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The Deammoniation Reaction of Ammonium X Zeolite

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The deammoniation of fully ammonium-exchanged zeolite X has been studied using differential thermal analysis. Deammoniation is shown to occur in two endothermic steps that correspond to the release of NH_3 from ammonium ions in small- and large-pore systems, respectively. Dehydroxylation of the resultant hydrogen-X zeolite occurs at a relatively low temperature of 175°C. The thermograms of NH_4X and NH_4Y deamnoniation are compared.

INTRODUCTION

Although the study of ammonium-exchanged Y zeolite using differential thermal analysis (DTA) has been previously reported (*1*, *2*), a similar investigation of its isotype, X zeolite, is not found in the literature. X- and Y-type zeolites are identical in framework structure but differ in Si/Al ratio. The resultant lattice-dimension differences between X and Y are small, with lattice parameter a = 24.86–25.02 Å for X-type zeolite and 24.61–24.85 Å for Y-type zeolite (*3*). Using DTA, we can compare these closely related zeolites with respect to their thermochemical nature and with supplementary experiments obtain an understanding of the acidity relative to Si/Al ratio. One apparent difficulty which has discouraged DTA studies on NH_4X in the past is the preparation of a pure, fully ammonium-exchanged X zeolite. In previously reported work the NH_4X samples were only partially exchanged and always accompanied by unwanted hydronium ion exchange. Kühl and Schweizer (*4*) reported a maximum 75% NH_4X with 12 hydronium ions per unit cell included in the structure. Bolton and Lanewala (*2*) obtained a 74% exchanged sample at reflux temperature using 10% NH_4Cl solution, the degree of hydronium exchange was not reported. The difficulty of NH_4X preparation and the accompanying hydronium uptake have also been observed by Olson (*5*) and Sherry (*6*). We have successfully prepared an essentially fully exchanged NH_4X sample with a minimum degree of hydronium exchange. The DTA thermograms of this NH_4X and some of its ion-exchanged derivatives will be reported in this paper together with the interpretation relative to deammoniation, dehydroxylation, and cation locations.

EXPERIMENTAL METHODS

Apparatus and Procedure

An R. L. Stone differential thermal analyzer Model DTA 202 was used with an SH-BE-type sample holder. Details of the equipment can be found elsewhere (*1*). The operating conditions of all the DTA runs were as follows:

A 10-mg sample was heated at a rate of 10°C/min with purge gas, purified N_2, flowing at the rate of 100 ml/min. Calcined

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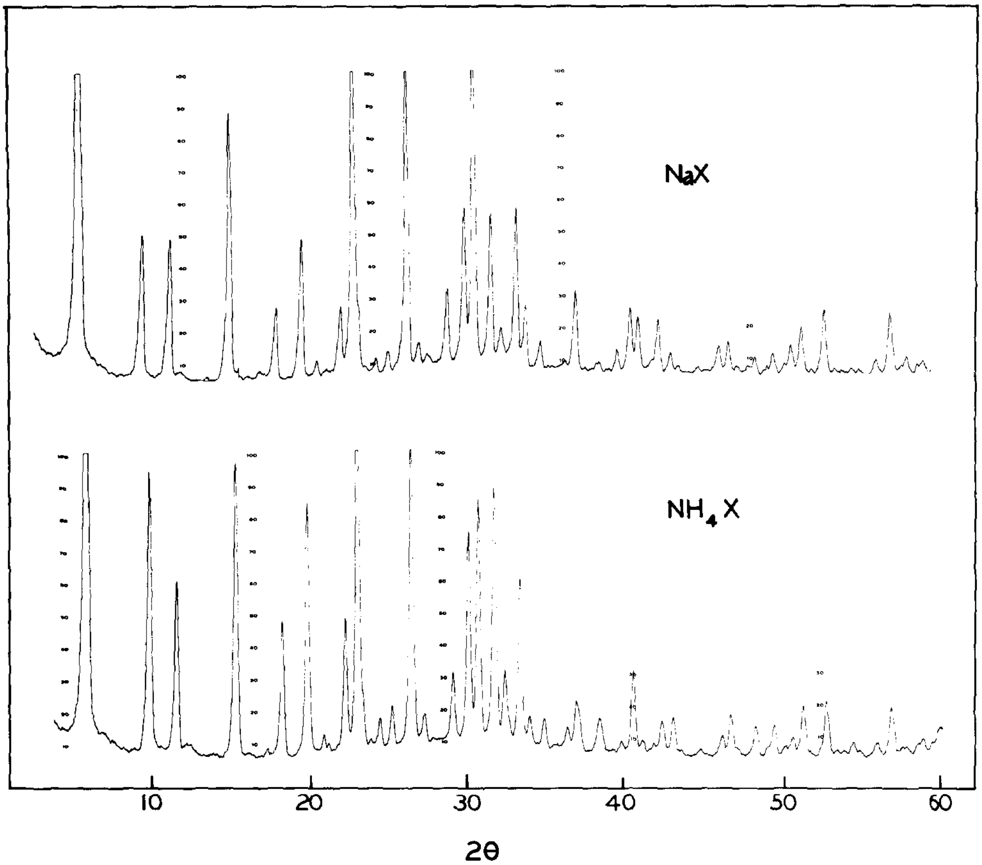

FIG. 1. X-Ray powder patterns of NH_4X and its NaX base.

tabular alumina, Alcoa T-61, of mesh size 100–140 was the reference material. The output range was set at 100 μV maximum.

A few TGA runs were done on a Dupont 990 thermal analyzer coupled with the automatic titration system from Radiometer of Copenhagen, Denmark. A procedure similar to that reported by Kerr and Chester (7) was used.

Sample Preparation

The samples used in this study were prepared from pure synthetic X-type faujasite obtained from the Linde Division of Union Carbide Corporation. Three different cationic forms were prepared by ion exchange.

1. 93% Exchanged NH_4X. Synthetic NaX was exchanged with a hot (80°C) 1:1 mixture of 0.5 *N* NH_4Cl and 0.5 *N* NH_4OH continuously. This procedure was chosen for the following reasons: (1) the presence of NH_4OH suppresses hydronium ions exchange; (2) the high temperature facilitates the Na removal in the small pores; and (3) continuous flow ion exchange is far more efficient than batch exchange. Samples were taken periodically and analyzed for the degree of exchange. The bulk of the sample was kept in wet cake form all the time. When the Na content was found to be lower than 0.2% (w/w), the entire sample was washed with about 200 ml of 0.2 *N* NH_4OH and dried under vacuum at room temperature.

The resultant NH_4X was highly crystalline. This is clearly shown by comparing its X-ray diffraction pattern with that of the original NaX in Fig. 1. There

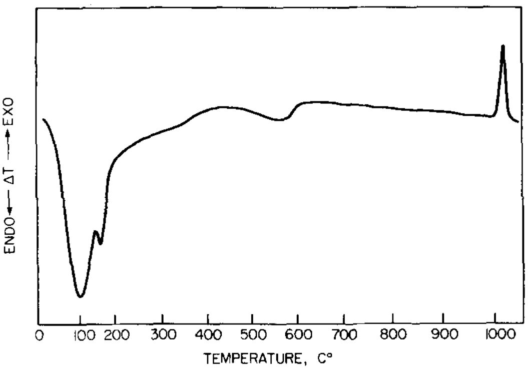

FIG. 2. DTA thermogram of NH_4X (residual Na: 0.1% w/w).

is considerable lattice expansion with the lattice parameter increasing from 24.95 to 25.14 Å, probably caused by the substitution of the larger NH_4^+ cation for Na^+ cation. Olson (*5*) has also observed a lattice expansion in his NH_4^+-exchanged X-type faujasite but to a lesser degree. Chemical analysis gave a unit cell composition of $(NH_4)_{78}(H_3O)_5NaAl_{84}Si_{108}O_{384}$.

A small portion of this NH_4X sample was back exchanged into Na form which was found to have the identical crystallinity, lattice parameter, and chemical composition of that of the original NaX base material. This result provides additional evidence that the prolonged high-temperature exchange procedure has neither affected the crystal integrity nor changed the Si/Al ratio of the X-type faujasite sample.

The possible contamination by physically sorbed NH_4^+ or NH_3 on the NH_4X due to the NH_4OH washing step was checked using a 0.2 NH_4OH-washed and vacuum dried NaX sample. The residual N content of the NaX sample was found to be negligible.

2. Partially exchanged (60%) NH_4X. Synthetic NaX was exchanged eight times with excess of the 0.5 *N* NH_4Cl and 0.5 *N* NH_4OH mixture at room temperature to produce a 60% exchanged NH_4X. Theng and co-workers (*8*) reported that the maximum extent of NH_4 exchange on NaX at room temperature is 62%. Our final NH_4OH-washed and vacuum-dried product had a unit cell composition of

$$(NH_4)_{50}(H_3O)_3(Na)_{31}Al_{84}Si_{108}O_{384}.$$

3. $CsNH_4X$. The previously described 93% ammonium-exchanged sample was exchanged with an excess of 0.1 *N* CsCl solution at room temperature. The sample was then water washed and vacuum dired. The product was found to have the unit cell composition

$$Cs_{53}(NH_4)_{30}NaAl_{84}Si_{108}O_{384}.$$

RESULTS AND DISCUSSION

The DTA thermogram of the 93% ammonium-exchanged X zeolite sample obtained in a N_2 atmosphere is shown in Fig. 2. There are three endotherms and one exotherm over the temperature range studied. The first endotherm at 100°C is the most intense one, representing the desorption of physically sorbed water from zeolite. The second endotherm reaches its peak at 175°C while the third endotherm is a broad shoulder on the second peaking at 270°C and terminating at about 350°C. These two endotherms at 175 and 270°C are found to be derived from the deammoniation reaction, as confirmed by the effluent gas titrations, and are assigned to NH_3 dissociation from NH_4^+ in the small-pore (sodalite cage) and large-pore (supercage) systems, respectively. The irregular small bump between 580 and 600°C should be ignored because its presence is seen in all the blank runs. The last peak at 1040°C is exothermic and is assigned to mullite formation. Crystallinity measurements of selected samples established the transition from amorphous to mullite at about 1040°C.

The crystal structures of X and Y zeolites have been determined (*9*) and they possess the same faujasite structure of connecting sodalite cages and supercages except that the ratio of Si to Al

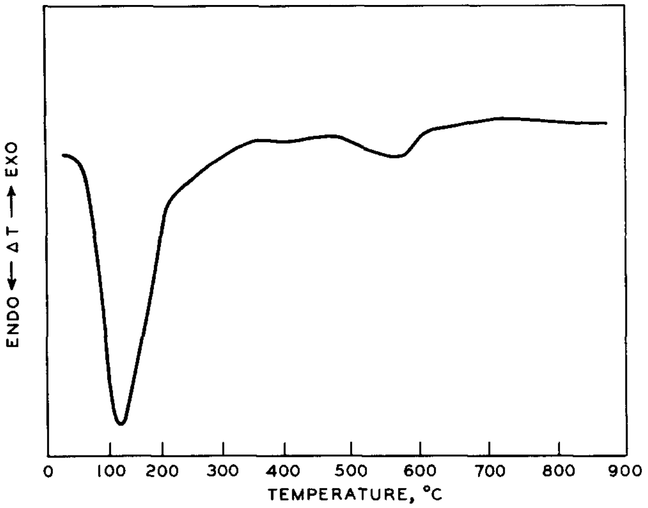

FIG. 3. DTA thermogram of partially exchanged NH_4X (residual Na: 5.5% w/w).

in X is 1.25 and that of Y zeolite is higher. The site occupancy and position of various cations in the structure have also been reported (*8–10*). Theng *et al.* (*8*) and Barrer *et al.* (*10*) have independently shown that NH_4 and Cs ions can only replace about 62% of the Na ions in X zeolite by ion exchange at room temperature. They believe that 32 out of the total 85 Na ions in NaX are located in small pores (sodalite cage) which are connected to the large pores through openings of 2.2 to 2.5 Å diameter. The NH_4 and Cs ions are too large to enter the sodalite cage at room temperature, and therefore, can only exchange those Na ions in the large pores (about 62% of the total). Using the same reasoning, the NH_4 ions in our partially ammonium-exchanged (60%) X zeolite should be located in large pores and those in the $CsNH_4X$ sample located in small pores. The DTA thermogram of the partially exchanged NH_4X (Fig. 3) shows no clear 175°C endotherm while retaining the 270°C shoulder and that of $CsNH_4X$ has essentially eliminated the 270°C broad

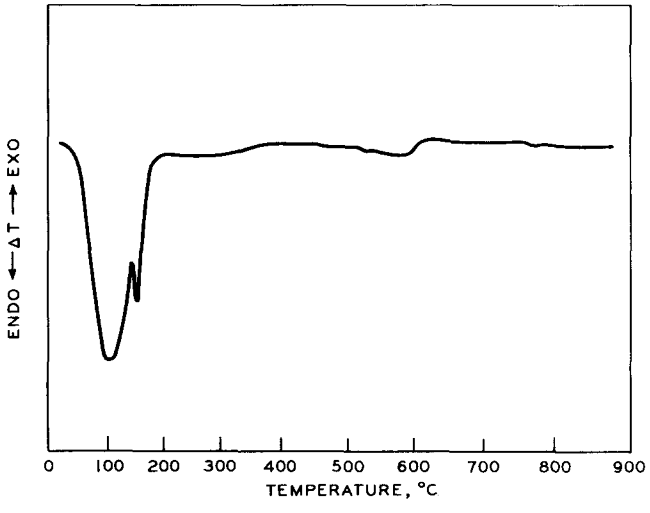

FIG. 4. DTA thermogram of $CsNH_4X$.

TABLE 1

Comparison of DTA Thermograms of NH_4X and NH_4Y Obtained in N_2 Atmosphere

Reaction	Endothermic temperature (°C)	
	NH_4X	NH_4Y
Physical H_2O desorption	100	100
NH_3 dissociation		
Small pore	175	250
Large pore	180–350[a]	250–400[a]
Dehydroxylation	—	650

[a] Approximate temperature range of the broad peak.

shoulder while retaining the 175°C peak (Fig. 4). These results support our endotherm assignment in NH_4X.

The corresponding endotherms of NH_4Y at 250 and 350°C, as reported earlier by Chu (*1*), were about 70°C higher. The temperature difference indicates that the dissociation of NH_3 from sites in NH_4X requires less energy than the similar reaction in NH_4Y. It also implies HX is a weaker acid than HY.

The differences between the thermograms of NH_4X and NH_4Y zeolites are summarized in Table 1, the following three findings are noteworthy.

(1) The deammoniation reaction of NH_4X in inert atmosphere is also endothermic as would be expected from the NH_4Y work.

(2) The deammoniation temperatures of NH_4X were 70°C lower than those of NH_4Y under same operating condition.

(3) There was no observable dehydroxylation peak in NH_4X.

The first observation confirms our previous conclusion (*1*) that deammoniation of ammonium-exchanged zeolite is an endothermic reaction and that the DTA thermogram of these zeolites obtained in inert atmosphere should consist of endotherms only.

The absence of a dehydroxylation peak in NH_4X thermogram is puzzling. X-Ray diffraction shows that the sample lost an appreciable amount of crystallinity even below 200°C and the sample is essentially amorphous at 400°C. It is, therefore, quite possible that the reactions of deammoniation, dehydroxylation, and loss of crystallinity proceed simultaneously and the less intensive endotherm of dehydroxylation is masked by the more intensive ones of deammoniation. A thermogravimetric analysis and titration were carried out to obtain the differential water loss accompanying deammoniation (*11*). Figure 5 shows the derivatives of the water evolution from the NH_4X and from sample of NH_4Y, $(NH_4)_{49}(H_3O)_3Al_{52}Si_{140}O_{384}$. The NH_4Y

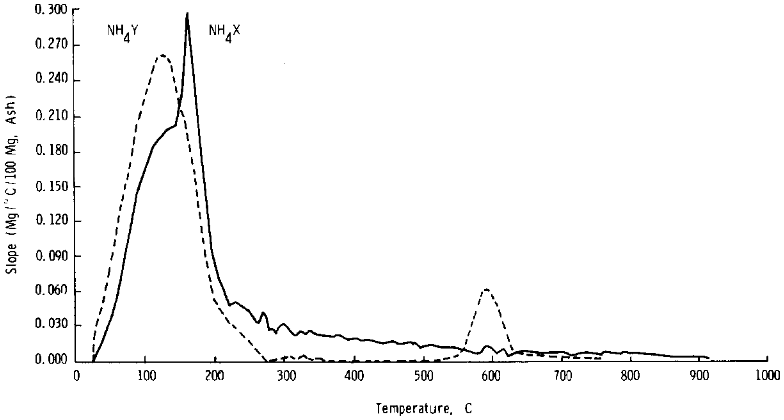

FIG. 5. Derivative H_2O loss of NH_4X.

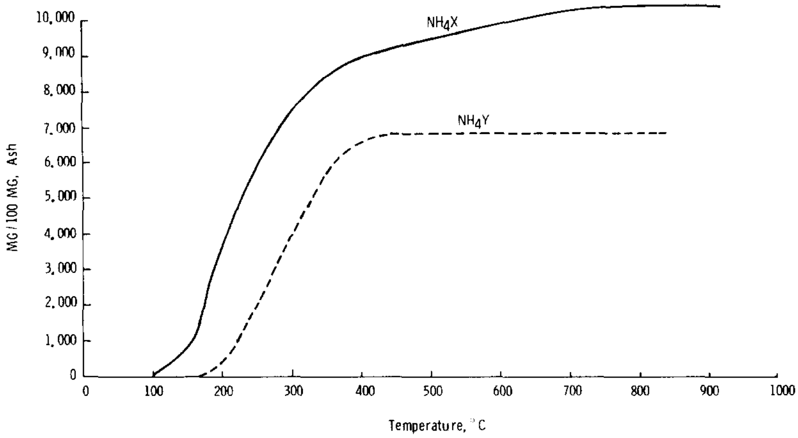

FIG. 6. NH_3 evolution of NH_4X and NH_4Y.

loses physically adsorbed water up to 300°C; then the water evolution ceases until dehydroxylation commences at about 525°C. The NH_4X also loses physically adsorbed water but suddenly a pronounced additional water loss peaks at around 175°C and a slow evolution of water continues as temperature is increased. At the same temperature range, the rate of NH_3 evolution from NH_4X is also intensified as shown in Fig. 6. The NH_3 evolution of NH_4Y is included for comparison. It is obvious that dehydroxylation and deammoniation are occurring simultaneously for NH_4X whereas they are separate and distinct steps for NH_4Y. The endotherm at 175°C in NH_4X thermogram might be partly attributable to dehydroxylation. The simultaneous crystallinity loss and dehydroxylation of NH_4X at a relatively low temperature have been reported by many other investigators (*2*, *5*, *12*).

We were concerned about the possibility of significant cation scrambling within the zeolite structure upon heat treatment. For example, Cs ions in $CsNH_4X$ might enter sodalite cages and conversely NH_4 ions migrate to the super cages. Such cation scrambling would cause uncertainty in our endotherm assignment. A CsNaX sample prepared by the same procedure as of $CsNH_4X$ was calcinated at 550°C for 10 h and then reexchanged with CsCl solution. Subsequent analysis shows no change in Cs and Na content in the zeolite sample. The Na ions in CsNaX are, therefore, indeed localized in sodalite cages even at high temperatures. This experiment gives some assurance that it is unlikely that ion scrambling will occur when one ion is restricted by its size, such as Cs ion in this case.

There are total eight supercages per unit cell in X zeolite. The total void space inside these cages can be calculated to be 9200 Å^3 by assuming the cages are spherical in shape and 13 Å in diameter (*3*). The volume of a hydrated ammonium ion is 152 Å^3 (hydrated ion radii of NH_4 = 3.31 Å (*13*)).

Therefore, assuming complete utilization of void space in the super cages, a maximum of 60 hydrated NH_4 ions can be accommodated in the eight super cages. This is in good agreement with the ion-exchange information that states a maximum of 62% NH_4^+ exchange or 52 NH_4 ions per unit cell when exchanged at room temperature since complete utilization of the supercage void volume is not probable. When NH_4 ion exchange is conducted at higher temperatures, the hydration shell is reduced and, hence, the radius of the hydrated ammonium ion. This reduction in hydration shell is apparently sufficient to allow penetration of the small sodalite cages by the NH_4 ions since a fraction of the NH_4 ions introduced by high-temperature exchange cannot be removed by back exchange at room temperature with Cs^+ that has a hydrated radius of 3.29 Å. Furthermore, since X and Y faujasite have the same supercage volume, the additional NH_4 ions resulting from the lower Si/Al in NH_4X vs NH_4Y must be located in the sodalite cages, i.e., 16 for NH_4Y and 32 for NH_4X.

SUMMARY

The NH_4X DTA thermogram has been obtained in inert atmosphere. The two endotherms at 175 and 270°C have been shown to be associated with the decomposition of NH_4 sites in small-pore and large-pore systems, respectively. The above temperatures are 70°C lower than the corresponding endotherms in NH_4Y. HX zeolite is a weaker acid than its isotype HY based on bond energy considerations.

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