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The Acidic Nature of Synthetic Zeolites: Acid Strength and Its Correlation with the Catalytic Activity

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The acidic characters of the X and Y zeolites exchanged by hydrogen, calcium, and lanthanum ions were investigated. Very characteristic features of the acid sites were found as compared with those of an amorphous silica-alumina cracking catalyst. The acidity is generally larger in the zeolites (2—3 meq/g) than in a silica-alumina (0.5 meq/g). The acid strength is more widely distributed in the zeolites ($H_0=+3.3$ —<-8.2) than in a silica-alumina ($H_0<-8.2$). Very important is the fact that the acid site increases not only in number but also in strength with an increase in the degree of ion exchange. The results on cumene cracking are in line with these results.

Zeolite catalysts exchanged by hydrogen ion or metal cations have been widely used in various reactions,[1] especially in the industrial cracking of gas oil.[2,3] The ion-exchanged zeolite catalyst has the ability to crack various hydrocarbons, the product distribution of which is similar to that obtained with a silica-alumina cracking catalyst.[4,5] These facts suggest that the zeolite catalyst is an acid solid. However, few data are available in the literature regarding the acidic character of zeolites, *i. e.*, the acid strength and its distribution, their correlation with the catalytic activity, and the difference in acidic character from amorphous silica-alumina.

The present work aims at clarifying the acidic characters of ion-exchanged zeolites by comparing them with that of silica-alumina.

Experimental

Materials. The X and Y zeolites were used, the former being Molecular Sieve 13X (a commercial product of Linde Co.) and the latter having been prepared in our laboratory by a method given in the literature.[6] Chemical analysis showed the compositions of $Na_2O\cdot$

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[1] P. B. Venuto and P. S. Landis, "*Advances in Catalysis*," Vol. 18 Academic Press, New York and London (1968), p. 259.

[2] C. J. Plank, E. J. Rosinski and W. P. Hawthorne, *Ind. and Eng. Chem., Product Research and Development*, **3**, 165 (1964).

[3] C. J. Plank and E. J. Rosinski, U. S. Pat. 3140253 (1964).

[4] V. J. Frilette, P. B. Weisz and R. L. Golden, *J. Catalysis*, **1**, 301 (1962).

[5] P. B. Weisz, V. J. Frilette, R. W. Maatman and E. B. Mower, *ibid.*, **1**, 307 (1962).

[6] D. W. Breck, U. S. Pat. 3130007 (1964).

$Al_2O_3 \cdot 2.69SiO_2$ and of $Na_2O \cdot Al_2O_3 \cdot 4.73SiO_2$ for the X and Y zeolites respectively. X-ray diffraction examination revealed a good crystallinity in both types of zeolites. A commercial amorphous silica alumina catalyst which was 13% Al_2O_3 (a fluidized cracking catalyst) was used.

Ion Exchange. The cation-exchange on zeolites was carried out by bringing the sodium ion form of zeolites in contact with a 0.2N solution of nitrates or of chlorides. The desired degree of ion exchange was controlled by the number of repeating the ion exchange process. The ion exchanged zeolite was calcined after repeated washings with pure water and after drying at 110°C. Zeolites exchanged by the calcium and the lanthanum ions were also prepared as has been described above. The protonated zeolite was obtained in a different way, by the calcination of the ammonium ion form of zeolite, which was prepared by bringing zeolite in contact with an ammonium chloride solution.

Acidity and Acid Strength. The acidic character was determined by the Benesi method[7,8] by the use of *n*-butylamine as a titer and Hammett indicators. Samples were calcined at 10^{-3}—10^{-4} mmHg for 2 hr and then transferred into weighing bottles in a dry box and measured.

The total acidity was defined as the amount of the acid determined with Butter Yellow ($pK_a = +3.3$). The acid strength was determined by using indicators of various pK_a's.

Catalysts and Cumene Cracking. Ion-exchanged zeolite powders (1—5 μ in diameter) were pressed into pellets, and then they were crushed into pilled catalysts 60—100 in mesh size. The cumene-cracking reaction was carried out over a pilled catalyst calcined at 600°C for 2 hr prior to use. This activity test was carried out in a flow system. Figure 1 shows a schematic diagram of the apparatus used for cracking.

A simple cracking reaction was conducted over various cationic forms of zeolites under definite conditions: weight of catalyst 0.6 g; reaction temperature, 450°C; LHSV, 1.2. The products were condensed for 1 hr after the start of the reaction. The condensate was then analyzed by gas chromatography in order to determine the amount of the conversion of cumene to benzene.

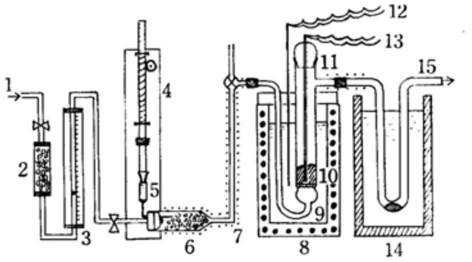

Fig. 1. Schematic diagram of apparatus for cumene cracking.

1	nitrogen gas	9	molten salt
2	drying tube	10	catalyst
3	rotameter	11	reactor tube of pyrex
4	cumene feeder	12, 13	thermocouple
5	syringe containing cumene		
6	cumene evaporator		
7	tape heater	14	dry ice bath
8	electric furnace	15	trap

In the case of the lanthanum ion exchanged form of the X zeolite, a more detailed experiment was undertaken in order to determine the correlation between the catalytic activity and the acidic character of zeolite. The reaction was carried out when the conversion of cumene was below ten percent, in which region the reaction rate was proportional to the amount of catalyst employed. Nitrogen gas was passed over the La–X catalyst for 1 hr at the reaction temperature, and then the cumene-nitrogen mixture was intoduced. The cracking activity was so high at the start that the sampling of products for 1 hr was begun 1 hr after the introduction of the reactant.

Results and Discussion

Acidic Character. The color changes of Hammett indicators, showing the end point of titration, were similar in both silica-alumina and zeolites, except that some of the latter catalysts showed less obvious color changes in the indicators. This is probably due to the difference in acid strength, as will be discussed below.

The distribution curve of the acid strength is cumulatively shown in Figs. 2 to 4 as a function of H_0, together with that of a FCC silica-alumina. In the figures and hereafter the symbols M–X and M–Y refer to the X and Y zeolites exchanged by the cation of the element, M. Figure 2 indicates that, in general, the zeolites have, in striking contrast to the silica-alumina, which has a strong acid site only, acid sites over a wide range of strengths and a larger acidity. The dotted line for the Ca–X (95.7) in Fig. 2 denotes that the detection of the color change of the indicators (benzalacetophenone, $pK_a = -5.6$; anthraquinone, $pK_a = -8.2$) was disturbed because of the yellow surface of this sample.

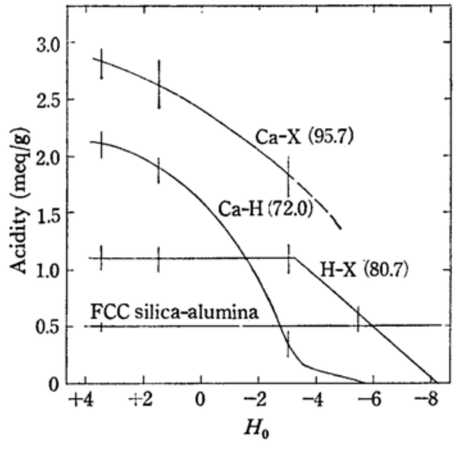

Fig. 2. Distribution of acid strength of the H–X, Ca–X and FCC silica-alumina.

The vertical lines and figures in bracket denote the uncertainty in titration and degree of the ion exchange, respectively. These remarks are also used in Figs. 3 and 4.

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[7] H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

[8] H. A. Benesi, *J. Am. Chem. Soc.*, **78**, 5490 (1956).

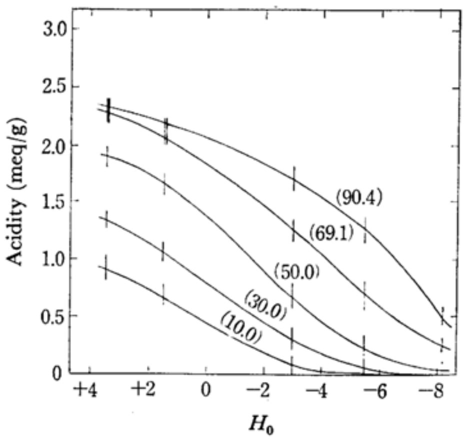

Fig. 3. Distribution of acid strength of the La–X with various degree of the ion exchange.

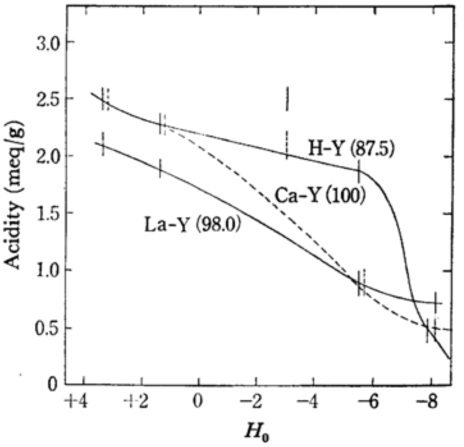

Fig. 4. Distribution of acid strength of the H–Y, Ca–Y and La–Y

Figure 3 shows the dependence of the distribution of the acid strength for the La–X on the degree of the ion exchange. The uniform crystalline structure of the zeolite leads us to expect that the distribution of the acid strength will be the same at any level of the ion exchange, whereas the total amount of acid will increase in proportion to the degree of the ion exchange. However, this is not the case. As may be seen in Fig. 3, stronger acid sites appear with an increase in the degree of ion exchange. Moreover, Figs. 2 and 3 show that the acid strength is dependent upon the kind of cation. These acidic characters are reasonable if the structure of the zeolite is considered. It has been established[9,10] that there are three kinds of sites occupied by sodium ions in the X and Y zeolites. It has also been found that, in the Ca-X, calcium ions occupied two kinds of sites, S_I and S_{II}, differing from each other in the number of oxygen atom coordinated to the calcium ion. The former site was located in the interior of the hexagonal prism, positioned between two puckered O_6 rings. It was effectively hidden from the surface of the large pore. The latter one was found in the O_6 ring, which formed a hexagonal face. It was positioned on the surface of the large pore. The results of the calculation of the electrostatic field strengths at these sites revealed that the charge distribution differed between the two sites, with the S_I site being energetically more stable than the S_{II} site. Thus, it follows that the calcium ion prefers the S_I site to the S_{II} site at a lower level of ion exchange.

Although the origin of the acid site in the zeolites has not been clarified well,[1] it is conceivable that the different states of the cation sites causes the occurrence of acid sites of different strengths.

Figure 4 indicates that the distribution of the acid strength also depends on the type of zeolite. A large proportion of the acid sites is distributed in the strong region in the Y zeolite, unlike as in the X zeolite. The total quantity of acid sites in the Y zeolite is less than that in the X zeolite, except for the protonated zeolite, corresponding to the difference in their ion exchange capacities. The X and Y zeolites are nearly the same in structure. The ratio of the silicon atom to the aluminum atom is higher in the Y zeolite. Rabo and his associates[9,10] have pointed out, however, that the electrostatic field strength at cation sites is much larger in the Y zeolite. It seems reasonable, therefore, that there is a difference in acid strength between the two types of zeolites.

In the case of the protonated zeolites, the H–X has less acidity than the H–Y. This can reasonably be explained by the results of the experiment given below. The crystalline structure of the NH_4–X collapsed, as was revealed by an X-ray diffraction

TABLE 1. CUMENE CRACKING ACTIVITY FOR VARIOUS TYPES OF ZEOLITES

Reaction temp. 450°C; LHSV=1.2;
weight of catalyst; 0.6 g

Sample	Degree of ion exchange (%)	Amount of cations in zeolite (meq/g)	Conv. of cumene (%)
H-X	80.7	4.48	79.8
H-Y	87.5	3.73	95.3
Ca-X	72.0	4.02	8.7
Ca-X	95.7	5.37	68.3
Ca-Y	100	4.26	96.3
La-X	95.7	5.37	86.0
La-Y	86.0	3.67	97.1

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[9] P. E. Pickert, J. A. Rabo, E. Dempsey and V. Shomaker, Proc. 3rd Intern. Congr. Catalysis, Amsterdam, 1964, Vol. I, Wiley, New York (1965), p. 714.

[10] J. A. Rabo, C. L. Angell, P. H. Kasai and V. Shomaker, *Discussions Faraday Soc.*, **41**, 328 (1966).

examination, during the formation of the H-X from the NH_4–X ($NH_4\text{–X} \xrightarrow{\text{heat}} \text{H–X} + NH_3\uparrow$), while the surface area of the zeolite was being lowered. The surface area of the H–X was found to be 371 m^2/g, only one half those of the Na–X (723 m^2/g) and Na–Y (898 m^2/g). On the other hand, the H–Y remains crystalline in spite of undergoing the same calcination step as in the H–X.

Cumene Cracking. Table 1 lists the results of cumene cracking conducted over various forms of zeolites under the definite reaction conditions described above. Figures 6 and 7 show the cumene cracking activity for the La–X as functions of degree of ion exchange and of the reaction temperature.

The kinetics of the reaction was analyzed as follows. The mechanism of cumene cracking may be supposed to be:[11)]

$$\text{Cumene} + \text{free site} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{cumene-site complex}$$

$$\xrightarrow{k_3} \text{benzene} + \text{propylene} + \text{free site}$$

Assuming the adsorption step in equilibrium during the reaction, the following relationship is derived:

$$P_c/r = 1/k_3B_0 \cdot P_c + 1/k_3B_0K, \; K = k_1/k_2 \qquad (1)$$

where:

P_c: partial pressure of cumene,
r: reaction rate,
B_0: number of active sites,
K: adsorption equilibrium constant.

The rate constant, k_3, is a measure of the ability to crack the complex. However, it is not determined directly because the value of B_0 is unknown. The value of k_3B_0, which is also a measure of the cracking activity, is determined from a reciprocal of the slope of a straight line plotted P_c/r *vs.* P_c, as is shown in Fig. 5.

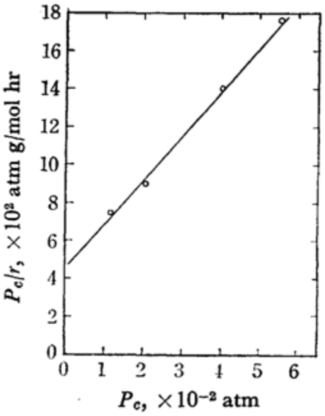

Fig. 5. Plots of P_c/r *vs.* P_c.
Catalyst: La–X (50.0);
Reaction temp.: 330°C

In the X zeolite the catalytic activity is in the following order:

La–X (percentage of the ion exchange: 95.7)> H–X (80.7)>Ca–X(95.7)>Ca–X(72.0); in the Y zeolite, although the amount of the cation exchange is less than that in the X zeolite, there is a very high activity in any cationic form. These results are in good agreement in order with the acid strength and not with the acidity, as is shown in Figs. 2 to 4. It is obvious from Figs. 6 and 7 that the catalytic activity increases more than linearly with an increase in the degree of ion exchange. Such a phenomenon,

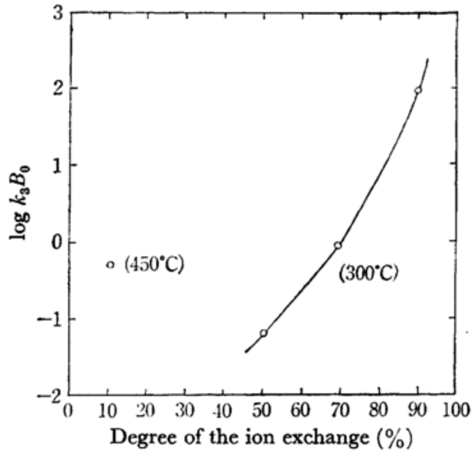

Fig. 6. Correlation between cumene cracking activity and degree of the ion-exchange for the La–X. Figures in bracket denote the reaction temperature.

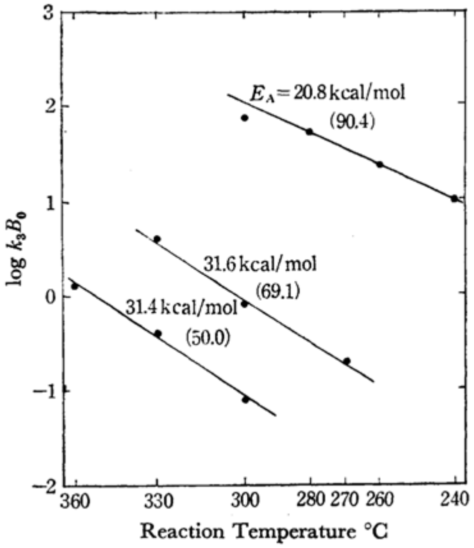

Fig. 7. Temperature dependence of cumene cracking activity and apparent activation energy for the La–X.

Figures in bracket denote degree of the ion-exchange.

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11) W. F. Pansing and J. B. Malloy, *Ind. and Eng. Chem., Process Design and Development*, **4**, 181 (1965).

suggesting the heterogeneity of the zeolite surface, has been observed with, for example, the benzene propylation over the Rare-earth-Y,[12] the cumene cracking over the H-Y[13] and over the Ca-X,[14] and the hexane isomerization over the Pt/Ca-Y.[15] These results may be interpreted in terms of the variation in acid strength with an increase in the degree of ion exchange, as may be seen in Figs. 2 and 3 for the Ca-X and La-X respectively.

The apparent activation energy for the cumene cracking over the La-X, shown in Figs. 7, seems to decrease at a high level of ion exchange. The change in the activation energy with the degree of ion exchange may be a reflection of the difference in the nature of the two kinds of active sites, S_I and S_{II}. At a lower level of ion exchange calcium ions occupy mainly the S_I site, while at a higher level they occupy S_I and S_{II} sites. The catalytic activities originate from the S_I and S_{II} sites at lower and higher levels of ion exchange respectively. Accordingly, there has been found a change in the activation energy from 32 kcal/mol for the La-X (50.0) to 23 kcal/mol for the La-X (90.4), dependent upon the degree of ion exchange.

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12) P. B. Venuto, L. A. Hamilton, P. S. Landis and J. J. Wise, *J. Catalysis*, **5**, 81 (1966).

13) J. Turkevich, F. Nozaki and D. Stamires, Proc. 3rd Intern. Congr. Catalysis, Amsterdam, 1964, Vol. I, Wiley, New York (1965), p. 586.

14) E. G. Boreskova, K. V. Topschiva and L. I. Piguzova, *Kinetika i Kataliz*, **5**, 903 (1964).

15) J. A. Rabo, P. E. Pickert, D. N. Stamires and J. E. Boyle, Actes 2nd Congr. Intern. Catalyse, Paris, 1960, Vol. 2, Editions Technip., Paris (1961), p. 2055.