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LETTERS TO THE EDITOR

The Effect of Faujasite Cations on Acid Sites

In a recent paper on this subject, Richardson (*1*) has purported to introduce a model in which the bond strengths of acidic hydroxyl groups are perturbed by the polarizing effects of neighboring cations in such a way as to increase the acid strength. We suggested (*2*) in 1963 "that the polarizing action of the field of the cation tends to free (make acidic) a proton of a hydroxyl group attached to an adjacent silicon or aluminum atom, or a proton of a water molecule adsorbed on the cation itself . . . The greater the field strength of the cation, the stronger would be the resultant acidity." This implicity requires a polarization such that the electrons in the O–H bond of the hydroxyl group be drawn away from the hydrogen atoms and toward the oxygen atoms, both for an adjacent silanol group as well as for a water molecule adsorbed on the cation. However, Richardson (*1*) has misunderstood our suggestion, and incorrectly attributed to us a model in which the polarization acts across the volume of the cavity in such a way as to make the proton less acidic.

There is nothing in our statement to imply that the polarization we envisaged operated across the cavity rather than by induction through the lattice. Our suggestion was made in a note added in proof and was thus necessarily rather brief. However, even if the polarization operated across the cavity, it does not necessarily follow, as alleged by Richardson, that it would result in decreasing the acidity of nearby silanol groups. The field of the cation would tend to orient the O–H dipole with the positive end (hydrogen atom) facing away from the cation; in this orientation the electrons in the O–H bond would be drawn away from the hydrogen atom, increasing the acid strength.

That inductive effects could be transmitted through solids and result in increased acidity of silanol groups was not a new concept even at the time of our note. Chapman and Hair (*3*) a few months earlier had explained the greatly increased acidity of fluorided porous glass as due to the inductive effect of an electronegative fluorine atom on an adjacent silanol group. Each cation is coordinated directly to several oxide ions in the zeolite lattice, and our concept was that this polarization, or shift of electronic charge, was transmitted through these oxide ions to nearby silanol groups by an inductive effect similar to that postulated by Chapman and Hair (*3*), which they considered analogous to inductive effects in organic chemistry.

The model described by Richardson (*1*) differs from the above only in details of terminology. He has formulated his model in the framework of band theory and expresses the electron-attracting ability of the zeolite cations in the form of positively charged surface defects. It would appear that qualitatively, at least, the two are essentially equivalent.

That we were not unaware of the possibility of a metal cation shifting electronic charge *within* the zeolite lattice, as alleged by Richardson, is indicated by the following statement (*4*): "If polyvalent metal ions occupy part of the S_I ion-exchange sites in a decationized Y zeolite, the negative charge binding a metal ion (or proton) to the lattice at adjacent S_{II} sites can be delocalized by the sharing of a single negative charge among several AlO_4 tetrahedra. Such a weakly-bound proton should be more acidic . . . " We have also suggested (*5*) that trigonal electron acceptor (Lewis) sites increase the acidity of two or more adjacent silanol groups in an amorphous silica-alumina catalyst in regions where we postulated that a zeolitelike local order existed; and that fluoriding alumina greatly increases its Brönsted acidity because of the inductive effect of fluoride ions on adjacent aluminol groups (*6*). All of these references (*4*–*6*) imply a perturbation of the bond strengths of acidic hydroxyl groups by a shift of electronic charge within the solid itself. As a matter of fact, a cation in an S_I site is completely surrounded by a double hexagonal ring of silica and alumina tetrahedra and could not polarize a hydroxyl group in the large zeolite cavity in any other way.

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In a recent Letter Hirschler (*1*) has criticized the novelty of a model I discussed (*2*) and has protested an alleged misinterpretation of his earlier remarks (*3*). The model in question pertains to the effect of faujasite cations on the acid activity of the catalyst and contains the following features:

(1) The origin of carbonium activity is the proton of hydroxyl groups in the supercage and not the electrostatic field of the cation as proposed by Pickert *et al.* (*4*).

(2) Increasing the ionic potential (e/r) of the cation results in a shift of electron charge distribution toward the vicinity of the cation via a mechanism described as an impurity conduction band in an insulator. This weakens the O–H bonds on the surface of the supercages, making them more acidic.

(3) The large number of possible environments for the hydroxyl groups introduces a wide acid strength distribution. Increasing the cation's ionic potential shifts the whole distribution to higher acid strengths.

(4) Only a very small concentration of active sites is necessary to account for observed rates. Acid strengths above a certain value will catalyze a particular reaction. Shifting the distribution to higher values moves more sites into the "active" region.

Recently, Ward (*5*) has agreed with the Brönsted activity of the hydroxyl groups but has proposed an alternate model for their dependence on the ionic potential. In this case water adsorbed on the cation is dissociated to provide a proton which then forms a hydroxyl group at a vacant S_{II} position, leaving behind OH^- associated with the cation. Acidity varies with ionic potential through a change in the dissociation constant of the bound water, so that higher values of e/r result in more hydroxyl groups. These sites are of constant energy and no energy distribution is required. Also Tung (*6*) has reaffirmed the hypothesis of