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LETTER TO THE EDITORS

On the Presence of Internal Silanol Groups in ZSM-5 and the Annealing of These Sites by Steaming

In a recent note on the framework hydroxyl groups of HZSM-5 zeolites (*1*), it was concluded that most, if not all, of the silanol groups responsible for the infrared band at 3745 $\mathrm{cm^{-1}}$ were located at the external crystal surface. For ZSM-5 samples having Si/Al atom ratios between 17 and 44, a direct relationship was observed between the number of 3745-$\mathrm{cm^{-1}}$ silanol groups and the external surface area of the crystals as measured by 1,3,5-trimethylbenzene sorption.

We recently reported that highly siliceous ZSM-5 exhibits cation-exchange capacity that, under certain conditions, is independent, and in excess, of the framework tetrahedral aluminum content (*2*). This aluminum-independent exchange was attributed to the presence of internal silanol groups in ZSM-5.

The intracrystalline nature of these silanol groups was confirmed by the fact that tetraethylammonium ions failed to exchange into calcined ZSM-5, whereas exchange with the smaller tetramethylammonium ions occurred readily. In addition, spectroscopic evidence has recently been reported confirming the presence of internal silanols in highly siliceous ZSM-5 (*3*).

FTIR STUDIES

We now wish to report additional evidence for the existence of internal silyloxy groups as counterions to TPA cations in as-synthesized forms of ZSM-5. High silica (Si/Al > 7000), TPA-containing ZSM-5 samples were synthesized. These samples were pelleted and placed in an evacuated chamber at less than 0.01 Torr inside a Nicolet 7199 FTIR spectrometer. FTIR spectra were taken every 100°C, as the zeolite was heated to 500°C.

The FTIR spectrum taken at 300°C, before decomposition of the TPA cation, was subtracted from that obtained at 500°C, after decomposition of the organic template. This difference spectrum is shown in Fig. 1.

This FTIR spectrum clearly reveals the formation of a nonacidic silanol O–H peak at 3740 $\mathrm{cm^{-1}}$, concomitant with the loss of organic C–H peaks in the 2800- to 3000-$\mathrm{cm^{-1}}$ region. These silanol groups do not exist in the as-synthesized zeolite and are only formed by decomposition of the organic cation, as shown in the equation

$$\mathrm{Si{-}O^{-}N^{+}(C_3H_7)_4} \rightarrow \mathrm{Si{-}O{-}H + (C_3H_7)_3N + C_3H_6}.$$

Any silanol groups present in the initial sample, such as those on the external crystal surface, do not appear in the difference FTIR spectrum by virtue of the subtraction technique used.

The formation of internal silanol groups during decomposition of TPA cations was also observed with a 35:1 Si/Al ZSM-5, which contained only 2.5 Al sites per unit cell to counterbalance 4 TPA ions per unit cell. The difference FTIR spectrum (500°C minus 200°C), which is shown in Fig. 2, reveals the formation of both acidic silanol groups adjacent to aluminum at 3610 $\mathrm{cm^{-1}}$ and nonacidic silanols at 3740 $\mathrm{cm^{-1}}$.

These results demonstrate that internal silanol groups exist in ZSM-5 and contribute to the infrared peak at 3740 $\mathrm{cm^{-1}}$, in addition to any terminating silanol groups located on the exterior of the crystals.

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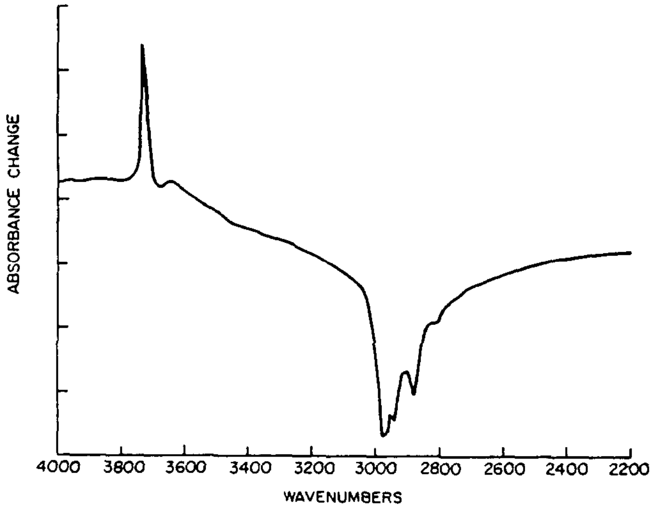


FIG. 1. FTIR difference spectrum (500–300°C) of a high-silica (Si/Al > 7000) ZSM-5.

MAS NMR EVIDENCE

Si MAS NMR studies provided additional evidence for the internal silanol groups in highly siliceous ZSM-5. In addition to a somewhat broad resonance at −113 ppm, a peak at −101 to −102 ppm was observed in the calcined H-form of ZSM-5. Quantitative Si spectra (60 s relaxation delay, T_1 = 7.5 and 6.1 s at −101 and −113 ppm) followed by a least-squares fit deconvolution (Fig. 3a) gave a concentration of 4.9 Si/unit cell for the −101 ppm species. This is at least an order of magnitude greater than that calculated for external surface silanol groups only.

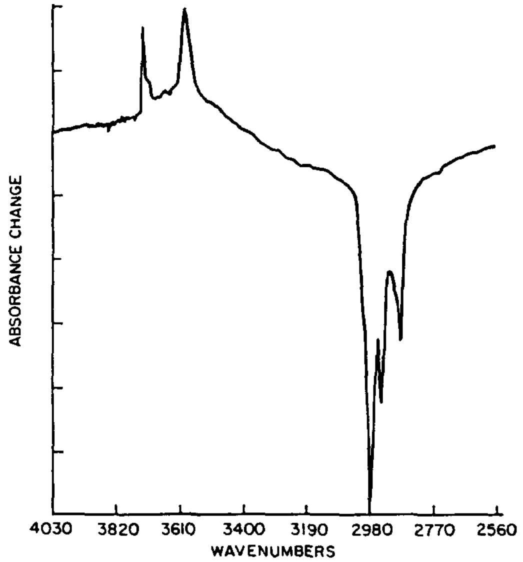


FIG. 2. FTIR difference spectrum (500–200°C) for a 35 : 1 Si/Al as-synthesized ZSM-5.

Silanol or silanoxy groups have been reported before by Si NMR of ZSM-5, but substantial concentrations of Al (*4*, *5*) or TPA (*6*) were present. Aluminum has been postulated to produce a downfield shift in adjacent silicons (*7*) and the rather large fraction (20%) of downfield silicons seen when TPA is present (*6*) makes it probable that the peak in this case is due to a shift similar to that observed for small organics (*8*, *9*). That the 4.9 Si/unit cell we observe at −101 ppm are silanols is confirmed by cross polarization experiments (Fig. 3b) in which the −101 ppm peak is found to cross polarize efficiently (*10*), with a four times increase in absolute intensity. Earlier work (*5*) showed an unexpected decrease in (absolute) intensity for the silanol peak under cross polarization conditions in a higher Al containing ZSM-5.

Since our HZSM-5 contained very little Al and no TPA and since the concentration of silicons at −101 ppm was at least an or-

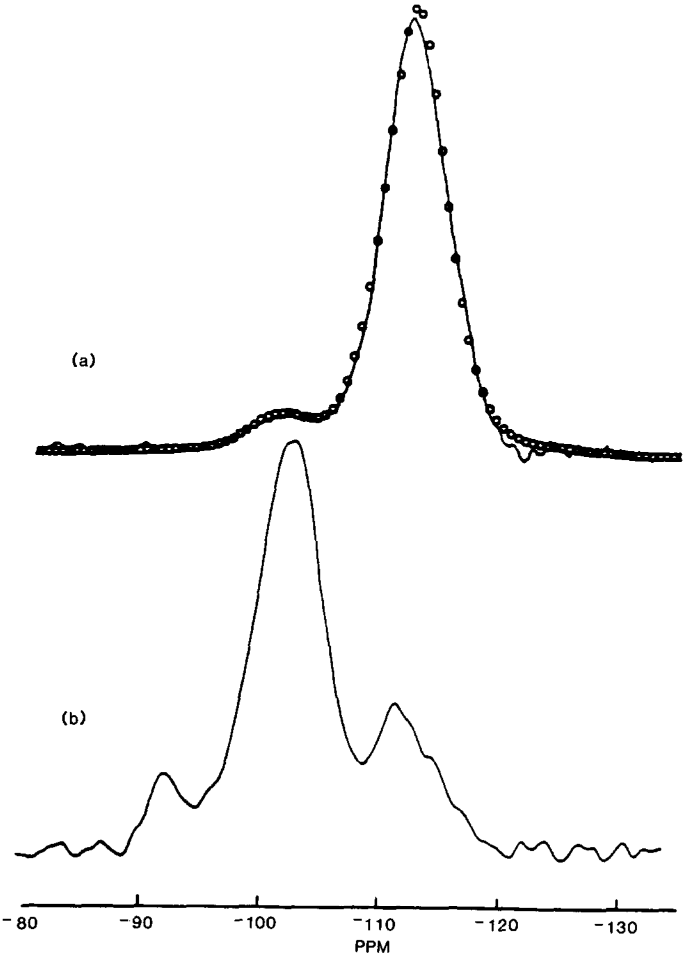
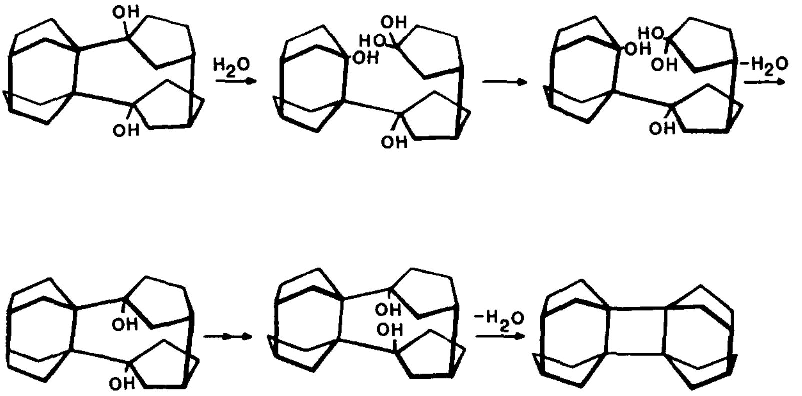


FIG. 3. Quantitative 39.6-MHz Si MAS–NMR spectrum (solid line) and least-squares fit simulation (circles) for a very low Al content HZSM-5 after calcination (a). CP-MAS Si NMR of a very low Al content HZSM-5 after calcination acquired using 4 ms single contacts and a proton field of 0.0012 T (b).

der of magnitude larger than that calculated for external terminating silanol groups, we conclude that the observed peak is due to internal silanols. The measured concentration of 4.9 silanols/unit cell is in excellent agreement with the 4.7 measured by TMA exchange.

EFFECT OF STEAMING—LOSS OF SILANOL SITES

The TMA exchange capacity of a calcined (2 h at 538°C) 13,000:1 Si/Al ZSM-5 (as measured by room temperature exchange in a solution 0.13 *M* in TMA^+Cl^- adjusted to pH 12 with TMA^+OH^-) was found to decrease dramatically from 0.76 meq/g to less than 0.05 meq/g upon steaming at 538°C. One hour of steaming in nitrogen containing 25 Torr water was sufficient to effect this reduction. A sample steamed in 1 atm of water for 2 h exhibited only 0.01 meq/g TMA exchange capacity. Consistent with their lower exchange capacities, these steamed samples were considerably less amenable to $AlCl_3$ activation via the procedure described earlier (*11*). α values for hexane cracking (*12*) after $AlCl_3$ activation were less than 15 for the steamed samples,



SCHEME 1. Plausible mechanism for annealing silanol defects (choice of location in four rings arbitrary).

whereas an α greater than 130 was obtained for the unsteamed precursor.

The facile loss of exchange capacity upon steaming is undoubtedly due to the structural rearrangement and annealing of isolated internal silanol defect sites, possibly via the mechanism shown in Scheme 1. Further evidence for the annealing of silanol sites is provided by Si MAS NMR and FTIR spectral changes induced by steaming. Figure 4 shows the Si NMR spectra obtained for a 2500 : 1 Si/Al calcined ZSM-5

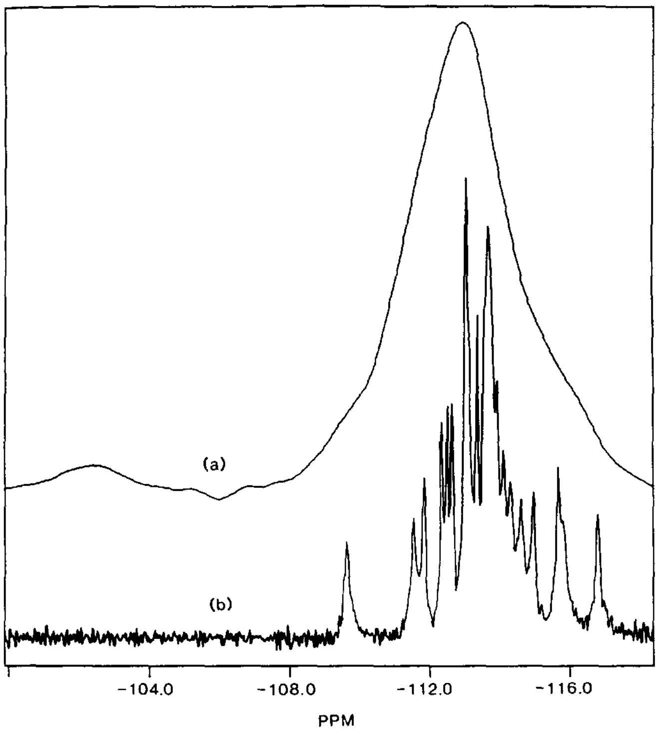


FIG. 4. 39.64-MHz Si MAS NMR spectra of a calcined high-silica ZSM-5 (Si/Al 2,500 : 1) before (a) and after (b) steaming.

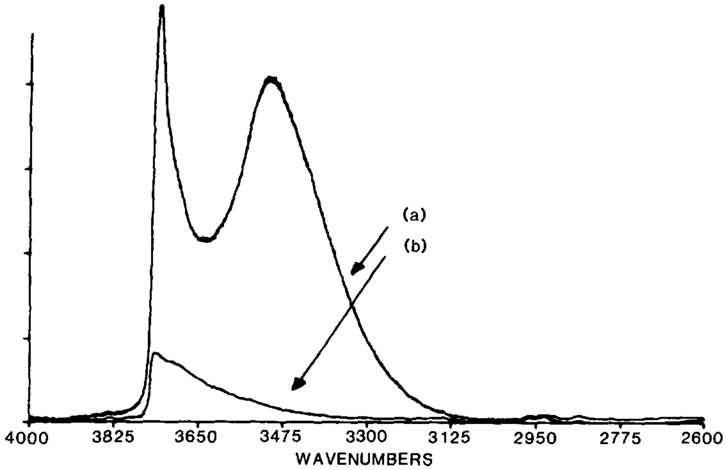


FIG. 5. FTIR spectra of a calcined high-silica ZSM-5 (Si/Al 13,000 : 1) before (a) and after (b) steaming.

before and after steaming. The internal silanol peak at −102 ppm is removed upon steaming, which in turn has a dramatic effect on the resolution of the main Si resonance at −113 ppm. Figure 5 shows analogous FTIR spectra for a 13,000 : 1 Si/Al ZSM-5. After calcination, and NH_4^+ exchange to remove residual Na^+, an additional band is present in the OH-stretching region at ~3500 cm^{-1}. This band is not present in the as-synthesized or calcined zeolite and appears to be induced by aqueous treatment. Upon streaming it can be seen that the intensity of absorption in the OH-stretching region is greatly reduced. The 3500-cm^{-1} band is essentially eliminated, and the 3740-cm^{-1} band is reduced to the level expected for external surface silanols.

Al MAS NMR of these samples indicate that the enhanced resolution of the Si NMR signal upon steaming is not due to loss of framework Al but rather to annealing of the internal silanol groups.

These results, taken in total, clearly demonstrate the presence of internal silanol groups in calcined forms of ZSM-5 and their facile removal by mild steaming.

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REFERENCES

1. Qin, G., Zheng, L., Xie, Y., and Wu, C., *J. Catal.* **95,** 609 (1985).
2. Chester, A. W., Chu, Y. F., Dessau, R. M., Kerr, G. T., and Kresge, C. T., *J. Chem. Soc. Chem. Commun.*, p. 289 (1985).
3. Woolery, G. L., Alemany, L. B., Dessau, R. M., and Chester, A. W., *Zeolites* **6,** 14 (1986).
4. Engelhardt, G., Fahlke, B., Magi, M., and Lippmaa, E., *Z. Phys. Chem. Lipzig* **266,** 1 (1985).
5. Nagy, J. B., Gabelica, Z., and Derouane, E. G., *Chem. Lett.*, p. 1105 (1982).
6. Boxhoorn, B., Kortbeek, A. G. T. G., Hays, G. R., and Alma, N. C. M., *Zeolites* **4,** 15 (1984). We have confirmed the 20% intensity of the peak at −101 ppm in a number of low-Al TPA-ZSM-5 materials.
7. Lippmaa, E., Magi, M., Samoson, A., Engelhardt, G., and Grimmer, A. R., *J. Amer. Chem. Soc.* **102,** 4889 (1980).
8. West, G. W., *Aust. J. Chem.* **37,** 455 (1984).

9. Fyfe, C. A., Kokotailo, G. T., Kennedy, G. J., and de Schutter, C. T., *J. Chem. Soc. Chem. Commun.*, p. 541 (1984).
10. Maciel, G. E., and Sindorf, D. W., *J. Amer. Chem. Soc.* **102,** 7606 (1980). Maciel and Sindorf found T_{1S} = 2–5 ms for silica; we find 11 ms for the internal silanols and 51 ms for the framework silicons adjacent to the silanols. In contrast, the −101 and −113 ppm silicons in TPA ZSM-5 both show T_{1S} = 35 ms confirming Lippmaa's conclusion (7) that cross-polarization is from the TPA cation and not from a silanol hydrogen.
11. Dessau, R. M., and Kerr, G. T.,. *Zeolites* **4,** 315 (1984); Chang, C. D., Chu, C. T-W., Miale, J. N., Bridger, R. F., and Calvert, R. B., *J. Amer. Chem. Soc.* **106,** 8143 (1984).
12. Weisz, P. B., and Miale, J. N., *J. Catal.* **4,** 527 (1965); Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966); Olson, D. H., Haag, W. O., and Weisz, P. B., *J. Catal.* **61,** 390 (1980); Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature* (*London*) **309,** 589 (1984).

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