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On the Proposed Clustering of Silanol Groups in ZSM-5

Recently, considerable evidence has emerged confirming the existence of internal silyloxy groups in ZSM-5. This evidence has been based on observations of aluminum-independent cation exchange (*1*, *2*), ^{29}Si MAS NMR studies (*3*, *4*), and FTIR results (*4*).

In the preceding letter (*5*), Kraushaar, De Haan, and Van Hooff proposed that these internal silyloxy groups are typically clustered as a nest of four terminal groups where one T atom is missing from the highly siliceous ZSM-5 lattice.

In the course of our work, we, too, considered the possibility of such silanol nests, especially since such hydroxyl nests had been proposed (*6*) as unstable intermediates formed during the dealumination of zeolites.

We, however, rejected this explanation of clustered silanols in favor of an alternate view, which regarded the silyloxy groups as relatively isolated from each other while attached to a ZSM-5 lattice with all framework T atoms in their proper locations. This choice was based on the following considerations.

Silanol nests, due to the proximity of OH groups, would be expected to contain delocalized protons. The FTIR spectra, upon TPA decomposition, clearly showed a sharp OH band characteristic of isolated sites at 3735 cm^{-1}. Delocalized hydrogen-bonded sites should appear at lower frequencies and should be much broader. Such sites, exhibiting a broad band at 3500 cm^{-1}, do indeed form upon aqueous exchange and can be eliminated by dry thermal treatment alone (under vacuum in the IR cell), whereas the sharp 3735-cm^{-1} band is unaffected in the absence of steam.

The total number of silyloxy groups in high-silica ZSM-5 is generally about four per unit cell based on ion exchange (*2*) and NMR studies (*4*). A low Al sample (<0.02 Al/unit cell) containing 0.6 sodium ions per unit cell contained 4.7 silanols per unit cell as measured by TMA ion exchange at pH 12. MAS NMR indicated 4.9 silanols per unit cell.

In contrast with dealuminated zeolites, there is no reasonable explanation why these silanols should be clustered essentially at one channel intersection while three other intersections remain free of silanols. Furthermore, FTIR studies have shown these silyloxy groups to be associated as counterions to the TPA cations (approximately four per unit cell), which are located at each channel intersection. This requires one silyloxy group at each intersection.

The facile exchange of four or more TMA ions per unit cell also argues against a cluster of four silanols, since it would be difficult, if not impossible, to accommodate four TMA ions in one channel intersection.

As for the trimethylchlorosilane silylation results used to support the clustering hypothesis (*7*), several questions remain: How quantitative were the results in terms of chlorosilane reacted per original silanol group? What fraction of the silane had merely reacted with the external surface of the zeolite crystallites, as TMCS might be expected to diffuse only slowly into ZSM-5? Undoubtedly, trimethylsilane derivatives were formed first and would have been observed if milder conditions had been employed. The high reaction temperatures (400°C) used resulted in decomposition to silenes (*8*), which then can react fur-

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ther with water or HCl or additional chlorosilane, or even the lattice itself, to yield products indistinguishable by NMR from the presumed polydentate siloxanes. The silylation data reported are, in our opinion, insufficient to support the concept of silanol clusters in ZSM-5.

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R. M. DESSAU
K. D. SCHMITT
G. T. KERR
G. L. WOOLERY
L. B. ALEMANY

Mobil Research and Development Corporation
Central Research Laboratory
Princeton, New Jersey 08540

Paulsboro Research Laboratory
Paulsboro, New Jersey 08066

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