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The Nature of Active Sites on Zeolites

XI. The Effects of the Silica-to-Alumina Ratio on the Acidity and Catalytic Activity of Synthetic Faujasite-Type Zeolites

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The acidity and catalytic properties of a series of magnesium and calcium synthetic faujasite-type zeolites have been studied as a function of the silica-to-alumina ratio of the zeolites. From measurements of the infrared spectra of adsorbed pyridine, the Brönsted acidity of the two cation series increases with silica-to-alumina ratio. All the magnesium forms were more acidic than the corresponding calcium forms. The acidity measurements can be understood in terms of the strength of the electrostatic field within the zeolite cavities.

The catalytic activity for the isomerization of *o*-xylene also increased with increasing silica-to-alumina ratio. The magnesium forms were more active than the corresponding calcium forms. The catalytic activity in each series appears to be directly related to the concentration of Brönsted acid sites.

INTRODUCTION

The influence of the exchangeable cation on the catalytic activity of molecular sieves has been the subject of a number of studies. In general, the catalytic activity for cracking, alkylation, and dealkylation increases with the increasing extent of replacement of sodium ions by hydrogen or multivalent cations (*1–4*). It has also been shown that the introduction of the more electropositive smaller cations results in the more active catalyst than the introduction of larger cations (cf. magnesium and barium) (*5–7*). It is shown that the calculated electrostatic field and potential decrease with increasing multivalent cation radius (*8*). It has also been shown that the number of Brönsted acid sites increases with increasing replacement of sodium by hydrogen or multivalent cation and with decreasing size of the multivalent cation (*7, 9, 10, 13*). It was suggested that the increase in acidity was due to the increasing electrostatic field (*7, 9, 10, 13*).

It has been reported that the Y-zeolites are more catalytically active than the X-zeolites (*11*). In general, the activity depends on the silica-to-alumina ratio of the zeolite and the radius and valency of the exchanged cation. Y-zeolites also have a stronger electrostatic field (*8*) and a greater concentration of Brönsted acid sites (*7, 12*). As is well known, the difference between X and Y sieves is the silica-to-alumina ratio. X-sieves generally have a silica-to-alumina ratio of about 2.4:1 while Y-zeolites have a ratio of about 5:1. Consequently, Y-zeolites contain fewer exchangeable cations per unit cell and the inter-aluminum distance is greater.

In this report, the variation of catalytic activity and acidity of several zeolites over a range of silica-to-alumina ratios has been studied in more detail. The magnesium and calcium forms were studied.

EXPERIMENTAL

The X-zeolites and the 4.1 silica-to-alumina ratio zeolites were laboratory preparations. The 3.4 and 4.9 silica-to-

TABLE 1
ANALYTICAL DATA FOR VARIOUS EXCHANGED ZEOLITES

Sample	Percent Exchanged	Percent Alumina	Surface Area, m^2g^{-1}
		Magnesium	
1	78	33.1	847
2	80	22.3	889
3	78	27.8	904
		Calcium	
4	96	31.4	851
5	94	26.6	927
6	93	23.3	885
7	93	20.5	872

alumina ratio zeolites were supplied by Linde Division of Union Carbide Corporation. The sodium forms were ion-exchanged with 10 percent aqueous solutions of calcium and magnesium nitrate. The physical properties are listed in Table 1. Catalytic activity for *o*-xylene isomerization was measured as reported previously (7, 9). The surface acidity was measured by means of the infrared spectra of chemisorbed pyridine using the previously reported procedures (7).

RESULTS

The spectra of the magnesium and calcium zeolites after chemisorption of pyridine are similar to those reported previously for pyridine adsorption on alkaline earth zeolites (7). The absorption band near 1545 cm^{-1} is due to chemisorbed pyridinium ions and is a measure of the concentration of Brönsted acid sites. Although a band is observed near 1446 cm^{-1} due to pyridine-cation interactions, no absorption band is detected near 1451 cm^{-1} due to adsorption of pyridine on the Lewis acid sites. In Fig. 1, the intensity expressed as absorbance per gram (peak height/sample mass) of the absorption band due to pyridine adsorbed on Brönsted acid sites is plotted against the percent alumina in the zeolites for both the magnesium and calcium samples.

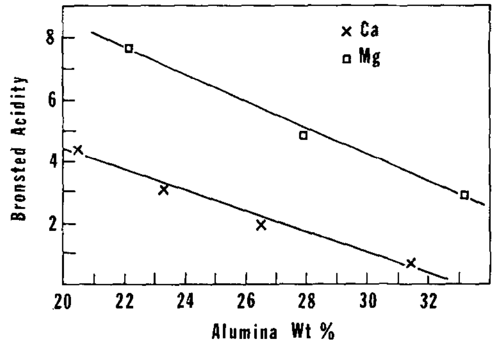

FIG. 1. Variation of Brönsted acidity with alumina content.

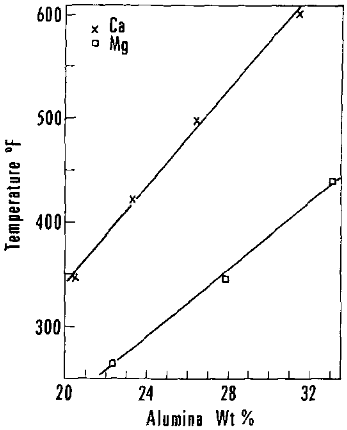

FIG. 2. Temperature for 20% isomerization of *o*-xylene as a function of alumina content.

In Fig. 2, the temperature for 20 percent conversion of the *o*-xylene to the meta- and para-isomers is plotted against the percent alumina. These data were derived from the linear plots of log conversion versus $1/T$. Figure 3 shows the catalytic ac-

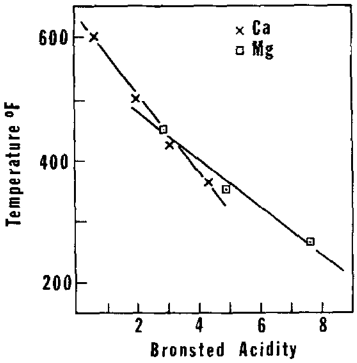

FIG. 3. Temperature for 20% isomerization of *o*-xylene as a function of Brönsted acidity.

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Discussion

For the divalent cation containing magnesium and calcium zeolites the present observations show that, at comparable degrees of ion exchange, the Brönsted acidity of the samples increases linearly with decreasing aluminum content. In agreement with previously proposed concepts of zeolite acidity, an increase in the concentration of Brönsted acidity with decreasing aluminum content would be expected since it is known that the electrostatic field increases with decreasing aluminum content (*8*) and hence it would be expected that according to the equilibrium,

$$M^{2+}OH_2 \rightleftharpoons MOH^+ + H^+,$$

the formation of protons and hence acidic hydroxyl groups would be favored. On the other hand, since the number of ion exchanged sites increases with increasing aluminum content and hence the potential number of acidic hydroxyl groups, it might be expected that the number of acid sites would increase with increasing aluminum content. Although the present results do not allow a definitive conclusion, it appears that the influence of the electrostatic field on the above equilibrium is the dominating factor and that the formation of MOH^+ species is more favored as the inter-aluminum distance increases. Hence a greater percentage of the possible potential acid sites is obtained as the silica-to-alumina ratio is increased.

Lewis acidity was not detected in any of the samples studied under the present experimental conditions. However, it is known that with higher temperature calcination, extensive dehydroxylation occurs with the concurrent formation of Lewis acid sites (*7*).

The catalytic activity for *o*-xylene isomerization follows a similar linear relationship to the Brönsted acidity as the aluminum contents of the zeolites are varied. The increase in activity with increasing silica-to-alumina ratio agrees with the results of Pickert (*11*) for gas oil cracking and Topchieva *et al.* (*11*) for cumene cracking. As shown by Fig. 3, for both the magnesium and calcium zeolites, there is a linear relationship between the Brönsted acid concentration and the catalytic activity. For all aluminum contents examined, the magnesium forms are more acidic and more active catalytically than the calcium forms, as shown previously for the extreme X and Y forms (*7, 12*). Again, as suggested previously, a greater acidity and activity of the magnesium forms is probably due to the greater associated electrostatic field (*7, 10*) which results in the formation of a greater percentage of MOH^+ groups and acidic protons. It is also possible that the acid sites in the magnesium form are of a different strength or effectiveness than those of calcium zeolites. The different temperature-acidity slopes shown in Fig. 3 suggest this possibility.

These results support previous deductions that the Brönsted acid sites formed by dissociation of adsorbed water, on divalent cation-containing zeolites are important active centers for proton acid catalyzed reactions such as *o*-xylene isomerization. Concentration of these sites has a marked influence on the activity but the acid strength may also be an important factor.

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