JOURNAL OF CATALYSIS 9, 225–236 (1967)

The Nature of Active Sites on Zeolites

I. The Decationated Y Zeolite

JOHN W. WARD

From the Union Oil Company of California, Union Research Center, Brea, California

Received June 19, 1967; revised August 30, 1967

The infrared spectra of ammonium Y zeolite have been observed after calcination at a series of temperatures up to 750°C. At least three different types of hydroxyl groups exist on the surface after the ammonium ions have been decomposed. The hydroxyl group concentration reaches a maximum at 350°C, remains constant to 550°C, and decreases with increasing temperature. The spectra of chemisorbed pyridine were observed on the zeolite after calcination. The concentration of pyridinium ion parallels that of the hydroxyl groups and is a measure of the concentration of Brönsted acid sites. The concentration of coordinately bound pyridine (Lewis acidity) is low below 475°C but increases rapidly with increasing calcination temperature. The hydroxyl groups are the Brönsted acid centers and the Lewis acid centers are tricoordinated aluminum atoms formed by dehydroxylation of the zeolite. Comparison of the hydroxyl group and Brönsted acid site concentrations with catalytic activity shows that the active centers are the acidic hydroxyl groups.

INTRODUCTION

Crystalline aluminosilicates have recently gained prominence as catalysts and adsorbents. The X and Y type zeolites have been investigated as catalysts for many reactions including cracking, isomerization, alkylation, and alcohol dehydration.

The structure has been described in detail (*1*). The crystal lattice consists of a three-dimensional network of silicon and aluminum atoms with mutual shared oxygen atoms. The negative charges on the aluminum-oxygen tetrahedra are satisfied by cations. The cations can be exchanged for other positive-charged ions. There are three different types of cation sites (*1*); these sites are located in the sodalite cages (cubooctahedra), in the bridge positions connecting sodalite cages, and in the giant supercages. The catalytic activity of the zeolites depends markedly on the type and location of the cation (*2*, *3*).

A number of theories regarding the nature of active sites on zeolites have been proposed. Plank *et al.* (*2*, *4*), Venuto *et al.* (*5*), and Benesi (*6*) have suggested that acidic hydroxyl groups are responsible for the catalytic activity while Pickert *et al.* (*7*) consider that the electrostatic fields produced by the cations are the seats of activity.

Turkevich *et al.* (*8*) have suggested that Lewis acid sites, produced by dehydroxylation of the molecular sieve which results in formation of tricoordinated aluminum atoms, are the active sites. Boreskova and co-workers (*9*) consider that the negatively charged aluminum-oxygen tetrahedra and the triply coordinated aluminum atoms in the decationated dehydroxylated form are active centers. It is, therefore, of interest and importance to attempt to discriminate between these different proposed seats of activity. This paper reports a study of the hydrogen or decationated Y zeolite.

Since this work was started, several papers have appeared which discuss the surface of Y zeolites. Uytterhoeven, Christner, and Hall (*10*) have reported an investigation of the decationated zeolites. They studied the hydrogen content of a Y zeolite as a function of temperature by means of deuterium exchange. They also studied the nature of the hydroxyl groups as a function of calcination temperature by infrared spectroscopy. Their results showed that the ammonium form on heating evolves ammonia. The proton formed reacts with lattice oxygen to form hydroxyl groups. Since the crystal lattice of the zeolite has several different types of oxygen, several different hydroxyl frequencies are not unexpected. They reported three principal hydroxyl frequencies at 3745, 3650, and 3545 cm^{-1}. The 3745-cm^{-1} band was assigned to hydroxyl groups at the edges of the crystallites which are thought to be similar to those observed on silica gel. The remaining two hydroxyl bands are assigned to Si–OH groups but their exact nature is uncertain. They result from deamination and subsequent reaction of the proton with the lattice oxygens. It is not clear whether the 3545-cm^{-1} band results from hydrogen bonding interaction between adjacent hydroxyl groups (*11*) or whether it represents hydroxyl groups at different locations in the lattice. Eberly (*13*) considers the two bands to represent hydroxyl groups in the cage and bridge positions in the structure. This conclusion was reached from observation of a preferential interaction of the 3650-cm^{-1} band with olefins. From a study of physically adsorbed molecules on Y zeolite, White *et al.* (*14*) reached the same conclusion on the grounds that the 3545-cm^{-1} band did not interact with nonpolar molecules.

Uytterhoeven *et al.* (*10*) showed that the 3650- and 3545-cm^{-1} bands behaved as Brönsted acids with respect to ammonia resulting in the formation of ammonium ions. In a later paper (*12*) Liengme and Hall showed that the 3650-cm^{-1} band, but not the 3545-cm^{-1} band, behaved as a Brönsted acid site with respect to pyridine for a zeolite calcined at 480°C. At higher calcination temperatures Lewis acid sites were detected. Uytterhoeven *et al.* (*10*) showed that most of the hydrogen could be driven from the structure and that water could not be added back to the structure.

The observations of hydrogen contents by Uytterhoeven *et al.* were made in Y zeolite which still contained 20% of the exchange capacity as sodium. Spectroscopic measurements were not made above 555°C. The studies of Liengme and Hall (*12*) were restricted to decationated zeolites still containing 55% of the exchange capacity as sodium and their reported base adsorption studies were restricted to two calcination temperatures, namely 300° and 600°C. Eberly's work (*13*) appears to have been restricted to samples calcined at 427°C and to olefin adsorption. Similarly, White *et al.* (*14*) restricted their observations to less than 350°C. Angell and Schaffer (*11*) investigated, after calcination at 500°C, Y zeolites with varying levels of ammonium exchange. They found that the intensities of the 3650- and 3545-cm^{-1} bands depended markedly on the degree of exchange.

No results have been reported of simultaneous studies of the structural hydroxyl groups and of pyridine adsorption as a function of temperature. Furthermore, no relationship appears to have been established between the nature of the surface groups and the catalytic activity of the Y zeolite.

We have studied a Y zeolite in which the sodium ions had been replaced to greater than 90% of the exchange capacity by ammonium ions. The infrared spectra have been studied at a series of calcination temperatures in order to determine the effects of temperature on the surface structural groups. Infrared spectra of chemisorbed pyridine adsorbed on the zeolite after calcination at various temperatures have also been obtained. The results from these studies have then been related to the activity of the zeolite for various reactions.

EXPERIMENTAL

Materials. The composition of the sodium Y zeolite starting material was 10.3% Na, SiO_2/Al_2O_3 ratio 4.9. Its nitrogen surface area was 901 m^2g^{-1}. The ammonium form was prepared by repeated exchange of the sodium zeolite with ammonium chloride solution at 80°C until the residual sodium content was 1.0%. The zeolite was washed free of excess chloride and dried at 110°C. X-Ray diffraction measurements showed the samples to be highly crystalline. Pyridine was Allied Chemical Research Grade. The heart-cut was collected after distillation from sodium hydroxide and dried over the 4A molecular sieve. It was further purified by the freeze–pump–thaw technique.

Apparatus and sample preparation. For spectroscopic studies, the samples were lightly ground in an agate mortar and pestle. Thin wafers, 1-inch in diameter, were prepared by compacting 0.03 to 0.07 g of the zeolite in a metallurgical die under 20 000 psi. The thickness ranged from 5 to 10 mg cm^{-2}. The samples transmitted about 10% of the incident infrared energy. Infrared spectra were recorded using either a Cary-White 90 or a Perkin Elmer 221G spectrophotometer. The spectral resolution was about 3 cm^{-1}. The infrared cell was similar to that of Parry (*15*) except that CaF_2 windows were used in place of NaCl windows and the furnace section of the cell was made from quartz. The cell could be attached to a conventional vacuum system. Vacua of 10^{-5} to 10^{-6} were maintained in the dynamic system. Sample calcinations and dosings with reagents were carried out with the cell attached to the vacuum system. The cell could be inserted in the spectrophotometer reproducibly. A simple evacuated gas cell was placed in the reference beam which was suitably attenuated by screening. A Stone differential thermal analysis apparatus and an Aminco Thermograv were also used.

Technique. The sample wafers were placed in the furnace end of the cell and evacuated. The temperature was raised to 110°C over 30 min and held until a vacuum of 10^{-4} was maintained. The temperature was then raised progressively to the desired calcination temperature. The sample was evacuated at the calcination temperature for 2 hr, at which time equilibrium had been established. The sample was cooled to room temperature and its spectrum was recorded. The procedure was repeated for each calcination temperature. The peak heights of the adsorption bands due to water, ammonium ion, and structural hydroxyl groups were measured.

For the pyridine adsorption studies, the same calcination procedure was used except a separate sample was used for each temperature. After the spectrum of the zeolite had been recorded at room temperature, excess pyridine was added. Two hours was allowed for equilibration and then the spectra of the adsorbate–adsorbent system were recorded as the pyridine was removed by evacuation at various temperatures. In some experiments, the pyridine was adsorbed at 110°C. Results were identical to room temperature adsorption. The addition of piperidine and water were similarly studied. Deuteration was carried out by contacting with deuterium oxide and then evacuating at 200°C.

The stability of the zeolite lattice was checked by X-ray diffraction studies. These showed that up to 800°C, only minor changes in the X-ray pattern occurred, indicating little loss of lattice structure.

Differential thermal analyses were conducted in flowing dry helium with a 10°C min^{-1} temperature program. Thermograms were recorded in flowing helium with a temperature program of 1°C min^{-1}.

Catalytic activity measurements were made in a flow microreactor at atmospheric pressure. A helium carrier gas was used at the flow rate of 50 cc/min. The helium was passed through a saturator containing cumene at 20°C. The reactor was a 2-cc Vycor bulb and contained 1 g of catalyst in the form of 20-mesh granules supported on quartz wool. Analysis of feed and product streams was made by gas chromatography using a 1-m column filled with a 20% mixture of 60% Silicone Fluid 96 and 40% Carbowax 20M supported on 60-80 mesh Chromosorb W. The column was maintained at 125°C. Conversions were measured after at least 16 hr on stream. At this elapsed time, the system had reached equilibrium.

RESULTS

Differential-thermal and thermogravimetric analysis curves for the zeolite are shown in Figs. 1 and 2. The off-gases were detected by effluent gas analysis. These show that the loss of physically adsorbed water occurs initially and is essentially nearing completion at 200°C. At this temperature the evolution of ammonia is appreciable and continues up to 300–350°C. No further loss of weight is observed until 500°C, when there is a marked weight loss accompanied by an endothermic heat change.

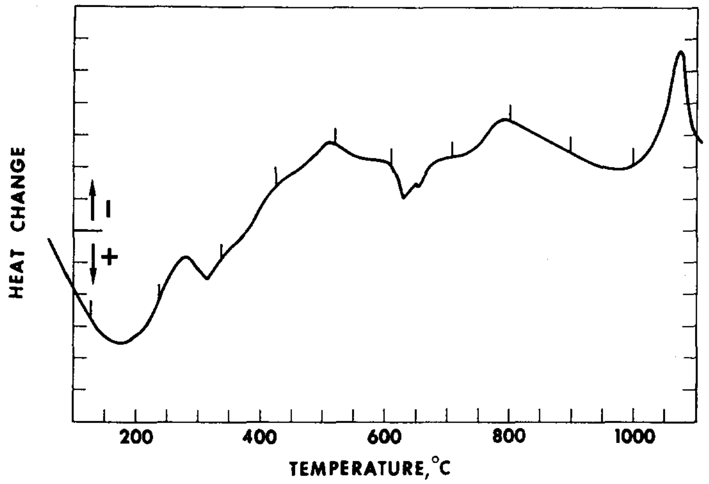


Fig. 1. Differential thermal analysis of NH$_4$Y in flowing helium.

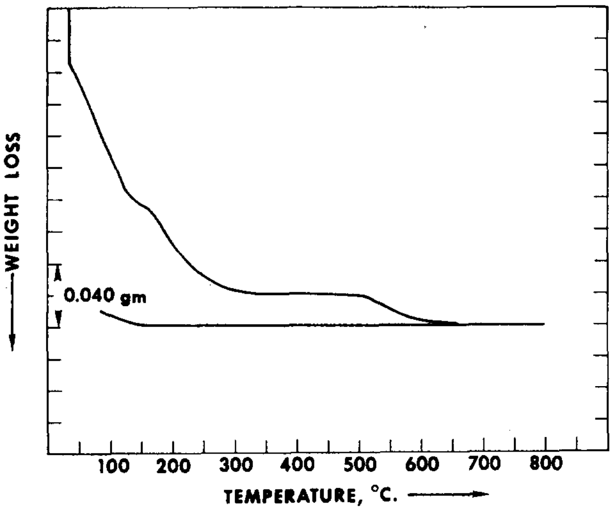


Fig. 2. Thermogravimetric analysis of NH$_4$Y in flowing helium.

The variation of the residual water, ammonium ion, and structural hydroxyl groups of the zeolite were investigated as a function of temperature by infrared spectroscopy. Figure 3 shows spectra from 4000 to 2800 cm^{-1} of ammonium Y zeolite at several temperatures from ambient up to 850°C. The adsorbed water present on the sieves at room temperature would be expected to absorb in the infrared at frequencies from 3750 to 2800 cm^{-1} and at about 1640 cm^{-1} and the ammonium ion would be expected to absorb from 3400 to 2900 cm^{-1} and near 1480 cm^{-1}. The chemically bound hydroxyl groups would be expected to absorb in the range 3750 to 3400 cm^{-1} but not near 1640 cm^{-1} since this absorption is characteristic of water molecules. As the temperature is raised stepwise from ambient, the spectra indicate several changes in the nature of the sieve. First, a marked decrease in the intensity of the 1640-cm^{-1} band due to desorption of adsorbed water is seen. Also there is a decrease in the absorption in the hydroxyl stretching region (3750–2800 cm^{-1}) which can be attributed to removal of physically adsorbed water.

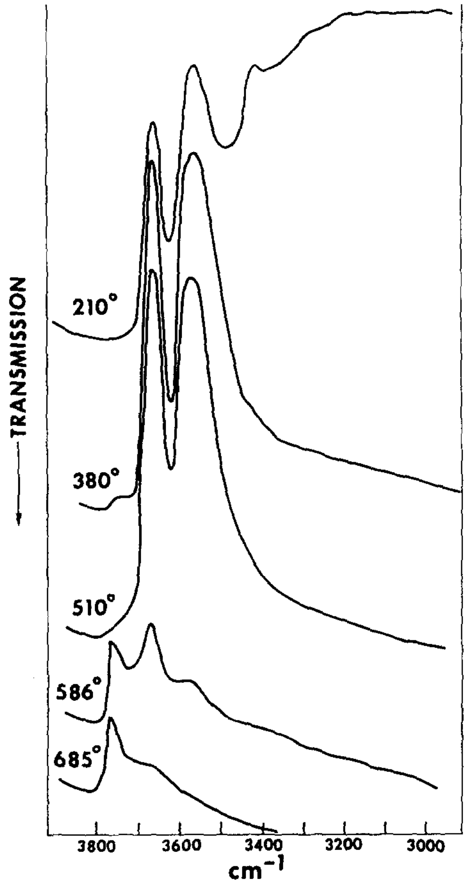


FIG. 3. Infrared spectra of NH_4Y after calcination at various temperatures.

The intensity of the 1640-cm^{-1} band can be used as an indication of the amount of adsorbed water on the zeolite. A plot of the intensity of this band as a function of temperature is shown in Fig. 4. This shows, in agreement with thermal analyses, that most of the water is removed by 250°C and remaining traces by 350°C.

The spectra of the ammonium form has absorption bands at 3423, 3200, 2900, 1680, 1485, and 1435 cm^{-1}. The band at 1485 is a good indicator of the ammonium ion and its intensity as a function of temperature is shown in Fig. 4. The ammonium ions appear to be unaffected by thermal treatment below 200°C and most of the ammonium ion is decomposed between 200° and 350°C. As the dehydration proceeds from ambient temperature, discrete absorption bands appear at 3742, 3643, and 3540 cm^{-1}. As the temperature is raised, the hydroxyl bands (except 3742 cm^{-1}) increase in intensity while those due to ammonium ions decrease such that at 420°C only discrete bands due to hydroxyl groups are observed. The only other absorption bands observed are those due to the skeletal vibrations of Al–O and Si–O groups below 1700 cm^{-1}. The maximum intensity of the hydroxyl group absorption bands was reached at 350°C. From this temperature to 500°C, the band intensities remained relatively constant. As the temperature is increased above 500°C, the 3643- and 3540-cm^{-1} bands decrease in intensity until at 800°C, very few hydroxyl groups are observed on the surface. In marked contrast, the 3742-cm^{-1} band intensity increases to a maximum at 640°C and then decreases. The band intensities versus temperature plots are shown in Fig.

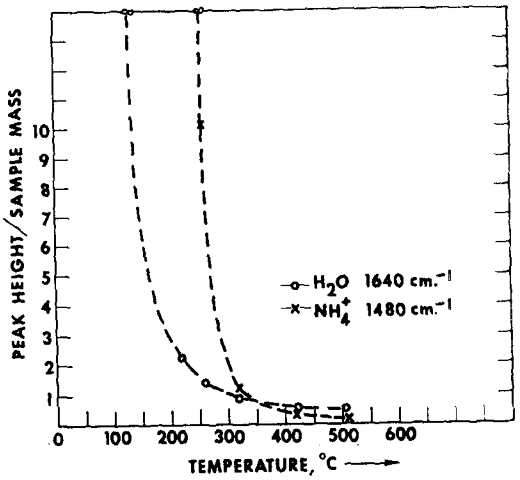


FIG. 4. Intensity of the 1640-cm^{-1} water absorption band and the 1485-cm^{-1} ammonium ion band as a function of temperature.

5. In agreement with other workers, no absorption bands were detected which could be attributed to H_3O^+ on the surface either during dehydration or when the zeolite was carefully rehydrated. On readdition of small amounts of water to the zeolite calcined at 800°C, only a broad absorption band is observed in the region 3700–2800 cm^{-1} and the characteristic water band at 1640 cm^{-1}. No sharp absorption bands suggesting reformation of surface hydroxyl groups is observed. The absorption bands are removed by evacuation at 330°C, indicating that water is simply adsorbed on the surface. If water is added back to the zeolite calcined at 520°C, all the hydroxyl groups become involved in hydrogen bonding to the water. On evacuating the adsorbed water, the structural hydroxyl groups reappear but these are considerably weaker than originally, indicating a collapse of the structure under the influence of water. Treatment of a hydrogen zeolite, after calcination at 500°C, with D_2O vapor and subsequent removal of the excess heavy water by evacuation at 230°C results in the appearance of three O–D bands at 2754, 2685, and 2617 cm^{-1} corresponding to the original three hydroxyl bands.

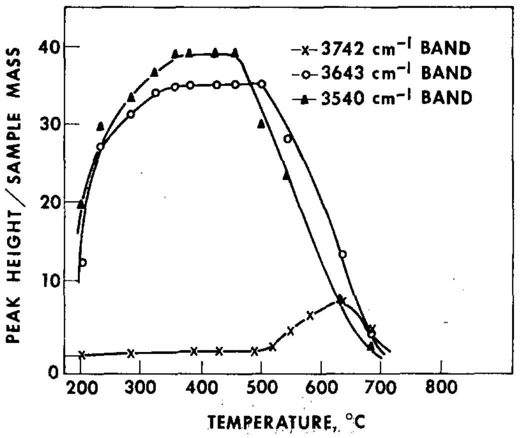


Fig. 5. Intensity of structural hydroxyl group bands as a function of temperature.

The effect of calcination temperature on the acidic character of the Y zeolite was studied by means of the spectrum of chemisorbed pyridine. The use of pyridine in the study of the acidity of surfaces has been reported (*15, 16*). The assignments of the bands observed in the spectrum of chemisorbed pyridine have been reported previously (*15, 16*). The band at 1545 cm^{-1} can be used to indicate proton acidity while a band (or bands) in the 1440–1455 cm^{-1} region indicates aprotic or Lewis acidity.

The spectrum of chemisorbed pyridine was observed for the zeolite after calcination over a range of temperatures between 200° and 800°C. Typical spectra are shown in Fig. 6. For samples calcined below 450°C, a strong band is observed at 1545 cm^{-1} but very little absorption in the 1440–1455 cm^{-1} region. As the temperature of calcination is raised the intensity of the 1545-cm^{-1} band decreases and a band at 1451 cm^{-1} is observed. The 1451-cm^{-1} band is attributed to coordinately bound pyridine on aprotic acid sites. This frequency is close to the 1450-cm^{-1} band reported by Basila *et al.* (*16*) and Parry (*15*) for

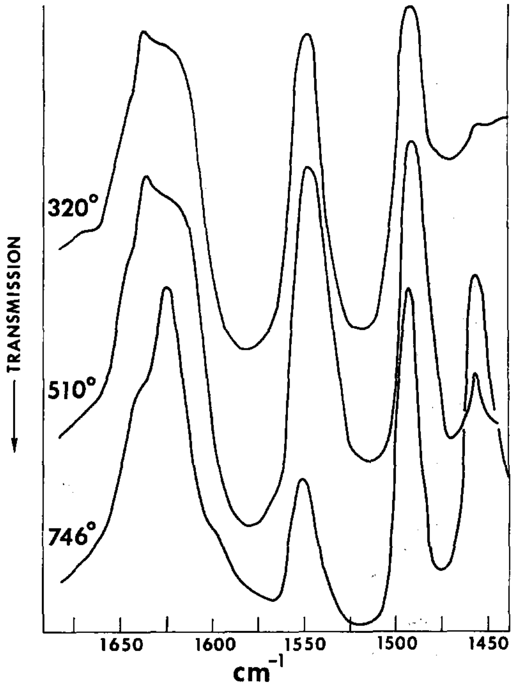


Fig. 6. Spectra of pyridine chemisorbed on ammonium Y zeolite after calcination at various temperatures.

pyridine chemisorbed on silica-alumina. In contrast to Hall and co-workers (*12*), no band is observed near 1445 cm^{-1} although this band has been served in cation zeolites (*17*).

In Fig. 7 the intensities of the 1545-cm^{-1} band (proton acidity) and the 1451-cm^{-1} band (aprotic acidity) are plotted as a function of temperature. The protonic or Brönsted acidity increases with calcination temperature up to about 325°C. It then remains constant to 500°C and then declines until at 800°C it is about one-tenth of its maximum value. The plot of aprotic or Lewis acidity against temperature shows virtually no acidity until a calcination temperature of 450°C is reached. It then increases slowly at first, and then, above 550°C rapidly as the Brönsted acidity decreases rapidly.

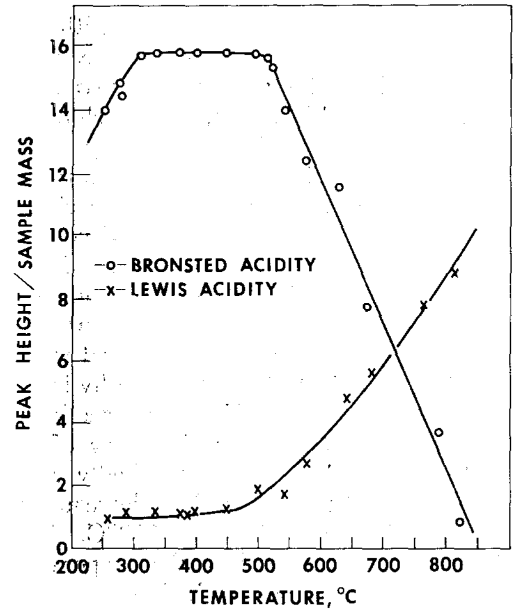


FIG. 7. Intensity of absorption bands of chemisorbed pyridine on Brönsted and Lewis acid sites.

The removal of excess pyridine from the Y zeolite as a function of temperature of evacuation was studied. Figure 8 shows the spectra of hydrogen Y zeolite (a) after calcination at 450°C, (b) after addition of excess pyridine, and (c) after removal of excess pyridine by evacuation at various temperatures. The 3643-cm^{-1} and the 3742-cm^{-1} bands were completely removed while the 3540-cm^{-1} band was considerably reduced in intensity. After evacuation, the 3540-cm^{-1} band was restored to its original intensity while the 3643-cm^{-1} band was not restored. Evacuation at temperatures of 150°C and above removed physically adsorbed and hydrogen-bonded pyridine leaving discrete absorption bands due to coordinately bound pyridine. These bands occur at 3250, 3160, 3130, 3060, 2980, 2885, 2840, 2770, and 2710 cm^{-1} in the bond-stretching region and at 1638, 1620, 1595, 1577, 1545, 1490, and 1451 cm^{-1} in the bending region and can be assigned to pyridinum ion and coordinately bound pyridine. At lower temperatures, due to overlap with bands of physically adsorbed and hydrogen-bonded pyridine, it is difficult to observe the Lewis acidity. However, it is seen that the 1545-cm^{-1} band due to Brönsted acidity increases markedly in intensity between evacuation of pyridine at

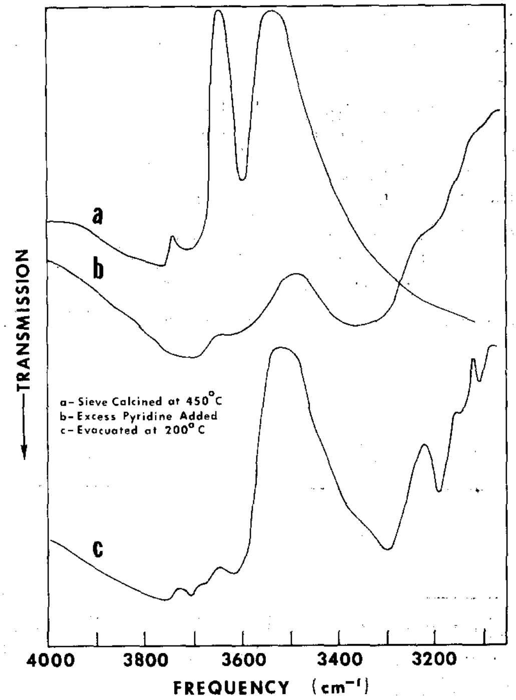


FIG. 8. Spectra of pyridine adsorbed on ammonium Y zeolite: (a) sieve-calcined at 450°C; (b) excess pyridine added; (c) evacuated at 200°C.

room temperature and 150°C. As the temperature of evacuation is increased the intensity of the bands of chemisorbed species decreases. The decrease in the 1545-cm^{-1} band is most rapid. At 500°C it has been almost completely eliminated whereas the 1451-cm^{-1} band still shows appreciable absorption. As the temperature is raised resulting in the decrease of the 1545-cm^{-1} band, the 3643-cm^{-1} band is gradually restored, showing a direct relationship between the Brönsted acidity and the hydroxyl group represented by the 3643-cm^{-1} band.

Spectra of chemisorbed piperidine showed an analogous behavior. This stronger base interacted very strongly with the 3643-cm^{-1} band and less strongly with the 3540-cm^{-1} band. Evacuation at 280°C, however, was required to restore the 3540-cm^{-1} band.

Data for the conversion of cumene over several Y zeolites are given in Table 1.

TABLE 1
CONVERSION OF CUMENE OVER
Y ZEOLITES AT 260°C

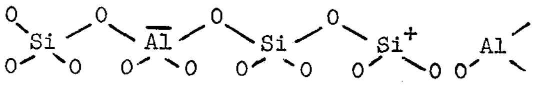
Zeolite	% Conversion
NaY	0
CaY	48
HY	96

They were obtained at 260°C. The conversion went cleanly to benzene and propylene.

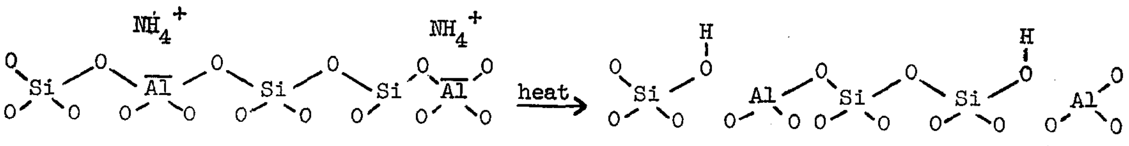
DISCUSSION

Calcination of Ammonium Y Zeolite

In agreement with Hall and co-workers, calcination of ammonium Y zeolite (I) is shown, by infrared spectroscopy, to result in the evolution of ammonia and the formation of the decationized zeolite (II) having hydroxyl bands at 3742, 3643, and 3540 cm^{-1}. Hall reports frequencies of 3745, 3650, and 3545 cm^{-1} (*11*). The hydroxyl bands at 3643 and 3540 cm^{-1} reach maximum intensity at 350°C compared to 290°C in Hall's studies (Fig. 5). In this study, the absorption band at 3540 cm^{-1} is also found to be more intense than that at 3643 cm^{-1} whereas Hall found the reverse. This effect is probably due to the different extents of exchange as reported by Angell and Schaffer (*11*). The greater the degree of exchange to the ammonium form, the stronger the 3540-cm^{-1} band. The temperature for first reaching maximum hydroxyl groups agrees closely with the temperature at which ammonia ceases to be evolved indicated by thermal analysis. In contrast to Hall's study, which shows a progressive decrease in the hydroxyl band intensity and hydrogen content determined by deuterium exchange, the results shown in Fig. 5 show a constant hydroxyl content up to 460°C for the 3540-cm^{-1} band and up to 510°C for the 3643-cm^{-1} band. The population of these hydroxyl groups then rapidly decreases as the temperature is raised until at 750°C virtually no hydroxyl groups are detected. When the zeolite is calcined above 500°C, the intensity of the 3742-cm^{-1} band increases markedly to a maximum at 640°C and then decreases to an insignificant value at 750°C. This phenomenon corresponds to the temperature at which there is a marked endothermic weight loss shown by thermal analysis and probably corresponds to some change in the crystal structure. The dehydration process has been envisaged as producing the following structure (III) (*10*) which contains



III



I

II

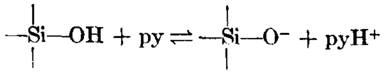
tricoordinated aluminum atoms (Lewis acid) and tricoordinated silicon atoms. The observation that hydrogen zeolites calcined above 600°C cannot be fully reconstituted by addition of water supports this conclusion.

In agreement with previous workers, the 3742-cm^{-1} band probably represents Si–OH groups terminating the lattice and are similar in character to those on silica. Alternatively, these hydroxyl groups could be associated with amorphous impurities present in the structure.

The hydroxyl groups corresponding to the 3643 and 3540 cm^{-1} bands have no reported analogy in other oxide systems. Since they can be deuterated and the frequency of the O–D absorption bands is displaced from the OH band frequencies by the expected isotope shift, they do not represent coupled vibrations (*14*). Angell and Schaffer (*11*) suggested that the 3540-cm^{-1} band represents interaction between adjacent hydroxyl groups. The variation in the ratio of the two bands with degree of decationization (*11*), time of calcination (*14*), temperature of calcination, and the different interactions with various adsorbate molecules (*14*) makes this unlikely. On the basis of a greater tendency of the 3643-cm^{-1} band to react with adsorbate molecules compared to the 3540 cm^{-1}, it has been suggested that the 3643-cm^{-1} band represents hydroxyl groups in the cage positions and the 3540-cm^{-1} band represents hydroxyl groups in the bridge positions (*13*). This seems unlikely since the bridging positions are not accessible to any but the smallest molecules whereas addition of excess pyridine, resulting in hydrogen bonding to the hydroxyl groups (Fig. 8), and the chemisorption of piperidine shows that the 3540-cm^{-1} hydroxyl groups interact with adsorbate molecules. The differences in the degree of interaction of the two bands with adsorbate molecules is probably an indication of the relative acidity of the two types of hydroxyl groups. Thus, bases of the strength of ammonia and piperidine are required for chemisorption on the 3540-cm^{-1} band whereas the 3643-cm^{-1} band interacts strongly with pyridine but not with ethylene. Although more work is necessary it appears that the two bands represent hydroxyl groups at different crystallographic locations. These are probably in the supercages.

The Nature of Acid Sites

If the calcination of ammonium zeolite involves the structures outlined above, the zeolite should undergo marked changes in acid character as a function of temperature. Structure (II) could function as a Brönsted acid while structure (III) could function as a Lewis acid. Liengme and Hall (*12*) have shown that after calcination at 300°C, the zeolite behaves as a Brönsted acid while after calcination at 600°C it behaves as both a Lewis and Brönsted acid. Their results were obtained from a study of the chemisorption of pyridine on a zeolite containing sodium in more than half of the ion-exchange positions. Their studies also showed that after evacuation at 150°C, pyridine was only chemisorbed on the 3643-cm^{-1} type of hydroxyl groups and hence only this type of hydroxyl group functioned as a Brönsted acid. The data in Fig. 8 confirm this conclusion. That the hydroxyl groups act as a Brönsted acid is also confirmed by the inverse dependence of the intensity of the 1545-cm^{-1} pyridinium ion band (Brönsted acidity) and the 3643-cm^{-1} hydroxyl band as the temperature of evacuation is increased. These observations probably indicate a transfer of a proton from the pyridinium ion to the surface with the liberation of pyridine.



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{py} \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^{-} + \mathrm{pyH}^{+}$$

Figure 6 shows a detailed study of the chemisorption of pyridine, used as a titrant, on the zeolite over a wide range of temperature. The 1545-cm^{-1} band is taken to correspond to Brönsted acidity and the 1451-cm^{-1} band to Lewis acidity. At temperatures up to 325°C, the Brönsted acidity increases in a parallel manner to the increase in hydroxyl group concentration represented by the 3643-cm^{-1} band. The Brönsted acidity then remains constant up to 500°C just as the intensity of the 3643-cm^{-1} band does. On further heating, the Brönsted acidity decreases along with the 3643-cm^{-1} hydroxyl band. If, then, the Brönsted acid sites are hydroxyl groups, a conversion to Lewis acid sites should occur with increasing temperature in an analogous manner to silica-alumina as the structure becomes more dehydroxylated and is converted from structure (II) to (III) by elimination of water and formation of tricoordinated aluminum atoms. Figure 6 shows that virtually no Lewis acidity is observed up to 475°C calcination temperature. The concentration then increases rapidly as the Brönsted acid concentration decreases rapidly. This behavior is expected from a consideration of the structure since no Lewis acid sites are present until some exposed tricoordinated aluminum atoms have been formed by dehydroxylation. The Lewis acid site concentration increases rapidly as the hydroxyl group population decreases rapidly until the structure is completely dehydroxylated. Since the dehydroxylation produces tricoordinated aluminum atoms, the Lewis acidity should be similar to that of an amorphous oxide. The frequency of the absorption band attributed to Lewis bound pyridine is within 1 cm^{-1} of that reported by Basila *et al.* (*16*) for pyridine chemisorbed on silica-alumina. Analogous to silica-alumina, readdition of small quantities of water to the zeolite after calcination at 550°C followed by pyridine shows the reconversion of Lewis acidity to Brönsted acidity. The Lewis acid sites, then are unlike those of alumina, which are not converted to Brönsted acid sites by water (*15*, *16*).

The nature of the acidity on zeolites is not totally accounted for by the hydroxyl groups. A study of the adsorption of pyridine on a sieve calcined at 800°C so as to eliminate hydroxyl groups shows that after heating the adsorbed pyridine to 200°C, pyridinium ions are formed, thus indicating the presence of Brönsted acidity (*17*). The nature of this acidity is not known at this time. If the dehydroxylation process is described by the transformation of structure (II) into (III), elimination of water should result in two Brönsted acid sites being converted into one Lewis acid site. Hence the concentration of Brönsted acid sites plus twice the concentration of Lewis acid sites should be constant. This is somewhat different from the mechanism of Trambouze (*18*), for amorphous silica-alumina, who envisaged a one-to-one conversion of sites. The relative band intensities of the Lewis and Brönsted acid bands were converted into relative numbers of acid sites by the method of Basila (*19*). Figure 9 shows plots of (a) [Brönsted acid sites] +2 [Lewis acid sites] and (b) [Brönsted acid sites] + [Lewis acid sites] against calcination temperature. Plot (a) gives a much closer approximation to a constant and thus lends support to the suggested mechanism of dehydroxylation. The decrease in total acidity at high temperature is probably due to loss of structure.

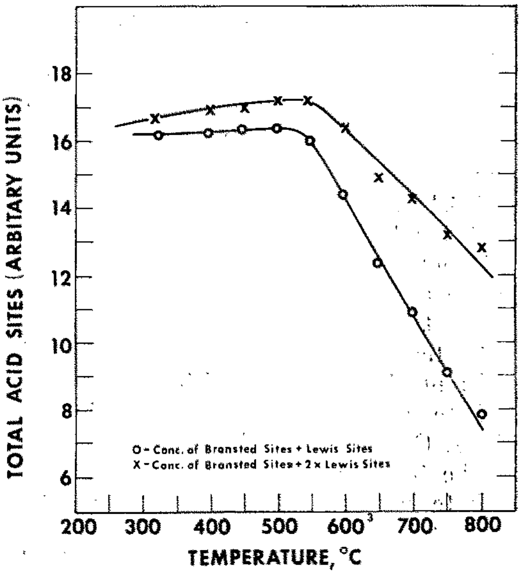


FIG. 9. Total acid site population as a function of temperature: ⊙, concentration of Brönsted sites + Lewis sites; X, concentration of Brönsted sites + 2 × Lewis sites.

Relationship of Acidity to Catalytic Activity

The hydrogen Y zeolite provides a catalyst system in which the ratio of Lewis to Brönsted acidity can be varied readily and in a controllable manner. Unfortunately, few reports of catalytic activity of hydrogen Y zeolites have been reported. Recently Benesi (*9*) has reported a study of the cracking of toluene over hydrogen Y zeolite as a function of calcination temperature. His results show that the conversion increases with calcination temperature up to about 570°C and then decreases with calcination temperature up to 800°C to one-twentieth of its value at 600°C. Readdition of water to the zeolite after calcination at 700°C restores its activity to 75% of the 600°C activity. These data correspond very well with the variation of the 3643-cm^{-1} hydroxyl band and the Brönsted acid population. They do not relate to Lewis acidity since in such a case the greater calcination temperature (without destroying the structure) should lead to greater activity.

The conversion of cumene over NaY, CaY, and HY at 260°C increases, as shown in Table 1, markedly along this series. Uytterhoeven *et al.* (*10*) showed that for their samples the respective hydrogen contents, from deuterium exchange experiments were 0.29, 0.61, and 11.2 $OH/g \times 10^{-20}$ at approximately 500°C calcination temperature. Infrared studies show a similar trend (*17*). Thus, there is a direct relation between cracking activity and hydrogen content. A similar study by Shi-thoang, Romanovskii, and Topchieva (*20*) showed the same relationship between exchanged ion and cumene cracking activity. They also showed that maximum activity for the hydrogen form was obtained when water was added corresponding to the number of sodium atoms removed, that is, activity is a maximum when the hydroxyl content is a maximum. Venuto *et al.* (*5*) have shown that alkylation reactions over the hydrogen zeolites involve hydrogen on the catalyst and suggest that the product distribution reflects the presence of strong protonic acids. Venuto and co-workers (*21*) have also shown that the activity for the ethylene–benzene alkylation reaction increases from 400° to 600°C and then declines on higher temperature calcination. The superactivity of hydrogen Y zeolites as cracking catalysts compared to silica-alumina can probably be related to the 20-fold greater concentration of Brönsted acid sites on the zeolites (*17*).

In conclusion, an investigation of the surface of the decationated Y zeolite has been made. The study, as a function of calcination temperature, of the structural hydroxyl groups and pyridine chemisorption shows that the hydroxyl groups function as Brönsted acid sites. At a calcination temperature of 475°C the zeolite is almost entirely in the Brönsted acid form. Increase of calcination temperature converts Brönsted acid sites into Lewis acid sites because of elimination of hydroxyl groups and formation of tricoordinated aluminum atoms. Comparison of the hydroxyl group behavior, and the acidity as a function of temperature with the catalytic activity shows that the Brönsted acidity is the seat of activity. No relationship with Lewis acidity is observed. The high concentration of Brönsted acid sites is responsible for the superactivity. Of course, it is always possible that a small concentration of unidentified sites on the zeolites may play some role in catalytic reactions.

ACKNOWLEDGMENT

The author is grateful to Mr. R. C. Hansford for the catalytic activity measurements and much advice.

REFERENCES

1. BRECK, D. W., *J. Chem. Educ.* **41**, 678 (1964).

2. PLANK, C. J., ROSINSKI, E. J., AND HAOTHOME, W. P., Division of Petroleum Chemistry, American Chemical Society Meeting, Philadelphia, April, 1964.

3. FRILETTE, V. J., WEISZ, P. B., AND GOLDEN, R. L., *J. Catalysis* **1**, 301 (1962); RABO, J. A., PICKERT, P. E., STAMIRES, D. N., AND BOYLE, J. E., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2**, 2055 (Editions Technip, Paris, 1961).

4. PLANK, C. J., *Proc. Intern. Congr. Catalysis 3rd, Amsterdam, 1964* **1**, 727. (Wiley, New York, 1965).

5. VENUTO, P. B., WU, E. L., AND CATTANACH, J., Society of Chemical Industry Conference on Molecular Sieves, London, 1967.

6. Benesi, H. A., *J. Catalysis,* **8,** 368 (1967).
7. Pickert, P. E., Rabo, J. A., Dempsey, E., and Schomaker, V., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1,** 714. (Wiley, New York, 1965).
8. Turkevich, J., Nozaki, F., and Stamires, D. N., *Proc. Intern. Congr. Catalysis 3rd, Amsterdam, 1964* **1,** 586 (Wiley, New York, 1965).
9. Boreskova, E. G., Lygin, V., I., and Topchieva, K. V., *Kinetics Catalysis (USSR) (Engl. Transl.)* **5,** 991 (1964).
10. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69,** 2117 (1965).
11. Angell, C. L., and Schaffer, P. C., *J. Phys. Chem.* **69,** 3463 (1965).
12. Liengme, B. V., and Hall, W. K., *Trans. Faraday Soc.* **62,** 3229 (1966).
13. Eberly, P. E., Division of Petroleum Chemistry, American Chemical Soc. Meeting, Miami, April, 1967.
14. White, J. L., Jelli, A. N., Andre, J. M., and Fripiat, J. J., *Trans. Faraday Soc.* **63,** 461 (1967).
15. Parry, E. P., *J. Catalysis* **2,** 371 (1962).
16. Basila, M. R., Kantner, T. R., and Rhee, K. H., *J. Phys. Chem.* **68,** 319 (1964).
17. Ward, J. W., unpublished results.
18. Trambouze, Y. J., de Mourges, L., and Perrin, M., *J. Chim. Phys.* **51,** 723 (1954).
19. Basila, M. R., and Kantner, T. R., *J. Phys. Chem.* **70,** 1681 (1966).
20. Shi-Thoang, H., Romanovskii, B. V., and Topchieva, K. V., *Dokl. Akad. Nauk SSSR* **168,** 1114 (1966).
21. Venuto, P. B., Hamilton, L. A., Landis, P. S., and Wise, J. J., *J. Catalysis* **4,** 81 (1966).