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.

References

1. Richardson, J. T., *J. Catalysis* **9,** 182 (1967).
2. Hirschler, A. E., *J. Catalysis* **2,** 428 (1963).
3. Chapman, I. D., and Hair, M. L., *J. Catalysis* **2,** 145 (1963).
4. Hirschler, A. E., *Am. Chem. Soc. Div. Petrol. Chem. Preprints* **11,** #4, A87 (Sept. 1966).
5. Hirschler, A. E., *J Catalysis* **6,** 1 (1966).
6. Hirschler, A. E., *Am. Chem. Soc. Div. Petrol. Chem. Preprints* **13,** #1, 142 (April 1968).

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The Effect of Faujasite Cations on Acid Sites

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 the direct polarizing action of the cationic field, but has further introduced the concept of a time-dependent polarization related to the mobility of the cations.

In his original footnote (*3*) Hirschler discussed a cation-dependent polarization of either adjacent hydroxyl groups or bound water molecules. His comments could then be construed to cover both the mechanisms Ward and I discussed. Unfortunately, neither at that time nor in the intervening period did Hirschler elaborate on his comments or distinguish between the consequences of the two possibilities. In developing my arguments it was necessary to rule out any probability that polarization across the cavity from the S_{II} cations could be the responsible mechanism. It is unfortunate that Hirschler has interpreted this essential clarification as a reflection on his proposal. However, even the factors that Hirschler claims must be implied from his statements do not completely cover all of the features outlined above. In his Letter he cites references that support his claims, yet these references repeatedly refer to the effect of the cations in *adjacent* hydroxyl groups. This overlooks the long-range interaction allowed by the band model interpretation, thus neglecting the energy distribution which provides for the small number of active sites required. Both of these are important features in the overall model and cannot be implied from any of Hirschler's statements.

The usefulness of such a model is the accuracy with which it describes the observed facts and the dependability of its predictions. Each of the models discussed above must be still regarded as hypothetical. The advantage of competing models is that their conflicts generate the critical experiments needed to resolve them. It is worthwhile to consider some of these critical experiments that have been or need to be performed in order to clarify the differences between these models.

The concept of the cation influencing the number of hydroxyl groups through its effect on the dissociation constant of the bound water is not only consistent with all the experimental facts as outlined by Ward, but is also not at variance with the small number of sites needed to explain the rate of cumene cracking. This explanation is more straightforward than used in my paper, since it is not necessary to explain why a certain acid strength site is needed or why the change in the active area under the distribution curve (i.e., heats of adsorption) fails to appear in the activation energies. However, Fig. 8 of ref. (*3*) and Fig. 4 of ref. (*7*) indicate that the cation must be exposed or dehydrated before activity is generated. The obvious follow-up experiment—the back-adding of water—has not been done. It would seem that experiments which *clearly* indicate the existence of $M^{+}OH$ and its direct relation to the appearance of acidity are needed. Ward's model does not require nor provide for a distribution of acid strengths. The only successful measurement of acid strength distributions is that of Benson *et al.* (*8*), who used ammonia adsorption to demonstrate the existence of a distribution with more of the moderate strength sites than in amorphous silica-alumina. However, Kubokawa *et al.* (*9*) have shown that cumene adsorption and decomposition on silica-alumina are unaffected by ammonia adsorption. The situation is still in doubt. Experimental measurement of the relationship between acid strength distribution and activity will be necessary.

The conclusion that only a small number of sites are necessary for cumene dealkylation is based on the assumption of zero order kinetics and acceptance of certain requirements in the absolute reaction rate theory. Maatman (*10*) has defended the latter in the cumene case and the former is based on sound considerations. However, studies using the technique of Prater and Lago (*11*) need to be carried out for confirmation. Possibly an alternate technique similar to that discussed by Bett and Hall (*12*) may be necessary. If confirmed, this small number of active sites needs to be reconciled with the poisoning experiments of Romanovskii *et al.* (*13*), who determined that the maximum number of active sites, although only a few percent of total number of decationized positions, is still several orders of magnitude larger than the kinetic site density.

The Ward model predicts that the acid faujasite is the ultimate since the role of other cations is to provide an increasing number of acid-type hydroxyl groups. The model in my discussion, however, predicts that a cation with high ionic potential (to provide polarization) mixed with the H-faujasite (to provide the OH concentration) could be more acidic than the pure acid faujasite. Indications that this is the case for a rare earth–hydrogen faujasite have been claimed (*14*) but for stability reasons. Experiments with acid strength distribution measurements are needed to decide this issue.

Finally, the role of direct cation interaction, although minimized for carbonium activity by many authors, still may play an important role for other types of reactions, e.g., the radical dehydrogenation of cumene (*3*). Measurements of the field strengths through spectroscopic or ESR techniques will be required, in addition to experimental verification of the cation time-dependent field proposed by Tung (*6*).

REFERENCES

1. HIRSCHLER, A. E., *J. Catalysis* **11**, 275 (1968).
2. RICHARDSON, J T., *J. Catalysis* **9**, 182 (1968).
3. HIRSCHLER, A. E., *J. Catalysis* **2**, 428 (1963).
4. PICKERT, P. E., RABO, J. A., DEMPSEY, E., AND SHOMAKER, B., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **2**, 1264 (Wiley, New York, 1965).
5. WARD, J. W., *J. Catalysis* **10**, 34 (1968).
6. TUNG, S. E., AND MCININCH, E., *J. Catalysis* **10**, 166 (1968).
7. RICHARDSON, J. T., *J. Catalysis* **9**, 172 (1967).
8. BENSON, J. E., USHIBA, K., AND BOUDART, M., *J. Catalysis* **9**, 91 (1967).
9. KUBOKAWA, Y., AND MIYATA, H., *J. Phys. Chem.* **72**, 356 (1968).
10. MAATMAN, R. W., LEENSTRA, D. L., LEENSTRA, A., BLANKESPOOR, R. L., AND RUBINCH, D. W., *J. Catalysis* **7**, 1 (1967).
11. PRATER, C. D., AND LAGO, R. M., *Advan. Catalysis* **8**, 298 (1956).
12. BETT, J. A. S., AND HALL, W. K., *J. Catalysis* **10**, 105 (1968).
13. ROMANOVSKII, V. B., THONG, H. S., AND TOPCHIEVA, K. V., *Kinetika i Kataliz* **7**, 197 (1966).
14. PLANK, C. J., AND ROSINSKI, E. J., U.S. Patent 3,140,253 (1964).

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Formation of Paramagnetic Surface Species during the Oxidation of Nonstoichiometric TiO_2(A), SnO_2, and ZnO

Iyengar, Codell, and Turkevich (*1*) recently published some ESR observations on the oxidation of nonstoichiometric rutile with oxides of nitrogen.

Similar measurements have been performed by us on TiO_2 (anatase), SnO_2, and ZnO and preceding a future and more detailed report we believe it relevant to summarize our results here, the more so, since they lead to a somewhat different explanation than that earlier given by Cornaz, van Hooff, Pluym, and Schuit (*2*) and van Hooff and van Helden (*3*).

TiO_2 (anatase) after outgassing at 500°C shows a similar signal as given by Iyengar *et al.* in their Fig. 1A. After admission (at room temperature) of O_2 and reevacuation (also at room temperature) this signal dis-