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# A Spectroscopic Study of the Surface of Y Zeolite

## III. Reexamination of the Temperature Dependence of the Infrared Spectra of Hydrogen Y Zeolite*

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The infrared spectra of several ammonium Y zeolites of different exchange levels were studied, after deammination at 470°C, as a function of temperature. In the temperature range of 200–470°C, the 3640-$cm^{-1}$ band changes in integrated intensity by about 35% of its 200°C value or 55% of its room temperature value. This change in intensity is too large to be due to simple thermal effects and is probably due to proton delocalization. No integrated intensity change was observed for the hydroxyl groups on Cab-O-Sil silica. The catalytic implications of these observations are discussed.

## INTRODUCTION

Several studies of the influence of temperature on the intensity of the absorption bands due to stretching vibrations of the hydroxyl groups of deamminated ammonium Y zeolite have been made. Uytterhoeven *et al.* (*1*) reported a 30% decrease in the integrated band intensity of the hydroxyl bands between 25 and 330°C for ammonium Y zeolite and predicted complete delocalization between 450 and 500°C. Unfortunately, their experimental conditions did not eliminate the interference of sample emissions at elevated temperatures. Eberly (*2*) was unable to observe any change in the hydroxyl group intensity but this may possibly be due to the total absorption of radiation by his samples at the hydroxyl group frequencies. Cant and Hall (*3*) studied the temperature dependence of the absorption bands due to structural hydroxyl groups on several oxides. For Y zeolite, they found that there was a 20% change in the integrated intensity of the 3640-$cm^{-1}$ band between 25 and 490°C. They considered this to be insufficient to necessitate an explanation other than the normal changes of band intensity of condensed phases with temperature (*4, 5*). Thus, Cant and Hall consider that their observations do not demonstrate the delocalization of hydroxyl groups. Previously, a similar study was made in these laboratories (*6*). Between 120 and 450°C, an optical density change for the 3640-$cm^{-1}$ band of 29% was found and the total band area under the 3640- and 3540-$cm^{-1}$ bands was found to change by 30% over the temperature range. This latter parameter was measured because the extensive overlap between the two hydroxyl bands in the sample used was such as to introduce large errors in the determination of the integrated intensities of the two separate bands. The band area was measured by means of a planimeter. The change in integrated band intensity was considered to be too great to be due to normal thermal effects (*4, 5, 7*), and was interpreted in terms of delocalization of hydroxyl groups. As pointed out by Cant and Hall (*3*) further experimentation appeared necessary to determine whether a conflict in findings or interpretation existed between the latter two studies

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* Part II. *J. Phys. Chem.* 72, 4211 (1968).

(*3*, *6*). In this paper, a temperature dependence of the hydroxyl groups on ammonium Y zeolites at several different degrees of exchange is reported. For comparison with the study of Cant and Hall (*3*), the temperature dependences of the hydroxyl groups on silica were also examined.

## EXPERIMENTAL METHODS

### *Materials*

The composition of sodium Y starting material was 10.3% Na, $SiO_2$–$Al_2O_3$ ratio 4.9, and its surface area was 901 $m^2\ g^{-1}$ [$(p/p_0)$ about 0.018]. The ammonium exchanged forms were prepared by ion exchange of the sodium Y zeolite with ammonium nitrate solution until the desired extent of exchange was obtained. The zeolites were washed free of excess nitrate and dried at 110°C. X-Ray diffraction showed the samples to be highly crystalline. The physical properties are listed in Table 1.

TABLE 1
COMPOSITION OF AMMONIUM Y ZEOLITES

| Sample | Sodium (%) | Ion exchange (%) | Surface area ($m^2\ g^{-1}$) |
|---|---|---|---|
| 1 | 6.8 | 31 | 926 |
| 2 | 3.7 | 64 | 981 |
| 3 | 1.3 | 88 | 956 |

The silica gel used was Cab-O-Sil H-5. It had a surface area of 145 $m^2\ g^{-1}$. The apparatus, sample preparation, and procedure were the same as used previously (*6*). The sample wafers weighed 0.02 to 0.04 g and were adjusted in weight such that the absorbance lay between 0.2 and 1.0.

Both optical densities and integrated intensities were measured. The absorption bands of the various hydroxyl groups were separated graphically and the area under the bands was determined by means of a planimeter. The accuracy of the area determination was considered to be ±2%.

## RESULTS

Figure 1 shows spectra of deamminated ammonium (hydrogen) Y zeolites of different degrees of ion exchange at a series of calcination temperatures up to the initial calcination temperature of 470°C. These spectra are, at least qualitatively, similar to those reported previously (*3*, *6*). The frequency of the band near 3640 $cm^{-1}$ (HF band) decreased with increasing temperature. The 3550-$cm^{-1}$ band (LF band) showed similar but smaller frequency shifts. Typical frequency dependences on temperature are shown in Fig. 2.

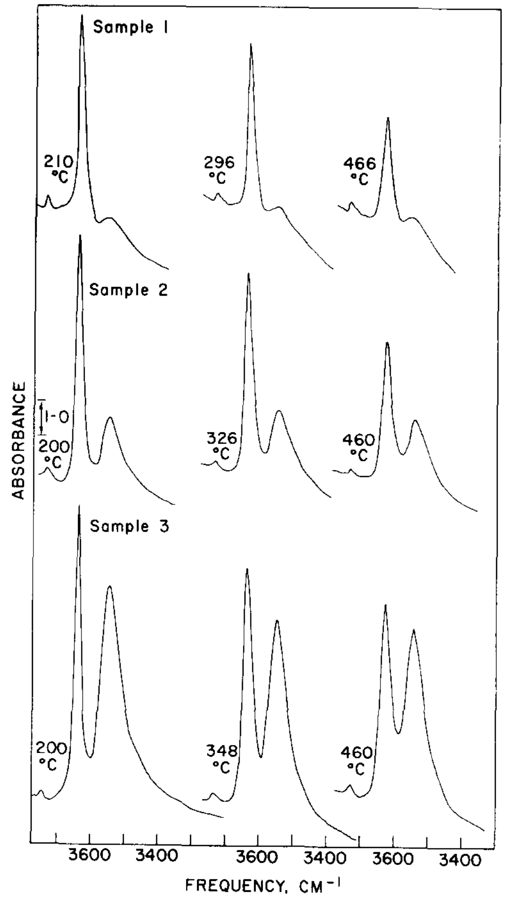


FIG. 1. Spectra of hydrogen Y zeolite, calcined at 470°C, as a function of temperature for Samples 1–3.

As the temperature was decreased from the initial calcination temperature, the optical density of the two principal absorption bands increased as reported previously, the HF band showed the larger increase in optical density. Over the temperature range studied, 200–470°C, the optical density of the HF band approxi-

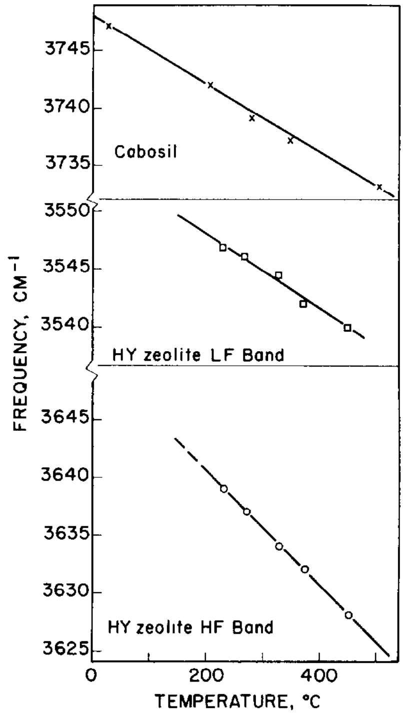


FIG. 2. Frequency of hydroxyl groups on Y zeolite as a function of temperature.

mately doubled compared to its 470° value and was 50% greater than the 200°C value, while that of the LF band increased by 28% for the sample which contained an appreciable concentration of LF hydroxyl groups (sample 3). Typical plots are shown in Fig. 3. At the same time, the half-bandwidth decreased substantially. These results are similar, but of greater magnitude, to those reported previously by Cant and Hall (*3*) and by us (*6*).

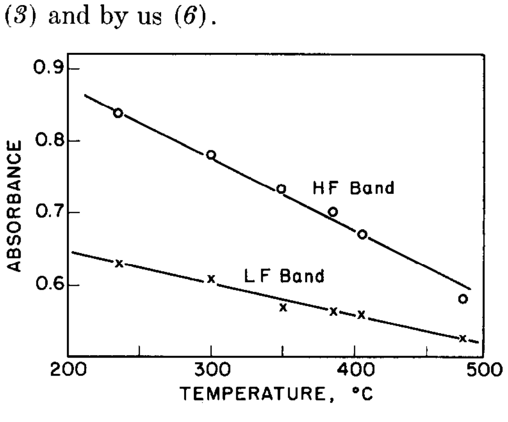


FIG. 3. Optical density of hydroxyl groups on Y zeolite as a function of temperature (Sample 3).

Measurement of the band area, as a measure of integrated intensity, also showed a change as a function of temperature. As the temperature was increased, the band area decreased for the HF band. Typical data are shown in Fig. 4. For the sample in which it was reasonably intense, the LF band remained virtually unchanged in integrated intensity. In the three samples studied, the HF band change in integrated intensity over the 200–470°C range by 35% of its intensity at 200°C or 53% of its intensity at 470°C. The integrated intensity appears to be a linear function of the temperature. If it is assumed that a linear relationship continues down to room temperature [it was previously shown to extend to 120°C (*6*)], the integrated intensity changes by 55% of its room temperature value or 120% of its 470°C value, over the room temperature to 470°C range. The observed values for the changes in integrated intensity are substantially less than the changes in optical density. These differences are due to changes in half-bandwidths as a function of temperature. The half-bandwidth typically changes from 20 $cm^{-1}$ at 230°C to 35 $cm^{-1}$ at 400°C.

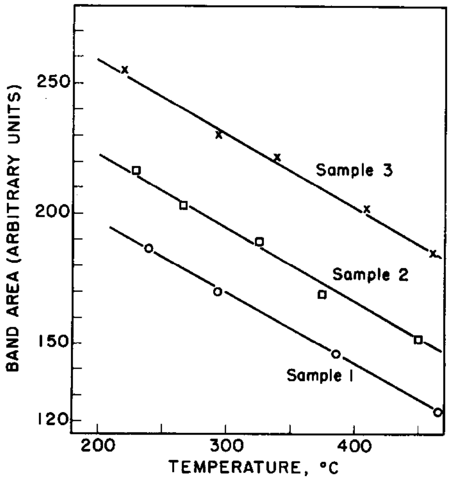


FIG. 4. Band area of HF hydroxyl groups on Y zeolite as a function of temperature.

Observations of the spectra of the hydroxyl groups on Cab-O-Sil over the same temperature range showed that the hydroxyl group frequency and optical density decreased with increasing temperature.

These measurements are shown in Fig. 5. However, over this temperature range, the band area remained constant within experimental error. These results for silica are completely analogous to those reported by Cant and Hall (*3*).

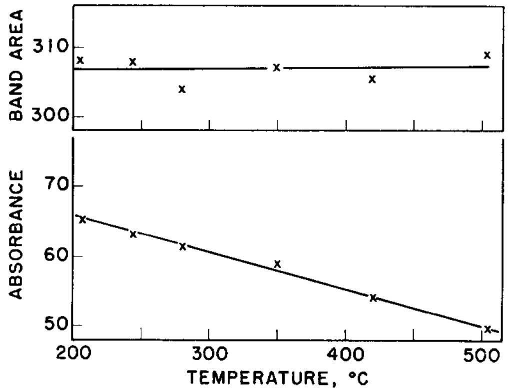


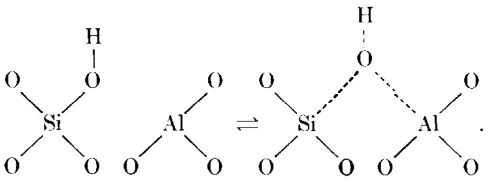
FIG. 5. Optical density and band areas of free hydroxyl groups on silica as a function of temperature.

## DISCUSSION

In agreement with previous observations of hydroxyl groups on inorganic oxides (*3*, *6–9*), changes in the optical density, half-bandwidths, and frequency of the hydroxyl stretching band frequencies occur as a function of temperature. The optical density and frequency decrease while the half-bandwidth increases as the temperature of the sample increases. Because of the simultaneous change in optical density and half-bandwidths, the use of optical density as a measure of absolute intensity is known to be unreliable and that the integrated band area is a much better criterion.

Observations of silica as a function of temperature indicate no measurable change in band area and, hence, it can be concluded that the hydrogen of silica gels is not delocalized at elevated temperature under the conditions used in this study despite the 30% change in optical density. This observation and interpretation is identical to that proposed by Cant and Hall (*3*). The observed 7-cm$^{-1}$ frequency shift between 200 and 500°C, as suggested by Cant and Hall (*3*), is probably due to increased thermal vibrations.

In contrast to the results of Cant and Hall (*3*) but in agreement with our previously reported results (*6*), marked changes are observed in the integrated band areas for the HF band of several ammonium Y zeolites. The magnitude of the band area changes are such as to be outside explanation in terms of simple temperature effects on a condensed phase system and require some other explanation. However, in agreement with previous workers, the optical density and absorption frequency decreased and the half-bandwidth increased with increasing temperature. Over the temperature range of 200–470°C, a frequency shift of 14 cm$^{-1}$ was observed which is comparable to that of 19 cm$^{-1}$ observed by Cant and Hall over the 25–490°C range and the 21 cm$^{-1}$ reported previously over the 25–430°C range (*6*). This frequency shift is considerably greater than that observed for silica above and for several other oxides (*3*). Hence, it appears probable that the shift is due to other factors than simple thermal influences on the spectra of condensed phases. As suggested previously, it is probable that the frequency shift indicates changes in the interactions between neighboring atoms in the structure, particularly the oxygen and aluminum.



This type of equilibrium is supported by the known details of the dehydration of hydrogen Y zeolites and the reconstitution of ammonium Y zeolites. The reformation of the Si–O–Al linkage occurs if the zeolite has not been extensively dehydroxylated.

A large change in integrated band area as a function of temperature suggests that hydroxyl groups are removed from the structure at elevated temperature but are reformed as the temperature is decreased. These results suggest that the bond between the proton and the lattice can be reversibly broken and reformed and that the protons are delocalized or mobile throughout the structure. This conclusion is the same as reached previously (*1*,*6*) and is now supported by other evidence. Thus, if the locations of the hydrogen in the zeolite structure determined by X-ray diffraction are correct (*8*), the ability of both types of hydroxyl groups to interact with the molecules such as piperidine, pyridine (*9*), and cumene (*10*) necessitates proton mobility. Furthermore, the interaction of cumene with the hydroxyl groups on zeolites seems to be a marked function of temperature. Also, wide-line proton magnetic resonance measurements have demonstrated proton mobility (*11*). If the protons are visualized as moving from oxygen to oxygen atom, the lifetime of a given OH bond must be very short ($< 10^{-4}$ sec). However other modes of accommodation of protons in the zeolite structure are possible.

The reason for the difference between these results and those of Cant and Hall are not clear. It may possibly lie in the fact that the present measurements were made in the presence of a stream of flowing dry helium whereas those of Cant and Hall were made under vacuum conditions. It may also lie in some unknown difference in experimental technique.

The occurrence of mobile protons on solid oxides possibly has important applications in catalysis. Thus, the number of delocalized protons on the surface of the deamminated Y zeolites is of the order of magnitude of the number of active sites estimated on these materials in acid-catalyzed reactions. These protons could function as strong acid centers. Note that in contrast to the hydrogen zeolites which are active proton acid catalysts, the silica gel studied, which is inactive in acid catalysis, showed no proton delocalization. Also note that although the LF band on hydrogen zeolite shows no change in integrated intensity, the hydroxyl frequency shift is intermediate between those of the HF band and of Cab-O-Sil. It is known that the HF hydroxyl groups protonate weaker bases than the LF hydroxyl groups, thus suggesting that the latter are weaker acid sites. Hence, there appears to be some relationship between the degree of delocalization and the magnitude of the frequency shift to the strength of the acidic hydroxyl groups. However, Cant and Hall (*3*) observed no delocalization on silica-alumina, which is an active proton acid catalyst. This point seems to merit further examination.

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