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INVESTIGATION OF THE DEALUMINATION OF ZEOLITE ZSM-5 BY SOLID-STATE MAGIC-ANGLE SPINNING NMR

C.A. FYFE,* G.C. GOBBI, and G.J. KENNEDY

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

The dealumination of ZSM-5 by various procedures has been monitored by ^{29}Si and ^{27}Al MAS NMR. The results suggest that ZSM-5 and 'Silicalite' are isostructural: Resolved signals from up to 15 crystallographically inequivalent Si tetrahedra are observed in the ^{29}Si spectra of highly dealuminated ZSM-5 materials identical with those observed in the spectra of very highly siliceous 'Silicalite' prepared by direct synthesis.

There has been considerable discussion on the structural relationship between ZSM-5[1] and the material Silicalite,[2] which is claimed to be the completely siliceous end member of the ZSM-5 substitutional series. Recently, we have reported[3] the investigation of a very crystalline and highly siliceous Silicalite sample by high resolution solid-state ^{29}Si and ^{27}Al MAS NMR at high field and have shown that, without recourse to resolution enhancement, it is possible to resolve at least nine separate ^{29}Si resonances for a considerable number of the crystallographically inequivalent silicon atoms in the unit cell (we consider the detection of crystallographic inequivalence to be typical of all highly siliceous crystalline zeolites.[4] Also, a clearly resolved ^{27}Al resonance is observed whose chemical shift value (δ = 55.3 ppm) indicates that it has tetrahedral co-ordination, and implies that the aluminium is present as an integral part of the silicalite framework.

Herein we report results from studies designed to further delineate the structural relationship between these two materials: We have attempted to dealuminate ZSM-5 by a variety of procedures to give 'Silicalite', and monitored the progress of the reaction by ^{29}Si and ^{27}Al MAS NMR. The results are complementary to those reported in the accompanying paper,[5] the two studies being carried out independently.

^{29}Si and ^{27}Al MAS NMR spectra were obtained at 79.5 MHz and 104.2 MHz, respectively, using previously described[6] equipment on a narrow-bore Bruker WH-400 spectrometer. Spectra are presented with appropriate line broadening without resolution enhancement. Dealuminations were carried out using standard literature techniques,[7-9] and XRD spectra were recorded on a diffractometer outfitted with an automatic divergence slit.

Figure 1 shows the ^{29}Si MAS NMR spectra together with the corresponding x-ray diffraction patterns for the starting material of Si/Al ≃ 125 (Fig. 1A) and the products formed by reaction with $SiCl_4$ at 550°C for 15 h. (Fig. 1B) and by two successive 24 h. hydrothermal dealuminations carried out at 850°C (Fig. 1C). Dealumination by $SiCl_4$ yields the same overall result as the hydrothermal dealumination, although the reaction is not as complete. Treatment with EDTA according to standard literature procedures[7] was found to be ineffective.

Dealumination of ZSM-5 with a relatively low Si/Al ratio (Si/Al ≃ 20) carried out hydrothermally (850°C for 5 d), gives the spectrum shown in Fig. 2C. As in Fig. 1, there was little change in the XRD spectra upon dealumination, indicating the structure remains the same. Figure 2A shows the ^{29}Si spectrum of a material obtained from direct synthesis and possessing a Si/Al of ≃ 900, while Fig. 2B depicts the spectrum of the product obtained from the hydrothermal dealumination (5 d at 850°C) of the material with Si/Al ≃ 125. From the detailed similarity of the spectra, it seems reasonable to suggest that the framework structures are indeed identical. In Fig. 2A, the linewidth is approximately 23 Hz and in Fig. 2B, where the linewidth is about 22 Hz, 15 crystallographically inequivalent silicon atoms are observed without using resolution enhancement. We have recently shown that the limiting linebroadening mechanism in low Si/Al zeolitic materials, which precludes the observation of site inequivalence, results from a distribution of ^{29}Si environments due to the distribution of second and further nearest neighbour aluminium atoms in the lattice.[4]

Figure 3 shows ^{29}Si MAS NMR spectra of a sample with a very low Si/Al ratio (≃7) and one of high Si/Al ratio (≃800) together with their corresponding ^{27}Al MAS NMR spectra. A well resolved peak at ca. 54 ppm with respect to $Al(H_2O)_6^{3+}$ (aq) as a reference is observed in the ^{27}Al spectrum in both cases, decreasing in absolute intensity at the higher Si/Al, with little accompanying change in chemical shift. The chemical shift value indicates that in both cases the Al present is in tetrahedral coordination. The lower spectrum (Si/Al ≃ 800/1) shows the fine structure previously reported for material of this composition.[3] Inspection of the ^{29}Si spectrum of the material of lowest Si/Al ratio (≃ 7/1) reveals that there are clearly several peaks in the ^{29}Si spectrum, shown resolved into Gaussian curves in the figure, corresponding to the different silicon environments Si(3Al), Si(2Al), Si(1Al), and Si(0Al).

The Si/Al ratio calculated from the ^{29}Si NMR spectrum is in excellent agreement with that found by chemical analysis, indicating that essentially all of the aluminium in the sample is accounted for. Thus, the aluminium atoms must be not only in tetrahedral coordination, as indicated by the observed chemical shift value, but must be directly incorporated into the lattice framework, since their effect is seen in the ^{29}Si spectrum indicating that they are directly attached (via oxygen bridges) to the silicon atoms.

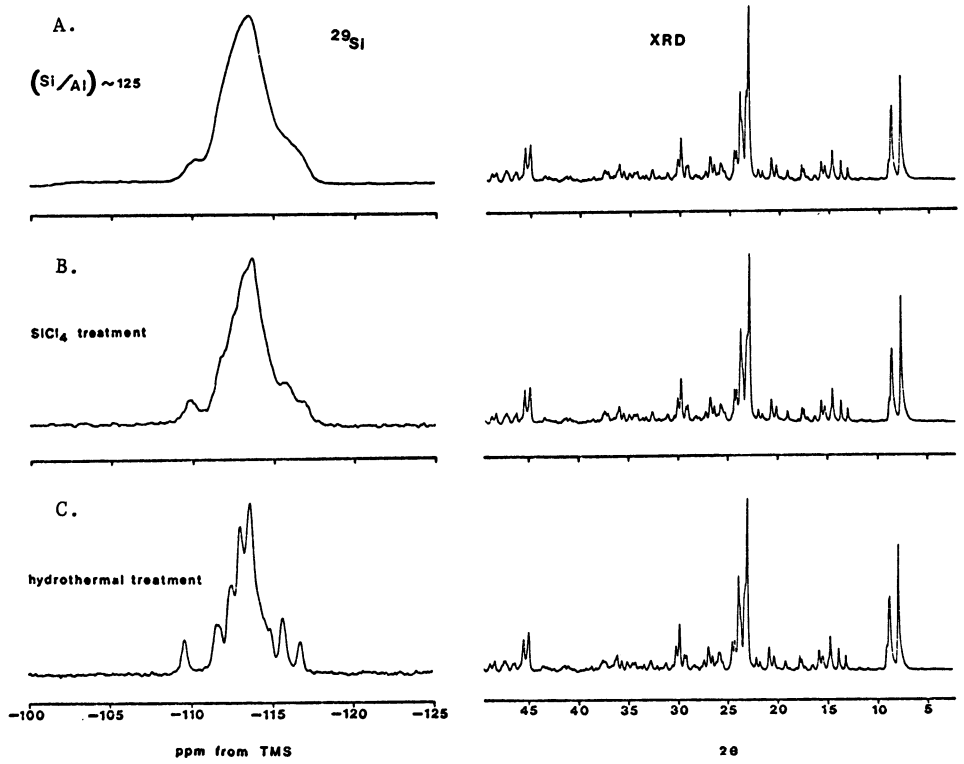

Fig. 1. ^{29}Si MAS NMR spectra obtained at 79.5 MHz with the corresponding XRD spectra for:
A. Material of Si/Al ≃ 125 (892 scans, 1 Hz linebroadening).
B. This material after reaction with $SiCl_4$ at 550°C for 15 h (210 scans, 3 Hz linebroadening).
C. This material after two successive hydrothermal dealuminations of the hydrogen form at 850°C for 24 h intervals (50 scans, 3 Hz linebroadening).

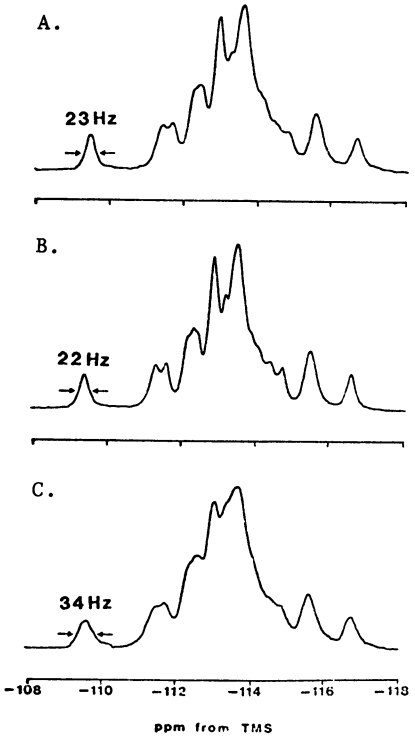

Fig. 2. ^{29}Si MAS NMR spectra obtained at 79.5 MHz for:
A. Material of Si/Al ≃ 900 obtained from direct synthesis. (500 scans, no linebroadening).
B. ZSM-5 of Si/Al ≃ 125 dealuminated hydrothermally at 850°C for 5 d (1560 scans, no linebroadening).
C. ZSM-5 of Si/Al ≃ 20 dealuminated at 850°C for 5 d (1500 scans, no linebroadening).

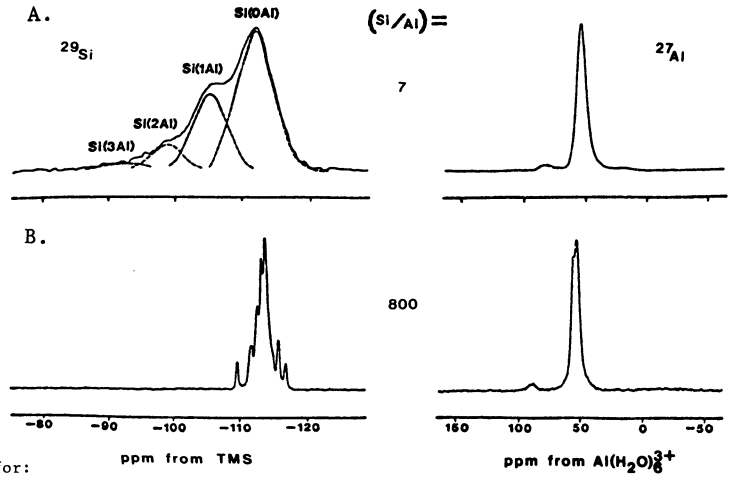

Fig. 3. ^{29}Si MAS NMR spectra obtained at 79.5 MHz, ^{27}Al spectra obtained at 104.2 MHz for:
A. Si/Al ≃ 7 (^{29}Si:2010 scans, 35 Hz linebroadening; ^{27}Al:1636 scans, 25 Hz linebroadening).
B. Si/Al ≃ 800 (^{29}Si:400 scans, 1 Hz linebroadening; ^{27}Al:123,000 scans, 25 Hz linebroadening).

The results described above confirm our previous findings[3] regarding the occurrence and lattice siting of aluminium atoms in 'Silicalite' and clearly imply that it is isostructural with ZSM-5 by the conversion of the latter to the former by dealumination.

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