Thermochimica Acta, 146 (1989) 263–269
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DETECTION OF UNIDENTIFIABLE CHANGES IN ZEOLITE-Y VIA TREATMENT WITH NH_4NO_3 USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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(Received 23 November 1988)

ABSTRACT

DSC measurements were carried out for zeolite-Y before and after long treatment with ammonium nitrate solution. Not only was the sodium ion in the zeolite exchanged with ammonium ion in this treatment, but changes in the acidity distribution of the zeolite were also detected; the quantity of acid sites increased, whereas their strength decreased. Triethylamine (TEA) was used as a probe base. The extent of Na^+ exchange with NH_4^+ in NH_4NO_3-treated NaY can be traced by at least one DSC effect in the thermograms of exchanged samples.

INTRODUCTION

Recently, Aboul-Gheit and co-workers [1–9] used thermoanalytical techniques to measure acidity distribution in zeolites and solid catalytic materials by desorbing and monitoring a presorbed base from the acid sites on these materials. Differential thermal analysis (DTA) seemed promising [1] but differential scanning calorimetry proved to be superior over DTA because of its higher sensitivity and quantitative response [10]. DSC provides enthalpy, ΔH, and activation energy, E_a, values for desorption of the base which are related to the quantity and strength of the acid sites respectively [2]. Acidity strength can also be correlated with desorption temperature in the thermograms. Moreover, DSC has been modified to overcome the effects due to the catalytic material [3]. The DSC technique has also proved successful in precise water determination in zeolites [4] and following the de-ammoniation of NH_4-zeolites [5].

Exchange of cations in zeolites with NH_4^+ is accomplished with NH_4NO_3 or NH_4Cl solutions [5,11]. However, in the present work we observed that longer exchange periods with NH_4NO_3 produced a shift of the TEA desorption peaks from the acid sites groups in the zeolite-Y to lower temperatures, i.e. the acidity strength decreased. Therefore, it is intended to

0040-6031/89/$03.50

increase the period of NH_4NO_3 treatment to 45 h although complete exchange with NH_4^+ has been found to be accomplished after only 18 h. DSC thermograms for the treated zeolites and their TEA desorption are given.

EXPERIMENTAL

Treatment with NH_4NO_3 solution

5 g samples of NaY zeolite were boiled in 50 ml of 1 M NH_4NO_3 solution under reflux. The boiling periods were 9, 13.5, 18, 27, 36 and 45 h. After each treatment period, the flask was allowed to cool overnight, was washed with distilled water until free of NH_4NO_3, filtered and dried overnight at 110 °C.

DSC measurements

A Mettler DSC-30 unit of the TA-3000 system was used with the following conditions: initial temperature, 50 °C; heating rate, 20 K; final temperature, 600 °C; full scale range, 25 mW; mass, 2.5 mg; purge gas, nil; and plot, 10 cm. The conventional DSC technique (reference cell empty

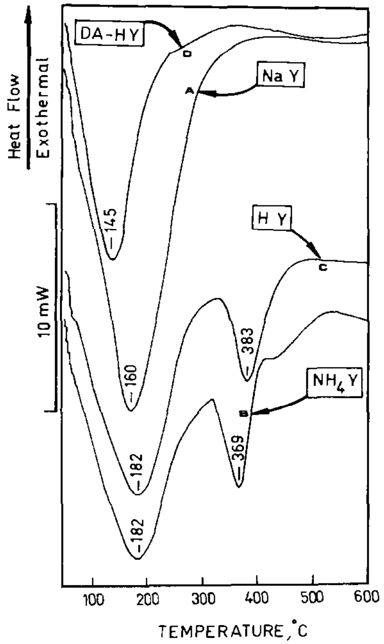

Fig. 1. DSC thermograms for the various forms of zeolite-Y.

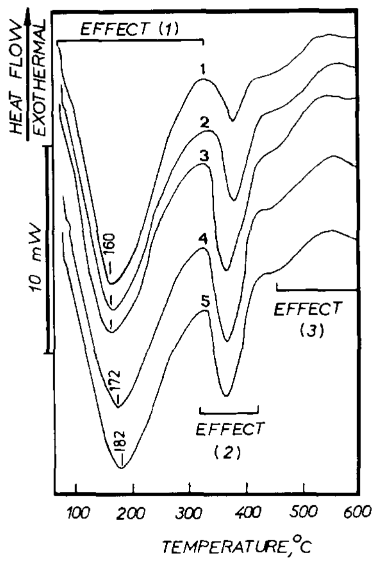

Fig. 2. DSC thermograms for NH_4-Y forms produced via treating Na-Y with NH_4NO_3 solutions for: 1, 9 h; 2, 13.5 h; 3, 18 h; 4, 27 h; and 5, 36 and 45 h.

aluminium pan) was used to obtain the DSC thermograms of the different zeolite forms (Fig. 1) and the NH_4NO_3-treated forms (Fig. 2), whereas the nullifying DSC technique was used for measuring acidity distribution (Fig. 3). In the nullifying technique, the sample cell contains a TEA-presorbing sample, whereas the reference cell contains the same weight of the corresponding TEA-free sample.

Presorption of TEA in the zeolite forms

The zeolites were calcined at 530 °C for 4 h, left to cool in the muffle furnace to 60 °C, and then soaked in TEA overnight. Excess TEA was removed before heating at 80 °C for 1 h before the DSC measurements.

RESULTS AND DISCUSSION

The DSC thermograms obtained for the different dried forms of zeolite-Y are given in Fig. 1. Thermogram A shows that NaY gives a single large intensity endothermal dehydration peak with a ΔH value of 578 J g^{-1} covering a temperature range of 50–350 °C with a maximum at 160 °C. The NH_4Y-form, prepared via long treatment with NH_4NO_3 (45 h) (thermogram B), gives two endotherms covering a temperature range of 50–400 °C with maxima at 182 and 369 °C and enthalpies of 322 and 76.5 J g^{-1} respectively, and a third exothermal effect between 435 and 600 °C with a maximum at around 530 °C. This high temperature effect is attributed to decomposition

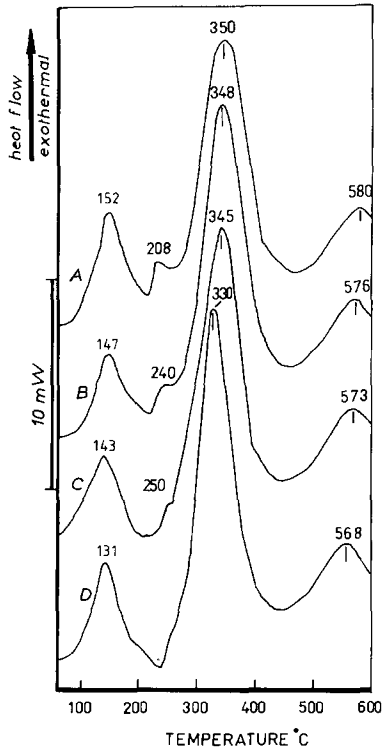

Fig. 3. DSC thermograms for TEA-desorption from the acid sites groups in H–Y zeolites produced via treating Na–Y with NH_4NO_3 solutions for: A, 9 h; B, 27 h; C, 36 h; and D, 45 h.

of the NH_4-form to the H-form and NH_3 gas. Such decomposition has been recently observed by the authors using the NH_4-forms of zeolons 400, 500, 700 and 900 [5].

$$NH_4\text{-}Y \xrightarrow{\text{heat}} H\text{-}Y + NH_3$$

A more distinct indication that the 369 °C endotherm is due to dehydration and not to ammonia evolution is the presence of the slightly shifted 383 °C endotherm in thermogram C for the NH_4-form calcined at 530 °C for 4 h. Such calcination completely decomposes NH_4Y to HY. Moreover, thermogram C (for HY) does not contain the 530 °C exotherm. The 369 and 383 °C endotherms in thermograms B and C (for the NH_4- and H-forms), respectively, yield more or less equal ΔH values, indicating an equal number of water molecules that are more strongly adsorbed on the NH_4- and H-forms than the water molecules adsorbed on NaY. As H^+ is less voluminous than NH_4^+, stronger water adsorption on the H-form (383 °C) than on the NH_4-form (369 °C) is logical.

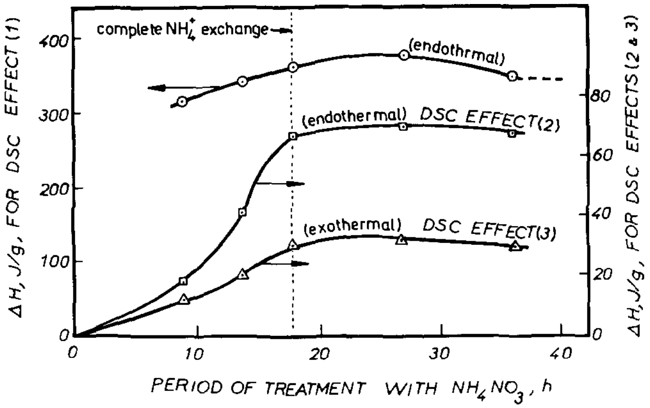

Fig. 4. Plot of ΔH values computed for effects 1, 2 and 3 in Fig. 2.

The dealuminated HY-form gives a weakly adsorbed water peak with lower enthalpy ($\Delta H = 215$ J g^{-1}), i.e. 37% of that in NaY and 54% of that in NH_4Y- and HY-types.

Influence of the period of treatment with NH_4NO_3 solution

Figure 2 shows the DSC thermograms obtained for several NH_4-exchanged Y samples produced by treating NaY with fresh NH_4NO_3 solutions for 9, 13.5, 18, 28, and 36 h. All thermograms give three DSC effects similar to thermogram B in Fig. 1. In thermogram 1 of Fig. 2, the first endotherm has a ΔH value of 315 J g^{-1} that increases with increasing the treatment period up to 374 J g^{-1} after 27 h, beyond which ΔH declines to 322 J g^{-1} after 36 h. The peak temperature is 160 °C for samples treated up to 18 h (Fig. 2, thermograms 1–3) then shifts to 172 and 182 °C after 27 and 36 h treatments (Fig. 2, thermograms 4 and 5), respectively. However, effect 2 in Fig. 2 (2nd dehydration peak) and effect 3 (de-ammoniation exotherm) do not seem to suffer temperature shift, although their ΔH values increase as is shown in Fig. 4 up to 18 h, beyond which insignificant ΔH change occurs.

The acidity strength distribution in the H-forms produced via different treatment periods with NH_4NO_3 solution is depicted in Fig. 3. TEA desorption from the groups of acid sites indicates: (a) a weak group in the low temperature region giving peaks with maxima in the range 131–152 °C; (b) an intermediate strength acid sites group with peaks having maxima between 330 and 350 °C; and (c) a strong group with peaks having maxima appearing between 568 and 580 °C. Figure 3 shows that the increase of the treatment period decreases the strength of the three acid sites groups irrespective of the Na/NH_4 exchange extent. Although Na^+ in NaY has been completely exchanged with NH_4^+ after an NH_4NO_3 treatment period

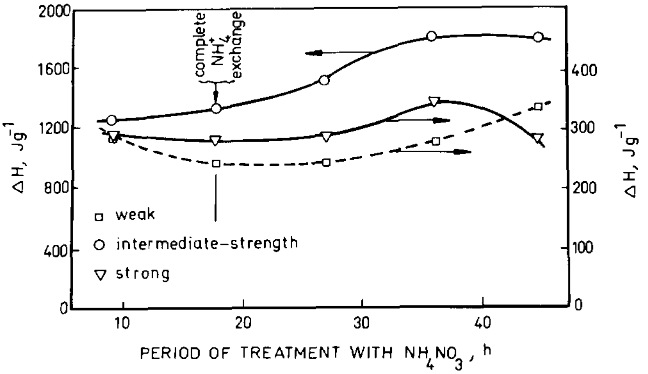

Fig. 5. Plot of ΔH values computed for TEA-desorption from the three groups of acid sites in H–Y for forms prepared via treating Na–Y at different periods.

of 18 hours, the NH_4NO_3 solution can still weaken the acidity strength of all acid sites groups for up to a period of 45 h, as well as varying the quantity of these acid sites, also for upto 45 h (Fig. 5). Figure 5 shows relative changes in the quantity of acid sites in HY-forms as a function of increasing the NH_4NO_3 treatment time of NaY. Figure 5 shows that acid sites of intermediate strength are the most numerous. Their ΔH values for the 9 h treated sample is 1260 J g^{-1}. ΔH then gradually increases with the treatment period up to a maximum of 1818 J g^{-1} after 36 h, beyond which ΔH remains almost unchanged up to 45 h. The weak and strong acid sites are of almost comparable quantities but are fewer in number than the intermediate stength sites. Samples treated up to 27 h seem to possess the same number of strong acid sites, then a maximum is reached after 36 h, beyond which the quantity gradually declines.

It is evident from this study that treatment with NH_4NO_3 has not only exchanged Na^+ with NH_4^+ but has also modified the acid sites strength distribution in the H-forms obtained by calcination of the NH_4-forms produced. This property is of prime importance in using zeolites as catalysts. Moreover, correlation of changes in the ΔH values obtained for DSC effects (2) and (3) of Fig. 4 as a function of NH_4NO_3 treatment period with Na content in treated zeolites (determined by atomic absorption) gives an excellent relationship. This indicates that either one or both DSC effects can be used to follow NH_4^+ exchange in, at least, NaY zeolite.

ACKNOWLEDGEMENT

Professor A.K. Aboul-Gheit thanks the Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt, for a leave of absence.

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