

## Effect of decationation and dealumination of zeolite Y on its acidity as assessed by ammonia desorption measured by differential scanning calorimetry (DSC)

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### Abstract

Zeolite NaY was decationated step-wise until the H-form was obtained (HY), and zeolite HY was dealuminated step-wise to increase its  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from 4.8 to 8.5. Ammonia was adsorbed on all the zeolite forms and was then desorbed thermally in a DSC cell, making use of the programmed temperature-increasing facility available in the DSC system. The total acidity of the zeolite was found to increase with decationation and decrease with dealumination. Strong acidity was found to increase with both decationation and dealumination, whereas weaker acidity decreased. The strength of strong acid sites increased further, whereas that of weaker acid sites decreased in both treatments.

### INTRODUCTION

The decationation and dealumination of zeolites lead to a marked change in their properties including acidity and shape selectivity which are of great importance in production of industrial catalysts [1]. Decationation increases the concentration of acid sites [2]. Barthomeuf demonstrated the linear decrease in the acid hydroxyl content and the increase in acid strength with dealumination [3,4]. Vedrine et al. [5] reported that the concentration of acid sites is higher in mordenites with lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. Mortier concluded that the acidity strength of zeolitic protons increases with increasing residual hydrogen charge and Al content [6], and confirmed that the catalytic efficiency increases linearly with residual hydrogen charge on the protons of several zeolites.

Titration with coloured indicators covering a whole  $\text{p}K_a$  range have been used to estimate the acidity distribution in acidic solids [7,8]. Differentiation between Lewis and Bronsted acid sites can be made using IR spectra of zeolites with presorbed pyridine [9] and their IR spectra after successive heating [10]. Temperature-programmed desorption (TPD) of presorbed pyridine is used for a rough estimate of the acid site distribution [11]. In this technique and in the DSC method under study, the strongest

acid sites desorb a presorbed base at the highest temperatures. However, the TPD method has been criticised [12]. Moreover, the IR methods (which are considered the most satisfactory) indicate that protons are not detectable in some strongly acidic Y zeolites [13] and that steamed mordenites [14] with no detectable IR OH-bands are active in toluene disproportionation.

## EXPERIMENTAL

### *Decationation of the zeolite NaY*

Decationation of the fully cationated zeolite NaY (10.25 wt.%) was carried out by exchanging with 1 M  $\text{NH}_4\text{NO}_3$  solution in cycles, using fresh solution in each cycle, to obtain  $\text{NaNH}_4$  Y-forms with decreasing Na contents. These forms were dried at 110 °C overnight, then calcined at 550 °C for 4 h in air. The NaHY forms produced ( $\text{NaHY}_1$ ,  $\text{NaHY}_2$ ,  $\text{NaHY}_3$  and HY) contained the Na contents given in Table 1, as determined by atomic absorption.

### *Dealumination of zeolite HY*

Zeolite HY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.8$ ) was dealuminated with hot N HCl solution under reflux in cycles of fresh acid solution, to obtain the successively dealuminated forms  $\text{DAHY}_1$ ,  $\text{DAHY}_2$ ,  $\text{DAHY}_3$  and  $\text{DAHY}_4$ . The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio determined for these forms is given in Table 1. The aluminium content was determined by atomic absorption.

TABLE 1

Effect of decationation and dealumination steps of zeolite Y on its acidity strength distribution

Zeolite form	Na (wt.%)	$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	Strong acid sites %	Weak acid sites %	Maximum of peaks (°C)	
					1st	2nd
NaY	10.25	4.8	1.9	98.1	175	341
$\text{NaHY}_1$	7.8	4.8	5.7	94.3	164	347
$\text{NaHY}_2$	5.2	4.8	7.7	92.3	154	363
$\text{NaHY}_3$	2.65	4.8	11.0	89.0	145	368
HY	0.0	4.8	14.1	85.9	135	371
$\text{DAHY}_1$	0.0	5.7	18.0	82.0	131	379
$\text{DAHY}_2$	0.0	6.6	22.0	78.0	127	390
$\text{DAHY}_3$	0.0	7.5	30.2	69.8	124	405
$\text{DAHY}_4$	0.0	8.5	44.2	55.8	120	423

### *Ammonia adsorption*

Ammonia adsorption on the zeolite forms obtained by decationation and dealumination, was carried out in a silica tube furnace in the form of pressed tablets. The tube was evacuated at  $5 \times 10^{-5}$  Torr whilst heating at  $530^\circ\text{C}$  to remove water, and then cooled under vacuum to  $50^\circ\text{C}$ . Ammonia was passed through the zeolite at a flow rate of  $50\text{ cm}^3\text{ min}^{-1}$  for one hour. The pelleted zeolite was ground rapidly into a powder and measured by DSC.

### *Ammonia desorption in the DSC system*

The apparatus used in this study was a DSC-30 unit of the Mettler system TA 3000, with a gold sensor. Standard aluminium crucibles with a hole in the centre of the cover were used in both sample and reference cells. Presorbed  $\text{NH}_3$  was desorbed in the DSC cell with nitrogen as eluent ( $50\text{ cm}^3\text{ min}^{-1}$ ) using the following conditions: start temperature,  $50^\circ\text{C}$ ; rate,  $10^\circ\text{C min}^{-1}$ ; end temperature,  $600^\circ\text{C}$ ; plot, 10 cm; full scale range, 25 mW.

## RESULTS AND DISCUSSION

This work is concerned with two treatments of zeolite Y; their effect was followed using differential scanning calorimetry (DSC). First, the Na form of zeolite Y (fully cationated) which contains 10.25 wt.% Na, was decationated in a step-wise manner using an ion-exchange procedure [15], through the forms  $\text{NaHY}_1$ ,  $\text{NaHY}_2$ ,  $\text{NaHY}_3$  and HY (Table 1) which contain, respectively, 7.8, 5.2, 2.65 and 0.0 wt.% Na, while the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was fixed at 4.8. Second, the HY form was dealuminated step-wise [15] through the forms  $\text{DAHY}_1$ ,  $\text{DAHY}_2$ ,  $\text{DAHY}_3$  and  $\text{DAHY}_4$  which possess, respectively,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 5.7, 6.6, 7.5 and 8.5. Ammonia was chemisorbed on these decationated and dealuminated forms of zeolite Y and was distributed on the different zeolitic acid sites of different strengths; the ammonia was then desorbed thermally in the DSC cell, making use of the programmed temperature-increase facility available in the DSC system. An inert atmosphere was used to exclude the possibility of oxidation. The ammonia desorption thermograms (Figs. 1 and 2) show, in general, two distinct DSC effects: a low-temperature peak appearing between  $50^\circ\text{C}$  and  $\approx 300^\circ\text{C}$ , which is attributed to  $\text{NH}_3$  desorption from the weaker acid sites in the zeolitic channels; and a high-temperature peak appearing between  $\approx 300^\circ\text{C}$  and  $\approx 500^\circ\text{C}$  which is attributed to desorption from the strong acid sites. It has been suggested that the strong acid sites occur in the deepest parts of the zeolitic channels, whereas the weaker acid sites are closer to the surface [16].

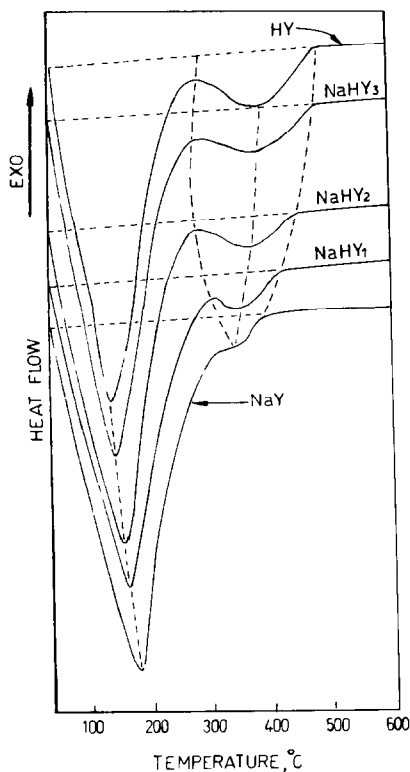


Fig. 1. DSC thermograms for  $\text{NH}_3$  desorption from the acid sites of zeolite Y forms with different Na contents.

Figure 1 shows that the low-temperature peak decreases somewhat as  $\text{Na}^+$  ions are progressively replaced by  $\text{H}^+$ , whereas the magnitude of the high-temperature peak increases. Figure 3 shows the enthalpy of ammonia desorption ( $\Delta H$ ) from the acid sites of zeolite Y forms, plotted quantitatively as a function of decationation. The total acid sites (weak + strong) increase linearly due to a significant increase in the number of strong acid sites which overcompensates for the decrease in the weaker sites. The fully cationated form ( $\text{NaY}$ ) gives a low  $\Delta H$  value of  $15 \text{ J g}^{-1}$  for  $\text{NH}_3$  desorption from its strong acid sites. The value increases successively with decationation to reach  $121 \text{ J g}^{-1}$  for the fully decationated form ( $\text{HY}$ ). However, the ammonia desorption enthalpy from weaker acid sites decreases from  $773$  to  $735 \text{ J g}^{-1}$ . It can thus be assumed that zeolite  $\text{NaY}$ , with only a negligible fraction of its acid sites being strong ones (which are important in catalysing many carbonium ion reactions), can acquire a significant number of strong acid sites on decationation. This may be in accordance with Wendlandt's view that alkaline and alkaline earth cations, when introduced in hydrogen mordenite, cause poisoning of its strong acid sites [2].

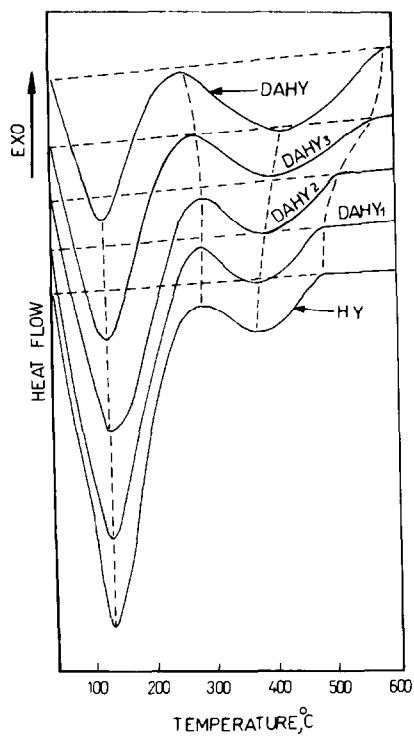


Fig. 2. DSC thermograms for NH<sub>3</sub> desorption from the acid sites of zeolite Y forms with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios.

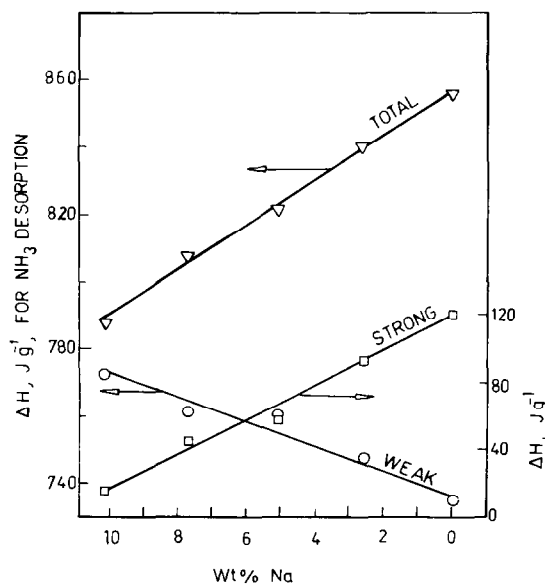


Fig. 3. Enthalpy of ammonia desorption from the acid sites of zeolite Y as a function of Na content.

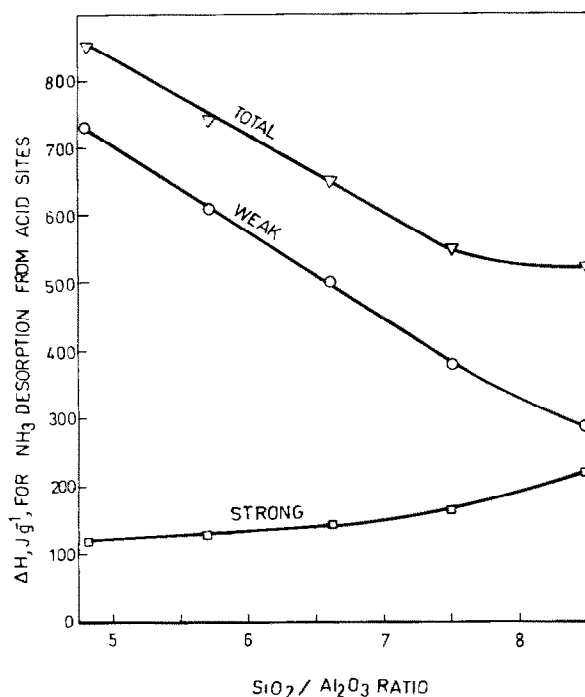


Fig. 4. Enthalpy of ammonia desorption from the acid sites of zeolite Y as a function of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio.

On the other hand, the step-wise increase of the silica/alumina ratio of HY via step-wise dealumination gives an additional increase in the number of strong acid sites (Fig. 2). The enthalpy obtained for ammonia desorption from the strong acid sites of HY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.8$ ) is increased from 121 to 231  $\text{J g}^{-1}$  after increasing its  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio to 8.5 by dealumination. The number of these acid sites (catalytically active) is almost doubled following dealumination of HY. Figure 4 shows that the total acid sites and the weak acid sites are decreased by successive dealumination, whereas the strong acid sites increase. Using IR spectroscopy, Barthomeuf [3,4] assumed that the acid strength of protons increases by dealumination, whereas applying an electronegativity model, Mortier [6] concluded that protons of higher acid strength are formed. Vedrine et al. [5] reported that the total concentration of acid sites is substantially higher in lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mordenite.

Figures 3 and 4 show that both decationation and dealumination decrease weak acidity, almost linearly, and increase strong acidity. However, decationation increases the total acidity, whereas dealumination decreases it. This is because decationation slightly decreases weak acidity, whereas dealumination significantly decreases it (from 735  $\text{J g}^{-1}$  for the HY form to 291  $\text{J g}^{-1}$  for the DAHY form).

Quantitatively, starting with NaY, strong acid sites increase from 1.9% of the total to 14.1%, following decationation to HY; they then increase to 44.2% of the total after dealumination of HY to yield an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 8.5.

Figure 1 and Table 1 also show that the maximum of the low-temperature endotherm shifts to a lower temperature with increasing decationation, i.e. the weak acid sites become of lower strength after decationation. This may indicate an increase in hydrogen-bonding acidity [12]. However, the maximum of the high-temperature DSC endotherm shifts to higher temperatures following decationation, i.e. strong acid sites become stronger on removing  $\text{Na}^+$  ions and replacing them with  $\text{H}^+$ . Protonic acidity, which is created by decationation, is known to be of high strength [6]. Figure 2 and Table 1 also show that step-wise dealumination has slightly shifted the maximum of the low-temperature endotherm, whereas it has significantly increased the temperature at which the maximum of the high-temperature effect appears.

It should be mentioned that the increase in the strength of the strong acid sites of zeolites brought about by removal of their cations and of aluminium, has been characterised by many techniques [1–6], whereas the decrease in the strength of the weaker acid sites by these treatments has not been previously recognised.

The use of DSC to follow the desorption of  $\text{NH}_3$  from zeolites in an inert atmosphere is very useful for characterising the acidity strength distribution of zeolites, as  $\text{NH}_3$  does not decompose in the temperature range employed. Moreover, the high temperature range used in the DSC measurements is also the range within which most of the reactions requiring zeolite catalysts take place. Hence, the characterisation of the acid site strength distribution by DSC may provide a true indication of the acidity. Other methods, such as the acid–base titration of the catalyst acidity which is carried out at room temperature, may not give a true evaluation of the acidity distribution at the reaction temperatures.

From the data of this work it is concluded that: decationation increases the total acidity of zeolite Y due to a greater increase in the number of strong acid sites which overcompensates for a smaller decrease in the number of weak acid sites, and, moreover, the strength of the weak sites becomes weaker whereas that of the strong acid sites becomes stronger; dealumination of HY decreases the total number of acid sites although the number of strong acid sites increases, and the weak acid sites slightly weaken in strength whereas the strong acid sites become stronger.

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