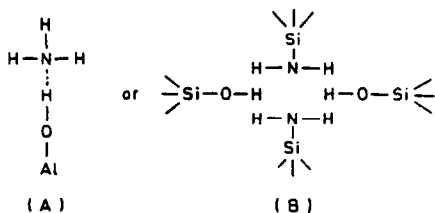


Evidence for Hydroxoaluminum Cation Formation during Dehydration and Decomposition of the Ammonium Ion in NH₄Y Zeolite. A Reply to G. T. Kerr

The early work of Cattanach *et al.* (1) showed quite conclusively that in the region of dehydration and deamination, the differential thermogravimetry (DTG) curves for "fresh" NH₄Y and "reconstituted" NH₄Y are substantially different in shape and in subtended areas for the individual peaks. Results with "fresh" NH₄Y could be interpreted as showing two major weight loss regions overall. The first region occurring near 100°C is attributed to desorption of physisorbed water. The second region, which is attributed to ammonium ion decomposition, is rather complex, indicating that a number of processes are taking place.

"Reconstituted" NH₄Y exhibits a less complex DTG curve, which contains three separate and distinct weight loss peak modes (1). Physisorbed NH₃ is lost in the region centered at about 110°C. The two remaining desorption peak modes are located at 180 and 280°C, with the actual quantities measured for each peak being consistent with the NH₃ adsorption mechanisms proposed by Breck and Skeels (2) for "reconstituted" NH₄Y:



Two NH₃ molecules are adsorbed in each of the 16 vacant sites as depicted in B. One NH₃ molecule is attached to each of the 16 hydroxoaluminum cations as depicted in A. The number of NH₃ molecules desorbed

during deamination agrees quite well with the number of desorbed NH₃ molecules obtained by Cattanach *et al.* (1) for "reconstituted" NH₄Y. The model of Breck and Skeels predicts that 32 and 16 NH₃ molecules per unit cell will be evolved during deamination. The actual values of Cattanach *et al.* were 30 and 22 NH₃ molecules per unit cell evolved in two steps during deamination of "reconstituted" NH₄Y. Thus, the total number of NH₃ molecules lost during deamination of both "fresh" and "reconstituted" NH₄Y is, and should be, identical, as predicted by the model.

The derivative curves for ammonia evolution shown by Kerr for "fresh" and "reconstituted" NH₄Y in his recent report (3) bear out the fact that the total evolved NH₃ is the same for either sample. However, neither curve shows the actual stepwise nature of the NH₃ evolution that others have found (1, 4). Perhaps the reason is that the Kerr data are not true TG data, but represent titrations of NH₃ present in the TG effluent. However, earlier data reported by Kerr and Chester (5) for a nearly identical experiment with "fresh" NH₄Y showed at least three separate NH₃ evolution steps. The experimental procedure, then, would seem to result in nonreproducible data. Hence, the argument of Kerr that the decomposition of "reconstituted" NH₄Y follows the exact same path as the decomposition of "fresh" NH₄Y is moot.

The additional evidence included in the Kerr report (3) that liquid water treatment of calcined NH₄Y causes a reduction in the ion exchange capacity is not surprising. Contacting calcined NH₄Y with liquid water or with water vapor also causes crystal

collapse (1, 2). Recent experiments were performed (6) where NH_4Y which had been calcined in a shallow bed under flowing dry air at 400°C , and cooled to room temperature, was subsequently put into 50 ml of distilled water for 2 h. X-Ray crystallinity of the dried water-treated zeolite product was less than 15% using standard diffraction peak intensity measurements and less than 35% when peak areas were measured. The X-ray peaks of the water-treated product are substantially broadened as well as reduced in intensity. In contrast, using essentially the same procedure but treating the calcined zeolite with 3 M NaCl solution, full crystallinity was retained, as previously reported by Breck and Skeels (2).

Evidence obtained recently from high-resolution solid-state NMR spectra of zeolite samples, utilizing magic-angle spinning, has clearly shown that dry-air calcination of NH_4Y results in the formation of extraframework aluminum species. Klinowski *et al.* (10) used ^{29}Si NMR and ^{27}Al NMR to show that calcination of NH_4Y at 400°C in air for 1 h resulted in removal of 23% of the framework aluminum. Bosacek *et al.* (11) used ^{27}Al NMR to show the formation of extraframework aluminum species as a result of 500°C air calcination. Maxwell *et al.* (12) concluded from their ^{29}Si NMR studies "that even during the relatively dry calcination conditions used for simple deamination to form the unstabilized HY zeolite, some loss of aluminum from the framework will occur."

The papers of Breck and Skeels (2, 7, 8) were the result of an extensive in-depth study of the physical and chemical properties of various air-calcined and steamed NH_4Y samples. The suggested models depicted the ideal species present in each step. Hydrogen Y as depicted by the equation



does not exist, nor does the calcined zeolite contain only hydroxoaluminum cations as the balancing cations. The models, based

on the experimental data, required formation of at least transient framework protons in order to form the various hydroxo-aluminum cation species. Further, some small fraction of the framework protons must be more than transient species in order to obtain the amount of water released during the dehydroxylation step at about 550°C (2). The models and equations suggested by Breck and Skeels do not preclude the existence of framework protons. They do preclude the existence of what has been called by Kerr (9) a "true" hydrogen form of the zeolite, that is, a framework containing only framework protons and devoid of any extraframework aluminum cations.

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