^{27}Al, ^{29}Si and ^{31}P MAS NMR of M^{n+}-SAPO-34 Prepared with Microwave Assisted Heating

R. Fu (NHMFL); A.J. Hernández-Maldonado (U. of Puerto Rico-Mayaguez, Chemical Engineering)

Introduction

Alkaline earth metal-based nanoporous silicoaluminophosphates (SAPOs) are CO_2 selective adsorbents in ultra-purification applications.[1-3] In order to reduce the framework faulting and enhance the adsorption capacity of these materials we have used a microwave heating assisted hydrothermal method. We have performed MAS NMR studies to verify this and the results are discussed below.

Experimental

^{27}Al and ^{29}Si MAS NMR measurements were performed on an ultra-narrow bore 19.6T magnet with a Bruker DRX NMR console where the ^{27}Al and ^{29}Si Larmor frequencies are 217.14 and 165.55 MHz, respectively, using a single resonance 4 mm MAS NMR probe. The samples were spun at 8 kHz. The ^{31}P measurements were carried out on a Bruker DMX 300MHz NMR spectrometer where the ^{31}P Larmor frequency is 121.52 MHz. A 4 mm Bruker MAS NMR probe was used with a sample spinning rate of 12 kHz for all ^{31}P measurements. For the ^{27}Al analyses, the chemical shifts were referenced to a $Al_2(SO_4)_3$ solution. 256 transients were used to record the ^{27}Al spectra with a recycle delay of 1s, pulse length of 1.0 μs (~10˚ flip angle), and 1024 FID points with 5 μs dwell time. For ^{29}Si, the chemical shifts were referenced to DSS. 512 transients were used to accumulate the ^{29}Si signals with a recycle delay of 10 s, pulse length of 2 μs (~15˚ flip angle), and 800 FID points with 10 μs dwell time. For ^{31}P, the chemical shifts were referenced to a Na_2HPO_4 solution. The experimental parameters were: 256 transients, 5 s recycle delay, 1.5 μs pulse length (~10˚ flip angle), and 1536 FID points, 5 μs dwell time.

Results and Discussion

Figure 1 shows the spectra for several material variants, including partially detemplated (PD) and ion-exchanged Sr-SAPO-34 samples. The strong ^{27}Al resonance peak at around 40 ppm corresponds to aluminum in a tetrahedral environment. Meanwhile, the small peak at 12 ppm may be due to aluminum with penta or hexa-coordination states. Another small peak shown at around 80 ppm is due to resonance contributions from other tetrahedral aluminum families. For the peak at ~ -10 ppm, the resonance should be attributed to octahedral aluminum species resulting from detemplation. For as-synthesized Na-SAPO-34 prepared for 36 h, the intensity of this peak decreased slightly after ion-exchange with Sr^{2+}, but still remained higher when compared to the intensity of the peak of Na-SAPO-34 prepared after 42 h. This indicates that the Al centers in the latter sample contain less octahedral environments. The ^{31}P spectrum of Na-SAPO-34 (MW-180-36) shows four distinct resonances. For the high resonance peak at -30.3 ppm, the coordination environment should be attributed to $P(OAl)_4$. Meanwhile, the remaining weak resonances could be related to non-equivalent P sites. After PD at 430˚C and 36 hours, the intensity of the peaks at -11.9 and -16.2 ppm decreased, disappearing after completion of the ion-exchange and calcination at 500˚C. Therefore, one may conclude that these peaks are related to the coordination of phosphorous with the template, while the peak at -20 ppm should be attributed to phosphorous coordinated to water molecules. All the samples showed a ^{29}Si peak at -90 ppm, which should be assigned to Si (4Al). Interestingly, the linewidth of the resonance at -90 ppm for many of the samples is about half when compared to the of Na-SAPO-34 (MW-180-36-16), which seems to inversely correlate with the linewidth of ^{27}Al at 40 ppm and ^{31}P at ~ -29.5 ppm. This is probably due to effects from the PD process. It should be noted that Na-SAPO-34 (MW180-42) does not show the peak broadening in the -100 to -120 ppm range, which indicates that its framework of silicon atoms are present mainly as Si(4Al) and, with minimal amount of faults.

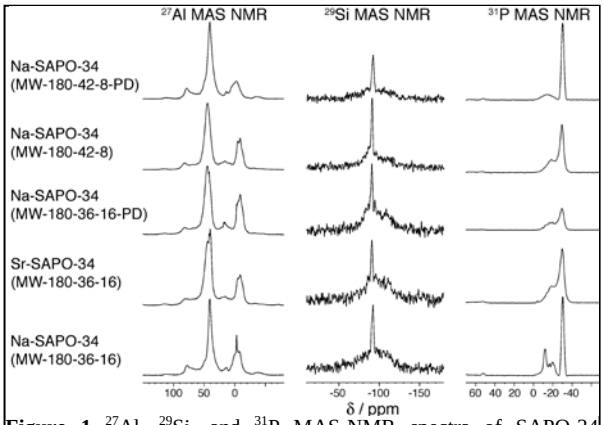

Figure 1 ^{27}Al, ^{29}Si, and ^{31}P MAS-NMR spectra of SAPO-34 materials. Data in parentheses represent temperature, synthesis time (hours)

Acknowledgements

This work was supported in part by the NHMFL and by the NASA award NNX08BA48A.

References

[1] Rivera-Ramos, M. E., *et al.*, Industrial & Engineering Chemistry Research, **47**, 5602-5610 (2008).
[2] Zhang, L., *et al.,* Journal of Physical Chemistry C, **114**, 14755-14762 (2010).
[3] Arevalo-Hidalgo, A. G., *et al.,* Industrial & Engineering Chemistry Research, **50**, 10259-10269 (2011).