

Thermochemical Reactions of Ammonium-Exchanged Y Zeolite and Its Derivatives

A. P. BOLTON AND M. A. LANEWALA

Union Carbide Corporation, Linde Division, Tarrytown, New York 10591

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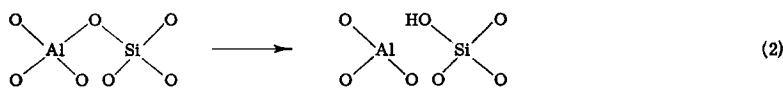
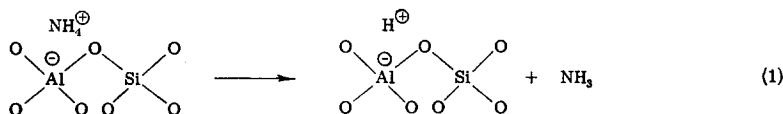
The thermal decomposition of ammonium-exchanged Y was studied using infrared, ion exchange, thermogravimetric, and differential thermal analyses. The deamination and dehydroxylation reactions constituting the thermal decomposition are shown to take place over large temperature ranges and overlap to a considerable extent. At 375°C, the temperature at which a 95% ammonium-exchanged Y having a SiO₂-Al₂O₃ molar ratio of 5 is completely deaminated, 25% dehydroxylation has already occurred. The temperature required to dehydroxylate the zeolite increases with increasing SiO₂-Al₂O₃ molar ratio and decreases with increasing extent of ammonium exchange. This study indicates that the intermediate derived by the deamination of ammonium-exchanged Y is the same species as that obtained by the mineral acid treatment of sodium Y. The reconstitution of ammonium-exchanged Y may be realized by adding water back to the dehydroxylated form over the entire temperature range the dehydroxylation takes place, prior to ammonia addition.

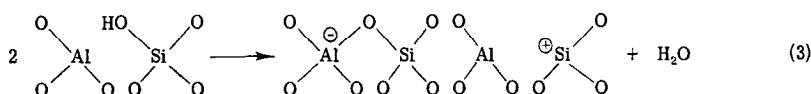
INTRODUCTION

The principal controversy over the mechanism of zeolite catalysis involves the role of the proton in the crystalline zeolite matrix. One of the most catalytically active forms is that derived from the thermal decomposition of the ammonium-exchanged zeolite. The initial concept of the decomposition mechanism was proposed by Rabo *et al.* (1) who envisaged the thermal decomposition of ammonium-exchanged Y to proceed through an intermediate hydrogen species formed by the evolution of ammonia. This protonic form was considered unstable at elevated temperatures and converted to the dehydroxylated form by

the liberation of water. Subsequent work by Uytterhoven *et al.* (2) has shown this concept to be essentially correct. Doubts about the existence of a hydrogen intermediate containing free protons have been allayed by proposing the reaction of these protons with lattice oxygens to form hydroxyl groups (2). The existence of this hydroxyl form is supported by the appearance of bands in the IR spectrum at 3640 and 3540 cm⁻¹ which corresponds to hydroxyl stretching frequencies (3).

The chemistry of the thermal decomposition of ammonium-exchanged Y may be represented by the following equations:





This study was concerned with the temperatures at which the steps constituting the thermal decomposition of the ammonium-exchanged form of zeolites occur and with the nature of the deaminated intermediate derived from the ammonium-exchanged form and the relation it bears to the mineral acid-treated form of the sodium zeolite.

EXPERIMENTAL METHODS

Materials

The samples used in this study were prepared from pure Type X and Type Y molecular sieve synthesized by Linde. The ammonium-exchanged forms were prepared by repeatedly contacting the zeolite powder with a 10% aqueous solution of ammonium chloride at reflux temperatures. The mineral acid-treated form of zeolite Y was prepared by repeatedly contacting the zeolite powder, having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.0, with 4 *N* HCl at room temperature. The products were washed with demineralized water until free of chloride ions and dried in ambient air.

Differential Thermal Analyses

A R. L. Stone differential thermal analyzer, Serial No. 17, was used in these experiments. In this equipment, the purge gas passes directly through the sample and reference cells. The operating conditions were as follows: A 100-mg sample was purged with helium or air at a flow rate of 2.3 liters/hr; the amplitude setting at 38 cm was equal to 30 μV ; the heating rate was 18°C/min; the differential thermocouple was platinum versus platinum plus 10% rhodium; the reference standard was calcined alumina (140 mesh). It is our experience that meaningful differential thermograms may be obtained only from systems in which the purge gas flows directly through the zeolite sample. If the purge gas flows over the sample holder as occurs in many differential analyzers, the

evolved products are not so effectively removed and this gives rise to artifacts in the thermogram which undoubtedly account for the wide discrepancies occurring in the literature (4-6).

Thermogravimetric Analyses

A duPont Model 950 thermogravimetric analyzer was used under the following conditions: the sample was purged with helium at 3 liters/hr; the heating rate was 18°C/min; the sample weight was 22.80 to 24.00 mg.

Infrared Analyses

The samples were run as self-supporting wafers and scanned on a Perkin-Elmer Model 621 spectrophotometer from 4000 to 1200 cm^{-1} . The wafer had a weight of ~ 6 mg/cm². Each sample was heated for 2 hr in a cell essentially the same as that described by Angell and Shaffer (3). Heating was carried out at various temperatures while the cell was purged with air. The cell was then cooled to room temperature and the spectrum was obtained.

X-Ray Diffraction

A Norelco diffractometer was used employing copper $K\alpha$ radiation at 50 kV and 40 mA. The sample was scanned over a 2θ range of 56 to 4° at 2°/min. An estimation of crystal structure retention was obtained by comparing the sum of the peak intensities at hkl values of (331), (440), (533), (642), (555), and (751) with that of the starting material.

RESULTS AND DISCUSSION

Thermal Analyses

Differential thermal analyses provide an excellent method of separating and identifying the individual steps constituting the thermal decomposition of ammonium-exchanged Y. Used in conjunction with thermal gravimetric analyses, a more complete account of this process is possible. Thermo-

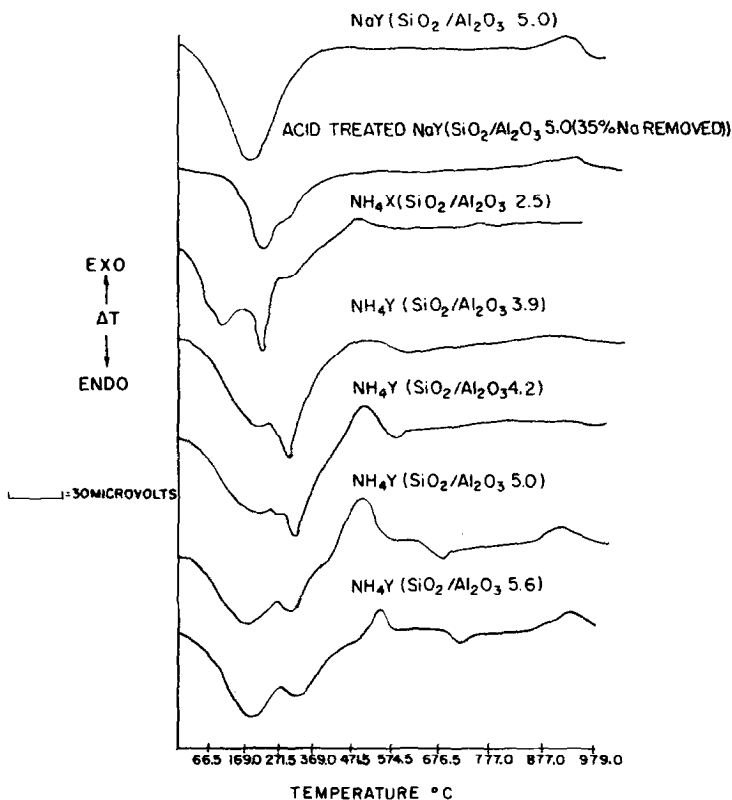


FIG. 1. Differential thermal analyses in a helium atmosphere.

grams, both differential and gravimetric, of ammonium-exchanged Type X and Y zeolites, together with an acid treated sodium Y having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.0, are shown in Figs. 1 and 2.

Chromatographic analyses of the effluent gases, as well as chemical analyses of samples withdrawn from the differential thermal analyzer, enabled characterization of the exothermic and endothermic peaks. The first endothermic peak is accompanied by the evolution of water and this peak has been attributed to the desorption of physically adsorbed water (4, 5). For an ammonium-exchanged Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.0, this process is essentially complete by about 250°C . The deamination process which occurs during the temperature range of the second endotherm, starts at about 250°C ; chromatographic analyses of the effluent gases and chemical analyses of samples withdrawn from the differential thermal analyzer, show that

over 90% of the ammonium cations are decomposed and evolved by 400°C . The exothermic peak in the differential thermogram of an ammonium-exchanged Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.0 with a helium purge, cannot be attributed to the dissociation of the ammonium cation or the subsequent desorption of ammonia since the latter has already been evolved. However, the size of this exothermic peak is proportional to the degree of ammonium exchange and thus must be associated with ammonium cation decomposition. The absence of this exotherm from the differential thermogram of the acid-treated Y would indicate that it might well be associated with the formation of the hydroxylated species, depicted in Eq. (2). This has been reported to be exothermic (2).

A differential thermogram of ammonium-exchanged Y having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.0, in air has an enhanced exothermic peak compared to that obtained in helium

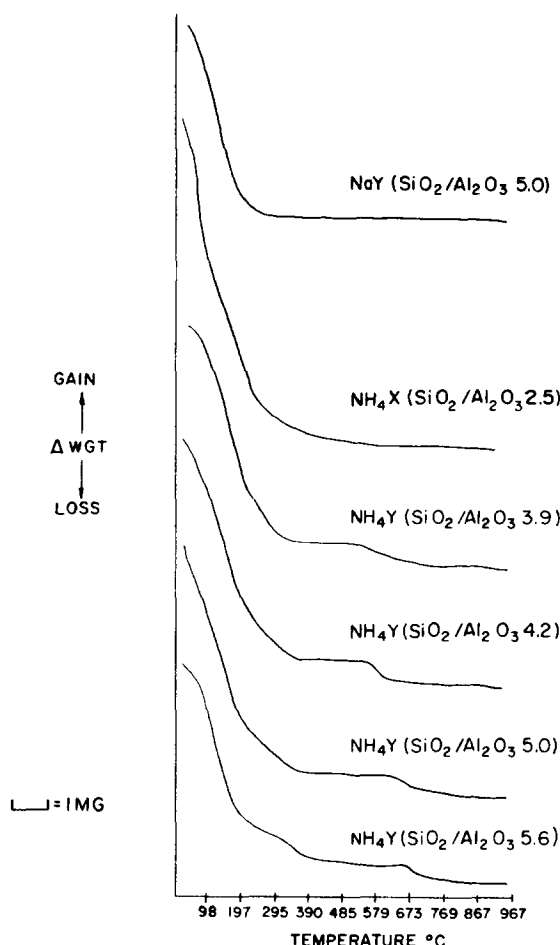


Fig. 2. Thermogravimetric analyses in a helium atmosphere.

and occurs at about a 50°C lower temperature in agreement with other studies (7). A mass spectrometric analysis of the gas evolved between 290 and 480°C in an oxidizing atmosphere (80% He and 20% O₂) showed nitrogen as well as ammonia to be present in the products. It is assumed that the enhanced exotherm in air is due to the partial oxidation of ammonia.

The differential thermogram of an ammonium-exchanged Y, having a SiO₂/Al₂O₃ molar ratio of 5.0, at higher temperature shows a small endothermic peak at 680° which would correspond to the dehydroxylation step. This is confirmed by thermogravimetric analysis which shows a weight loss from 500 to 900°C. This has been shown to correspond to the theoretical weight loss for this reaction. This weight loss is due to the

formation of one molecule of H₂O from two OH groups which, from Eq. (1) are derived from two ammonium cations. The observed weight loss derived from thermogravimetric analysis only matches the calculated value if the former is taken over the temperature range 500 to 900°C. Although the gravimetric thermograms in Fig. 2 show a major dehydroxylation weight loss over a more limited temperature range, 650 to 700°C in the case of a 95% ammonium-exchanged Y starting material having a SiO₂/Al₂O₃ molar ratio of 5.0, this is insufficient to account for the calculated value. The additional weight losses outside this limited temperature range and beginning at 500°C is required to satisfy the calculated value.

Measurements of unit cell dimension of samples removed from the differential

TABLE 1
THE VARIATION IN UNIT CELL DIMENSION
WITH TEMPERATURE

Temp (°C)	65% NH ₄ ⁺ Y SiO ₂ /Al ₂ O ₃ 5.0 (A°)	Acid-treated NaY (35% Na) SiO ₂ /Al ₂ O ₃ 5.0 (A°)
Ambient	24.93	24.62
310	24.93	24.62
400	24.61	24.61
480	24.61	24.61
590	24.61	24.61
680	24.24	24.22
700	24.22	24.22
780	24.22	24.22

analyzer at different temperatures show that a change of a_0 accompanies this endothermic peak. Such a contraction would not be unexpected since, according to Eq. (3), lattice oxygens are removed during dehydroxylation. These data, given in Table 1, also show that the change in unit cell dimension of acid-treated sodium Y with temperature is identical to that found with the ammonium-exchanged form.

Thermal data together with X-ray diffraction patterns of samples removed from the differential thermal analyzer showed

that ammonium-exchanged X having a SiO₂/Al₂O₃ molar ratio of 2.5 and ammonium exchanged to 74%, deaminates, dehydroxylates, and loses crystallinity simultaneously in the temperature range 175–400°C. In the same temperature range, Type Y having SiO₂/Al₂O₃ molar ratio of less than 4 and exchanged to over 75% with ammonium cations deaminates without significant loss in crystallinity but undergoes dehydroxylation and some loss in crystallinity simultaneously. The differential thermograms, Fig. 1, show that the deamination temperature increases with increasing SiO₂/Al₂O₃ molar ratio. The temperature required for complete dehydroxylation, as shown in Fig. 2, also increases with SiO₂/Al₂O₃ molar ratio, being about 500°C for a 3.9 ratio material and 700°C for a 5.6 ratio material. The effect of degree of ammonium exchange upon the dehydroxylation temperature is shown in Fig. 3 and Table 2 to increase from 625°C for a 97% ammonium-exchanged material to 780°C for a 30% ammonium-exchanged material. Dehydroxylation, as defined by Eq. (3) is the condensation of two hydroxyl groups. The activation energy of this reaction will depend on the proximity of the hydroxyl groups which in turn will be a

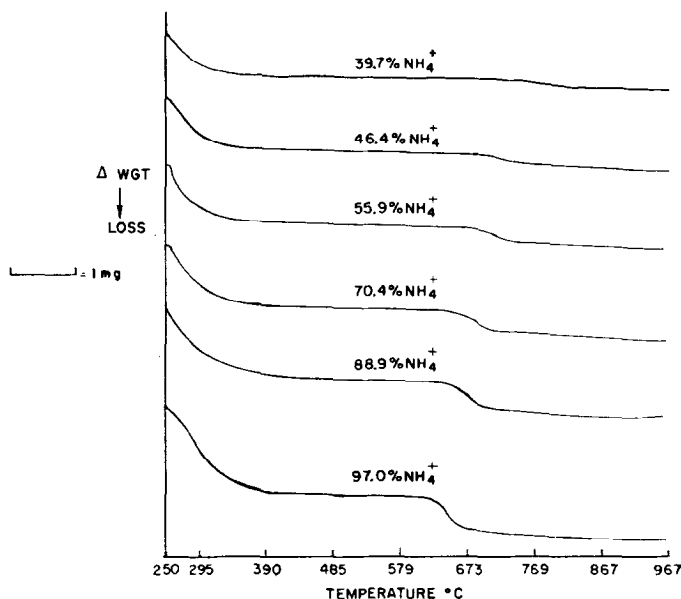


FIG. 3. Gravimetric thermograms of ammonium exchanged Y, SiO₂/Al₂O₃ molar ratio 5.0, in air.

TABLE 2
TGA DATA FOR VARIED AMMONIUM-EXCHANGED Y, $\text{SiO}_2/\text{Al}_2\text{O}_3$
MOLAR RATIO 5.0, IN AN AIR ATMOSPHERE

% NH_4^+ exchange	No. NH_4^+ / unit cell	Total wt-loss (%)	% Wt-loss, 500-900°C		Initial temp for major dehydroxylation wt-loss
			Observed	Calculated for dehydroxylation	
0	0	22.9	0.05	—	—
29.8	15.9	25.9	0.80	0.85	780
34.7	19.1	26.0	0.92	0.95	740
39.7	21.8	26.0	1.10	1.15	715
46.4	25.4	26.2	1.30	1.40	700
55.9	30.5	27.5	1.70	1.70	660
70.4	38.6	28.7	2.10	2.10	655
88.9	48.7	31.0	2.65	2.70	640
97.0	53.3	30.0	2.95	3.00	625

function of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio as well as the degree of ammonium exchange. A plot of the temperature at which dehydroxylation begins, as derived by thermogravimetric analysis and the number of ammonium cations per unit cell, is shown in Fig. 4. The break in the curve at between 20 to 25 hydroxyl groups per unit cell for this $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio

material indicates that there are two distinct cation sites. It would appear that the ammonium cations and thus the subsequently formed hydroxyl groups occupy one position in the lattice until 50% sodium removal corresponding to 20-25 hydroxyl groups for this $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio material is achieved. At this point the ammonium cations occupy another position where

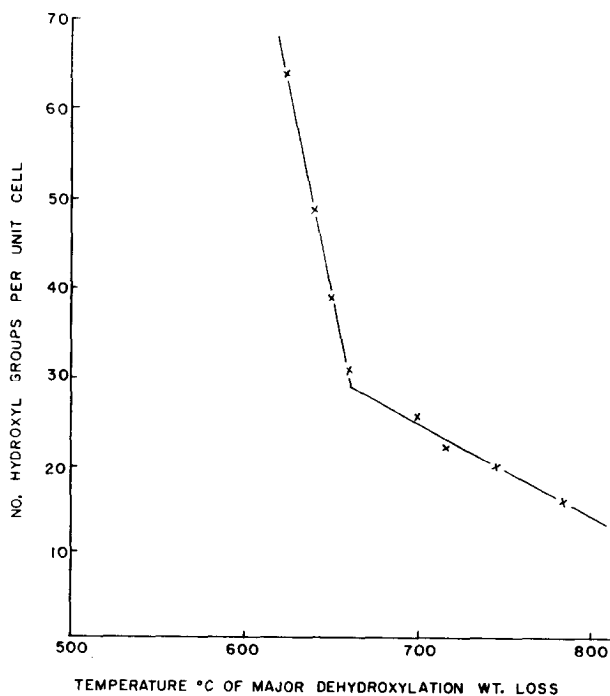


FIG. 4. Hydroxyl content vs. dehydroxylation temperature; ammonium-exchanged Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.0$).

the distance to a neighboring hydroxyl group is much reduced. The variation in the relative intensities of the 3640 and 3540 cm^{-1} bands with ammonium exchange would support this hypothesis (3, 8).

Isothermal Studies

The thermal data reported in the previous section were obtained under dynamic or nonequilibrium conditions and the temperatures reported for the completion of the various steps will not match those occurring under isothermal conditions. Correlation of thermal data with subsequent infrared, ion exchange, and reconstitution studies requires a knowledge of the temperature at which the constituent reactions are complete. These studies were carried out using a 97% ammonium-exchanged zeolite Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.0. The temperature at which deamination is complete was first investigated by placing the sample in a crucible and heating in a muffle furnace with a helium purge at a predetermined temperature. The samples were chemically analyzed after treatment. The analyses showed that complete deamination occurs after 2 hr at 375°C in agreement with other studies (5, 9). The extent of dehydroxylation was determined using the same technique, followed by examination of the treated samples for the presence of hydroxyl groups by infrared. Dehydroxylation was found to be essentially complete by about 625°C. In a subsequent thermogravimetric analysis, the absence of a weight loss in the 600–900°C region confirmed this conclusion.

Infrared Analyses

The thermal decomposition of ammonium-exchanged Y was next followed by infrared analysis. The sample was 97% ammonium exchanged and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.0. The data in Fig. 5 show the 3540 and 3640 cm^{-1} bands, attributed to hydroxyl groups, to be present at 200°C, the minimum temperature at which the masking effect of adsorbed water is sufficiently removed. Thus, some deamination has already taken place at this temperature. On raising the temperature, the

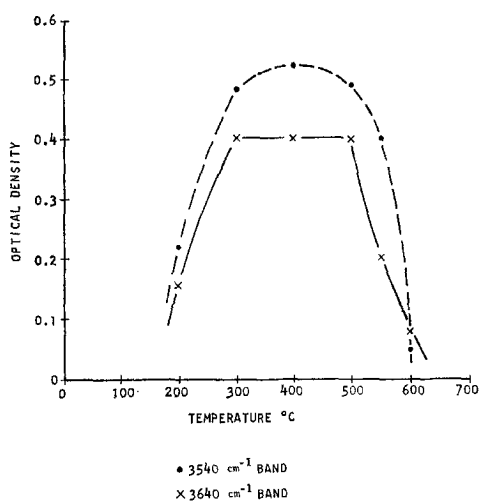


FIG. 5. The intensity of structural hydroxyl¹ group bands as a function of temperature; 97% ammonium exchanged Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.0$).

maximum hydroxyl concentration remained constant with increasing temperature until 500°C, after which it rapidly decreased to zero at about 600°C. These data are essentially the same as those obtained by Ward (5). A comparison was then made of the temperatures required, in a nitrogen purge,

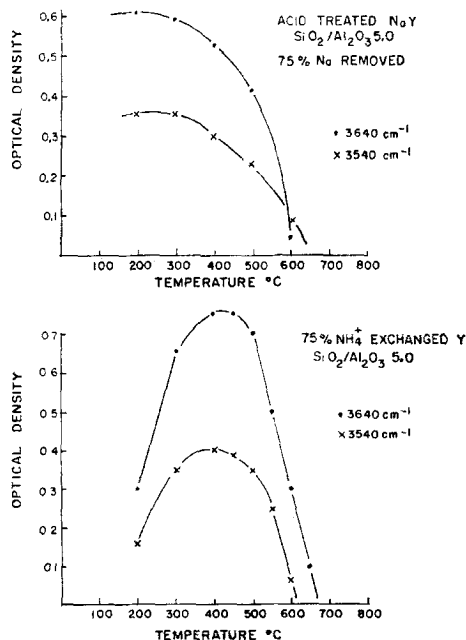


FIG. 6. The intensity of structural hydroxyl group bands as a function of temperature.

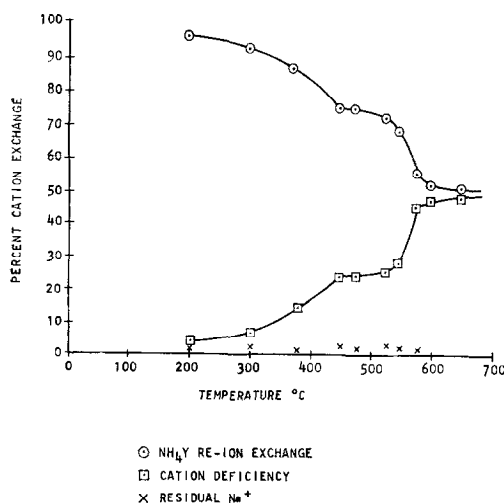


Fig. 7. The effect of temperature on ion exchange capacity of 95% NH_4^+ -exchanged Y ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 5.0).

to form and remove the hydroxyl groups on a 75% ammonium-exchanged Y and an acid-treated sodium Y in which 75% of the sodium cations had been removed; both samples had $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 5.0. The data in Fig. 6 of the 75% ammonium-exchanged Y are similar to that of the higher ammonium-exchanged material with the

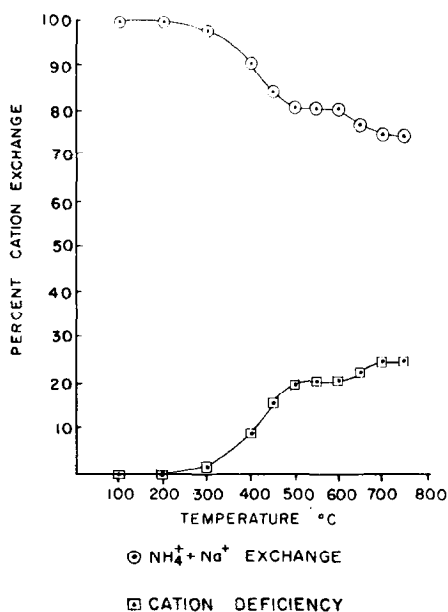


Fig. 8. The effect of temperature on ion exchange capacity of 47% NH_4^+ -exchanged Y ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 5.0).

exception that the hydroxyl bands were removed at about a 50°C higher temperature. The hydroxyl groups at 3540 and 3640 cm^{-1} are not only present in the acid-treated sodium Y at 200°C , but also at their maximum concentrations. Further increasing the temperature resulted in a gradual loss in these bands and their disappearance at about 650°C .

Ion Exchange

The formula representing the dehydroxylated species in Eq. (3) requires that only one-half of the original ion exchange capacity be retained. Thus, the extent of ion exchange capacity after calcination at a particular temperature should be a measure of the extent of dehydroxylation. Data from such experiments, starting with a 95% ammonium-exchanged Y $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.0, are shown in Fig. 7 and confirm that the ion exchange capacity of the zeolite calcined at 575°C is indeed 50% of its initial capacity as originally suggested by Rabo *et al.* (1). However, Fig. 7 also shows that the zeolite does not retain all of its ion exchange capacity at intermediate temperatures. Since X-ray crystallinity and surface area measurements indicate complete retention of crystallinity over the temperature range studied, some dehydroxylation must have already occurred at lower temperatures.

Previous thermogravimetric analyses indicated the occurrence of some dehydroxylation at intermediate temperatures. These analyses also showed that decreasing ammonium exchange results in a higher dehydroxylation temperature. Accordingly, the ion exchange capacity of a 47% ammonium-exchanged Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.0, was determined after calcination at a series of temperatures. The results in Fig. 8 show that a temperature of 700°C is required to effect the 50% retention of ion exchange capacity indicative of complete dehydroxylation. The different extents of dehydroxylation at intermediate temperatures, derived from the re-ion exchange data, undergone by these two ammonium-exchanged samples, is shown in Fig. 9.

The apparent constant concentration of

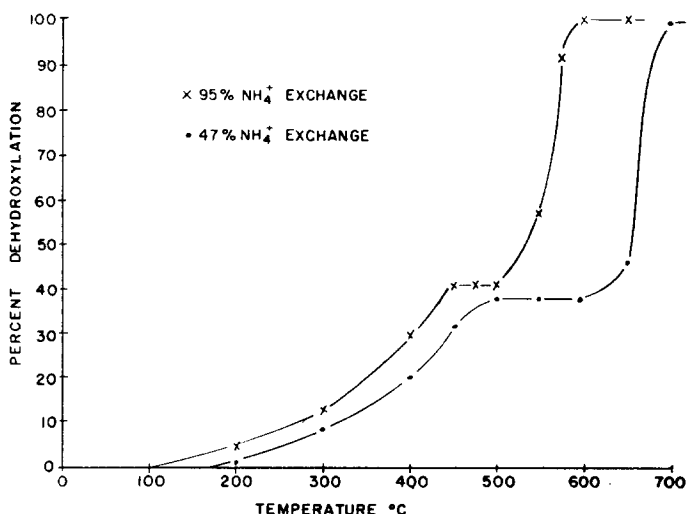


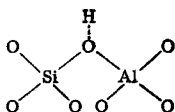
Fig. 9. The effect of temperature on the extent of dehydroxylation of NH_4Y ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.0).

the hydroxyl groups as indicated by infrared analysis of a 95% ammonium-exchanged Y having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.0, over the temperature range of approximately 300 to 500°C would not appear to be in agreement with the ion exchange data. An explanation of this discrepancy is not immediately apparent.

The acid-treated form of sodium Y has been shown by infrared to exist as an hydroxylated species, as does the intermediate in Eq. (2) derived from the deamination of ammonium-exchanged Y. However, the acid treated form of NaY possesses cation exchange capacity and can undergo ion exchange as the following chemical analysis indicates:

Molar or atom ratio	Acid-treated sodium Y	Lanthanum-exchanged product
$\text{SiO}_2/\text{Al}_2\text{O}_3$	5.0	5.0
Na/Al	0.30	0.24
$\text{La}/3\text{Al}$	—	0.75
Cation deficiency/Al	0.70	0.01

Thus, the proton, even though identified as being in the hydroxylated state, also exists as an exchangeable cation and the intermediate might better be represented as:



Reconstitution

The variation of ion exchange capacity of ammonium-exchanged Y with calcination temperature, Fig. 7, shows that the deamination and dehydroxylation reactions overlap to a considerable extent. At 375°C, the temperature at which deamination has been shown to be complete, 25% dehydroxylation has already occurred as shown by loss in ion exchange capacity. Thus, for the successful reconstitution of ammonium-exchanged Y from dehydroxylated Y, it is necessary to reintroduce water over the entire temperature range that dehydroxylation is observed to occur. Conditions other than these would explain the failure of previous attempts to reconstitute ammonium-exchanged Y from its dehydroxylated derivative (2, 9).

Accordingly, a sample of ammonium-exchanged Y was heated in a nitrogen purge for 2 hr at 600°C which from infrared, ion exchange, and isothermal data is a sufficient temperature for complete conversion to the dehydroxylated form. The sample was then cooled over a period of 2 hr in a nitrogen purge saturated with water vapor to 400°C. Ammonia was then added to the water saturated nitrogen purge and the sample was further cooled to 100°C, after which the sample was purged with dry nitrogen at room temperature. The following anal-

yses show that 78% of the exchanged sites were reconstituted.

Molar or atom ratios	Starting material; ammonium-exchanged Y	Re-constituted product	Lanthanum-exchanged reconstituted product
SiO ₂ /Al ₂ O ₃	5.0	5.0	5.0
Na/Al	0.04	0.03	0.02
NH ₄ /Al	0.96	0.78	0.00
La/3Al	—	—	0.86

Complete reconstitution of the ammonium-exchanged sites was not achieved, but sufficient reconstitution above the 50% level required by Eq. (3) provides an adequate demonstration of the reversibility of this step. That the dehydroxylated form must be rehydroxylated before conversion to the ammonium-exchanged form was demonstrated by repeating the reconstitution omitting the addition of water. The following chemical analyses and ion exchange data show the complete absence of ammonium cations and the retention of approximately 50% of ion exchange capacity.

Molar or atom ratios	Starting material	Re-constituted product	Lanthanum-exchanged reconstituted product
SiO ₂ /Al ₂ O ₃	5.0	5.0	5.0
Na/Al	0.04	0.04	0.04
NH ₄ /Al	0.96	0.00	0.00
La/3Al	—	—	0.44

CONCLUSIONS

This study shows that the deamination and dehydroxylation reactions occurring during the thermal treatment of an ammonium-exchanged Y overlap to a considerable extent. For example, at 375°C, the temperature at which a 95% ammonium-exchanged Y having a SiO₂/Al₂O₃ molar ratio of 5.0 is completely deaminated,

25% dehydroxylation has already taken place. The temperature required to dehydroxylate an ammonium-exchanged Y has been shown to increase with SiO₂/Al₂O₃ molar ratio and decrease with increasing extents of ammonium exchange. It is proposed that the dehydroxylation temperature is related to the number of hydroxyl groups per unit cell. The re-ion exchange of calcined ammonium-exchanged Y showed that reconstitution of this form can only be realized if water is added back to the dehydroxylated species over the entire temperature range over which dehydroxylation occurs. This observation enabled the reversibility of Eqs. (1) and (3) to be demonstrated by the partial reconstitution of the ammonium-exchanged form from the dehydroxylated form.

An important conclusion from this study is that infrared, ion exchange, thermogravimetric, and differential thermal analyses, used in conjunction can yield meaningful information on the thermochemical reactions of the ammonium-exchanged zeolites and their derivatives. Used alone, however, any one of these tools can lead to erroneous conclusions.

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