

Structural Stability of Sodium Ammonium Zeolite X

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The crystallinities of NaHX samples obtained by calcination of NaNH_4X were determined from the cyclohexane sorption capacities. The zeolite X crystal structure was found to be thermally stable if the Na/Al atomic ratio is at least about 0.6, corresponding to 32 protons/unit cell. Generalized, the results suggest that the faujasite structure with any Si/Al ratio is perfectly stable to calcination of the ammonium form, if not more than 32 protons/unit cell are generated.

The structural stability of NaHX to recalcination after water sorption was also found to be a function of the Na/Al ratio. Above a Na/Al atomic ratio of 0.6, the crystallinities were somewhat greater and, below this value, somewhat lower than a linear relation would predict. The cross-over point is expected to depend on the Si/Al ratio.

INTRODUCTION

Early work on the preparation of hydrogen zeolites led to the conclusion that zeolites of low silica to alumina ratio could not be converted completely to the hydrogen form. Attempts to prepare these hydrogen zeolites resulted in loss of crystal structure. Several papers have appeared in the literature which touch on this subject (1,2). However, these contributions do not provide sufficient information for understanding the loss of structure over the entire range of ammonium ion exchange.

Kerr's work (3) has given a clear structural picture of the effects accompanying the decomposition of NH_4^+ ions in ammonium zeolite Y under various conditions. The thermal chemistry of partially ammonium-exchanged zeolite A was reported in a recent paper (4). The thermal and hydrothermal stabilities of partially ammonium-exchanged zeolite X are discussed below.

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EXPERIMENTAL METHODS

Apparatus

Thermal analyses and some sorption capacity measurements were carried out with a DuPont Model 950 thermogravimetric (TG) analyzer. The ammonia appearing in the TG analyzer effluent was determined by passing the effluent through a solution containing 2 ml of aqueous 4% boric acid and 50 ml of water, and titrating at regular temperature intervals with sulfamic acid with methyl purple as indicator. This procedure and modifications to the TG analyzer were described by Kerr (3).

Sorption measurements at constant partial pressure were made in a Pyrex sorption unit with a mercury-switched solenoid pressure controller (5). X-Ray diffraction patterns were recorded on a Siemens horizontal powder diffractometer with $\text{CuK}\alpha$ radiation.

Reagents

The zeolite samples were prepared by ion exchange of Linde 13X zeolite (Lot No. 13970) with 0.1 N ammonium chloride solution at ambient temperature.

TABLE 1
COMPOSITION OF ZEOLITE SAMPLES (EXCLUDING SORBED WATER)

| Sample no. | Av unit cell composition | Atomic ratios | | |
|----------------------------------|---|-----------------|---------|-------|
| | | N/Al formula | Na/Al | |
| | | | Formula | Found |
| Starting material (Linde 13X) | $\text{Na}_{85}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | — | 1.0 | 1.0 |
| 1 | $(\text{NH}_4)_{10}(\text{H}_3\text{O})_9(\text{Na})_{66}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.118 | 0.776 | 0.774 |
| 2 | $(\text{NH}_4)_{22}(\text{H}_3\text{O})_9(\text{Na})_{54}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.259 | 0.635 | 0.640 |
| 3 | $(\text{NH}_4)_{34}(\text{H}_3\text{O})_8(\text{Na})_{43}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.400 | 0.506 | 0.510 |
| 4 | $(\text{NH}_4)_{42}(\text{H}_3\text{O})_8(\text{Na})_{35}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.494 | 0.412 | 0.427 |
| 5 | $(\text{NH}_4)_{48}(\text{H}_3\text{O})_8(\text{Na})_{29}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.565 | 0.341 | 0.342 |
| 6 | $(\text{NH}_4)_{64}(\text{H}_3\text{O})_{12}(\text{Na})_9[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.753 | 0.106 | 0.110 |
| 7 ^a | $(\text{NH}_4)_{29}(\text{H}_3\text{O})_4(\text{Na})_{52}[\text{AlO}_2]_{85}[\text{SiO}_2]_{107}$ | 0.341 | 0.612 | 0.614 |

^a Exchanged with 0.2 N NH_4OH .

Reagent grade chemicals were used for all ion exchange preparations. The ion-exchanged samples were characterized by complete chemical analysis. The results, calculated on a unit cell basis, are summarized in Table 1.

For the sorption measurements, reagent grade hydrocarbons dried over 13X molecular sieve pellets were used as sorbates.

Procedures

Initial decompositions were carried out by heating approximately 50 mg of sample in the TG analyzer in a helium flow of 190 ml/min at 30°C/min. The He was dried by passing it through a bed of P_2O_5 . Slower heating rates were tried with several samples (Nos. 1, 5, 6, 7) but no change in any of the measured properties was found. Therefore, the faster heating rate was used. It was always possible to separate the decomposition of the ammonium ions from the loss of chemical water at this heating rate.

To regenerate the ammonium zeolite from the hydrogen zeolite, dry ammonia gas was passed through the sidearm of the TG unit while He was passed over the balance portion of the unit. When a constant weight was reached, the ammonia flow was

turned off and the He was saturated with H_2O which desorbed physically sorbed ammonia. The hydrated ammonium zeolite could then be analyzed in the same way as the original sample.

The sorption capacity of the zeolite was determined using the TG analyzer. The He gas was saturated with the desired sorbate in a gas wash bottle. The gas mixture then passed through the TG unit over the zeolite sample at ambient temperature; the weight was recorded as a function of time. When the sample weight was constant, pure He was switched on and the He saturated with the sorbate was turned off. At the flow rate used, the partial pressure of the sorbate was reduced to less than 0.1 Torr in 3 min. These conditions cause the sorbate on the amorphous aluminosilicate portion of the sample to desorb very rapidly; the sorbate in the zeolite begins to desorb, too, but at a very much slower rate, particularly at less than 30°C. It was found experimentally that after 15 min purging with pure He, the amount of sorbate on the zeolite corresponded closely to the sorption capacity measured at a low partial pressure of the sorbate. A typical experimental run is shown in Fig. 1. At point A, pure helium was switched on and the

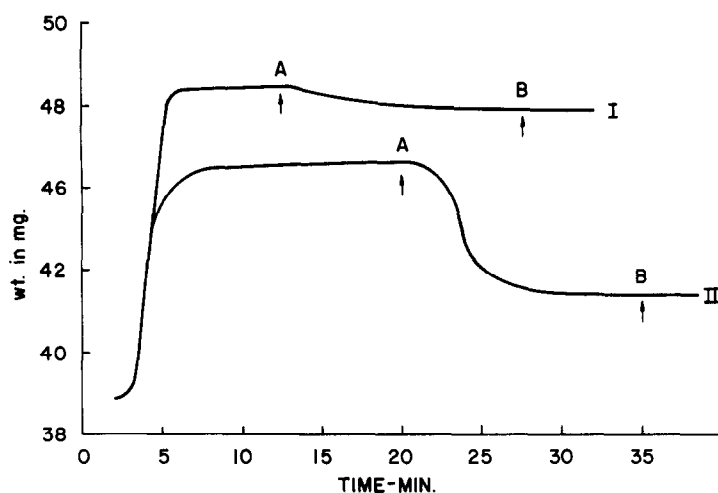


FIG. 1. Typical experimental data: cyclohexane sorption by NaHX . Unit cell composition of sample: $[\text{H}_{50}\text{Na}_{35}(\text{AlO}_2)_{85}(\text{SiO}_2)_{107}]$; He flow rate, 190 ml/min; (I) after thermal activation; (II) after sorbing H_2O on (I) and recalcining.

sorbate-loaded helium was turned off. The sorption capacity was determined from the weight at point B.

Although the experimental procedure attempts to measure an equilibrium property under nonequilibrium conditions, the displacement from equilibrium is very small for the faujasite framework structure. Sorption capacities were measured in the TG unit and at 20 mm Hg in a constant pressure apparatus (5) with cyclohexane as the sorbate. Sorption capacities determined by the two procedures agreed

within about 2.5% of each other (Table 2). The differences in the sorption capacities are similar to the reproducibility of the measurement in the constant pressure apparatus. However, the agreement of the two methods may not be as good for other zeolite structures.

RESULTS AND DISCUSSION

Ammonium Ion Exchange

Data in Table 1 show that ammonium exchange with ammonium chloride solu-

TABLE 2
SELECTED SORPTION DATA—CONSTANT PRESSURE VS TG UNIT VALUE^a

| Sample | Cyclohexane sorption | | | |
|--|----------------------------------|-----------------|------------------------|-----------------|
| | Constant pressure $p/p_0 = 0.21$ | | TG unit as described | |
| | g/100 g SiO_2 | mol/g-unit cell | g/100 g SiO_2 | mol/g-unit cell |
| NaX , $[\text{Na}_{85}(\text{AlO}_2)_{85}(\text{SiO}_2)_{107}]$ | 37.2 | 28.4 | 37.4 | 28.6 |
| 1 | 37.9 | 29.0 | 37.4 | 28.6 |
| 5 | 31.4 | 24.0 | 30.8 | 23.6 |
| 4 (after hydrothermal treatment) | 17.6 | 13.5 | 17.25 | 13.2 |
| CaX , $[\text{Ca}_{42}\text{Na}_1(\text{AlO}_2)_{85}(\text{SiO}_2)_{107}]$ | 37.3 | 28.5 | 37.1 | 28.4 |
| NiX , $[\text{Ni}_{28}\text{Na}_{29}(\text{AlO}_2)_{85}(\text{SiO}_2)_{107}]$ | 37.4 | 28.6 | 38.0 | 29.0 |
| NH_4Y , $[(\text{NH}_4)_{50}(\text{AlO}_2)_{50}(\text{SiO}_2)_{142}]$ | 24.9 | 25.2 | 25.4 | 25.8 |
| NaY , $[\text{Na}_{52}(\text{AlO}_2)_{52}(\text{SiO}_2)_{140}]$ | 28.9 | 28.9 | 28.2 | 28.2 |

^a $T = 25^\circ\text{C}$.

tion is always accompanied by hydronium ion (H_3O^+) exchange (pH of 0.1 N NH_4Cl solution is about 5). In most samples, 8 to 9 H_3O^+ /unit cell were found. Sample 6 received a more extensive ammonium chloride treatment and accepted 12 hydronium ions. In order to reduce the degree of hydronium exchange, sample 7 was prepared by ion exchange with about 0.2 N ammonium hydroxide (pH about 10), washed with ammonium hydroxide and dried at ambient temperature by passing air through the filter cake overnight. This sample had only 4 H_3O^+ /unit cell.

The selectivity for hydronium ions of certain sites in zeolite X must be very high, since they are capable of removing these ions from solution of such a low concentration. Incidental hydronium ion exchange was observed previously upon ammonium exchange of sodium zeolite A (4) and upon exchange of zeolite Y with methyl-substituted ammonium ions (6).

Since we could not eliminate exchange with hydronium ions, their presence must be recognized when the results are interpreted.

Thermal Stability

Careful decomposition of ammonium cations in zeolite X, with immediate removal of the decomposition products in an inert gas stream, produces hydrogen zeolite X, if the degree of ammonium ion exchange is small. The product can be converted back to the ammonium form by reaction with ammonia. Sorbing water on this ammonium zeolite produces a material indistinguishable from the original sample. The crystallinity of NaHX can be determined by measuring the cyclohexane sorption capacity. In Fig. 2, Curve 1, the cyclohexane sorption capacity is plotted as a function of the ratio of the sodium ions to aluminum. It is evident that the zeolite X structure remains intact upon calcination, if the Na/Al atomic ratio is at least about 0.6. At lower Na/Al ratio, the degree of crystallinity after calcination decreases with reduction of the Na/Al ratio. Simultaneously, changes caused by partial loss of crystal structure are observed in the X-ray diffraction pattern.

The tetrahedron AlO_4^- is isoelectronic with SiO_4 , and it can be predicted that the

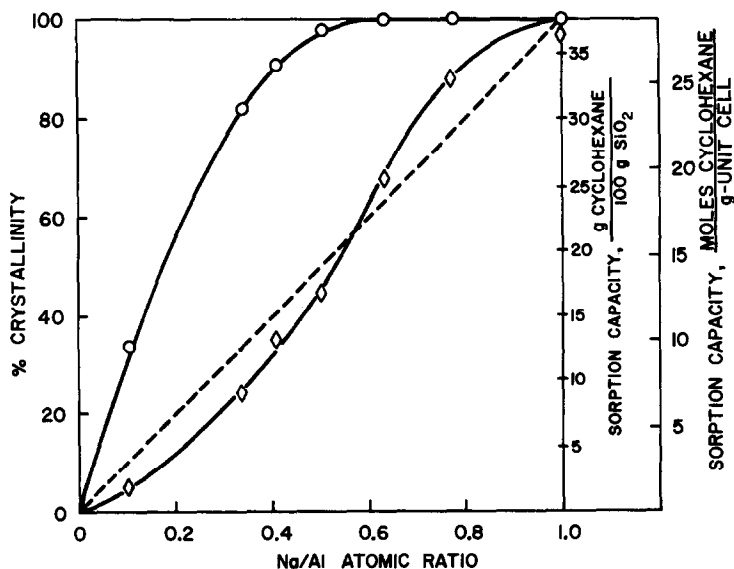


FIG. 2. Crystallinity of NaHX as determined by cyclohexane sorption. Curve 1: after calcination at $30^\circ\text{C}/\text{min}$ in flowing He (\circ —); Curve 2: after calcination at $30^\circ\text{C}/\text{min}$ in flowing He, water sorption and recalcination (\diamond —).

bonds extending from either tetrahedron are of approximately identical strength. Most cations associated with the AlO_4^- tetrahedron, especially those that do not form strong complexes with framework oxygen (e.g., Na^+), do not exert a major influence on the strength of these bonds. Indeed, Kerr (7) observed that the endotherms associated with the breakdown of the crystal structure occur at about the same temperature for NaY (940°C) and NaX (935°C). On the other hand, a proton, as formed by thermal decomposition of an ammonium ion, reacts so intimately with a framework oxygen that the Al-O bond is considerably weakened. It appears, therefore, that the concentration of protons in the zeolite structure is of much greater consequence to the stability of the zeolite than the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of a zeolite structure is raised by substituting NaAlO_4 with SiO_4 . A sodium hydrogen zeolite X, NaHX , should have approximately the same stability to calcination (differences in the temperature at which dehydroxylation occurs are discussed below) as a hydrogen zeolite Y, if the $(\text{SiO}_2 + \text{NaAlO}_2)/\text{HAlO}_2$ molar ratio of NaHX is identical to the Si/Al atomic ratio of HY . For a constant $\text{SiO}_2/\text{Al}_2\text{O}_3$ of zeolite X, the ratios $(\text{SiO}_2 + \text{NaAlO}_2)/\text{HAlO}_2$ correspond to certain $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios, so that the hydrogen zeolite Y's are related to NaHX as follows:

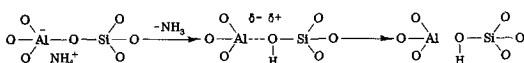
| HY of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio | Corresponds to | NaHX ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.52$) of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio |
|---|----------------|---|
| 4.00 | | 0.247 |
| 4.40 | | 0.294 |
| 4.62 | | 0.318 |
| 4.86 | | 0.341 |
| 5.11 | | 0.365 |
| 5.38 | | 0.388 |
| 5.68 | | 0.412 |
| 6.00 | | 0.435 |

In Table 2 the sorption data are given in

grams of cyclohexane sorbed per 100 g of SiO_2 in the zeolite structure. This dimension is convenient if the number of Si atoms per unit cell is constant, for instance, for samples ion-exchanged to varying degrees. It cannot be used when zeolites of identical structure, but different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are to be compared, e.g., X and Y. A convenient dimension for such comparison is moles of cyclohexane per g-unit cell (Table 2, Fig. 2). If a sorbate is physically sorbed, i.e., without strong interaction with the cations of the zeolite, the number of molecules of the particular sorbate per unit cell is practically independent of cations and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. A saturated hydrocarbon represents such a sorbate of low polarity. It can, therefore, be expected that a g-unit cell (unit cell weight in grams, corresponding to mol and g-atom) of a faujasite of any composition sorbs approximately the same amount of cyclohexane. Sodium zeolite X ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.52$), containing 107 Si/unit cell, sorbed 37.4 g of cyclohexane/100 g of SiO_2 or 28.6 mol of cyclohexane/g-unit cell. Sodium zeolite Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.32$) containing approximately 140 Si/unit cell, sorbed 28.2 g of cyclohexane/100 g of SiO_2 or 28.2 mol of cyclohexane/g-unit cell. This value corresponds to 99% crystallinity compared with the sorption of sodium zeolite X and is within the experimental accuracy. Ammonium zeolite Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.70$), containing about 142 Si/unit cell, was carefully calcined as described above. The hydrogen form sorbed 25.4 g of cyclohexane/100 g of SiO_2 or 25.8 mol of cyclohexane/g-unit cell, corresponding to 90% crystallinity. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of this HY corresponds closely to a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of NaHX ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.52$) of 0.413. Curve 1 (Fig. 2) shows that this NaHX had a crystallinity of 91%. This result agrees very well with the 90% crystallinity found for the HY .

A NaHX , if perfectly stable to calcina-

tion, has at least about 0.6 Na/Al according to Curve 1 (Fig. 2). It is interesting to note that a NaHX with a Na/Al atomic ratio of 0.62 contains 32 H⁺/unit cell (=4 H⁺/sodalite cage). A hydrogen zeolite Y with 32 H⁺/unit cell would have a SiO₂/Al₂O₃ molar ratio of 10. Such a material with a perfect lattice is not known. An aluminum deficient faujasite appears to sorb more cyclohexane, probably because of lattice defects. Kerr (8) reported a dealuminized zeolite Y (SiO₂/Al₂O₃ = 8.7; 29 H⁺/unit cell) to sorb 24 g of cyclohexane/100 g of zeolite; this sorption capacity corresponds to 30.2 mol of cyclohexane/g-unit cell or 106% crystallinity. Upon calcination of an ammonium zeolite, one Al-O bond is weakened by each proton obtained by thermal decomposition of the ammonium ion. If many of these bonds are weakened, the crystal structure collapses:



Even at 200°C, this reaction proceeds: Sample 6 was heated to 200°C in the TG apparatus and the temperature held at 200°C for 0.5 hr; at the end of this time, 75% of the ammonium ions had decomposed (leaving 16 NH₄⁺/unit cell) and the cyclohexane sorption capacity was only 72% of the sorption capacity of the original sodium zeolite. This is about the value expected for a sample containing 25 cations (9 Na⁺ and 16 NH₄⁺), (Na⁺ + NH₄⁺)/Al = 0.29 (Fig. 2).

Hydrothermal Stability of NaHX

Sorbing water on sodium hydrogen zeolite X, then recalcining, reduced the cyclohexane sorption capacity approximately by the same proportion (based on the sorption of the sodium X starting material) as the sodium content, e.g., 60% of initial sorption at a Na/Al molar ratio of 0.6, Curve 2

(Fig. 2). However, it is evident that the samples with Na/Al molar ratios above 0.6, which were thermally stable, are slightly more stable to hydrolysis than the degree of exchange would predict. Conversely, the samples with Na/Al molar ratios below about 0.6 which were not thermally stable, were slightly less crystalline after this treatment than the Na/Al ratio might lead one to anticipate. It is to be expected that the point at which the sigmoidal curve crosses the diagonal line, representing an assumed linear relation, depends on the silica to alumina ratio of the zeolite and would be at Na/Al = 0.33 for SiO₂/Al₂O₃ = 6 and would reach 0 for a theoretical SiO₂/Al₂O₃ = 10.

If an ammonium zeolite is calcined without removing the bulk of the adsorbed water prior to thermal decomposition of the ammonium ions, water vapor attacks the zeolite framework at the site of the proton (3). Aluminum is removed from the framework, and the protonic site is irretrievably lost. When we carefully calcined sample 1, containing 10 NH₄⁺ and 9 H₃O⁺/unit cell, in the TG unit, then sorbed ammonia to neutralize the acid sites generated, and finally sorbed water to desorb any physically sorbed ammonia, the analysis showed that there were only 10 NH₄⁺ ions/unit cell. Evidently, thermal decomposition of the hydronium ions did not yield the same kind of acid protons as the decomposition of NH₄⁺ ions. It appears to be likely that hydrolysis of framework-Al occurred.

One might expect that, by sorbing water on a hydrogen zeolite, the proton is rehydrated and a hydronium zeolite is formed. Curve 2 (Fig. 2) indicates that a sample of rehydrated NaHX with Na/Al = 0.89, corresponding to 9 H₃O⁺/unit cell, would lose about 3% of its sorption capacity upon calcination. Sample 1 does contain 9 H₃O⁺ (and 10 NH₄⁺)/unit cell, but no detectable loss of sorption capacity was found after calcining this sample (Curve 1). From the

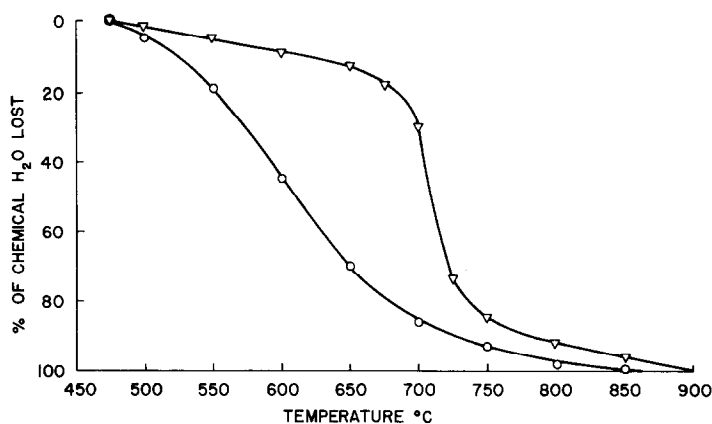


FIG. 3. Dehydroxylation of HY and NaHX. He flow rate, 190 ml/min; heating rate, 30°C/min; (▽)[$\text{H}_{50}(\text{AlO}_2)_{50}(\text{SiO}_2)_{142}$]; (○)[$\text{H}_{50}\text{Na}_{35}(\text{AlO}_2)_{85}(\text{SiO}_2)_{107}$].

presently available data it cannot be decided whether the loss in sorption capacity is too small to be detected, whether a hydronium zeolite, as prepared by ion-exchange, is different from the material obtained by sorbing water on a hydrogen zeolite, or whether the slowly released ammonia reacts in some way that stabilizes the crystal structure.

Since we did not determine complete sorption isotherms, but measured only the sorption capacities at one pressure, X-ray diffraction patterns of sample 6 (Curve 1) and samples 2 and 5 (Curve 2) of Fig. 2 were taken as a check of the crystallinity. If we plot Fig. 2 with the relative intensity of a particular X-ray line on the ordinate, the points for these samples fall within $\pm 10\%$ of the points of the plots with sorption capacity on the ordinate. Since the relative X-ray line intensities vary with exchange of H^+ for Na^+ , better agreement using individual lines cannot be expected.

Loss of Chemical Water

We found by thermogravimetric analysis that 97% of the theoretical amount of chemical water was retained after calcination at 200°C. This result agrees with findings by Uytterhoeven and co-workers (1), that no dehydroxylation occurs at this low

temperature. However, our result shows that, for low Na/Al ratios, the crystal structure collapsed before dehydroxylation occurred. Uytterhoeven *et al.* stated that "structure collapse accompanies dehydroxylation." This apparent disagreement may be explainable with the Na/Al ratio, which is more than double for Uytterhoeven's zeolite than for our sample 6. Uytterhoeven also observed that "there was considerable overlap between the deammoniation and dehydroxylation reaction in the case of the X-samples." Our experiment separated these two reactions, although the deammoniation was still incomplete after 0.5 hr.

In the thermogravimetric experiment, sodium hydrogen zeolite X loses chemical water at a lower temperature than does hydrogen zeolite Y (Fig. 3). Dehydroxylation of sodium hydrogen zeolite X is also drawn out over a wider temperature range, and it is likely that prolonged calcination at even lower temperatures will cause dehydroxylation. If a constant temperature is used, e.g., 550°C, sodium hydrogen zeolite X loses chemical water at a faster rate than hydrogen zeolite Y.

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