Introduction

Alkaline earth metal-based nanoporous silicoaluminophosphates (SAPOs) are CO₂ selective adsorbents in ultra-purification applications. 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

27Al and 29Si MAS NMR measurements were performed on an ultra-narrow bore 19.6T magnet with a Bruker DRX NMR console where the 27Al and 29Si 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 31P measurements were carried out on a Bruker DMX 300MHz NMR spectrometer where the 31P 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 31P measurements. For the 27Al analyses, the chemical shifts were referenced to a Al₂(SO₄)₃ solution. 256 transients were used to record the 27Al 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 29Si, the chemical shifts were referenced to DSS. 512 transients were used to accumulate the 29Si 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 31P, the chemical shifts were referenced to a Na₂HPO₄ 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 27Al 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 Sr²⁺, 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 31P spectrum of Na-SAPO-34 (MW-180-36-16) shows four distinct resonances. For the high resonance peak at -30.3 ppm, the coordination environment should be attributed to P(Al)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 phosphorus with the template, while the peak at -20 ppm should be attributed to phosphorous coordinated to water molecules. All the samples showed a 29Si 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 27Al at 40 ppm and 31P 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.

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References