

Comment on the Letter to the Editors Written by R. M. Dessau, K. D. Schmitt, G. T. Kerr, G. L. Woolery, and L. B. Alemany, Entitled "On the Presence of Internal Silanol Groups in ZSM-5 and the Annealing of These Sites by Steaming"

In a recent interesting letter Dessau *et al.* presented FTIR and ^{29}Si (CP) MAS NMR results providing further evidence for the presence of internal silanol groups in ZSM-5. The decrease in the silanol groups during a steaming procedure accompanied by a dramatic enhancement of the resolution of the Q^4 signal in ^{29}Si MAS NMR spectra was reported (1).

Recently, we described a very similar ordering of the lattice and decrease in internal silanol groups that we observed during prolonged heat treatment in laboratory air of high-silica ZSM-5 in the presence of alkaline ions. By means of XPS the Na^+ or K^+ ions were found to concentrate at the external surface of the zeolite particles during this procedure (2).

Depending on the synthesis procedure we always find considerable amounts of Na^+ or K^+ ions (typically 0.75 to 1.3 ions per unit cell) in high-silica ZSM-5 even after thoroughly washing with water. They are located in terminal siloxy groups that can be converted into silanol groups upon ion exchange with diluted hydrochloric acid. Regrettably, the amounts of alkaline ions in the samples studied by Dessau *et al.* are not described very precisely. Only once do they mention an ion exchange with ammonium ions in order to remove Na^+ . But the corresponding FTIR spectrum does not exhibit the typical $\nu(\text{NH})$ bands which should indicate that the ion exchange was effective

(3). Therefore, we think it to be possible that sodium ions were still present during steaming in that case. However, it is interesting to conclude from Dessau's work that heat treatment at an increased vapor pressure of water probably accelerates the process of lattice improvement.

While the evidence for internal silanol groups in ZSM-5 is rather convincing we would like to propose a different view concerning the arrangement of silanol groups and the mechanism of rearrangement in the lattice. Silylation of silanol groups in our ZSM-5 with trimethylchlorosilane (TCS) and subsequent analyses of the products by means of ^{29}Si CP MAS NMR clearly indicate that silanol groups are not isolated but rather clustered (2, 4). Isolated silanol groups as suggested by Dessau *et al.* should yield exclusively trimethylsiloxysilanes. Instead, we find the secondary and tertiary products (dimethyldisiloxysilanes and methyltrisiloxysilanes) which can be formed only if further neighboring silanol groups are present. The ease of the formation of tertiary silylation products as compared with the silylation of, e.g., silica gels, indicates that in the ZSM-5 samples silanol groups are in arrangements favoring the insertion of TCS. We think that high-silica ZSM-5 typically contains clusters of four terminal groups each (e.g., silanol groups) where T atoms are missing in the lattice. During prolonged heat treatment (or steam-

ing) these vacancies migrate toward the external surfaces of the zeolite particles, possibly via a T-jump mechanism. This would explain why alkaline ions are found to concentrate at the external surface.

The activation of high-silica ZSM-5 with AlCl_3 mentioned by Dessau *et al.* clearly confirms this idea since Brønsted acidity is achieved by insertion of AlCl_3 in lattice vacancies rather than by linking with an isolated silanol group.

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