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Evidence that Breck and Skeels Prepared Hydrogen Zeolite Y

In a series of papers, Breck, Skeels, and Flank (*1–4*) proposed that hydrogen zeolite Y, the expected thermal decomposition product of ammonium zeolite Y (Eq. (1)), does not exist.

$$NH_4Y \rightarrow HY + NH_3. \qquad (1)$$

They thermally decomposed the ammonium zeolite following the "shallow-bed" procedure first described by Kerr (*5*) and then characterized the calcined product by various treatments with aqueous salt solutions. The work reported here presents very strong evidence that "shallow-bed" calcination of ammonium zeolite Y yields the true hydrogen form of the zeolite as described earlier (*5*).

A sample of the ammonium zeolite [empirical formula of the anhydrous salt: $Na_{0.06}(NH_4)_{0.94}(AlO_2)(SiO_2)_{2.69}$] was thermally decomposed in a DuPont 951 thermogravimetric analyzer (TGA) by a previously described method (*6*) which included the continuous and essentially instantaneous quantitative analysis of evolved ammonia. The ammonia, expelled from about 150 to about 500°C at a programmed heating rate of 10°C/min, amounted to 0.423 mmole/100 mg of ash (sample weight at 1000°C). Beginning at about 600°C, 0.216 mole of chemical or constitutive water/100 mg of ash was evolved up to about 900°C.[1] Hence, almost 0.50 mole of chemical water was evolved per mole of evolved ammonia, in agreement with the stoichiometry dictated by the complete decomposition of the ammonium salt of a Brønsted oxyacid to yield ammonia, water, and the oxyacid anhydride.

In another TGA experiment, ammonium zeolite Y was heated to 500°C at 10°C/min, while the evolved ammonia was measured continuously and quantitatively. After cooling to room temperature, the sample was treated with dry gaseous ammonia and heated isothermally at 100°C until the ammonia evolved was less than 0.001 mg over a 10-min period. The sample was then heated and evolved ammonia measured as described above. The derivatives of the ammonia evolution curves are shown in Fig. 1. The shapes and areas of the two curves show that the evolution of ammonia from the original ammonium zeolite and that from the ammoniated sample are essentially identical. This very strongly suggests that reaction (1) is reversible.

Breck and Skeels claimed that 28 to 29% of the tetracoordinate-framework aluminum of the initial ammonium zeolite was removed from the framework and converted to six-coordinate aluminum on calcination at temperatures of 200 to 700°C. It is highly unlikely that such a substance would have the properties described in the present study. That such a substance would thermally desorb ammonia after ammonia chemisorption in exactly the same quantity and at the same temperatures as the original ammonium zeolite is very highly unlikely. Moreover, that the product proposed by Breck and Skeels would lose the very same quantity of constitutive water as calculated for the hydrogen form of the zeolite is also difficult to accept.

The proposal of Breck and Skeels was based on their observations of the behavior of the calcined product upon treatment with aqueous salt solutions. Work in this laboratory has shown that upon contact with liquid water at room temperature, the ion exchange capacity of the zeolite decreases. This was determined by contacting samples

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[1] See Fig. 1 of Ref. (*5*).

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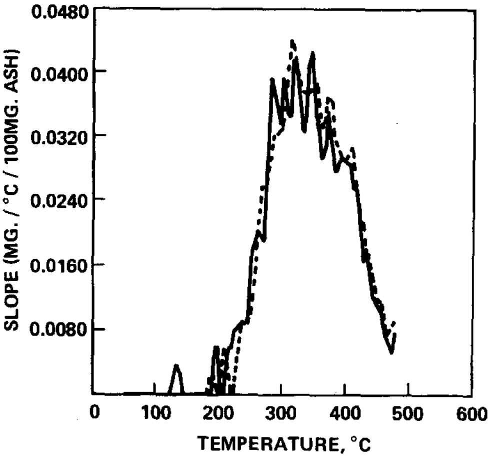

FIG. 1. Derivatives of ammonia evolution curves: ——, original sample: ----, reammoniated sample.

of carefully calcined ammonium zeolite Y in liquid water for various times and then adding concentrated ammonium hydroxide to the zeolite–water slurries to effect formation of ammonium ions by direct ammoniation of protons or hydronium ions in the zeolite. The solid products were analyzed for ammonium ion content. The results showed that after contact with water for only 10 to 15 s, 80% of the initial ammonium ion content was obtained and after 15 min contact 70% of the initial ammonium content was realized. These observations are in agreement with the proposal that hydrogen zeolite Y reacts with water to effect hydrolysis of tetracoordinate aluminum, thereby reducing the ion exchange capacity of the zeolite and leading to the formation of six-coordinate-nonframework aluminum (*5*). If water can effect such reactions it would be expected that aqueous salt solutions would be at least equally effective.

These results indicate that the experimental techniques used by Breck, Skeels, and Flank to characterize their product significantly change the properties of the material. Instead of observing the nature of hydrogen zeolite Y they actually studied the properties of the hydrolysis product of the hydrogen zeolite.

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