

The Nature of Active Sites on Zeolites

II. Temperature Dependence of the Infrared Spectra of Hydrogen Y Zeolite

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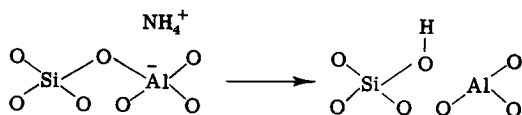
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An in situ infrared spectroscopic study of the thermal decomposition of ammonium Y zeolite has been made. The spectra are similar to those reported for room-temperature investigations except that the absorption band near 3640 cm^{-1} is moved about 15 cm^{-1} from its room-temperature frequency. The effects of temperature on the intensity of the 3640-cm^{-1} and 3540-cm^{-1} bands have been observed on a sample calcined at 450°C . On cooling to 120°C , the intensities of the bands increase by 29%. The change in intensity is probably due to delocalization of the hydrogen. The temperature dependence of the 3640-cm^{-1} and 3540-cm^{-1} bands suggests that the latter is not due to hydrogen bonding interactions of adjacent hydroxyl groups. The relation of the delocalized hydrogen to catalysis is discussed.

INTRODUCTION

Infrared spectroscopic studies (1-5) have shown that on heating the ammonium form of Y zeolite, ammonia is evolved and the protons liberated attack the lattice to form hydroxyl groups. Three principal absorption bands are observed in the 4000 to 3200 cm^{-1} region of the spectrum and can be attributed to different hydroxyl groups. The 3745-cm^{-1} band has been assigned to silanol groups either terminating the zeolitic lattice or present in amorphous material. The intensities of the two strong bands at 3640 and 3540 cm^{-1} increased with increasing exchange of cations by ammonium ions. These bands have been assigned to silanol groups introduced by the attack of the protons liberated by the ammonium ions.



There is considerable disagreement as to where these hydroxyl groups are located in the zeolite lattice (1-4). From a study of their interaction with adsorbed pyridine,

the hydroxyl groups are probably situated at different geometrical locations in the zeolite supercages (6, 12).

The decomposition studies by Uytterhoeven *et al.* (1) used spectroscopic measurements at room temperature while White *et al.* (3) report decompositions at 200°C . No in situ thermal decomposition studies have been reported.

Recently, it has been shown that hydrogen on the surface of oxides can become delocalized. For example, Fripiat *et al.* (7, 8) have shown a marked dependence of the hydroxyl groups of boehmite and mica on temperature. Eberly (4) reported spectra of the hydrogen (or decationated) Y zeolite at 427°C . He observed spectra similar to those recorded at room temperature.

If hydrogen on the surface of solid oxides becomes delocalized or mobile at elevated temperature, it could play a very important role in catalyst activity. Recently, Tung and McInnish (9) have attributed the cracking activity of alumina above 400°C to the thermal activation of hydrogen present in the lattice.

An infrared study of the in situ decomposition of ammonium Y zeolite is re-

ported in this paper. Results of a study of the influence of temperature on the hydroxyl groups remaining on the zeolite after calcination at 450°C are also presented.

EXPERIMENTAL

Materials. The composition of the sodium Y zeolite starting material was 10.3% Na, SiO₂/Al₂O₃ ratio 4.9. Its nitrogen surface area was 901 m² g⁻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.

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 on a Cary-White 90 spectrophotometer. The chopping of the radiation before, and not after the sample in the spectrophotometer prevents radiation emitted by the sample and heater from reaching the detector. Thus true absorption spectra of the sample are recorded.

An infrared cell in which it is possible to heat the sample to 900°C while in the spectrophotometer beam was used (10). Pressure of 10⁻⁶mm to 1 atm could be used. The sample temperature was measured by means of the thermocouple in contact with it. The spectral resolution was 3 cm⁻¹ and the scan speed 1 cm⁻¹/sec.

Procedure. Molecular-sieve-dried helium was passed over the sample in the cell at the rate of 50 ml min⁻¹. This served to sweep out the decomposition products and prevented reabsorption of water and carbon dioxide. The sample was gently heated and the temperature raised slowly until a temperature of 125°C was reached. The sample was maintained at this temperature for 2 hr and the spectrum recorded. The pro-

cedure was repeated at approximately 50°C temperature intervals until a final temperature of 450°C was reached. Spectra were recorded from 4000 to 2800 cm⁻¹ and 1700 to 1400 cm⁻¹. The temperature was then decreased in small steps. After allowing 1 hr for equilibrium at each temperature, the spectrum in the 4000–2800 cm⁻¹ region was recorded. After lowering the temperature to 120°C, it was stepwise increased again to 450°C.

RESULTS

In situ decomposition. Figures 1 and 2 show the spectra of the ammonium Y zeolite in the 4000 to 2000 cm⁻¹ and 1700 to 1400 cm⁻¹ ranges as a function of temperature. The results are basically similar to those reported previously for decomposition studies recorded spectroscopically at room temperature (1, 5). It is interesting to note that even without cooling the sample for recording, the protons liberated from the ammonium ions attack the lattice structure and form discrete hydroxyl groups. The intensity of the hydroxyl groups near 3640 and 3540 cm⁻¹ increases progressively as the ammonium ions are decomposed (characteristic absorption bands at 3160, 3030, 1620, and 1420 cm⁻¹) until all the ammonium ions have been removed at about 380°C (Figs. 1 and 2). This temperature is considerably higher than that reported (1) and is probably due to the higher ammonium ion content. Table I lists the absorbance of the 3640- and 3540-cm⁻¹ bands as a function of temperature. Above 396°C, the peak

TABLE I
INTENSITY OF HYDROXYL BANDS AS A FUNCTION
OF TEMPERATURE DURING DECOMPOSITION

Temperature (°C)	Absorbance	
	3640-cm ⁻¹ band	3540-cm ⁻¹ band
210°	0.17	0.31
266°	0.47	0.61
306°	0.63	0.65
373°	0.76	0.70
396°	0.78	0.71
450°	0.74	0.69
300° ^a	0.78	0.70

^a Cooled from 450°C.

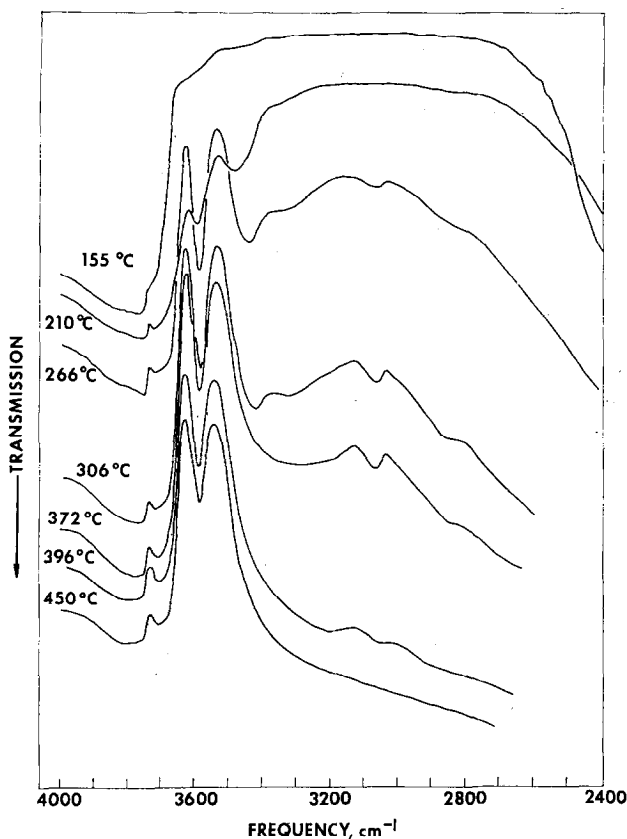


FIG. 1. Spectra of ammonium Y zeolite decomposition as a function of temperature in the 4000 to 2000 cm^{-1} region.

absorbance appears to decrease with rising temperature. However on cooling the sample down to 300°C, the band intensity increases to within experimental error of that observed at 396°C on the heating step. It is also seen that at 372°C and above, the depth of the well separating that 3640 and 3540 cm^{-1} bands has decreased compared to that observed at 300°C.

Effects of temperature on the hydroxyl groups of the zeolite precalcined at 450°C. Figure 3 shows the spectra of the decalcinated zeolite at a series of temperatures up to the initial calcination temperature of 450°C. Intensities were not recorded below 120°C because the bands became too intense for accurate measurements. (Spectra were recorded in the absorbance mode [$\log 1/\text{transmission}$] to give greater accuracy in measuring intensity.) Intensities were

measured by measuring the peak absorbance of the 3640- and 3540- cm^{-1} bands and also by measuring the area under the absorption bands between 3800 and 3200 cm^{-1} . As the temperature of the sample was lowered, the intensity of the two absorption bands near 3640 and 3540 cm^{-1} increased progressively. On raising the temperature again, the band intensities decreased. Table 2 lists the absorbances of the two bands and their ratio as a function of temperature. Figure 4 is a plot of the results. Figure 5 plots the band area against temperature. Increase of the sample temperature caused a reversible decrease in the band intensities. No temperature observations were made on the 3742- cm^{-1} band because of its weakness. The band frequencies remained constant during the temperature change with the exception of

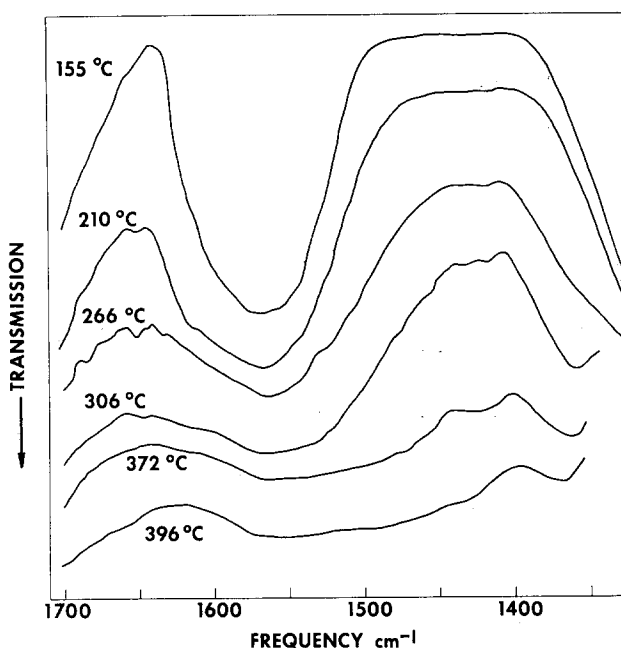


FIG. 2. Spectra of ammonium Y zeolite decomposition as a function of temperature in the 1700 to 1400 cm^{-1} region.

the band near 3640 cm^{-1} . This decreased in frequency as the temperature was raised, as shown in Fig. 6. The frequencies are listed in Table 3. It is also noticed in Fig. 3 that as the temperature was raised the well between the two absorption bands decreased in depth.

DISCUSSION

In Situ Decomposition

The in situ study of the decomposition of ammonium Y zeolite yielded results very similar to those obtained by conducting the spectroscopic measurements at room

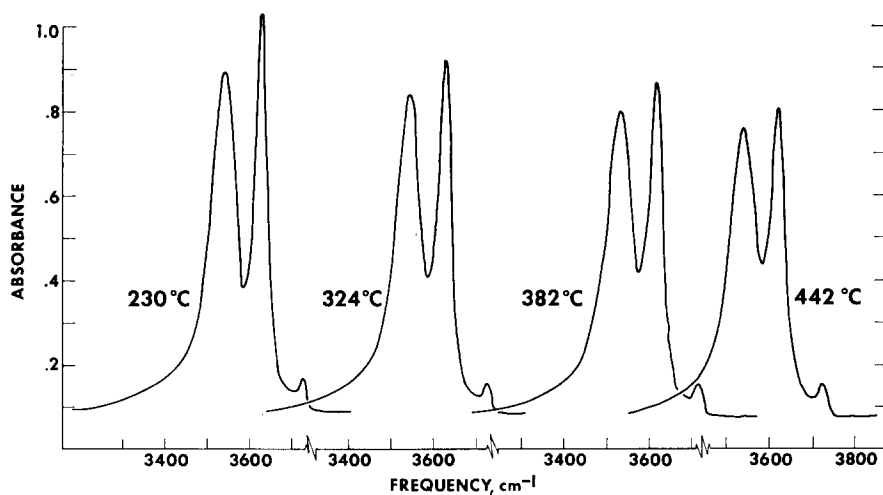


FIG. 3. Spectra of hydrogen Y zeolite, calcined at 450°C , as a function of temperature.

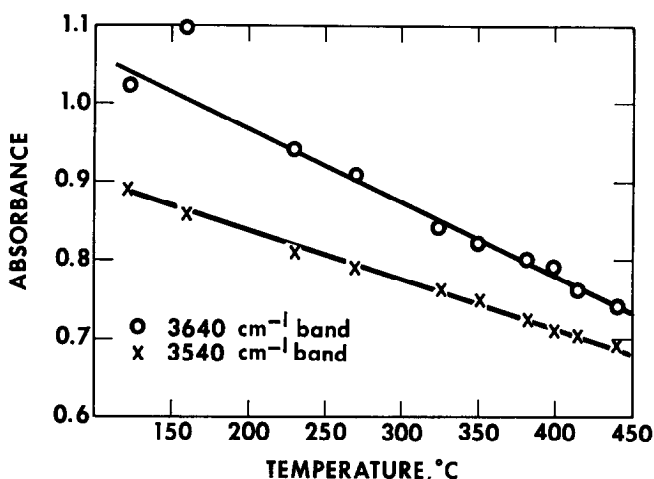


Fig. 4. Absorbance of the 3640- and 3540-cm⁻¹ bands as a function of temperature.

TABLE 2
INTENSITY OF HYDROXYL BANDS OF A CALCINED
ZEOLITE AS A FUNCTION OF TEMPERATURE

Temperature (°C)	Absorbance		Ratio	Band area, (inches ²)
	3640-cm ⁻¹ band	3540-cm ⁻¹ band		
122°	1.02	0.89	1.15	—
160°	1.10	0.86	1.28	12.25
230°	0.94	0.81	1.16	11.70
270°	0.91	0.79	1.15	11.32
324°	0.84	0.76	1.10	11.04
350°	0.82	0.75	1.10	10.53
382°	0.80	0.72	1.11	10.62
399°	0.79	0.71	1.11	10.31
414°	0.76	0.70	1.09	10.22
442°	0.74	0.69	1.07	10.20
345 ^a	0.81	0.74	1.09	—
430 ^a	0.75	0.70	1.07	—

^a Reheated.

temperature. The protons liberated in the ammonium decomposition appear to have reacted rapidly with the lattice to form hydroxyl groups. No evidence was found for any intermediates during the decomposition. This is not unexpected since, unless the liberated protons form bonds with other, different atoms or molecules, they will not have an infrared spectrum. The frequencies of the hydroxyl groups observed are similar to those reported previously (5). The band near 3640 cm⁻¹ is the only one showing any appreciable change from

TABLE 3
FREQUENCY OF 3640-CM⁻¹ BAND AS A
FUNCTION OF TEMPERATURE

Temperature (°C)	Frequency
25°	3643
160°	3636
270°	3631
355°	3624
430°	3622

room-temperature measurements (3642 cm⁻¹). The lowering of the frequency with increasing temperature may be a reflection of greater interaction of the silanol grouping with the neighboring aluminum atom.

Effects of Temperature of Sample

It is generally agreed that the band near 3640 cm⁻¹ represents hydroxyl groups attached to silicon, formed in the deamination process. These hydroxyl groups are located in the lattice at points readily accessible to adsorbate molecules, probably in the supercages close to the face of a six-membered oxygen ring (6). The location of the hydroxyl groups responsible for the 3540-cm⁻¹ band is in doubt. Liengme and Hall (11) and White *et al.* (3) have concluded that hydroxyl groups are inside the sodalite units while Eberly (4) has suggested that they are in inaccessible bridge

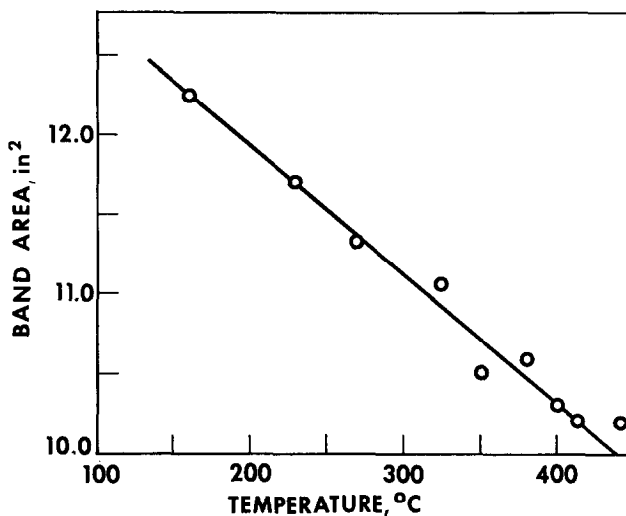


FIG. 5. Band area of hydroxyl absorption as a function of temperature.

positions located between two sodalite units. Hughes and White (12) concluded that the hydroxyl groups are attached to oxygen atoms protruding into the large cavity. Angell and Schaffer (2) on the other hand suggest that the band represents adjacent hydroxyl groups involved in hydrogen bonding. If this is the case and the 3640-cm^{-1} band represents free hydroxyl groups, the ratio of the intensities of the two bands should be a function of temperature (13). Examination of Table 2 shows

that the band ratio remained relatively constant, the 3640-cm^{-1} band showing most temperature dependence over the 200°C range. The temperature dependence of the bands is the opposite to that expected for hydrogen bonding. Therefore, location at different points in the lattice is favored.

In contrast to the report by Eberly (4), the results of this work show a distinct effect of sample temperature on the spectra of the hydroxyl groups on zeolites. Because of the frequency range studied, the

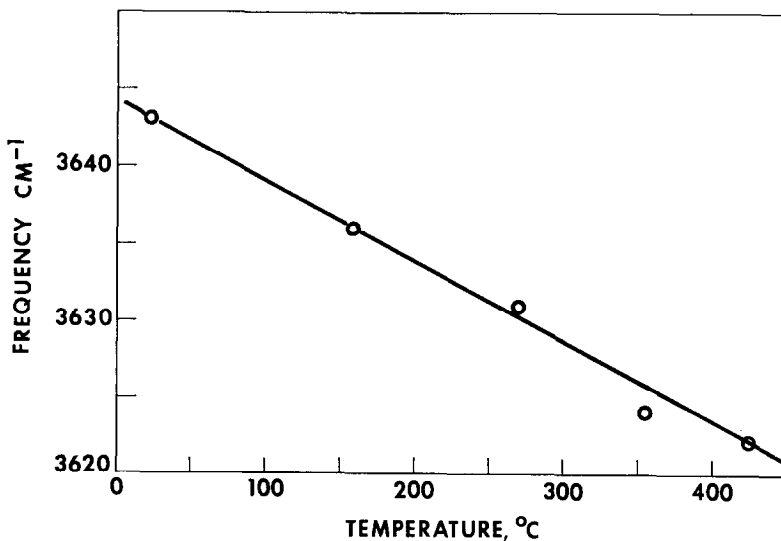


FIG. 6. Frequency of "3640"- cm^{-1} band as a function of temperature.

temperature effects are unlikely to have any appreciable contribution from changes in the energy level populations (14). The decrease in intensity of the hydroxyl group bands and their change in frequency probably indicate interaction of the silanol groups with neighboring atoms. This can probably be represented by the following scheme:



Such a scheme has been suggested by Liengme and Hall (11) to account for the re-formation of ammonium ions on addition of ammonia to the zeolite.

The movement of the absorption frequency of the 3460-cm^{-1} band to lower frequencies and the decrease in depth of the well between the 3640- and 3540-cm^{-1} bands with increasing temperature both support more involvement of the hydroxyl group with neighboring aluminum atoms. The reconstituted ammonium zeolite can be converted to the sodium form by ion exchange. The re-formation of the Si-O-Al linkage occurs if the zeolite is not extensively dehydrated. Increase of dehydration appears to bring about permanent changes in the structure. Under the conditions used here only a small proportion, if any, of the hydroxyl groups would have been eliminated from the surface.

The failure of Eberly (4) to observe any change in hydroxyl group intensity was probably due to the total absorption of radiation by his samples at the hydroxyl group frequencies. The data of Table 2 show that between 150° and 450°C , the hydroxyl peak decreases by 29%. Thus about one-third of the hydrogen in the zeolite is delocalized or mobile at temperatures of catalytic interest. According to the data of Uytterhoeven *et al.* (1), this would amount to about 10^{20} OH g^{-1} . This is of the same order of magnitude as the number of active sites determined by cumene cracking (15). Recently Tung and McInnish (9) have shown that alumina be-

haves as Brönsted acid above 400°C from examination of the cracking pattern of cumene. They suggested that this was due to delocalization of protons in the lattice. It is possible, then, that the hydrogens of hydroxyl groups in Y zeolites, which become delocalized at elevated temperatures are significant active centers in zeolite catalysts and may be responsible for the superactivity.

Examination of Fig. 4 shows that the temperature dependence of the 3640-cm^{-1} band intensity is greater than that of the 3540-cm^{-1} band. This implies that the hydroxyl groups represented by the 3640-cm^{-1} band more readily interact with the adjacent aluminum atoms and that the hydrogen atoms are more easily delocalized. This would be expected in the light of the reported greater interaction of the 3640-cm^{-1} band with adsorbate molecules (1, 3, 5, 11).

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