Thermochimica Acta, 160 (1990) 193–200
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF HUMIDITY, Na^+ ION EXCHANGE AND SILICA/ALUMINA RATIO OF ZEOLITE H–Y ON ITS PHYSICAL PROPERTIES AS ASSESSED BY WATER DESORPTION USING DIFFERENTIAL SCANNING CALORIMETRY

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(Received 24 August 1989)

ABSTRACT

Zeolite H–Y gives two widely separated endotherms in the DSC curve which are attributed to water desorption from large supercages and small β-cages. Water is still present in the β-cages after 50% dehydration of the zeolite, whereas water in the supercages is linearly dehydrated. Increasing the Na^+ ion exchange in H–Y, prevents water molecules from reaching the β-cages but increases the multi-layers of water in the supercages. Dealumination of H–Y appears to destroy the β-cages but decreases the internal surface area and widens the supercages and, hence, decreases the water uptake. The size of the endotherms and, hence, their ΔH values, together with the shift of the endotherm maxima, give useful information.

INTRODUCTION

The nature of the interaction of water vapour and the surface of a solid is determined not only by its physical properties, such as specific surface area and porosity, but also by its chemical composition. However, it is difficult to assess the influence of physical and chemical properties separately. Paterson [1] has claimed that such an assessment may be possible from DSC thermograms.

In this work, successive stages of the change of zeolite H–Y to different forms is traced by DSC while using the ΔH values obtained for the DSC effects appearing in the thermograms to describe such changes, i.e. the

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water-desorption peaks in the DSC thermograms are correlated from qualitative and quantitative points of view.

EXPERIMENTAL

Zeolite treatments

Zeolite H–Y was prepared from commercially available Na–Y (Linde SK-40) by exchanging with NH_4NO_3 solution to remove the Na^+ ions, dried at 110 °C overnight and then decomposed at 530 °C for 4 h to produce the H–Y form [2].

Preliminary work indicated that dehydration of the produced H–Y is completely reversible. Dehydration was carried out under vacuum (10^{-5} Torr) over P_2O_5, then the product was equilibrated at relative humidities between 5% and 80% [1]. The fully hydrated sample contained 26.1 wt.% water, as determined thermogravimetrically, and was assumed to possess 100% relative humidity (R.H.).

Samples of H–Y were exchanged with $NaNO_3$ solutions such as to contain relative Na^+ ion exchange (R.E.) of 38% and 75%. The fully cationated zeolite (Na–Y), assumed to contain 100% R.E., was found to possess 10.25 wt.% sodium on a dry basis.

H–Y samples with increased SiO_2/Al_2O_3 ratios (5.7, 6.6 and 7.5) were prepared by dealuminating the H–Y form (SiO_2/Al_2O_3 ratio = 4.8) using HCl leaching [3,4].

DSC measurements

The DSC measurements of all samples were done by the conventional technique where the sample crucible contained 10 mg of the zeolite and the reference crucible was kept empty. Standard Al crucibles were used. A DSC-30 unit of the Mettler TA-3000 system was used at atmospheric pressure in air atmosphere without purge gas. The DSC conditions were: initial temperature, 50 °C; programmed heating rate, 20 K; final temperature, 600 °C; plot, 10 cm; and full-scale range, 25 mW.

RESULTS AND DISCUSSION

The unit cell of zeolite Y is cubic with large dimensions, 25 Å, and the framework structure contains the largest void space of any known zeolite, i.e. about 50 vol.% of the dehydrated crystal. These properties confirmed the suitability of this zeolite for this study as its water-adsorption capacity is relatively large. Furthermore, preliminary work showed that the DSC thermogram obtained for the H–Y form gives two widely separated endotherms due to water desorption, which are not normally obtained for other zeolites.

Effect of relative humidity on zeolite H–Y

Curve a in Fig. 1 is the DSC curve for the fully hydrated zeolite H–Y (relative humidity, R.H. = 100%) composed of two more or less symmetrical endotherms with maxima at 182° C and 383° C. Such a wide separation of water-desorption endotherms is actually uncommon in zeolites [5]. This indicates the presence of at least two distinct groups of pores or channels having widely different diameters. The low-temperature endotherm (182° C) is attributed to water molecules adsorbed in wide pores, the supercages of the zeolite Y structure, whereas the high-temperature endotherm (383° C) is attributed to water molecules in the narrow β-cages. Thermogravimetry (TG) showed that the 182° C peak corresponds to 21.0 wt.% water, whereas the 383° C peak corresponds to 5.1 wt.% of the fully hydrated zeolite. This implies that the total volume of the micropores (in β-cages) comprises 19.1% of the total pore volume in zeolite H–Y.

Figure 1 shows the changes in the DSC curves obtained for zeolite H–Y

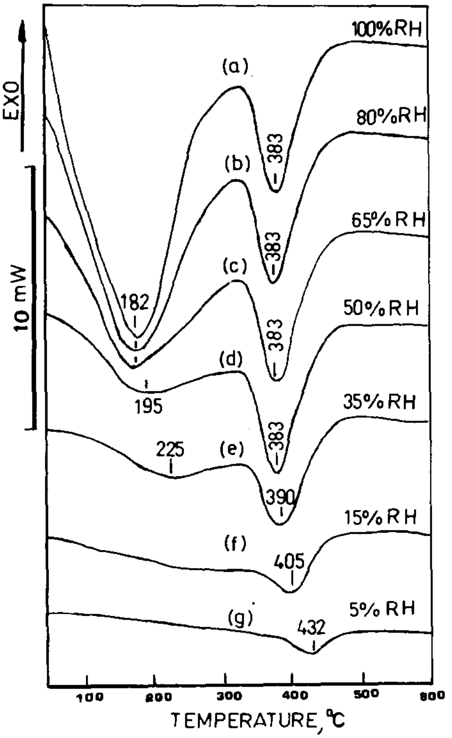

Fig. 1. DSC curves for zeolite H–Y with different relative humidities (R.H.).

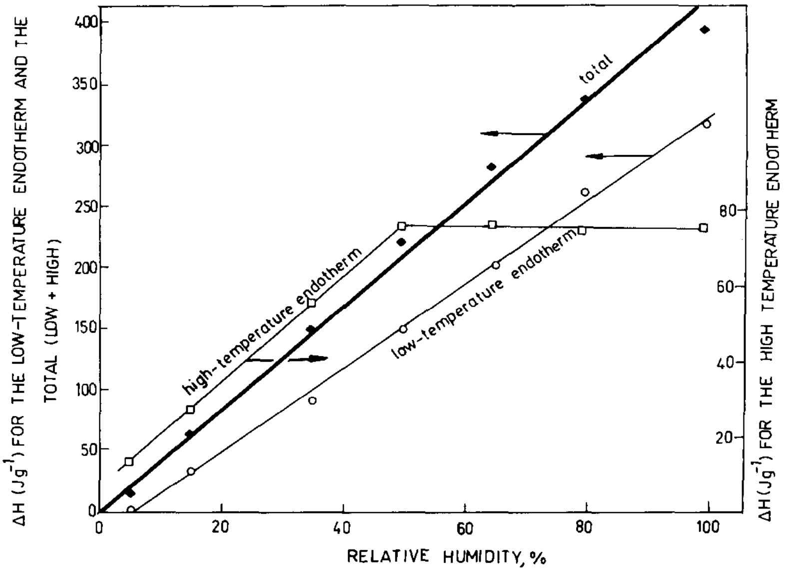

Fig. 2. Effect of relative humidity of zeolite H–Y on the ΔH values of the dehydration endotherms.

at different R.H. values. Decreasing the R.H. of the zeolite to 50% (curve d) results in the successive decrease in the size of the low-temperature peak, and hence its ΔH value (Fig. 2), whereas the size of the high-temperature peak remains unchanged ($\Delta H = 77$ J g^{-1}). This indicates that the β-cages in zeolite H–Y are occupied by very strongly bound water molecules which remain in their positions even after removal of 50% of the zeolite water content. However, the shape of the low-temperature peak may indicate the presence of some supercages with different diameters because the peak is asymmetrical (curves b–e).

Figure 2 shows that beyond 50% R.H., a linear decrease of the ΔH values obtained for the high-temperature endotherm is a function of decreasing R.H. according to

$$\Delta H = 5.0 + 2.0\text{R.H.} \tag{1}$$

Nevertheless, the relationship between R.H. and ΔH for the low-temperature endotherm is

$$\Delta H = -20 + 3.5\text{R.H.} \tag{2}$$

and for the total value of ΔH for both endotherms

$$\Delta H = 4.2\text{R.H.} \tag{3}$$

Aboul-Gheit et al. [5] have also found that the relationship between the TG water content of different zeolites and their DSC ΔH values is linear.

Figure 1 also shows that the maxima of the low- and high-temperature endotherms are shifted towards higher temperatures as the R.H. decreases.

This indicates that both supercages and β-cages may exhibit different diameters and/or that some cages of both types are much more deeply situated. Moreover, the very fine nature of the particles of the zeolite under study may contribute to such peak shifts [1].

Effect of Na^+ ion exchange on zeolite H–Y

Curves a and d in Fig. 3 are the DSC curves for the completely decationated zeolite, H–Y (i.e. with a relative sodium exchange, R.E., of 0%), and the fully sodium-exchanged zeolite, Na–Y (R.E. = 100%), respectively. The 100% R.E. zeolite shows complete absence of the 383° C endotherm characteristic for H–Y, but the low-temperature endotherm appears much larger. In positions intermediate between curves a and d, curves b and c show intermediate stages of decreasing size of the 383° C peak and increasing size of the 182° C peak as a function of increasing R.E. of sodium, see Fig. 3. Figure 4 shows the change in ΔH for the endotherms as R.E. increases. The increase of the low-temperature-peak-ΔH is gradual on increasing the R.E. from 0% to 75% but it is largely enhanced beyond 75% R.E. This indicates that Na^+ ions enhance water adsorption in the supercages. Breck [6] assumed that cations in hydrated zeolites are surrounded by as many water molecules as is spatially possible, as long as they do not lie

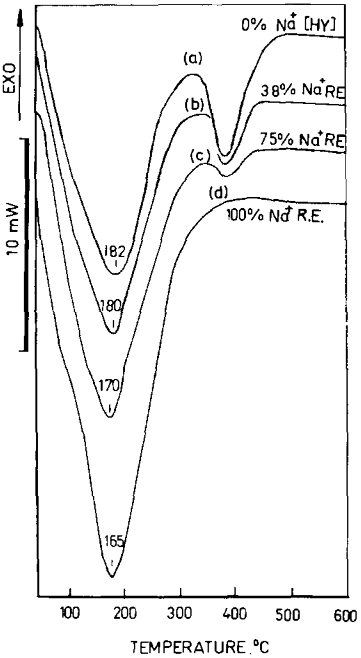

Fig. 3. DSC curves for zeolite H–Y with different relative Na^+ ion exchanges (R.E.).

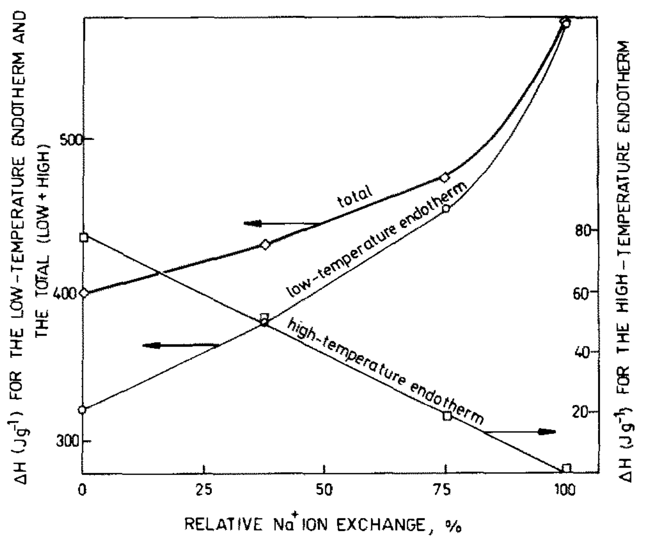

Fig. 4. Effect of relative Na^+ ion exchange of zeolite H–Y on the ΔH values of the dehydration endotherms.

too far away from the alumino-silicate framework and the negative charge distribution. On the other hand, ΔH for the high-temperature endotherm decreases linearly as a function of increasing the R.E. according to

$$\Delta H = 77 - 0.77\text{R.E.} \qquad (4)$$

Since all of these samples are fully hydrated, the steady disappearance of water from the β-cages of the zeolite with the introduction of Na^+ ions may be due to their impeding the presence of water molecules in these cages, e.g. by blocking them. This presumption may be substantiated by observing that no shift of the high-temperature peak maxima occurs as a function of increasing the R.E. If, however, the dimension of the β-cages is decreased by adsorbing Na^+ ions within them (because the volume of the sodium atom is 23.7 W/D, whereas that of the hydrogen atom is 14.1 W/D), the peak maximum would have been considerably shifted to higher temperatures.

Nevertheless, the maximum of the low-temperature endotherm undergoes a slight shift to lower temperatures as the R.E. increases: from 182 °C at 0% R.E. to 165 °C at 100% R.E. This may indicate that Na^+ ions cannot change the dimensions of the large supercages, but can only increase the capacity of the zeolite to adsorb more multi-layers of water such that its desorption in the DSC cell takes place at lower temperatures. Cation blocking-effects in zeolites are known [6].

Effect of dealumination on zeolite H–Y

Figure 5 shows that the increase of the silica/alumina ratio of zeolite H–Y by leaching with HCl results in a continuous decrease of the size of

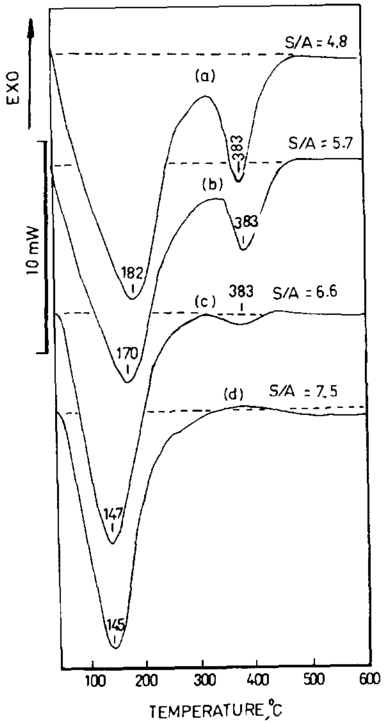

Fig. 5. DSC curves for zeolite H–Y with different silica/alumina ratios (S/A).

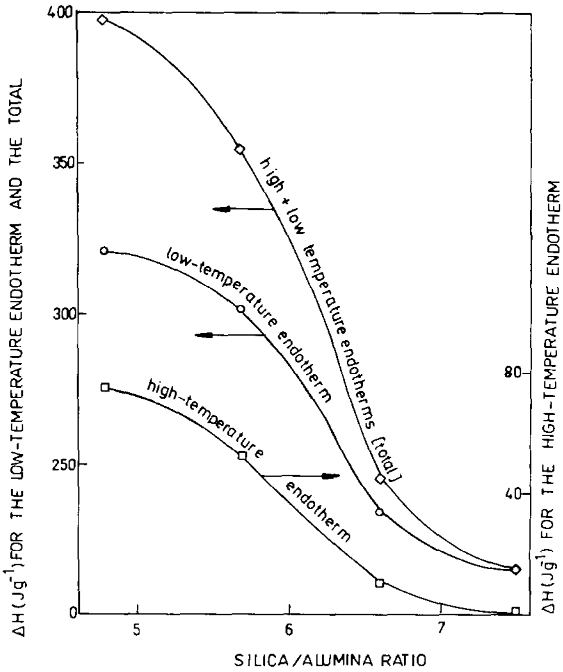

Fig. 6. Effect of silica/alumina ratio of zeolite H–Y on the ΔH values of the dehydration endotherms.

both the low- and high-temperature endotherms. At a ratio of 7.5 (curve d), the high-temperature endotherm completely disappears. Figure 6 shows the decrease in ΔH for the endotherms with the increase in SiO_2/Al_2O_3 ratio.

The unit cell dimensions, as well as the framework structure of the zeolite, should have been changed by changing the silica/alumina ratio. The decrease in ΔH for the high-temperature endotherm can be attributed to the destruction of the micropores (β-cages), whereas the decrease in the ΔH value for the low-temperature endotherm can be attributed to an overall decrease in the internal surface area of the zeolite by an excessive widening of the macropores (supercages). The shift of the maximum of this endotherm from 182°C to 145°C by removing some alumina implies an easier water desorption, which can be achieved by widening the cages. However, the unshifted maximum of the high-temperature endotherm implies the disappearance of cages rather than a change in their diameter. Dealumination decreases the surface area of zeolite Y [7].

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