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Zeolitic Aluminosilicate

III. Dynamic (Time Variant) Bronsted Acidity

SHAO E. TUNG*

Research and Development Department, Continental Oil Company

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The dielectric response to the temperature and electrical frequency reveals that there are a great deal of ionic movements on the zeolitic surfaces whereas relatively few such movements prevail on the surfaces of amorphous aluminosilicates, silica, and alumina.

A concept of *dynamic Bronsted acidity* (i.e., the variation of acid strength with time) is proposed. Together with the previously proposed *dynamic field* and *dynamic Lewis acid,* a possibility exists that the observed difference in activity between the zeolitic and amorphous aluminosilicates could well be as much due to a difference in the kind of sites (i.e., dynamic vs. static) as to a difference in degree (e.g., number and strength of the sites).

In two previous papers (*1, 2*), the significance of ionic movements on zeolitic surfaces and its implication to catalytic activity were discussed. The discussion dealt with the *dynamic surface field* and the *dynamic Lewis acid sites.* The dynamic characteristics render the sites (either field or Lewis acids) capable of activated adsorption and subsequent desorption and thereby continuously promote catalytic reactions in a cyclic manner. It is easily conceivable that a reaction which will not proceed at all on static Lewis acids might proceed on dynamic Lewis acid sites with considerable facility. If the amorphous aluminosilicate surfaces are much less dynamic than the zeolitic surfaces, then a possibility exists that the difference in the observed activities on these two kinds of surfaces might well be due to a difference in kind of sites (dynamic versus static) as much as it might be in degree (stronger or more numerous acid sites).

It would be interesting to verify experimentally whether the amorphous aluminosilicates are in fact less dynamic than zeolites. For this purpose, we have measured the dielectric constants of both aluminosilicates under alternating current excitation covering wide spans of frequency and temperature. The results are presented in Fig. 1. For comparison, the data of silica and alumina are also included. The details of the measurements were described elsewhere (*3*). Fig. 1 shows that zeolites, as exemplified by CaY—70%, responded to the frequency and temperature change much more vigorously than the three amorphous solids. Decationized Y and CaX catalysts behave similarily to the CaY catalysts (*4*).

It can be shown (*4*) that the observed dielectric response of the CaY—70% zeolite was largely due to the ionic movements. The individual ions jump back and forth, contributing a polarization analogous to the orientation of permanent dipoles (*5*). In addition, the translational movement of ions and their subsequent piling up at the barriers caused space polarization. Electronic polarization due to the distortion of the electron clouds and atomic polariza-

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*Present address: Arthur D. Little, Inc., 20 Acorn Park, Cambridge, Massachusetts 02140.

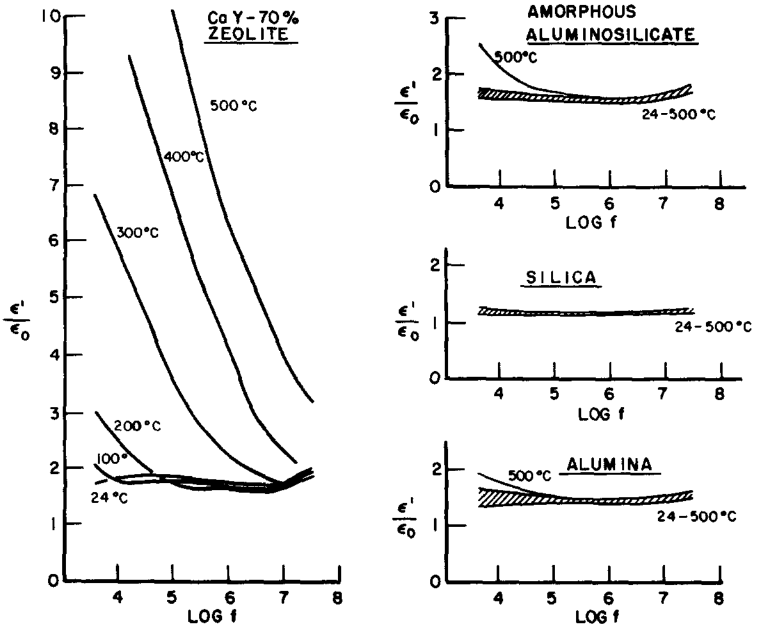
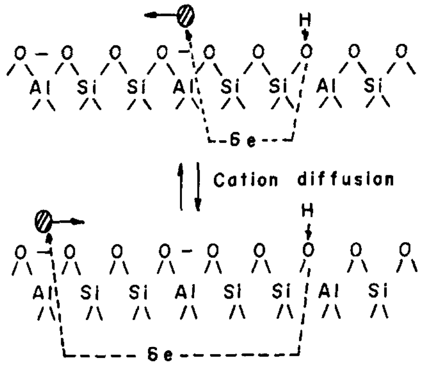


FIG 1. Relative dielectric constant versus log frequency.

tion arising from the displacement of positive and negative ions relative to each other contributed rather insignificantly. Hence, the strong response of the CaY—70% zeolite to the frequency and temperature change suggests many ionic movements on the zeolitic surfaces. On the other hand, the lack of response of the silica, alumina, and amorphous aluminosilicate portrays a relatively static situation over these surfaces. This interpretation is consistent with the dielectric loss measurement. At 500°C and 91.8 kHz ac excitation, the dielectric loss of CaY—70% was found to be 50-fold larger than that of amorphous silica alumina.

The catalytic activity of zeolites has been attributed to Bronsted acids (*6–9*), Lewis acids (*10*), and surface electric field (*11*). The implication of *dynamic field* and *dynamic Lewis acids* has been discussed (*1, 2*). It remains now to examine the influence of ionic movements on the activity of the Bronsted acid sites.

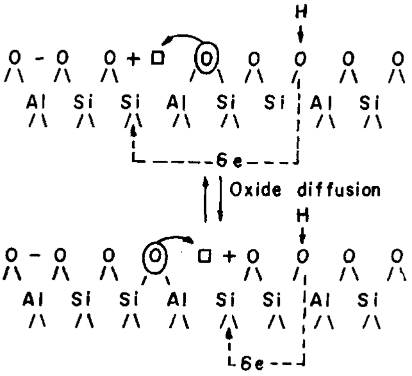
The Bronsted acidity on zeolitic surfaces has been associated with the structural hydroxyl groups (*9*), in particular, the hydroxyl groups responsible for the 3640-cm^{-1} absorption band. The bond strength of these acidic hydroxyl groups (and therefore the acid strength) may be perturbed by the polarizing effect of the neighboring cations. Thus, Hirschler (*12*) pictured that the polarizing action of the field tended to free a proton from a hydroxyl bond. The greater the field strength of the cation, the stronger would be the resultant acidity. Richardson (*13*) proposed that the inductive influence was exerted via the intervening crystal structure. The neighboring defect sites may also act inductively on the structural hydroxyl groups as was discussed by Lunsford (*14*). Now, if this inductive model is valid, then it readily follows that ionic movement will cause the Bronsted acid strength to fluctuate. As the ion (or defect) moves, the separation between the ion (or defect) and the structural hydroxyl group will necessarily change. The inductive influence of the ion (or defect) and the acid strength of the hydroxyl group will vary accordingly. If the ion (or defect) jumps back and forth, the acid strength of the hydroxyl group will fluctuate. For a multivalent cation zeolite such as a CaY this may be illustrated as follows:



Here, the shaded circle denotes a cation which could be a metal ion or another proton. The metal ion could be in one of several forms, Na^+, Ca^{++}, $Ca(H_2O)^{++}$, and $Ca(OH)^+$, and the distribution among them depends upon the degree of Ca^{++} for Na^+ exchange as well as the calcination temperature and the conditions under which the zeolite is subsequently exposed. The influence of the movement of a proton is electrically equivalent to the movement of a monovalent metal ion such as Na^+.

Support of the induction effect of the neighboring ion on the protonic acidity is afforded by the observed frequency shift of the acidic hydroxyl band upon the polarizing power (e/r) of the neighboring cation. Thus for NaY, BaY, CaY, MgY, and decationized-Y, the observed band frequencies are 3652, 3647, 3645, 3643, and 3636 cm^{-1}, respectively. It has been estimated (*13*) that a shift of 16 cm^{-1} in band frequency may correspond to a change in peak position of the acid distribution curve from $pKa = -3.3$ to $pKa = -4.9$. This inductive influence not only depends on the polarizing power of the polarizing ion but also depends on its proximity to the hydroxyl group being polarized. Since the field strength imposed on a hydroxyl group by a neighboring polarizing ion varies in accordance with an inverse square relation with the separation between them, the inductive influence depends on the distance rather strongly. Hence, the variation of the proton acid strength due to the movement of a neighboring ion could be quite substantial.

When a multivalent cation zeolite is calcined at temperatures higher than 500°C, Lewis acid sites may form as discussed by Ward (*15*) and by Uytterhoeven (*16*) *et al.* Lewis acids also prevail on the decationized —Y catalysts after dehydroxylation. With these catalysts, diffusion of oxide ions could cause the Bronsted acid strength to fluctuate such as:



Here the squares denote the anion vacancies.

Completely analogous to the previously discussed *dynamic Lewis acids* (*2*) and

$$H^+(\text{strong}) + C_6 \longrightarrow H^+(\text{strong})\,H^- + C_6^+ \tag{1}$$

$$C_6^+ \longrightarrow C_6^+(\text{iso}) \tag{2}$$

$$H^+(\text{strong})\,H^- \xrightarrow{\text{Cation or oxide diffusion}} H^+(\text{weak})\,H^- \tag{3}$$

$$H^+(\text{weak})\,H^- + C_6^+(\text{iso}) \longrightarrow H^+(\text{weak}) + C_6(\text{iso}) \tag{4}$$

$$H^+(\text{weak}) \xrightarrow{\text{Cation or oxide diffusion}} H^+(\text{strong}) \tag{5}$$

$$C_6 \longrightarrow C_6(\text{iso}) \tag{6}$$

dynamic field (*1*), this *dynamic* nature (time-variance-characteristic in acid strength) of the *Bronsted acids* will facilitate the promotion of both activated adsorption and subsequent desorption and thereby enhance their catalytic activity. Using the hexane isomerization and cracking as examples, it may be illustrated as follows: and

$$H^+(\text{strong}) + C_6 \longrightarrow H^+(\text{strong})\ H^- + C_6^+ \qquad (7)$$

$$C_6^+ \longrightarrow C_n^+ + C_{6-n}\ (\text{olefin}) \qquad (8)$$

$$H^+(\text{strong})\ H^- \xrightarrow{\text{Cation or oxide diffusion}} H^+(\text{weak})\ H^- \qquad (9)$$

$$H^+(\text{weak})\ H^- + C_n^+ \longrightarrow H^+(\text{weak}) + C_n \qquad (10)$$

$$H^+(\text{weak}) \xrightarrow{\text{Cation or oxide diffusion}} H^+(\text{strong}) \qquad (11)$$

$$C_6 \longrightarrow C_n + C_{6-n}\ (\text{olefin}) \qquad (12)$$

Because of the variation in acid strength, reactions (1), (4), (7), and (10) are further enhanced. A possibility, therefore, exists that Bronsted acids on zeolites, because of their dynamic nature, may promote some reactions more effectively than Bronsted acids of comparable strength on the amorphous aluminosilicate surfaces. Since polarization is a long range interaction, the inductive influence on any hydroxyl group does not come from one neighboring cation alone, as is represented in a simplistic fashion here. In actuality, it is the sum total effect of the influences of many neighboring ions, with the nearer ions exerting greater shares of influence.

REFERENCES

1. TUNG, SHAO E., AND MCININCH, E., *J. Catal.* **10**, 166 (1968).

2. TUNG, SHAO E., AND MCININCH, E., *J. Catal.* **10**, 175 (1968).

3. TUNG, SHAO E., to be published.

4. TUNG, SHAO E., to be published.

5. DEBYE, P., "Polar Molecules," p. 105. Chem. Catalog Co., New York, New York, 1929.

6. PLANK, C. J., "Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964." Vol. 1, p. 727. Wiley, New York, 1965.

7. VENUTO, P. B., AND LANDIS, P. S., "Advances in Catalysis and Related Subjects," Vol. 18. Academic Press, New York, 1968.

8. BENESI, H. A., *J. Catal.* **8**, 368 (1967).

9. WARD, J. W., *J. Catal.* **9**, 225 (1967).

10. TURKEVICH, J., NOZAKI, F., AND STAMIRES, D. N., "Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964." Vol. 1, p. 586. Wiley, New York, 1965.

11. PICKERT, P. E., ROBO, J. A., DEMPSEY, E., AND SCHOMAKER, V., "Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964." Vol. 1, p. 714. Wiley, New York, 1965.

12. HIRSCHLER, A. E., *J. Catal.* **2**, 428 (1963).

13. RICHARDSON, J. T., *J. Catal.* **9**, 182 (1967).

14. LUNSFORD, J. H., *J. Phys. Chem.* **72**, 4163 (1968).

15. WARD, J. W., *J. Catal.* **10**, 43 (1968).

16. UYTTERHOEVEN, J. B., SCHOONHEYDT, R., LIENGME, B. V., AND HALL, W. K., *J. Catal.* **13**, 433 (1969).