JOURNAL OF CATALYSIS 11, 251–258 (1968)

The Nature of Active Sites on Zeolites

VI. The Influence of Calcination Temperature on the Structural Hydroxyl Groups and Acidity of Stabilized Hydrogen Y Zeolite

JOHN W. WARD

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

Received March 24, 1968

The infrared spectra of magnesium ammonium Y zeolite have been observed after calcination at temperatures up to 800°C. Thermogravimetric, differential thermal, and X-ray diffraction analyses were also made. The observations are similar to those previously reported for ammonium Y zeolite except no indications of structural collapse were observed. The spectra of chemisorbed pyridine were observed for the zeolite after calcination. The concentration of pyridinium ion parallels that of the hydroxyl groups represented by the 3643-cm^{-1} absorption band and is a measure of the Brönsted acid site concentration. The concentration of Lewis acid sites increases with increasing calcination temperatures and decreasing hydroxyl content. The concentration of Brönsted acid sites plus twice the concentration of Lewis acid sites remains constant over a wide range of temperatures. As for ammonium Y zeolite, the acidic hydroxyl groups are considered to be the catalytically active centers. No hydroxyl groups attached to magnesium cations are detected.

INTRODUCTION

The catalytic properties of hydrogen Y zeolite were first reported by Rabo, Pickert, Stamires, and Boyle (*1*).

The influence of calcination temperature on the structural hydroxyl groups and acidity of hydrogen (decationized) Y zeolite has recently been discussed (*2–5*). In general, as the ammonium Y zeolite starting material is decomposed, the concentration of structural hydroxyl groups increases with calcination temperature until all the ammonium ions have been decomposed. On further heating at increasing temperatures, the concentration of hydroxyl groups decreases until at 800°C, few hydroxyl groups remain. The concentration of Brönsted acid sites follows a similar trend. Both Hughes and White (*2*) and Ward (*3*) observed that up to 450°C, the concentration of Lewis acid sites was small. However, whereas Ward observed that the Lewis acid concentration increased with increasing calcination temperature up to 800°C, the maximum temperature used, Hughes and White observed a maximum near 600°C. Both sets of workers found that the total concentration of acid sites decreased with increasing calcination temperature above 550°C. A notable difference between the investigations was that whereas Hughes and White made all observations on one sample, Ward used a fresh sample for each observation. The differences in results could, then, probably be attributed to the different experimental techniques since high temperatures and hydrothermal conditions are known to result in destruction of the zeolite lattice framework unless special care is taken (*6*).

It is known that the thermal stability of the hydrogen zeolites can be improved by incorporation of multivalent cations so as to fill the S_I ion exchange positions in the structure (*6*). Since several workers (*6–9*) have shown that the calcination temperature can markedly affect the catalytic activity of zeolites, it is of interest to clarify these divergences.

In this paper, the influence of calcination temperature on the structural hydroxyl groups and acidity of a Y zeolite stabilized by incorporation of magnesium ions is studied. The uncertainties due to loss of structure are minimized in this system.

EXPERIMENTAL

Materials. The magnesium ammonium Y zeolite was prepared from a sodium Y zeolite. The starting material had a silica-to-alumina ratio of 4:9 and a nitrogen surface area (measured at $P/P_0 \approx 0.02$) of 901 m^2g^{-1}. The ammonium form was prepared by repeated exchange of the sodium Y zeolite with a 10% ammonium nitrate solution at 80°C until the residual sodium content was 1%. The zeolite was then washed free of nitrate. The ammonium form was then ion-exchanged with sufficient 10% magnesium nitrate solution to yield the magnesium ammonium zeolite containing 2.9% magnesium. X-Ray diffraction and surface area measurements showed the zeolite to be highly crystalline. Pyridine was Allied Chemical Research Grade. The heart cut was collected after distillation from sodium hydroxide and dried over activated 4 A 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 a Cary-White 90 Spectrophotometer. The spectral resolution was about 3 cm^{-1}. The infrared cell was similar to that of Parry (*13*) 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 used. X-Ray powder diffraction patterns were obtained with a Norelco diffractometer using filtered copper $K\alpha$ radiation.

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 absorption 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 were 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. Acidity data were calculated from measurements after desorption of the pyridine at 250°C.

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}. X-Ray diffraction patterns were recorded on the samples after calcination at various elevated temperatures up to 800°C.

Catalytic activity measurements were made in a flow microreactor at atmospheric pressure. A helium carrier gas was used at a 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 20 M supported on 60–80 mesh Chromosorb W. Conversions were measured after at least 16 hr on stream. At this elapsed time the system had reached equilibrium.

Surface areas were measured by nitrogen adsorption at $P/P_0 \approx 0.02$.

Results

Spectra of the magnesium ammonium zeolite in the 4000 to 2800 cm^{-1} region for several temperatures from ambient up to 800°C are shown in Fig. 1. The variations in residual water and ammonium ion were also observed and are shown in Fig. 2. The adsorbed water on the zeolites would be expected to absorb from 3750 to 2800 cm^{-1} and at about 1640 cm^{-1}; the ammonium ion would be expected to absorb from 3400 to 2900 cm^{-1} and at 1480 cm^{-1}. The chemically bound hydroxyl groups would be expected to absorb in the region 3750 to 3400 cm^{-1} but not near 1640 cm^{-1} since this absorption is characteristic of water molecules. As the temperature is increased stepwise from ambient, a marked decrease in the intensity of the 1640-cm^{-1} band due to desorption is first seen. There is a simultaneous decrease of the absorption in the hydroxyl stretching region due to removal of physically adsorbed water. The intensity of the 1640-cm^{-1} band is a measure of the amount of adsorbed water on the zeolite. The plot of band intensity versus temperature in Fig. 2 shows that most of the adsorbed water is removed by 250°C with traces remaining up to 350°C. This is confirmed by the thermogravimetric and differential thermal analysis results shown in Fig. 3.

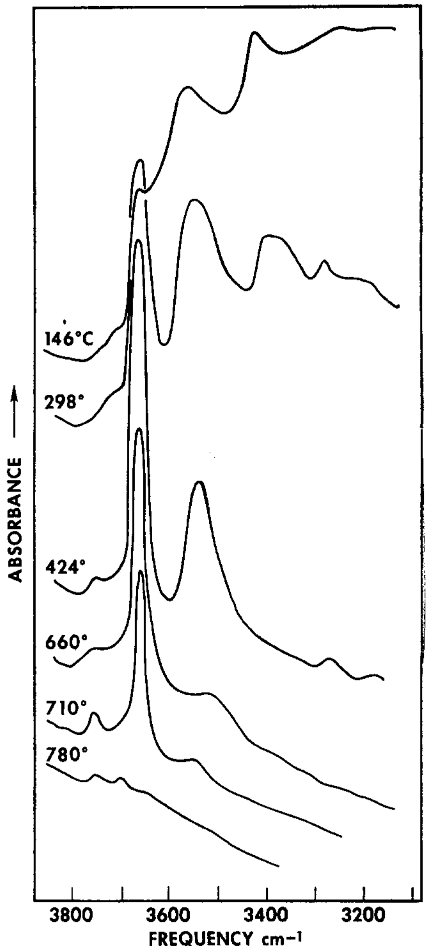


Fig. 1. Infrared spectra of $MgNH_4Y$ after calcination at various temperatures.

The resulting anhydrous zeolite has absorption bands at 3423, 3200, 2900, 1680, 1485, and 1435 cm^{-1}. The band at 1485 cm^{-1} is a good indicator of the ammonium ion concentration, and its intensity as a function of calcination temperature is also shown in Fig. 2. The ammonium ion is unaffected by thermal treatments below 200°C and most of the ammonium ion is decomposed between 200° and 350°C. This temperature range for the ammonium ion decomposition is confirmed by the thermogravimetric and differential thermal analysis. Similar temperature ranges have been observed for the decomposition of

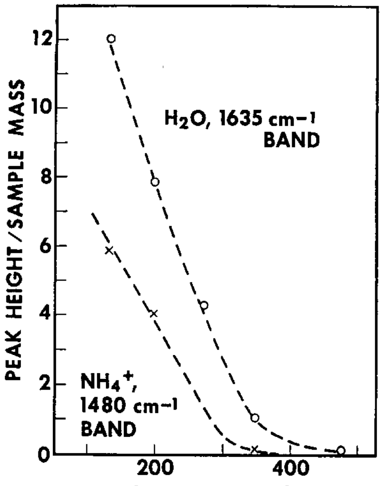


FIG. 2. Intensity of the 1640-cm^{-1} water absorption band and the 1485-cm^{-1} ammonium ion band as a function of temperature.

ammonium Y zeolite (*3*, *10*). Discrete absorption bands due to structural hydroxyl groups are observed at 3742, 3643, and 3540 cm^{-1}, similar to those observed during the decomposition of ammonium Y zeolite (*2–5*, *11*). As the calcination temperature is raised, the hydroxyl group band at 3643 cm^{-1} increases in intensity while bands due to ammonium ions decrease such that at 400°C only discrete bands due to hydroxyl groups are observed. The 3643-cm^{-1} band reaches a maximum intensity near 425°C. As shown in Fig. 4, the hydroxyl population remained relatively constant until a temperature of 575°C was reached. On further increase in temperature, the intensity of the 3643-cm^{-1} absorption band decreased until at about 800°C, the intensity was very low, indicating that most of the hydroxyl groups had been removed from the structure. These observations are similar to those reported for ammonium Y (*2*). In marked contrast to the results observed for ammonium Y zeolite the absorption band due to hydroxyl groups at 3540 cm^{-1} decreases steadily with increasing calcination temperature. Also, in contrast to ammonium Y zeolite, the absorption band at 3742 cm^{-1} remains at constant intensity. As with ammonium Y zeolite, no absorption bands were detected which could be attributed to H_3O^+.

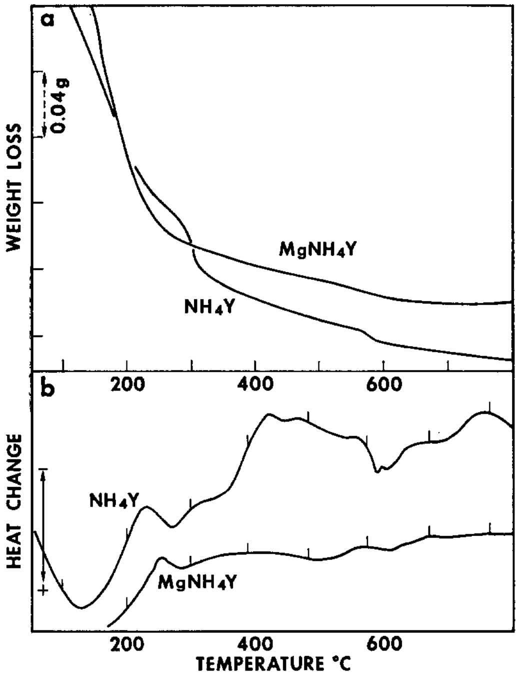


FIG. 3. Differential thermal and thermogravimetric analyses of NH_4Y and $MgNH_4Y$ in flowing helium.

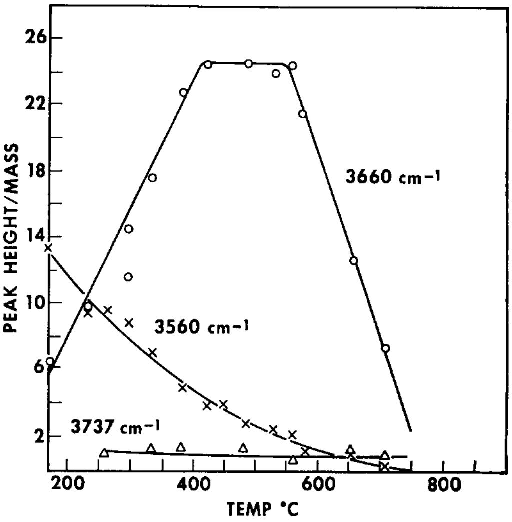


FIG. 4. Intensity of structural hydroxyl group bands as a fuction of calcination temperature.

The thermogravimetric analysis curves of magnesium ammonium Y zeolite and ammonium Y zeolite show a distinctly different behavior. Although weight losses due to loss of physically adsorbed water and decomposition of ammonium ion are observed in both cases, the magnesium ammonium Y system does not exhibit the abrupt weight loss near 550°C. Similarly no sharp endothermic heat change is observed near 550°C in differential thermal analysis observations on the magnesium ammonium Y zeolite. A similar absence of heat change is found in differential analysis studies of stabilized hydrogen Y zeolite (*12*). The absence of these thermal effects and of a maximum in the intensity of the 3742-cm^{-1} absorption band as found for ammonium Y probably indicates the greater stability of the magnesium ammonium Y structure.

The stability of the magnesium ammonium Y structure was confirmed by surface area measurement and X-ray analysis of the zeolite after calcining at 300°, 500°, 600°, 700°, and 800°C. The summed intensities of the 331, 533, 642, and 751 peaks and surface areas are given in Table 1.

TABLE 1

SURFACE AREAS AND X-RAY DIFFRACTION PEAK INTENSITIES OF MAGNESIUM AMMONIUM Y ZEOLITES AFTER CALCINATION AT VARIOUS TEMPERATURES

Temperature (°C)	Surface area (m^2g^{-1})	Diffraction peak intensity[a]
300°	—	178
410°	763	201
470°	—	181
510°	791	174
570°	886	187
600°	—	171
620°	837	163
660°	—	169
740°	871	174
800°	—	187

[a] Sum of peak heights for (331), (533), (642), and (751, 555) reflections.

The effect of calcination temperature on the acidic character of the zeolite was investigated by means of the spectrum of chemisorbed pyridine. The use of pyridine in the study of surface acidity has been reported previously (*13*, *14*). The absorption band of chemisorbed pyridine at 1545 cm^{-1} is indicative of Brönsted acidity while a band near 1451 cm^{-1} indicates Lewis acidity.

The spectrum of chemisorbed pyridine was observed after calcination of the zeolite over a range of temperatures between 200° and 800°C. Typical spectra are shown in Fig. 5. They are similar to those reported previously for ammonium Y (*3*). For samples calcined below 500°C, a strong absorption band is observed at 1545 cm^{-1} but very little absorption is observed at 1451 cm^{-1}. A band observed at 1446 cm^{-1} is due to interaction of the pyridine with the magnesium cations. The intensity of the 1545-cm^{-1} band increases as the calcination temperature is increased from 300° to 425°C. It remains constant as the calcination temperature is increased to 600°C and then declines sharply as the temperature is increased to 800°C.

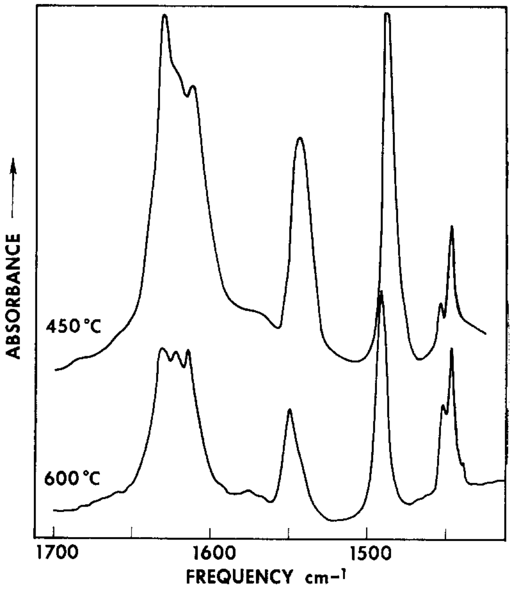


FIG. 5. Spectra of pyridine chemisorbed on $MgNH_4Y$ zeolite after calcination at various temperatures.

The band at 1451 cm^{-1} (indicative of Lewis acidity) remains weak and constant until the calcination temperature reaches 550°C. It then increases rapidly as the 1545-cm^{-1} band decreases rapidly. The changes in the 1545-cm^{-1} (Brönsted acidity) and 1451-cm^{-1} (Lewis acidity) band intensities with calcination temperature are shown in Fig. 6. As in the case of ammonium Y zeolite, only the hydroxyl groups represented by the 3643-cm^{-1} band are sufficiently acidic to form pyridinium ions. The 3540-cm^{-1} band type of hydroxyl group hydrogen-bonds to pyridine at room temperature if excess pyridine is present (for example, a residual gas-phase pressure of 2 torr) but does not hydrogen-bond to or transfer a proton to pyridine at 250°C like ammonium Y zeolite (*2*).

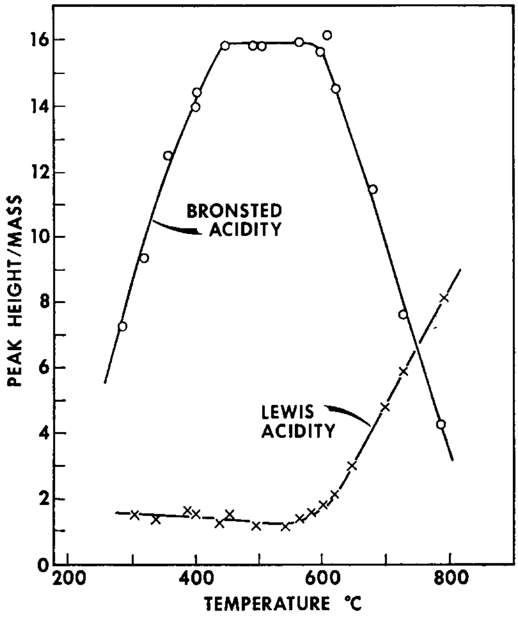


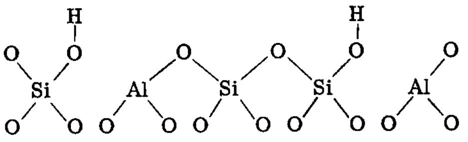
Fig. 6. Intensity of absorption bands of chemisorbed pyridine on Brönsted and Lewis acid sites.

Discussion

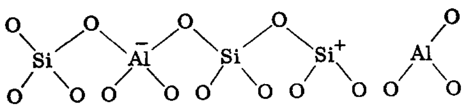
Influence of Calcination Temperature on Structural Hydroxyl Groups

The X-ray diffraction, thermogravimetric, and differential thermal analyses indicate that the magnesium ammonium Y zeolite is stable up to high calcination temperatures. Hence observations made with it are not subject to the same degree of uncertainty due to lattice collapse as are results obtained with ammonium Y zeolite (*2, 3*).

The decomposition of magnesium ammonium Y zeolite by calcination is very similar to that previously reported for ammonium Y zeolite (*1–5, 11*). Infrared spectroscopy, thermogravimetric, and differential thermal analyses show that after loss of physically adsorbed water, ammonia is evolved from the structure to yield the decationized zeolite.



The three absorption frequencies at 3742, 3643, and 3540 cm^{-1} characteristic of decationized Y zeolite are observed. In contrast to decationized Y zeolite, the maximum intensity of the 3643-cm^{-1} band is not reached until 425°C and does not start to decline until 575°C. As noted above, the 3540-cm^{-1} band declines constantly with increasing calcination temperature and the 3742-cm^{-1} band remains constant in marked contrast to the decationized Y zeolite. These differences from the decationized zeolite together with the absence of an endothermic weight loss near 550°C must be attributed to the stabilizing effects of the magnesium ions. The observed intensity of the hydroxyl band at 3643 cm^{-1} is less than that reported for the decationized Y zeolite, presumably due to the smaller original concentration of ammonium ions in the zeolite. No absorption band which could be attributable to hydroxyl groups attached to magnesium ions is observed. It has been suggested that such a band would be observed near 3595 cm^{-1} (*15*). The loss of hydroxyl groups on calcination at temperatures in excess of 575°C probably occurs in the same manner as suggested for the decationized Y zeolite (*2, 4*) to yield the dehydroxylated zeolite



which contains tricoordinated silicon and aluminum atoms. The similarity of the frequencies and behavior of the hydroxyl groups on magnesium ammonium zeolite to those on the decationized zeolite suggests that they are in similar locations.

Influence of Calcination Temperature on the Acid Sites

Since X-ray studies (*16*) have indicated that alkaline earth cations preferentially exchange into a zeolite in the S_I positions, one might expect a cation ammonium Y zeolite in which magnesium ions have been exchanged to fill only the S_I positions, to behave similarly to ammonium Y zeolite. Such behavior would be expected since the S_{II} and S_{III} sites will either be occupied by ammonium ions or be empty.

In previous publications on calcination effects (*2, 3*) it was shown that the Brönsted acidity passed through a maximum near 450°C and decreased to a very low value at 800°C. The Lewis acidity was shown to be small up to 450°C and then to increase rapidly as the Brönsted acidity decreased. Figure 6 shows that very similar temperature functionality occurs with magnesium ammonium zeolite. The Brönsted acidity increases in a parallel manner to the hydroxyl group concentration. Whereas the ammonium Y zeolite reached an initial maximum near 325°C, the Brönsted acidity of magnesium ammonium Y increases up to 425°C. It remained approximately constant to 600°C (500°C for NH_4Y) and then decreased rapidly with increasing calcination temperature. The range of maximum Brönsted acidity occurring at higher temperature than for ammonium Y zeolite, corresponds closely to the higher temperature range for formation and elimination of hydroxyl groups. It would appear, then, that the presence of magnesium ions thermally stabilizes both the ammonium ion decomposition and the dehydroxylation process. Analogously to ammonium Y zeolite, pyridine chemisorbs only on the 3643-cm^{-1} band type of hydroxyl groups. The hydroxyl groups corresponding to the 3643-cm^{-1} band are considered to be the Brönsted acid sites. The hydroxyl groups represented by the 3540-cm^{-1} band will interact to form carbonium ions with the stronger base piperidine.

The formation of Lewis acid sites, indicated by the absorption band at 1451 cm^{-1}, with increasing calcination temperatures is analogous to the observation for ammonium Y zeolite (*2, 3*) and shows that as the zeolite is dehydroxylated, Brönsted acid sites are converted into Lewis acid sites, that is, tricoordinated aluminum centers. That is, the zeolite is transformed from predominantly Structure I above to Structure II. As in the case of ammonium Y zeolite and of silica-alumina, readdition of small quantities of water to the zeolite after calcination at 600°C followed by chemisorption of pyridine shows that the Lewis acid sites are converted into Brönsted acid sites.

Finally, if the magnesium ammonium Y zeolite behaves similarly to ammonium Y zeolite, the concentration of Brönsted acid sites plus twice the concentration of Lewis sites should remain constant since according to Structures I and II, two Brönsted acid sites are converted into one Lewis acid site. A plot of the acid site concentration against calcination temperature is given in Fig. 7. A plot is also shown of the concentration of Brönsted acid sites plus the Lewis acid sites which would be expected to be constant according to the scheme of Trambouze (*17*) in which one Brönsted acid site is converted into one

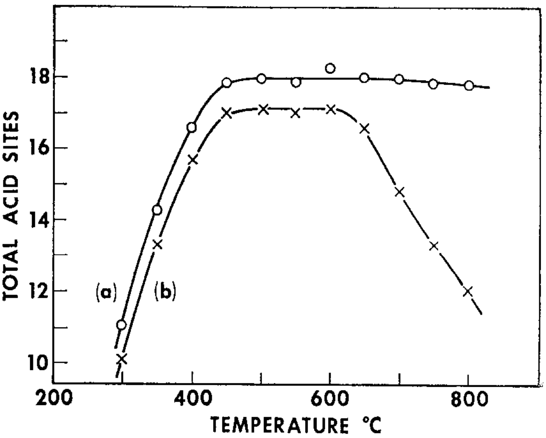


FIG. 7. Total acid site concentration as a function of temperature: (a) concentration of Brönsted sites plus 2x Lewis sites; (b) concentration of Brönsted sites plus Lewis sites.

Lewis acid site on silica-alumina. Plot (a) gives a much closer approximation to a constant suggesting that the dehydroxylation mechanism outlined occurs.

Comparison of the maximum Brönsted acidities for ammonium Y zeolite (*2*) and the magnesium ammonium Y zeolites shows them to be equal. This is to be expected if sufficient magnesium ions are incorporated only to fill the S_I crystallographic positions. The ammonium ions (hydroxyl groups after calcination) will occupy completely the accessible sites which will be equal in number. Cumene cracking data in Table 2 show both zeolites to be equally active, as expected from the equal number of Brönsted acid sites.

TABLE 2

CONVERSION OF CUMENE OVER Y ZEOLITES AT 260°C

Zeolite	Conversion (%)
NaY	0
HY	96
MgHY	95

In conclusion, the surface chemistry of a stabilized hydrogen Y zeolite has been studied. Under conditions for which the unstabilized hydrogen Y maintains its structure, the two zeolites have very similar properties. At calcination temperatures near 500°C, the zeolites are almost entirely in the Brönsted acid form. Increase in calcination temperature converts Brönsted acid sites to Lewis acid sites by elimination of hydroxyl groups. Comparison of calcination effects on the Brönsted acidity and hydroxyl group concentrations suggests that the hydroxyl groups represented by the 3643-cm^{-1} absorption band are the Brönsted acid sites. Because of the greater thermal stability of the magnesium hydrogen Y zeolite, calcination effects could be studied at temperatures where dehydroxylation is extensive without the uncertainties introduced by possible structural destruction.

ACKNOWLEDGMENTS

The determinations of catalytic activity by Rowland C. Hansford and the X-ray measurements obtained by Dr. E. Goldish of this laboratory are acknowledged.

REFERENCES

1. RABO, J. A., PICKERT, P. E., STAMIRES, D. N., AND BOYLE, J. E., *Actes Intern. Congr. Catalyse 2ᵉ, Paris, 1960* **2**, 2055 (Editions Technip, Paris, 1961).

2. HUGHES, T. R., AND WHITE, H. M., *J. Phys. Chem.* **71**, 2192 (1967).

3. (a) WARD, J. W., *J. Catalysis* **9**, 225 (1967); (b) WARD, J. W., *J. Catalysis* **9**, 396 (1967).

4. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69**, 217 (1965).

5. LIENGME, B. V., AND HALL, W. K., *Trans. Faraday Soc.* **62**, 3229 (1966).

6. PICKERT, P. E., BOLTON, A. P., AND LANEWALA, M. A., *Chem. Eng. Progr. Symp. Ser.* **73** (No. 63) (1967).

7. VENUTO, P. B., HAMILTON, L. A., AND LANDIS, P. S., *J. Catalysis* **5**, 484 (1966).

8. BENESI, H. A., *J. Catalysis* **8**, 368 (1967).

9. PLANK, C. J., Comment on Paper of PICKERT, P. E., RABO, J. A., DEMPSEY, E., AND SCHOMAKER, V., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 727 (Wiley, New York, 1965).

10. TURKEVICH, J., AND CIBOROWSKI, S., *J. Phys. Chem.* **71**, 3208 (1967).

11. ANGELL, C. L., AND SCHAFFER, P. C., *J. Phys. Chem.* **69**, 3463 (1965).

12. MCDANIEL, C. V., AND MAHER, P. K., "Conference on Molecular Sieves." Society of Chemical Industry, London, 1967.

13. PARRY, E. P., *J. Catalysis* **2**, 371 (1962).

14. BASILA, M. R., KANTNER, T. R., AND RHEE, K. H., *J. Phys. Chem.* **68**, 3197 (1964).

15. WARD, J. W., *J. Catalysis* **11**, 238 (1968).

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

17. TRAMBOUZE, Y. J., DE MOURGES, L., AND PERRIN, M., *J. Chim. Phys. (France)* **51**, 723 (1954).