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Chemistry of Crystalline Aluminosilicates

VII. Thermal Decomposition Products of Ammonium Zeolite Y*

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Two distinct products can be obtained on the thermal decomposition of ammonium zeolite Y at 760 torr and 500°. The geometry of the zeolite bed during calcination determines the nature of the product. Where the geometry permits rapid removal of ammonia from the bed, the expected hydrogen zeolite is obtained. Bed geometries that impede removal of ammonia from the bed yield an ultrastable product. This material contains cationic aluminum; the cations are derived from a portion of the tetrahedrally coordinated aluminum ions which were initially part of the zeolitic framework. A mechanism is proposed to explain this transition of the aluminum ions.

INTRODUCTION

Ammonium zeolites, like most ammonium salts, would be expected to yield ammonia and a Brönsted acid on thermal decomposition. This reaction has been observed for ammonium zeolite Y (*2–4*) and ammonium mordenite (*4*). Hydrogen or acid zeolites, being Brönsted oxyacids, would be expected to lose constitutive or chemical water at elevated temperatures to yield the acid anhydride. This reaction has also been reported by several workers (*2–4*) and is generally known as dehydroxylation. McDaniel and Maher reported a third thermal decomposition product of ammonium zeolite Y; this material, having greater thermal stability than the normal hydrogen zeolite Y, was named ultrastable faujasite (*5*). Two recent reports briefly described the nature of this material, the factors leading to its formation, and a mechanism to explain its formation (*1, 6*). The present study describes in more detail the formation and properties of ultrastable faujasite.

METHODS

The ammonium zeolite Y used in the present work had the unit cell formula $Na_2(NH_4)_{48}(AlO_2)_{50}(SiO_2)_{142} \cdot 267H_2O$. Thermal decompositions of the ammonium zeolite were conducted in a Temco type 1500 electric furnace at 500°. Sample sizes in all cases amounted to 7.0 g of the ammonium zeolite. Two sample geometries were used. "Shallow bed"(SB) calcination was conducted in a weighing dish having an inside diameter of 7.0 cm. "Deep bed" (DB) calcination was done in a weighing jar having an inside diameter of 2.3 cm. The SB samples were 0.3 cm deep and the DB samples were 2.9 cm deep. The samples were placed directly into the furnace at 500°. About 1 and 4 hr were required for complete loss of ammonia from the SB and DB samples, respectively, as determined with moist pH indicator paper. Several dozen SB and DB samples were prepared and studied as described below. The samples discussed in this report are typical SB and DB products.

The instrumental procedures used in this study were previously described (*1, 7*). Cation exchange was effected by slurrying the zeolite samples (about 1 g) in 100 ml of 0.1 *N* NaOH solution for 1 hr followed by filtration, washing with 50 ml of water, and drying. The samples were then ana-

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[*] Part VI: Ref. (*1*).

lyzed. Anhydrous gaseous ammonia was used for ammoniation of the calcined products. Physically adsorbed ammonia was removed from the samples by slurrying the zeolites in water for about 1 hr with a 10% excess of Amberlite IRC-50, a carboxylic acid cation exchange resin in the hydrogen form. The resin in this form readily reacts with free bases, such as ammonia, but is too weakly acidic to effect salt splitting of the ammonium zeolite. Prior to contact with the zeolites, fines were removed from the 50 mesh resin using a 100 mesh stainless steel screen. After reaction, the zeolite and resin beads were completely separated using this screen. The zeolite samples were then collected on a Büchner funnel and dried before analysis. The removal of only sorbed ammonia by this method was tested using a standard and a blank; the standard was an ammonia-loaded sodium zeolite Y and the blank was a hydrated ammonium zeolite Y. Ammonia was completely removed from the sodium zeolite but less than 5% of the ammonium ion was removed from the ammonium zeolite.

RESULTS

Sorptive properties and stabilities. The DB calcined product sorbed 17.9% cyclohexane at 20 mm and 27.9% water at 12 mm. (Percent sorption = g of sorbate at equilibrium and 25°/100 g of activated sample.) After desorption of the water-loaded zeolite by heating at 350° with a nitrogen purge, the zeolite sorbed 17.3% cyclohexane. The SB calcined product sorbed 19.9% cyclohexane and 31.5% water. After thermal desorption of the water from the water-loaded sample, the cyclohexane sorptive capacity was 0.38%. X-Ray diffraction analyses of the samples just described disclosed that all samples were crystalline except that which sorbed only 0.38% cyclohexane; this sample was also found to be completely amorphous prior to the cyclohexane sorption. The DB sample had undergone a contraction of the lattice of about 1% relative to the SB sample; similar contractions have been previously reported (*1*, *5*). Differential thermal analyses showed that the DB product loses crystallinity at 1050° and the SB product at 850°.

Thermogravimetric analyses. The results are shown in Fig. 1. The weight losses below 300° were sorbed water that was picked up by the samples during loading on the balance pan. Analyses of the purge gases during these experiments indicated that both calcined products were ammonia free; the weight losses above 500° shown by the thermograms can therefore be attributed to the removal of chemical water from the samples. The chemical water content of the DB product amounted to 0.51 moles of

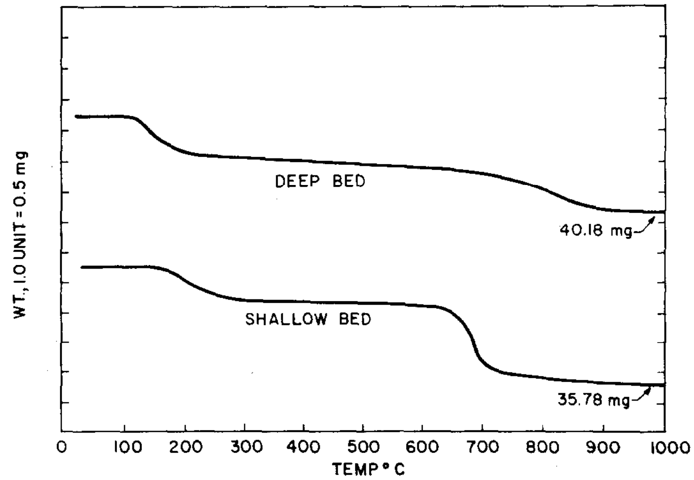

FIG. 1. Thermograms of ammonium zeolite Y calcination products.

H_2O/mole of Al_2O_3 in the zeolite; for the SB product this ratio was 0.97/1.00.

Reactions with ammonia. Samples of DB and SB calcined products were converted to the ammonium forms and analyzed. Both samples had the same Si/Al atom ratio as the initial ammonium zeolite (2.85/1.00); the Na/Al atom ratios of both samples was 0.03/1.00. The N/Al atom ratios were 0.24/1.00 for the DB sample and 0.86/1.00 for the SB sample.

Cation exchange properties. The Na/Al atom ratios of the SB and DB products after exchange with sodium hydroxide solution were 0.96 and 0.92, respectively. The Si/Al ratio of the SB sample after exchange was 2.79 compared with 2.85 for the initial ammonium zeolite. Sodium hydroxide treatment of the DB sample removed a significant portion of aluminum, giving a product with Si/Al atom ratio of 3.58.

DISCUSSION

The various chemical and physical properties of the SB sample are those expected of the normal hydrogen zeolite Y. The temperature of lattice collapse and the hydrothermal instability have been reported for hydrogen zeolite Y (*1*, *5*). The thermogravimetric results found for the SB sample are essentially identical with those reported earlier for the hydrogen zeolite (*4*, *8*). Reconstitution of the ammonium zeolite from the hydrogen form was recently described (*8*). Conversion of the SB sample to the sodium form, in which the Na/Al atom ratio approached unity with no significant change in the Si/Al ratio, is further evidence that it is the normal hydrogen zeolite.

A shallow bed at atmospheric pressure as compared with a deep bed, more nearly approaches the conditions inherent in vacuum calcination where gaseous products are rapidly and effectively removed from the environs of the zeolite. The studies which most convincingly demonstrated the existence and nature of hydrogen zeolite Y were conducted on small samples (1 g or less) obtained from the ammonium zeolite at atmospheric pressure or from small samples obtained from the ammonium form under vacuum.* The only work reported thus far in which relatively large quantities of ammonium zeolite Y (100 g) were calcined at atmospheric pressure showed that the hydrogen zeolite was not obtained, but rather the ultrastable form resulted; the geometry of the ammonium zeolite during calcination apparently was not considered important as it was not mentioned nor described in the report (*5*).

The DB calcined product has several properties in common with the ultrastable faujasite of McDaniel and Maher (*5*): a contracted lattice relative to normal hydrogen zeolite Y, greater stability than either the hydrogen or dehydroxylated forms of zeolite Y, a lower cation exchange capacity than that expected from the normal hydrogen form of the zeolite, and a lower chemical water content than hydrogen zeolite Y.

The properties which the DB product and the ultrastable faujasite share can be readily explained by assuming that a portion of the tetrahedrally coordinated aluminum of the zeolite framework has been removed. Previous studies of both sodium and hydrogen forms of zeolite Y from which a portion of the aluminum was removed, disclosed that these materials had contracted lattices, had greater stability than the forms containing the full complement of tetrahedrally coordinated aluminum, and had lower cation or proton contents than the normal forms (*1*, *7*). The DB sample contains the normal total quantity of aluminum. Therefore, if the assumption is correct that a portion of the framework aluminum has been removed, this material must contain still another form of aluminum in addition to that which is tetrahedrally coordinated. The removal of a portion of the aluminum from the DB sample on treatment with sodium hydroxide solution supports the assumption. The sodium form of the DB product contains only tetrahedrally coordinated aluminum as shown by the Na/Al atom ratio of nearly 1/1. Calculated on the unit cell basis, the sodium exchange reac-

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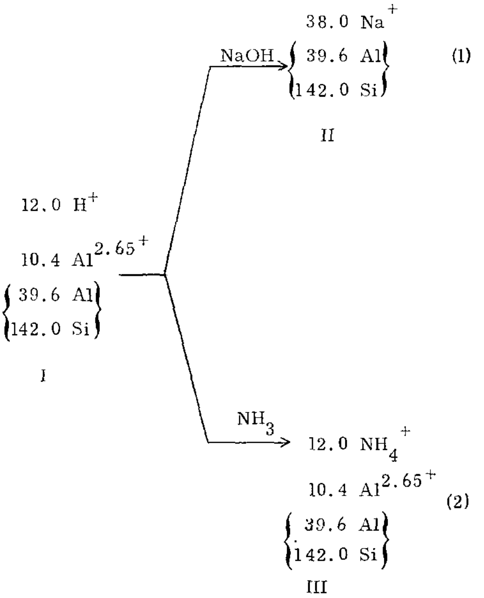
* Refs. (*2*-*4*) are examples of such studies.

tion involved the removal of 10.4 aluminum ions from the zeolite and exchange of 38 sodium ions into the zeolite. The reaction of the DB sample with ammonia indicates that 12 Brönsted acid sites are present per unit cell.

The reactions of this material with sodium hydroxide solution and ammonia can be explained by Eqs. (1) and (2) in which unit cell compositions are used; the Si and Al atoms enclosed by brackets represent tetrahedrally coordinated ions in the zeolite framework. Other ions are in cation or proton sites.



The DB calcined product has the composition shown by (I) and the products of reaction with sodium hydroxide solution and ammonia are shown by (II) and (III), respectively. These compositions are in agreement with the analyses. Studies of several dozen DB samples showed that the number of aluminum cations per unit cell ranged from about 9 to 15 and the number of Brönsted acid or protonic sites from about 10 to 20. The average valence of the aluminum cations varied from about 1 to 3.

Products similar to the DB calcined ammonium zeolite Y have been obtained directly from the normal hydrogen form by two procedures: heating hydrogen zeolite Y at 700–800° in a closed reactor (*6*) and contacting the hydrogen form with ammonia in a closed reactor at 500° (*9*). Both procedures appear to involve reaction of the hydrogen zeolite with a portion of the chemical water which becomes labile under these reaction conditions. The prolonged retention of ammonia in the DB calcination surely fosters the formation of chemical water which in turn leads to the formation of the ultrastable product. A mechanism [Eqs. (3) and (4)] is presented which explains the formation of the ultrastable form.

The extreme instability of water-loaded hydrogen zeolite Y at elevated temperatures (*1*) might be attributed to reaction (3). High water concentrations in the zeolite could cause reaction (3) to occur at a much more rapid rate than reaction (4) thus effecting a catastrophic removal of aluminum from the framework. An earlier study showed that removal of about 60% or more of the tetrahedral aluminum resulted in loss of crystal structure (*7*). The proposed mechanism suggests that in the formation of the DB sample, reaction (4) serves as a control or governor on the degree of hydrolysis of aluminum associated with proton sites via neutralization of the proton sites by aluminum hydroxide. This means that reactions (3) and (4) must

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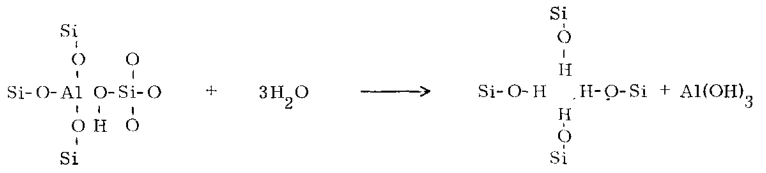
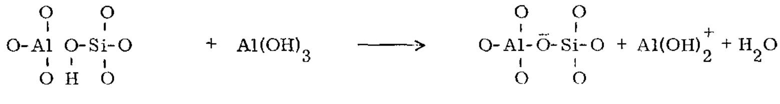


$$\mathrm{Si{-}O{-}\underset{\underset{Si}{O}}{\overset{\overset{Si}{O}}{Al}}\;\underset{H}{O}{-}\underset{O}{\overset{O}{Si}}{-}O \;+\; 3H_2O \longrightarrow Si{-}O{-}H\;\;\underset{\underset{\underset{Si}{O}}{H}}{\overset{\overset{\overset{Si}{O}}{H}}{}}\;H{-}O{-}Si \;+\; Al(OH)_3} \qquad (3)$$



$$\mathrm{O{-}\underset{O}{\overset{O}{Al}}\;\underset{H}{O}{-}\underset{O}{\overset{O}{Si}}{-}O \;+\; Al(OH)_3 \longrightarrow O{-}\underset{O}{\overset{O}{Al}}{-}\ddot{O}{-}\underset{O}{\overset{O}{Si}}{-}O \;+\; Al(OH)_2^+ \;+\; H_2O} \qquad (4)$$

occur at nearly the same rate, otherwise excessive hydrolysis would occur resulting in loss of crystal structure.

The charge of the cationic aluminum species has been found to vary from about 1 to 3, depending on the reaction conditions. The $Al(OH)_2^+$ ion formed in reaction (4) might react further with protons to yield $Al(OH)^{2+}$ and Al^{3+} ions. The four silanol groups in the product of reaction (3) should condense at elevated temperatures to yield water and form new Si–O–Si bonds as discussed earlier (*1, 6, 7*). The water molecules shown in reaction (3) are assumed to originate from the dehydroxylation reaction. The degree of dehydroxylation in these materials is not known, but it is reasonable to assume that it is limited because of the high hydrothermal stability of these substances. The usual dehydroxylated zeolite Y is extremely unstable to water (*8*). Since water is a product of reaction (4), only a limited amount of chemically-derived water is initially necessary to hydrolyze a portion of the tetrahedral aluminum. The disposition of the 0.5 H^+/Al in the DB sample, as shown by thermogravimetric analysis, is not known but could be present as hydroxyl groups on aluminum and as silanol groups, as shown in reaction (3), in addition to Brönsted acid protons.

CONCLUSIONS

These studies show that the ultrastable faujasite of McDaniel and Maher is formed because of the geometry of the ammonium zeolite Y during thermal decomposition. To obtain the expected, normal hydrogen zeolite Y, conditions must be controlled so that gaseous products formed during calcination of the ammonium zeolite are rapidly removed from the environs of the zeolite. Even vacuum calcination of large quantities of the ammonium zeolite or of tightly compacted samples might yield the aluminum-deficient product. As a result of the studies described in this article, one may reasonably ask "How many reports on the chemical and catalytic properties of hydrogen zeolite Y (or "decationized" or "decationated" zeolite Y) in fact describe the framework-aluminum-deficient zeolite?" Studies are now underway in this laboratory to determine if other hydrogen zeolites undergo aluminum removal as observed in hydrogen zeolite Y to yield products of increased thermal and hydrothermal stability.

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