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The Nature of Active Sites on Zeolites

IX. Sodium Hydrogen Zeolite

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The acidic and catalytic properties of a series of sodium hydrogen Y zeolites have been studied as a function of the zeolitic sodium content. The structural hydroxyl groups were investigated after the zeolite had been calcined at 480°C. The characteristic hydroxyl groups of hydrogen Y zeolite with frequencies near 3745, 3640, and 3540 cm^{-1} were observed. The intensity of the 3640-cm^{-1} band increases almost linearly with decreasing sodium content. The 3540-cm^{-1} band is very weak until about half of the sodium ions of the zeolite have been exchanged. The intensity of the band then increases rapidly until at low sodium contents, the 3640- and 3540-cm^{-1} bands are of equal intensities. Evidence for the 3540-cm^{-1} band type of hydroxyl groups being located in the hexagonal prisms of the structure is discussed.

The acidities of the zeolites were measured by means of the infrared spectra of chemisorbed pyridine. After calcination at 480°C, the zeolites are mostly in the Brönsted acid form. The concentration of Brönsted acid sites increases linearly with decreasing sodium content of the zeolite until 60–70% of the sodium ions have been replaced in the structure, corresponding to sodium ions remaining only in the hexagonal prisms of the structure; the Brönsted acidity then remains approximately constant.

The catalytic activity for *o*-xylene isomerization was measured. The activity increases with decreasing sodium content of the zeolite. The activity per site also increases with decreasing sodium content. The changes in catalytic activity with sodium content are considered in terms of the structure of the zeolite. The hydroxyl group concentration, Brönsted acidity, and catalytic activity all increase in a parallel manner with decreasing zeolite sodium content. Brönsted acid sites are probably the primary catalytic centers. However, because of the known changes of activity with calcination temperature, other types of sites are probably involved, either simultaneously or sequentially, in reactions over zeolites.

INTRODUCTION

In a previous paper in this series (*1*), the influence of calcination temperature on the hydroxyl groups and acidity of hydrogen (or decationated) Y zeolite was discussed. In agreement with other studies (*2–6*) it was shown that there are at least three distinct types of hydroxyl groups in the structure of the deamminated zeolite. It was shown that the populations of these hydroxyl groups depend markedly on the calcination temperature. The population reaches a maximum near 400°C and declines to a very small number at 700°C. The Brönsted acidity of the zeolite was shown to follow a similar temperature dependence to the 3640-cm^{-1} band type of hydroxyl groups. The Lewis acidity was shown to be very low up to about 500°C calcination temperature and then to increase rapidly with increasing calcination temperature as the dehydroxylation of the structure became more extensive. It was suggested that the 3640-cm^{-1} band type of hydroxyl groups were the sources of Brönsted acidity. By comparison with catalytic activity measurements, it was suggested that the Brönsted acid sites played an important role in catalytic reactions.

In a subsequent paper (*7*), it was shown that the concentration of Brönsted acid sites under constant calcination conditions varied with the nature of the exchangeable cation. It was suggested that the electrostatic field associated with the cations promoted the dissociation of adsorbed water, thus yielding protonic centers:

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

Comparison of the catalytic activity and Brönsted acid site concentrations again suggested an important role for Brönsted acid centers in zeolite catalysis.

In the current study, a series of sodium hydrogen Y zeolites, with a wide range of sodium contents, has been studied. Catalyst acidities were measured by means of the spectroscopic studies of chemisorbed pyridine and catalyst activities were measured for *o*-xylene isomerization. This reaction is considered to be Brönsted acid-catalyzed.

In other studies of the sodium hydrogen Y system, Turkevich, Nozaki, and Stamires (*8*) have found that the cumene cracking activity of sodium Y zeolite increases as the sodium ions are progressively replaced by hydrogen ions or decationated sites. They also found that the number of free radicals formed from the adsorption of triphenylamine was proportional to the degree of ion exchange. In a further study, Turkevich and Ciborowski have shown that the H_2–D_2 equilibration rate increases as the replacement of sodium by ammonium ions is increased (*9*). Pickert, Bolton, and Lanewala (*10*) have also shown that the rate of benzene alkylation with propylene increases with the extent of decationization.

EXPERIMENTAL

All samples of zeolite were made from a common parent sodium Y zeolite. This zeolite had a silica-to-alumina ratio of 4.9, a sodium content of 10.3% and a surface area of 901 m^2g^{-1} (determined at $P/P_0 \simeq 0.02$). X-Ray diffraction measurements showed the zeolite to be highly crystalline.

Batches of the sodium Y zeolite were ion-exchanged with ammonium nitrate solutions at 95°C so as to yield products containing a wide range of ammonium ion concentrations. The analytical data for the series of zeolites are given in Table 1.

TABLE 1
ANALYTICAL DATA FOR NaHY ZEOLITES

Sample	% Na	% Ion-exchanged	No. of Na Atoms	Surface area (m^2g^{-1})
1	0.2	99.8	<1	931
2	1.3	88	7	956
3	3.4	67	18	945
4	3.6	65	20	920
5	3.8	63	21	981
6	5.1	50	28	968
7	6.9	32	38	926
8	8.3	19	45	898
9	10.3	0	56	901

The chemisorption of pyridine on the zeolites was observed spectroscopically as described previously (*7*). Spectra of the structural hydroxyl groups were also recorded after calcination of the zeolite at 480°C. A Cary-White 90 infrared spectrophotometer was used. The spectral slitwidth was 3 cm^{-1} and the scan speed was 1 cm^{-1} sec^{-1}. The samples weighed 0.04 to 0.08 g.

The *o*-xylene isomerization was studied using the microreactor described previously (*7*). The catalyst, in the form of 20–40 mesh granules, was dried in flowing helium and the temperature was gradually increased to 480°C. The catalyst was then calcined for 3 hr in flowing helium at this temperature and then cooled to 200°C. The helium purge gas was then diverted through a thermostated *o*-xylene saturator and the stream was passed over the catalyst. The products were intermittently sampled and analyzed by gas chromatography. The temperature was adjusted until a suitable conversion (5–10%) of the feed was obtained. When the system had reached steady state, accurate measurements of the conversion were made. Conversions were subsequently measured at three or four higher temperatures, the maximum conversion being kept below 40% of the feed. The logarithms of the conversions were plotted against the reciprocal of the absolute temperature in the conventional manner. From the linear relationships, the temperatures for 10%, 25%, and 50% conversions were calculated. Surface

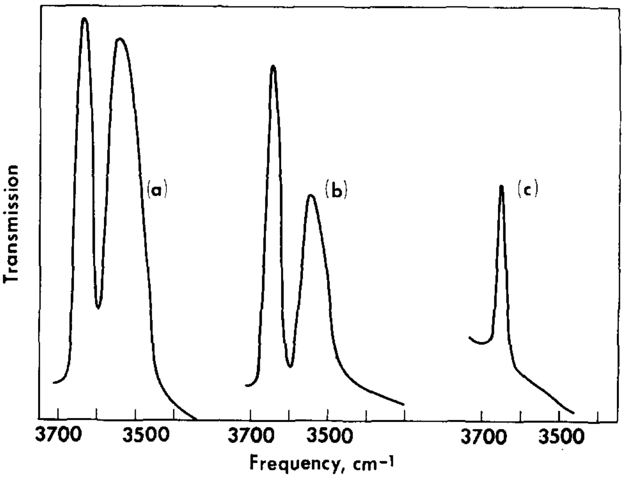


FIG. 1. Spectra of hydroxyl groups on various NaHY zeolites after calcination at 480°C: (a) 0.2% Na, (b) 3.6% Na, (c) 6.9% Na.

area and X-ray diffraction measurements on the samples used in the reactor showed no detectable loss of zeolite structure.

RESULTS

The spectra in the hydroxyl stretching region for several of the samples are shown in Fig. 1. The zeolites had been calcined for 12 hr at 480°C before the spectra were recorded. Three hydroxyl group absorption bands are seen with frequencies near 3742, 3640, and 3540 cm^{-1} similar to those observed for hydrogen Y zeolites (*1–4, 6*). The invarient 3742-cm^{-1} band is omitted from Fig. 1. The intensities of the bands increase with increasing ion exchange and the band intensities relative to each other vary considerably. As the extent of ion exchange increases, the ratio of the intensity of the 3640-cm^{-1} band to that of the 3540-cm^{-1} band decreases so that for the highest

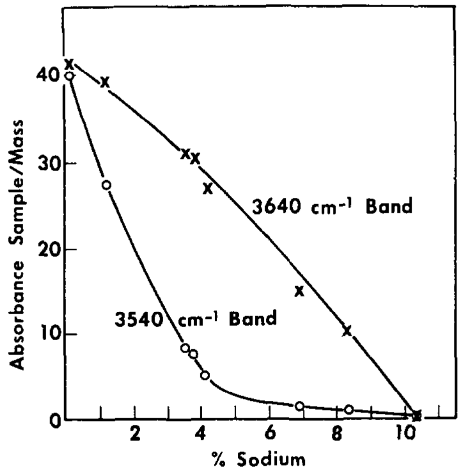


FIG. 2. Absorbance of the 3640- and 3540-cm^{-1} hydroxyl bands as a function of zeolite sodium content.

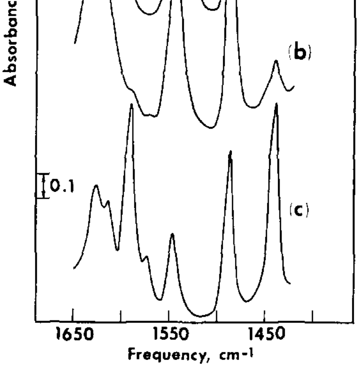


FIG. 3. Spectra of pyridine chemisorbed on various NaHY zeolites after calcination at 480°C: (a) 0.2% Na, (b) 3.6% Na, (c) 6.9% Na.

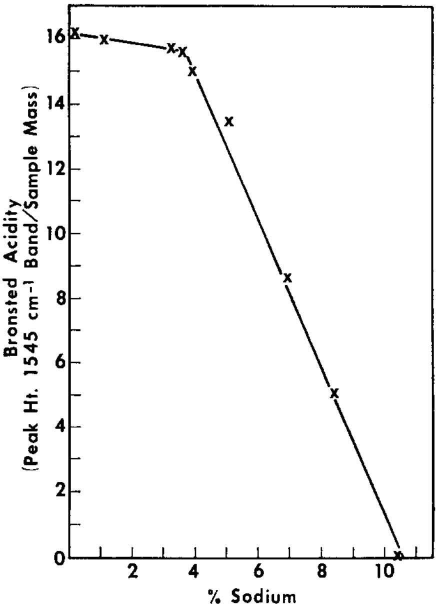


FIG. 4. Absorbance of 1545-cm^{-1} band as a function of zeolite sodium content.

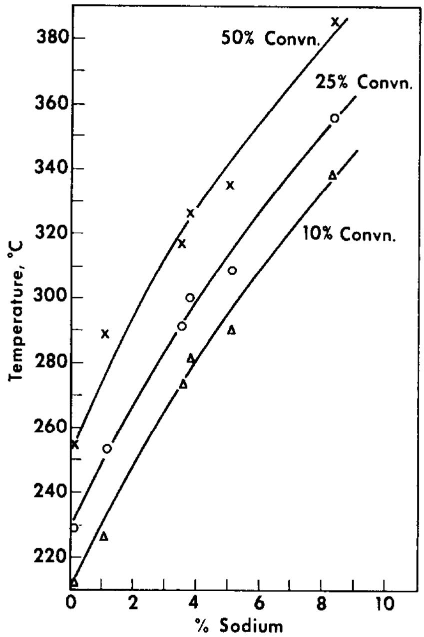


FIG. 5. Temperature required for 10%, 25%, and 50% conversion of o-xylene as a function of zeolite sodium content.

exchanged form, the two bands are of equal intensities. The intensities of the bands are plotted against the sodium contents of the zeolites in Fig. 2.

The spectrum of adsorbed pyridine was observed after equilibrating the zeolite with excess pyridine followed by desorption for 2 hr at 250°C. Typical spectra are shown in Fig. 3. After the spectrum of adsorbed pyridine had been observed, a small amount of water (3 μmoles) was equilibrated with the sample followed by evacuation at 250°C. The spectrum was again recorded. This procedure was followed to see if any significant dehydroxylation had occurred, since it has been shown that readdition of water to a dehydroxylated zeolite results in an increase in the 1545-cm^{-1} band (*2*). No effect or only very small effects were observed on the concentration of pyridinium ions, as indicated by little change in intensity of the 1545-cm^{-1} absorption band, thus showing that little dehydroxylation had taken place. It has previously been shown that the ab-

TABLE 2

BRÖNSTED ACIDITY AND CATALYTIC ACTIVITY OF NaHY ZEOLITES

Sample	Peak ht. 1545-cm^{-1} band / Sample mass	Temperature (°C) for— 10%	25% conversion	50%	Percent conversion at 250°C
1	16.2	212°	228°	254°	45.8
2	15.8	226°	253°	288°	25.1
3	15.6	—	—	—	—
4	15.5	272°	291°	317°	7.7
5	14.9	282°	300°	326°	5.7
6	13.4	290°	308°	335°	4.4
7	8.6	—	—	—	—
8	5.2	337°	356°	385°	0.8
9	0	—	—	—	0.0

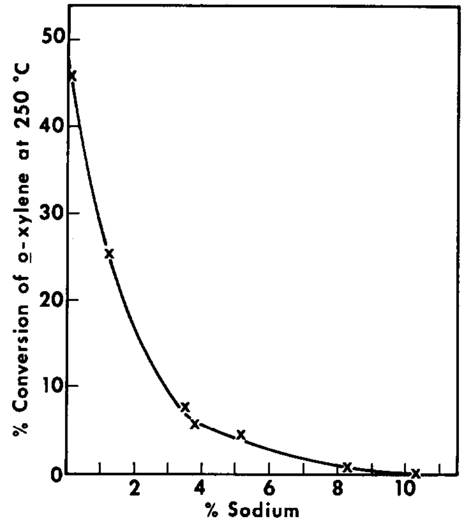


FIG. 6. Percentage conversion of *o*-xylene at 250°C as a function of sodium content.

absorption band near 1545 cm^{-1} in the spectrum of chemisorbed pyridine is characteristic of pyridinium ions and hence Brönsted acidity of the solid catalyst, while a band near 1451 cm^{-1} is characteristic of pyridine adsorbed on Lewis acid sites (*1*, *2*, *6*, *11*, *12*). In Table 2, the intensities of the 1545-cm^{-1} band, characteristic of Brönsted acid sites, are tabulated. These data are plotted against the sodium content of the zeolite in Fig. 4. Only very weak absorption bands corresponding to pyridine adsorbed on Lewis acid sites were observed.

Data for the conversion of *o*-xylene over the various catalysts are also given in Table 2. Temperatures required to achieve the various conversions and the percentage conversion at 250°C are listed. These data are plotted against the zeolite sodium contents in Figs. 5 and 6.

DISCUSSION

Structure of Sodium Y Zeolite

The structural framework and the location of the cations in Y zeolites have been discussed by several workers (*13–15*). It has been found that the sodium ions occupy several different crystallographic positions in the zeolite lattice, the exact positions depending upon whether the zeolite is hydrated or not. According to Breck (*13*), the sodium ions in the hydrated zeolite are distributed so that there are 16 cations located in the centers of the hexagonal prisms (site S_I), 32 cations are located on the six-membered oxygen rings of the cube octahedra (S_{II} sites), and 8 cations are located on the walls of the channels (S_{III} sites). For the dehydrated zeolite, Eulenberger, Shoemaker, and Keil (*14*) locate 8 cations at the S_I sites, 19 cations at S'_I sites, which are situated in the sodalite units approaching the hexagonal prisms, and 30 cations in the S_{II} position. The locations of ammonium ions have not been reported, and hence the discussion of sodium hydrogen zeolites is difficult. In aqueous solution, it has been shown by Sherry (*16*) that the last 16 sodium ions are much more difficult to ion-exchange out of the zeolite than the other sodium ions. Hence, the sodium ions in the hexagonal prisms are most likely to be the last to be exchanged. It is also known that the ions in the S_I sites are only accessible to molecules which can pass through a ring of about 2.2-Å diameter whereas sites II and III are accessible to molecules up to 9-Å diameter. These considerations led Hughes and White (*2*) and Ward (*17*) to consider that the 3540-cm^{-1} band did not represent hydroxyl groups located in the S_I positions, since these hydroxyl groups interacted with piperidine and pyridine, both molecules being too large to enter the hexagonal prisms.

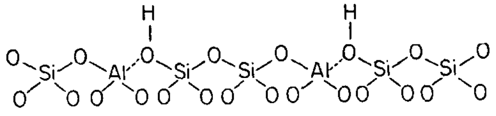
The results of the present study can be interpreted in terms of the structural concepts of the zeolite.

Structural Hydroxyl Groups

It is now reasonably well established that pure sodium Y zeolite contains no structural hydroxyl groups while hydrogen Y zeolite possesses two intense absorption bands due to hydroxyl groups (*1–4*, *6*, *18*, *19*). Angell and Schaffer (*3*) examined three zeolites which were 7%, 32%, and 84% ion-exchanged to the ammonium form. Their studies showed that the relative intensities of the two bands at 3640 and 3540 cm^{-1} varied markedly with the extent of ion exchange. The more detailed results of the present study confirm and extend the results of Angell and Schaffer. In Fig. 2, it is seen that the intensity of the 3640-cm^{-1} hydroxyl band increases fairly linearly with decreasing sodium content of the zeolite. On the other hand, the 3540-cm^{-1} hydroxyl band increases very little until the sodium content has been reduced to about 5% by weight. The 3540-cm^{-1} band then increases in intensity rapidly with decreasing sodium content and becomes comparable in intensity to the 3640-cm^{-1} band at very low sodium contents. These results indicate, as previously suggested by Hughes and White (*2*) and Uytterhoeven *et al.* (*20*), that the 3640-cm^{-1} band represents the most accessible hydroxyl groups. This study shows that they are formed by replacement of the most readily exchanged sodium ions, most likely those located in the S_{II} and S_{III} positions in the hydrated zeolite. Hence, it is to be expected that these hydroxyl groups will readily interact with adsorbing molecules, as shown in several studies (*1–3*, *6*, *18*, *19*). Because the 3540-cm^{-1} band appears only at high degrees of ion exchange, it is likely that these hydroxyl groups are formed during the replacement of the sodium ions in the S_I positions. Indeed, the 3540-cm^{-1} band occurs to any extent only during the replacement of the last 22 to 25 sodium ions. Since the S_I sites are filled with about 16 sodium ions and the 3640-cm^{-1} band is still increasing in intensity when there are only 25 residual sodium atoms left in the structure, it seems highly probable that the 3540-cm^{-1} band type hydroxyl groups are associated with the removal of the sodium ions from the S_I sites. It would then seem possible that the 3540-cm^{-1} band type of hydroxyl groups are within the hexagonal prisms. If this is correct, these hydroxyl groups would be inaccessible to most molecules which cannot enter the hexagonal prisms. It has been shown that these hydroxyl groups do not interact with many molecules with which the 3640-cm^{-1} band type of hydroxyl groups interact (*19*, *21*). However, the 3540-cm^{-1} band type hydroxyl groups have been shown to interact with basic molecules (*2*, *17*), although the interaction is weaker than with the 3640-cm^{-1} band type hydroxyl groups. Because the 3540-cm^{-1} band type hydroxyl groups interact with bases, Hughes and White (*2*) suggested that these hydroxyl groups are not in the hexagonal prisms but that the O_4 oxygen atoms form the oxygens of these hydroxyl groups. However, recently, it has been shown that delocalization of the hydrogen atoms can occur at elevated temperatures (*19*, *22*) and hence the hydrogen atoms or ions could migrate into the larger cavities in which they could interact with adsorbates. It also seems probable that if the adsorbates have sufficient attractive powers, the hydrogen atoms could be separated from the hydroxyl groups even at room temperature. This point will be considered again below. The present studies, then, suggest that the 3540-cm^{-1} band type of hydroxyl groups could be located in the hexagonal prisms and yet still be free to interact with adsorbates if the attraction of the adsorbate is sufficiently strong or the temperature high enough to delocalize the hydrogen atoms. The study also confirms the increase in population of both the 3640- and 3540-cm^{-1} band types of hydroxyl groups with increasing sodium removal previously suggested (*3*). A very recent X-ray study by Olson and Dempsey (*33*) has shown that the hydrogen atoms are attached to the O_1 and O_3 oxygen atoms.

Acidity of the Sodium Hydrogen Zeolites

Readdition of small amounts of water (3 μmoles) to the zeolites had negligible influence on the concentration of acid sites. Hence it can be concluded that the calcination procedure resulted in little dehydroxylation of the structure. Examination of the spectra of chemisorbed pyridine showed little evidence for the presence of Lewis acid sites. This would be expected from the structure of the hydrogen zeolite when little dehydroxylation has occurred, as shown by the scheme below:



In Fig. 4, the concentration of Brönsted acid sites is shown as a function of the sodium content of the zeolite. Because the pyridine molecule is too large to enter the hexagonal prisms, the detected acid sites must be located in the supercages or the sodalite portions of the structure. This is borne out by the results of Fig. 4. It can be seen that the Brönsted acid site concentration increases linearly with the percentage of sodium removed until only about the last 16 sodium ions are left in the structure, corresponding to the occupancy of the S_I positions. If the hydrogen atoms replacing these sodium ions are inside the hexagonal prisms, they would be incapable of chemisorbing pyridine. This has been shown previously (*1*, *2*, *18*), although it has also been shown that these same hydroxyl groups chemisorb the stronger base, piperidine (*2*), and also weakly hydrogen-bond with pyridine (*1*). However, it should be remembered that the acidity measurements were made at room temperature. At elevated temperatures, it is probable that the hydrogen atoms become mobile and can diffuse into parts of the zeolite which are accessible to larger molecules. Such mobility or delocalization has been indicated in previous studies (*19*, *22*). It has also been shown that cumene interacts with the 3540-cm^{-1} band hydroxyl at temperatures above 380°C but not at lower temperatures (*23*). However, at 260°C, Eberly (*18*) has shown that the 3540-cm^{-1} band hydroxyl does not interact with pyridine. Hence if these hydroxyl groups are mobile and accessible at this temperature, they are either nonacidic or only very weakly acidic.

As reported previously (*7*), the sodium Y zeolite was found to be nonacidic. The results also confirm previous conclusions that the 3640-cm^{-1} band type of hydroxyl are the sites of Brönsted acidity since, under the conditions used, only these hydroxyl groups are capable of protonating pyridine. It is seen from Figs. 2 and 4 that the intensity of the 3640-cm^{-1} band and the concentration of Brönsted acid sites increase together as the sodium content is reduced, thus suggesting that each 3640-cm^{-1} band type of hydroxyl group is an acid center. The very small concentration of Lewis acid sites and its nondependence on the degree of ion exchange are to be expected from the accepted structure of the hydrogen Y zeolite shown above. However, if dehydroxylation occurs at elevated temperatures, as suggested by several workers (*1*, *2*, *4*, *5*, *8*, *10*, *20*, *21*), and predicted from the structure, the Lewis acid site concentration would be expected to increase with the extent of ion exchange as the number of potential accessible tricoordinated aluminum atoms increases.

Catalytic Activity

The results of the *o*-xylene isomerization studies are shown in Figs. 5 and 6. It is seen that for the reaction over the zeolite calcined at 480°C, the activity progressively increases with the increasing removal of sodium ions. The present results show a near-linear relationship between the temperature required for a given conversion at various levels of conversion and the percentage sodium in the zeolite. However, there appears to be a definite deviation from linearity at lower sodium levels, suggesting that the catalytic activity increases more rapidly with increasing sodium removal. This phenomenon is clearly shown in Fig. 6 in the plot of conversion at 250°C as a function of sodium content. Similar effects were observed previously for other reactions (*8–10*). If each sodium ion is replaced by an ammonium ion and then on calcination by a hydroxyl group, which forms an active center, the results indicate an increasing effectiveness per site with increasing ion exchange. A similar conclusion was reached by Turkevich *et al.* from studies of cumene dealkylation (*8*). This result is surprising since it would be expected that the last 16 hydroxyl sites to be introduced would be inaccessible to the xylene molecules and the results of the acidity measurements show that, under the conditions used in this study, the last 16 hydroxyl groups do not contribute to the acidity. However, as suggested elsewhere (*19*, *22*, *23*), it appears that the hydrogen of the hydroxyl groups can become delocalized and mobile. Since it is known that the 3540-cm^{-1} band type of hydroxyl groups do interact with cumene at elevated temperatures (above 380°C), whereas they do not at lower temperatures (*23*), it may be expected that these hydroxyl groups, which are nonacidic and inaccessible under the conditions of the acidity measurements, can function as active centers under reaction conditions. It is also possible to envisage mutual enhancement of the sites as their separation decreases. Such an enhancement could be particularly important if mobile protons are the important seats of activity.

Relationship between Acidity and Catalytic Activity

The catalytic activity of zeolites has been attributed to Brönsted acid sites, Lewis acid sites, and the electrostatic field within the zeolite structure. The results of the present study show that as the sodium content of the zeolite is decreased, the hydroxyl content, the Brönsted acid site concentration, and the catalytic activity increase. For the calcination conditions used, the concentration of Lewis acid sites remained very small and constant. Hence, it would appear that Lewis acid sites as such are not responsible for the catalytic activity. This conclusion is supported by the previous results, which showed that the alkaline earth Y zeolites were active for cumene dealkylation but possessed only Brönsted acid sites (*7*), and by the lack of a relationship between toluene cracking activity and Lewis acid content of hydrogen Y zeolites (*9*, *24*). The observations that proton donors increase the catalytic activity of strongly dehydrated zeolites also tends to indicate that Lewis acid sites are not the primary active centers (*24–26*). Hence, it must be concluded that the Brönsted acidity or the electrostatic fields are the active centers.

The simultaneous increase in the concentration of Brönsted acid sites and the increase in catalytic activity suggest that the Brönsted acid sites are important centers for catalytic activity. Furthermore, the relationships of acidity and activity to hydroxyl group concentrations suggest that the 3640-cm^{-1} band type of hydroxyl groups are the principle Brönsted acid sites, while the 3540-cm^{-1} band hydroxyls can be active centers under some conditions. Other evidence for the active sites being Brönsted acids has been discussed elsewhere (*7*, *24*, *27*, *28*).

The results of this study shed little light on the question of the electrostatic field being responsible for the catalytic activity. However, since the products of the reaction and the activation energy for *o*-xylene isomerization over the zeolites and over amorphous silica-alumina cracking catalysts are similar (*29*), it does not seem necessary to invoke any type of site different from those present on silica-alumina. Furthermore, it is difficult to rationalize the poisoning effects of bases such as ammonia (*24*) and quinoline (*8*) if acid sites are not involved in the reactions. Other reasons for discounting electrostatic fields as the primary seats of catalytic activity have been discussed previously (*7*).

Although the results of this study indicate the importance of Brönsted acid sites in zeolite catalysis, other factors must also be involved. Comparisons of catalytic activity of zeolites as a function of calcination temperature (*24*, *30*, *31*) with measurements of the Brönsted acidity as a function of calcination temperature (*1*, *2*, *32*) show that the catalytic activity reaches a maximum near 600°C whereas the Brönsted acid site concentration is only about one-half of its maximum value. In fact, at 600°C, there are approximately equal numbers of Brönsted and Lewis acid sites (*1*, *32*). Hence, it is possible that two sites are involved, simultaneously, or sequentially, in the zeolite system. Dual-site mechanisms have been postulated previously (*34*) and are known in biological systems. It is also possible that partial dehydroxylation of the surface removes low activity sites and increases the accessibility of the residual sites. Further studies are needed to clarify these points.

ACKNOWLEDGMENT

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