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The Nature of Active Sites on Zeolites

XIV. The Influence of Alkaline Earth Cations on the Catalytic Activity of Hydrogen Y Zeolite*

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The rate constants for *o*-xylene isomerization over two series of alkaline earth ammonium Y zeolites have been measured. The series differed in sodium contents of the zeolite. All forms examined were exchanged to the same extent with the alkaline earth cations. It was found that the catalytic activity was a function of the calculated electrostatic field and potential of the cation. The magnesium ammonium form was more active and the calcium, strontium and barium forms were less active than the parent ammonium Y. The sodium level had greatest influence on the most active catalyst and little influence on the least active. Since all the zeolites had the same measured acid site concentration, it is believed that the cations are influencing the acid site strength.

INTRODUCTION

Many studies have now been reported which relate the catalytic activity of zeolites in reactions involving carbonium ions to the presence of acid sites (*1*). In particular, the active centers appear to be related to the presence of Bronsted acid sites rather than Lewis acid sites or to the influence of the electrostatic field associated with the exchangeable cations.

Most of the discussions of relationships between catalytic activity and acidic properties of the zeolites have considered the concentration of acidic sites. Although in many cases good relationships have been found between the acid site concentration and the catalytic activity, a sufficient number of exceptions has been reported that it appears desirable to investigate other factors which might be contributing significantly to the catalytic activity.

One of the many possible factors which could influence the catalytic activity is the strength of the acid sites. Few studies have been made of this phenomenon in zeolites although its importance has been suggested several times.

Hirschler (*2*) has suggested 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." Thus, the acid strength should increase with increasing charge and decreasing size of the cation. Hence, it would seem that water molecules associated with the cations could become acid centers and that the cations could influence the acid strength of hydroxyl groups already present in the structure.

Richardson (*3*) has discussed a somewhat similar concept in relating catalytic activity for cumene cracking to cation properties. He considered that the ionic potential (e/r) of the cation results in a shift of electron charge distribution towards the vicinity of the cation via a conduction

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band model. Such an interaction would weaken the O–H bonds on the surface of the supercages and thus modify the acidity of the hydroxyl groups. Both of these proposals consider the role of the cation in modifying the nature of hydroxyl groups existing already in the zeolite structure (*2, 3*) or of water associated with the cation without specific formation of new structural hydroxyl groups (*2*). An interesting portion of the proposals of Richardson is that modifications of the activity of hydrogen Y zeolite can be anticipated. Thus, whereas the discussion of cation and hydrogen Y zeolites above would lead to expectation that hydrogen Y zeolite would be the most acidic faujasite type zeolite, introduction of a cation with a high ionic potential into a hydrogen Y zeolite could produce a more acidic faujasite (*3*). Studies of rare earth hydrogen and alkaline earth hydrogen Y zeolites (*4, 5, 10*) have indicated such an effect. The proposals of Richardson also suggest that a distribution of acid strengths exists which is compatible with the necessity for only a small fraction of the total acid site population being necessary for catalytic conversions. Tung and McIninch (*6*), and Tung (*7*) have discussed a different type of mechanism for the modification of acid site strengths. They visualized the existence of a dynamic (time variant) surface field and Bronsted acidity. Movements of the ion exchanged cations were visualized as generating changes in the surface field strengths and in the strengths of proton acid sites. These considerations stemmed from the studies of dielectric constants of the zeolites in the presence of an alternating electrostatic field. Variations in the acid site strength have also been reported by Benson, Ushiba and Boudart (*8*). Lunsford (*9*) has proposed that defect sites formed in the zeolite structure have important modifying effects upon the acidity of the structural hydroxyl groups.

In this paper, the influence of the acid site strength is investigated. Previous studies of alkaline earth zeolites, which show the indirect influence of the cation field on catalytic activity, led to an investigation of the influence of multivalent cations on the activity of ammonium Y zeolite (*10*). In the study of magnesium and calcium hydrogen Y zeolites, it was seen that for a range of divalent ion contents between approximately 35 and 55% exchange, the activity is independent of the cation content. These results were extended so as to consider the alkaline earth hydrogen zeolites containing about 40% of the exchange capacity as alkaline earth. At this level of exchange, the cations are present in inaccessible parts of the structure.

EXPERIMENTAL METHODS

Materials

Two samples of ammonium Y zeolite were prepared by conventional ion exchange of sodium Y zeolite ($SiO_2/Al_2O_3 = 4.9$). The ammonium Y zeolites had sodium contents of 1.1 and 0.1 wt %, respectively. The alkaline earth ammonium Y zeolites were prepared by ion exchange of the parent ammonium Y zeolites (surface area 965 m^2 g^{-1} after heating in flowing helium at 400°C) with suitable salt solutions. The zeolites contained the alkaline earth cations in a concentration equivalent to 40 ± 2% of the exchange capacity.

Technique

Catalytic activity of the various zeolite samples for *o*-xylene conversion was measured as reported previously (*5*). Conversions of *o*-xylene were measured at a series of temperatures. From the Arrhenius plots, the rate constant at 260°C was calculated. The surface acidity was measured by means of the infrared spectra of chemisorbed pyridine using the previously reported procedures (*5*).

RESULTS AND DISCUSSION

Measurements of the concentration of Bronsted acid sites on the zeolite catalysts by pyridine chemisorption showed the parent ammonium Y zeolite and the various cation exchanged zeolites to have the same concentration of acid sites. This would be expected since at the level of exchange, the cations are believed to occupy inaccessible positions and thus should not influence the concentration of acid sites. The results for magnesium and calcium were reported previously (*10*).

In Fig. 1, the rate constants for the isomerization of *o*-xylene at 260°C are plotted as a function of the calculated electrostatic potential and field for the four cation containing forms containing 1.1 wt % sodium. Good straight line relationships were obtained. Hence, the inaccessible cations are markedly modifying the catalytic activity of the ammonium Y zeolite. The catalytic activity appears to be closely related to the electrostatic properties of the cations exchanged into the zeolite. The smaller the cation and hence the greater the resultant electrostatic field, the greater the catalytic activity.

It should be noted that the catalytic activity of the magnesium hydrogen form is greater than that of the parent hydrogen form, whereas that of the calcium, strontium and barium–hydrogen forms is less. Since the activities can be related to the polarizing powers of the cations and are distributed on both sides of the hydrogen Y activity, it would appear that the fields generated by the cations are influencing the strengths of the acid sites. Magnesium ions must increase the catalyst acidity while calcium, strontium and barium decrease the acidity.

An interesting observation in this study is that the cations and the active sites are believed to be located in different parts of the zeolite structure and hence the effects of the cations must encompass large distances through the structure. The cations are probably located in the small pore system of the zeolite whereas the hydroxyl groups are probably located in the supercages. Hence in contrast to the reports (*2*, *3*, *6*) the polarizing effects of the cations must encompass relatively large distances in the structure.

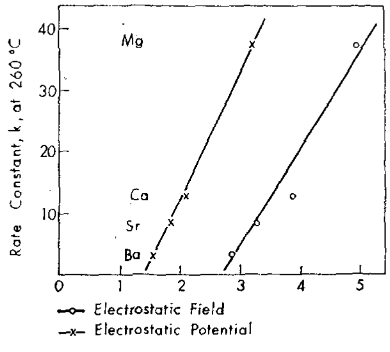

FIG. 1. Rate constant for *o*-xylene isomerization over alkaline earth hydrogen Y as a function of cation.

Previously reported studies of various zeolites have suggested that the catalytic sites are the acidic structural hydroxyl groups with infrared absorption bands near 3650 and 3550 cm^{-1} (*1*). The previous study (*10*) on the influence of the degree of exchange of calcium or magnesium into ammonium Y zeolite upon the hydroxyl group and acid site concentration and on the catalytic activity suggests that the 3550 cm^{-1} hydroxyl groups are not important catalytic sites since their concentration does not follow the changes in acid site concentration or catalytic activity. However, the hydroxyl groups represented by the 3650 cm^{-1} band are probably active centers since their concentrations closely follow the acidity and catalytic activity. Bolton and Bujalski (*11*) recently reached a similar conclusion. Hence the cations must be influencing the nature of this type of hydroxyl group presumably by altering the polarity and hence the acidity of the hydroxyl group. Depending on the radius of the ion, the site strength and catalytic activity can be greater or less than that of the parent ammonium Y zeolite. However, observations of the frequency of the hydroxyl groups show no change with changing cation radius, which might have been expected.

The type of mechanism or effect by which the inaccessible cations can influence the catalytic properties of the structural hydroxyl groups is not clear at this time. It is possible that a shift in electron charge distribution via a conduction band model as suggested by Richardson occurs (*3*) or via an inductive effect suggested by Lunsford (*9*).

Figure 2 shows the influence of the residual sodium level on the activity of the cata-

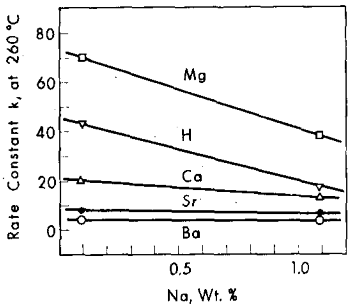

FIG. 2. Rate constant for *o*-xylene isomerization over alkaline earth hydrogen Y as a function of sodium content.

lysts. In all cases, except barium, the lower sodium level results in a more active catalyst. It is of greater interest to note that the more active catalysts respond more to the sodium levels than the less active catalysts. Thus lowering the sodium level from 1.1 to 0.1% results in almost 100% increase in the activity of magnesium hydrogen Y but only about 50% increase for calcium hydrogen Y. In like manner the hydrogen form and the strontium hydrogen forms were respectively more and less sensitive to the sodium level than the calcium hydrogen form. Hence small amounts of sodium (less than 10% of the exchange capacity) can have pronounced effects on the catalytic activity. It is well known that the level of sodium markedly influences the activity of hydrogen Y zeolite (*12–14*). The activity apparently increased rapidly with decreasing sodium content and it was suggested that the activity per site was increasing. In the present case, the number of sites are constant. Hence, it would appear that the most active sites are being poisoned by sodium in each case. It also appears that the sites generated by the removal of the last 10% of the sodium are those which respond most to the multivalent cation. The role of sodium in these systems is being further explored so that its influence on the catalytic sites can be more fully understood.

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