to the results of Beaumont and Barthomeuf, is too high. In any case, as is implied above, we should be looking at square faces.

The most probable arrangement for square faces—figure 1c—presents an even worse case than that for the hexagons, with only 8 aluminum atoms/unit cell being easily removable. If we can justify the distribution of aluminum atoms of Fig. 1d, however, we find good agreement with Beaumont and Barthomeuf. Two aluminum atoms per sodalite cage, or 16/unit cell, are easily removed, leaving 40 to be associated with strongly acidic proton sites, and to be related to the aluminum content of ultrastable Y. In other words, 29% of the aluminums must be removed to produce a material having only strong acidity.

This discussion not only provides a simple basis for explaining the results of Beaumont and Barthomeuf; it also uses the results of these authors to say something about the probable distribution of aluminum atoms on the square faces of the sodalite cages of the Si/Al = 2.43 material and of ultrastable Y.

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