

# Characterization of hydroxyl groups of Y zeolites by infrared spectra\*

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Received 19 July 1974

The preparation of Y type decationized zeolites was studied in various conditions. It has been found that an increase in the activation temperature leads to a gradual loss of hydroxyl groups. Decationized zeolites, prepared *in vacuo*, are less stable than zeolites prepared in static atmospheric conditions or in an atmosphere enriched in water vapour. The zeolite stability was evaluated on the basis of the thermal resistivity of the —OH groups formed and of the resistance of the lattice to amorphization during rehydration.

Был изучен процесс приготовления свободных от катионов цеолитов типа Y при различных условиях. Было определено, что повышение температуры активации ведет к последовательной потере гидроксильных групп. Свободные от катионов цеолиты приготовлены в вакууме менее стабильны чем цеолиты приготовлены в статических атмосферических условиях или в атмосфере обогащенной водяным паром. Стабильность цеолитов была характеризована термической стойкостью возникших —OH групп и стойкостью решетки к аморфизации при регидратации.

Decationized zeolites are formed by thermal decomposition of the appropriate ammonium form of the zeolite. Ammonium ions decompose by thermal treatment with formation of gaseous ammonia and of protons which are bound to some lattice oxygens in the zeolite skeleton, thus forming structural —OH groups (*ca.*  $10^{21}$ /g zeolite).

The —OH groups on the zeolite surface are important since they may become active centres, *e.g.* in acid-base catalytic reactions, or adsorption centres during formation of adsorption complexes. Therefore a profound knowledge of the mechanism of their formation and their properties, *e.g.* thermal stability, resistance towards water vapour, reactivity, and location in the lattice, is inevitable.

In the present paper, the formation of structural —OH groups of the Y zeolite will be discussed. These groups are formed during thermal decomposition of the appropriate ammonium form *in vacuo* (at 350°C), in air under atmospheric pressure (at 600–800°C) or in atmosphere enriched in water vapour (at 570°C). Besides,

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\* Presented at the 1st Czechoslovak Seminar on Adsorption, Bratislava, June 4–5, 1974.

the thermal stability of the —OH groups formed in this way and the properties of the absorption bands of structural —OH groups in the i.r. spectra will be dealt with.

### Experimental

As the starting sample, Y zeolite with faujasite structure was used, with the composition  $0.96\text{Na}_2\text{O} \cdot 0.041\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 5.04\text{SiO}_2$ , which was converted into the ammonium cycle by ion exchange in a solution of  $\text{NH}_4\text{NO}_3$  at  $80^\circ\text{C}$ ; its composition was then,  $0.29\text{Na}_2\text{O} \cdot 0.033\text{CaO} \cdot 0.72(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.95\text{SiO}_2$ , and it will be denoted as  $\text{NH}_4\text{Y-70}$ , or HY-70. This sample was provided by the Research Institute for Oil and Hydrocarbon Gases in Bratislava under cooperative agreements. The i.r. spectra were taken using transparent samples with a thickness equivalent to  $8\text{--}14\text{ mg/cm}^2$ , which were pressed from pulverized zeolite at about  $1000\text{ kg/cm}^2$ . The pellet was placed in a cell provided with  $\text{CaF}_2$  windows. The cell formed a part of the vacuum apparatus described earlier [1]. The spectra were obtained with the Perkin—Elmer 621 spectrophotometer using the standard programme and a double slit. An attenuator was placed in the reference beam in order to modify the transparenance scale.

### Results and discussion

#### *Decomposition of the ammonium form of the $\text{NH}_4\text{Y-70}$ zeolite in vacuo*

The decationized  $\text{NH}_4\text{Y-70}$  zeolite was prepared by a thermal treatment at  $350^\circ\text{C}$  for 4—5 hrs *in vacuo* of  $10^{-5}\text{--}10^{-6}$  torr. This decomposition temperature is optimal for maintaining the maximum number of —OH groups on the surface. No absorption bands corresponding to the  $\text{NH}_4^+$  cation were found in the i.r. spectrum, which verifies the completeness of the decomposition of the ammonium cation.

The i.r. spectrum exhibits three typical absorption bands [2] at 3740, 3640, and  $3550\text{ cm}^{-1}$  (Fig. 1, curve 1) in the region of —OH group stretching vibrations.

The band at  $3740\text{ cm}^{-1}$  is independent of the degree of decationization and is attributed to the terminal —OH group in the zeolite crystal.

The band at  $3640\text{ cm}^{-1}$ , denoted as a high-frequency (HF) band, is narrow and symmetrical and its intensity depends on the degree of decationization. Ward [3] has found that these —OH groups are located in large cavities of the Y zeolite; hence they are easily accessible and can be affected by sorption of saturated and unsaturated hydrocarbons. It has not been unambiguously determined at which oxygen these —OH groups are located.

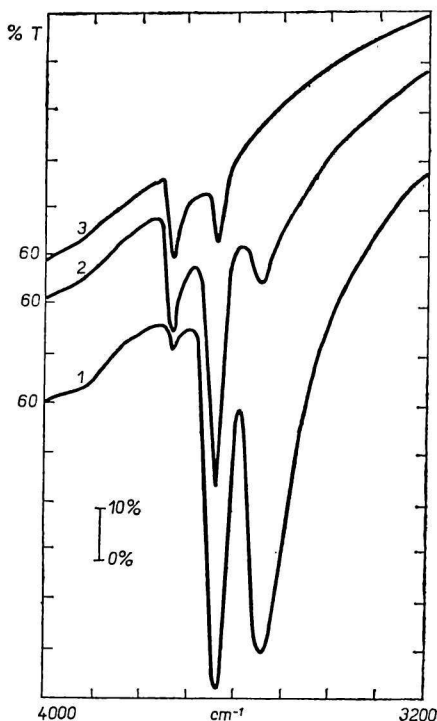
The band at  $3550\text{ cm}^{-1}$ , denoted as a low-frequency (LF) band, is broad, asymmetrical and it also depends on the degree of decationization. The —OH groups corresponding to this band are located in sodalite units of the zeolite structure and, although we assume that the protons in these groups are more loosely bound than those in the previous case, these —OH groups are not sensitive with respect to the sorption of nonpolar molecules or olefins because of their inaccessibility.

At temperatures above  $400^\circ\text{C}$ , the surface of the Y zeolite becomes damaged due to dehydroxylation, *i.e.* to the loss of structural —OH groups by desorption of  $\text{H}_2\text{O}$ .

The sample was first decomposed at  $350^\circ\text{C}$  and then activated at  $500^\circ\text{C}$  for 4 and 24 hrs. As it can be seen in Fig. 1 (curves 2 and 3), the intensity of the band

Fig. 1. Decomposition of the  $\text{NH}_4\text{Y-70}$  zeolite *in vacuo*.

1.  $350^\circ\text{C}$ , 4 hrs; 2.  $500^\circ\text{C}$ , 4 hrs; 3.  $500^\circ\text{C}$ , 24 hrs.



at  $3550\text{ cm}^{-1}$  decreased, while that of the band at  $3740\text{ cm}^{-1}$  simultaneously increased. This is in agreement with the literature [3], which shows decreasing frequency of  $-\text{OH}$  group stretching vibrations in dependence on temperature; thus at  $500^\circ\text{C}$  the band with the lowest wavenumber,  $3550\text{ cm}^{-1}$ , disappears fastest since the most labile  $-\text{OH}$  groups are most easily removed. From this aspect also the high thermal stability of the  $-\text{OH}$  groups represented by the band at  $3740\text{ cm}^{-1}$  can be explained; the band disappears only at about  $650^\circ\text{C}$  when the zeolite surface is already dehydroxylated, the lattice collapsing between  $700$  and  $800^\circ\text{C}$ .

The zeolite decationized *in vacuo* is very sensitive to water vapour. During repeated hydration—dehydration cycles, the sorption capacity measured with argon decreased to almost one half of the original value, the lattice partially decomposed and the i.r. spectra changed. Hence it follows that the zeolite decomposed in this way is a quite unstable material, undergoing fundamental changes when handled in conditions other than *in vacuo*.

#### *Decomposition of the ammonium Y zeolite in air at higher temperatures*

In this case the decationized  $\text{NH}_4\text{Y-70}$  zeolite was prepared in air at  $600^\circ\text{C}$  and the sample was then evacuated for one hour at  $350^\circ\text{C}$  (Fig. 2). This process was repeated three times (curves 1—3) and then followed by evacuation at  $600^\circ\text{C}$  (curve 4).

Four bands appear in the spectrum. The band at  $3740\text{ cm}^{-1}$  is substantially more intense than in the case of the zeolite decomposed *in vacuo*, the band at  $3660\text{ cm}^{-1}$

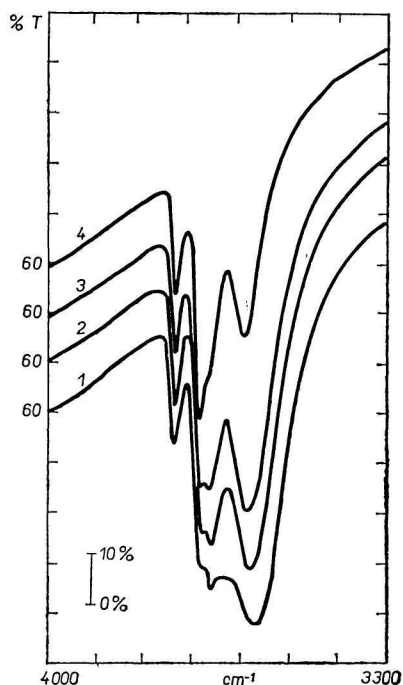


Fig. 2. Decomposition of the  $\text{NH}_4\text{Y-70}$  zeolite under static atmospheric conditions at  $600^\circ\text{C}$ . 1.  $600^\circ\text{C}$ , 4 hrs in air followed by evacuation at  $350^\circ\text{C}$  for 1–2 hrs; 2. air introduced and the process represented by curve 1 repeated; 3. air introduced and the process represented by curve 1 repeated once more; 4. evacuated at  $600^\circ\text{C}$  for 2 hrs.

is the typical HF band for zeolites decomposed *in vacuo*, though it is somewhat shifted [4] and the band at  $3550\text{ cm}^{-1}$  is absent.

The bands at  $3685$  and  $3575\text{ cm}^{-1}$  are new bands, characteristic of zeolites decomposed in conditions other than *in vacuo*. At repeated activation in air they shift to higher frequencies, up to  $3690$  and  $3600\text{ cm}^{-1}$ . The ratio of the intensities of the bands at  $3690$  and  $3600\text{ cm}^{-1}$  changes in favour of the band at  $3690\text{ cm}^{-1}$ .

As it follows from curve 4, the  $-\text{OH}$  groups formed are thermally more stable and the corresponding absorption bands are intense even when evacuated at  $600^\circ\text{C}$ .

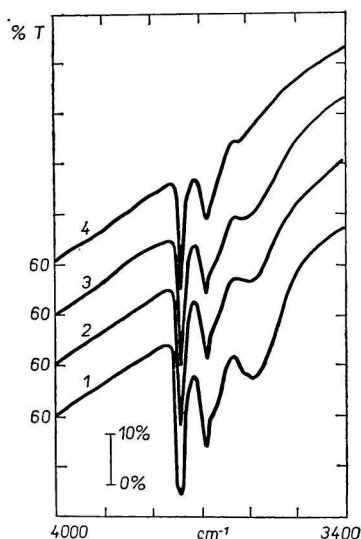
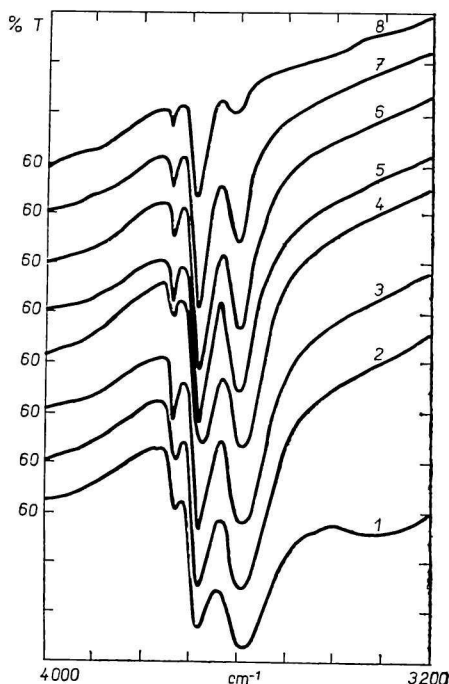
If the decomposition process is performed in the same manner, but at  $800^\circ\text{C}$ , a similar picture is obtained (Fig. 3). Now the band at  $3740\text{ cm}^{-1}$  is more intense and the intensity of the bands at  $3690$  and  $3590\text{ cm}^{-1}$  is decreased. Nevertheless, at least some of the  $-\text{OH}$  groups represented by the band at  $3690\text{ cm}^{-1}$  remain on the zeolite surface and are not decomposed at the temperature of  $800^\circ\text{C}$ , at which the zeolite decomposed *in vacuo* disintegrated.

Both the decomposition of the ammonium form of the Y zeolite *in vacuo* and decomposition at higher temperatures in air were carried out directly in the apparatus for the measurement of the i.r. spectra.

#### *Decomposition of the ammonium form of the Y zeolite in an atmosphere enriched in water vapour*

This decomposition, leading to the so-called stabilized form, was performed at  $570^\circ\text{C}$  at atmospheric pressure and at a partial pressure of water vapour of about

*Fig. 3.* Decomposition of the  $\text{NH}_4\text{Y}$ -70 zeolite under static atmospheric conditions at  $800^\circ\text{C}$ . 1.  $800^\circ\text{C}$ , 4 hrs in air followed by evacuation at  $350^\circ\text{C}$  for 1–2 hrs; 2. air introduced and the process represented by curve 1 repeated; 3. air introduced and the process represented by curve 1 repeated once more; 4. evacuated at  $800^\circ\text{C}$  for 2 hrs.



*Fig. 4.* Thermal stability of the decationized HY-70 zeolite, prepared in an atmosphere enriched in water vapour and evacuated at: 1.  $150^\circ\text{C}$ , 4 hrs; 2.  $350^\circ\text{C}$ , 4 hrs; 3.  $450^\circ\text{C}$ , 4 hrs; 4.  $550^\circ\text{C}$ , 4 hrs; 5.  $600^\circ\text{C}$ , 4 hrs; 6.  $650^\circ\text{C}$ , 4 hrs; 7.  $700^\circ\text{C}$ , 4 hrs; 8.  $800^\circ\text{C}$ , 4 hrs.

38 mmHg without using the apparatus. Then a pellet was pressed and transferred into the i.r. spectrometer.

After evacuation at  $350^\circ\text{C}$  for 4 hrs three bands at  $3740$ ,  $3680$ – $3690$ , and  $3600\text{ cm}^{-1}$  appear in the spectrum. Upon increasing temperature up to  $800^\circ\text{C}$  the intensity of the band at  $3680\text{ cm}^{-1}$  somewhat decreases (Fig. 4). From this it follows that the zeolite surface remains partially hydroxylated even after this type of decomposition of the zeolite ammonium form, perfect crystallinity being preserved as was verified by X-ray measurements. Using i.r. spectral measurements and measurement of the sorption capacity, we found that this material is stable, its properties do not change during handling in the air and it is not sensitive to the effects of water vapour.

### Conclusion

When the properties of the above three types of decationized HY-70 zeolites are compared, the following tendencies are observed:

1. An increase in the activation temperature always leads to a gradual loss of hydroxyl groups. With zeolites prepared *in vacuo*, this dehydroxylation simultaneously leads to a partial or complete destruction of the zeolite structure.

2. With zeolites prepared under static atmospheric conditions the dehydroxylation proceeds more slowly, and the stability of —OH groups and of the lattice skeleton increases.

3. The zeolite prepared in an atmosphere enriched in water vapour exhibits a further increase in the stability of the —OH groups and the lattice, and increased resistivity to the effect of H<sub>2</sub>O vapours. The tendency to stabilization of —OH groups is accompanied by shifts in the frequencies of structural —OH groups toward higher wavenumbers. It is probable that the acidity of the bound protons simultaneously changes.

In conclusion we would like to emphasize the importance of the proceeding in which the ammonium forms of the Y zeolite are decomposed; the final product is a so-called ultrastable zeolite [5].

### References

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Translated by Z. Tvarůžková