

MULTIPLE QUANTUM ^{27}Al MAS NMR OF SAPO-44 MOLECULAR SIEVES

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Incorporating silicon atom into phosphorus T site of the aluminophosphate framework produces Silicoaluminophosphates (SAPOs). The bridging hydroxyl in the framework may be formed in the Al-O-Si position, which is an active motif participating in many catalytic reactions.

MAS NMR is widely used for the characterization of Al species in zeolites. ^{27}Al has a nuclear spin value greater than $1/2$, therefore its electric quadrupole moment is expected to interact with the electric field gradient at Al created by the electronic surroundings. This quadrupolar interaction is often so strong that only the central transition ($-1/2, 1/2$) remains observable in its powder spectra. In 1995, Frydman and Harwood proposed multiquantum MAS (MQ MAS) method as an alternative to obtain high resolution isotropic spectra.^[1] This paper reports the results of the application of ^{27}Al MQ MAS NMR method to elucidate new structural insights in SAPO-44.

The triple (3MQ) and quintuple-quantum (5MQ) ^{27}Al MAS 2D-NMR spectra were recorded at 78.2 MHz on a Bruker ASX-300 NMR Spectrometer. The 4 mm rotors were spun at 12 kHz. Three SAPO-44 samples were synthesized in this study and their atom ratio (Si:Al:P) are 0.08:0.50:0.42 (a), 0.10:0.50:0.40 (b) and 0.12:0.50:0.38 (c).

In the ^{27}Al 3Q MAS NMR spectrum of sample a, three resonances are clearly resolved. The resonance at $\delta_{\text{iso}}^{27}\text{Al} \approx 40.1$ ppm with a SOQE = 2.8 MHz is assigned to framework tetrahedral aluminum connected with four phosphorus atoms (signal A). For signal B, the $\delta_{\text{iso}}^{27}\text{Al} \approx 42.3$ ppm, but a much higher SOQE value of 6.0 MHz is obtained. No significant line narrowing is observed suggesting that a substantial distribution of isotropic parameters exist in the species. B is the result of a weak second order interaction between four-

coordinated framework aluminum with molecular templates, which tends to increase the electric field gradient at Al. We found that this peak ridge disappeared after calcinations of the molecular sieves. Signal C is located at $^{27}\text{Al} \approx 17.7$ ppm, and based on its chemical shift and its ridge position it can be assigned to five-coordinated Al species.

When the quantity of Si atoms is increased in the samples, a new signal, D, with an isotropic chemical shift of ≈ 57 ppm and a SOQE of 2.3 MHz is detected. The chemical shift of D is almost identical to the chemical shifts of tetrahedral species enclosed by various silicon atoms as the nearest neighbor found in the zeolite Y and the zeolite ZSM-5. It has been suggested that Si patches exist in these systems.

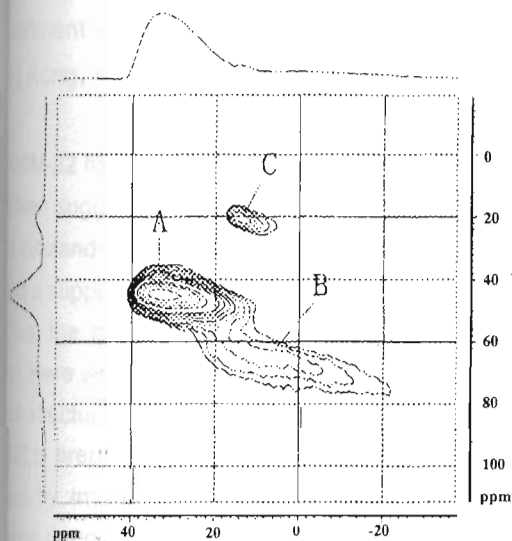


Fig. 1. 3MQ MAS NMR ^{27}Al of SAPO-44 with Si:Al:P = 0.08:0.5:0.42

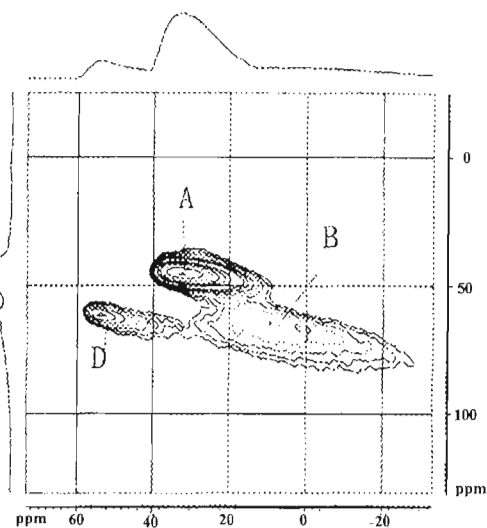


Fig. 2. 3MQ MAS NMR ^{27}Al of SAPO-44 with Si:Al:P = 0.1:0.5:0.4

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