Solid-State NMR Study of Magnesium Incorporation in Aluminophosphate of Type 20

S. Prasad and James F. Haw*

Laboratory of Magnetic Resonance and Molecular Science, Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received October 3, 1995. Revised Manuscript Received November 28, 1995[⊗]

Magnesium aluminophosphate of type 20 (sodalite structure) was synthesized with two different levels of metal substitution. The amount of Mg from the gel entering into the crystal framework upon hydrothermal treatment varied to maintain Mg ordering in the lattice. The occluded tetramethylammonium hydroxide molecules could not be removed when the structure contained >1 Mg/sodalite cage. At 1 Mg/sodalite cage, calcination resulted in the partial removal of Mg into the extraframework sites. Nevertheless, the calcined material contained two different bridging hydroxyl groups located at P(2Al,2Mg) and P(3Al,1Mg) sites corresponding to resonances at −19.3 and −27.7 ppm in the ^{31}P spectrum, respectively.

Introduction

Sodalites comprise a class of materials having three-dimensional structures built up of corner-sharing TO_4 tetrahedra with T = Si^{4+}, Al^{3+}, Ge^{4+}, Ga^{3+}, etc.[1] The truncated octahedra (also known as the sodalite cage or the β cage) thus formed have many potential applications in the design of advanced materials.[2] Recent studies demonstrated the formation of phosphate-based sodalite frameworks.[3] The analogue of sodalite in the aluminophosphate family is $AlPO_4$-20, which has a neutral framework.[3a] Substitution of divalent metal, e.g., Zn, Co, Mn, Mg, etc., in place of aluminum results in the corresponding MeAPO-20 structure having an anionic framework.[4] There has been a brief report on the study of the magnesium-substituted structure MAPO-20.[5] In the present paper we report a detailed NMR characterization of MAPO-20 with two different substitution levels of magnesium. Our study shows that the occluded template could be removed completely only when the metal content is low; even then a *demetallization* is observed. Two different types of acid sites corresponding to protons located at P(3Al,1Mg) and P(2Al,2Mg) sites could be distinguished by ^{1}H−^{31}P CP-MAS NMR spectroscopy.

Experimental Section

MAPO-20 samples with two different gel compositions were synthesized following the patented method of Wilson and Flanigen.[4] The sources of raw materials were CATAPAL-B alumina (Vista), phosphoric acid (85%, Mallinckrodt, AR) and tetramethylammonium hydroxide pentahydrate (Aldrich). Two different gel compositions, $\{(1 - x) + 0.005\}Al_2O_3 \cdot 2x MgO \cdot 1.0P_2O_5 \cdot 1.0TMAOH \cdot 50H_2O$, where $x = 0.085$ and 0.335 were used. Gels were hydrothermally treated in Teflon-lined autoclaves at 473 K for 24 h under static conditions. To stop the crystallization process, the reaction mixture was cooled, and the crystals were filtered, washed with distilled, water and dried at room temperature.

All MAS NMR spectra were acquired using a Chemagnetics 360 spectrometer operating at 93.73, 145.62, and 359.73 MHz for ^{27}Al, ^{31}P, and ^{1}H, respectively. $Al(NO_3)_3$ solution (0 ppm), the upfield signal of (−)-(2*S*,3*S*)-bis(diphenylphosphino)butane (*S*,*S*)-chiraphos (−13.3 ppm with reference to 85% phosphoric acid), and acetone (2.11 ppm with reference to TMS) were used as chemical shift references for ^{27}Al, ^{31}P, and ^{1}H, respectively. Kaolinite was used to set up ^{1}H−^{27}Al match. The following NMR experiments were performed: ^{27}Al, single-pulse excitation, pulse delay = 2 s, pulse length = 1 μs (<10°), 400 transients; CP, contact time = 0.8 ms, pulse delay = 3 s, pulse length = 5 μs (90°), 400 transients; ^{31}P, single-pulse excitation with proton decoupling, pulse delay = 30 s, pulse length = 5.2 μs (90°), 64 transients; CP, contact time = 0.1−10 ms, pulse delay = 5 s, pulse length = 4.3 μs (90°), 128 transients; ^{1}H, single pulse excitation, pulse delay = 10 s, pulse length = 5 μs (90°), 64 transients. Samples were packed in 7.5 mm zirconia rotors and a spinning frequency of 4 kHz was used in all the experiments. X-ray powder diffraction patterns were obtained using a Seifert-Scintag powder diffractometer PAD 5 fitted with Cu Kα radiation. Scanning electron microscope (SEM) photographs were taken on a JEOL JSM-T330A microscope at the Texas A&M University Electron Microscopy Center. Chemical analysis was carried out by Galbraith Laboratories. Calcination was done in a muffle furnace (1 g of sample, 2 mm bed depth). In the case of sample B, calcination was also attempted with flowing nitrogen or oxygen.

Results and Discussion

As-Synthesized Forms. The samples are designated as sample A $\{(Mg/Al)_{gel} = 0.092\}$ and sample B $\{(Mg/Al)_{gel} = 0.5\}$, respectively. The X-ray diffraction patterns of both samples in their as-synthesized forms (Figure 1) resemble those of aluminosilicate sodalite. The peaks are sharper for sample B which has a higher Mg content. The sharper peaks are reflected in the size and shape of the crystals. The SEM photograph of sample A shows spherical crystals with an average diameter of 1 μm, while sample B crystals are formed of aggregates of platelets having a size of 50 μm (Figure 2). Duke et al.[6] observed changes in the morphology of

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) Depmeier, W. *Acta Crystallogr., Sect. B* **1984**, *B40,* 185−191.

(2) Stein, A.; Ozin, G. A.; Macdonald, P. M.; Stucky, G. D.; Jelinek, R. *J. Am. Chem. Soc.* **1992**, *114*, 5171−5186.

(3) (a) Wilson, S. T.; Lok, B. M.; Flanigen, E. M. US Patent 4,310, 440, 1982. (b) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508−510.

(4) Wilson, S. T.; Flanigen, E. M. US Patent 4,567,029, 1986.

(5) Barrie, P. J.; Klinowski, J. *J. Phys. Chem.* **1989**, *93*, 5971−5974.

(6) Duke, C. V. A.; Hill, S. J.; Williams, C. D. *J. Chem. Soc., Chem. Commun.* **1994**, 2633; *Zeolites* **1995**, *15*, 413−420.

0897-4756/96/2808-0861$12.00/0

Table 1. Product Compositions of MAPO-20 Samples

sample	bulk chemical composition[a]	framework composition[b]	$(Mg/Al)_{gel}$	$(Mg/Al)^a$	$(Mg/Al)^b$
A (as-syn)	$(Mg_{0.04}Al_{0.46}P_{0.5})O_2$	$(Mg_{0.92}Al_{0.408}P_{0.5})O_2$	0.092	0.086	0.224
A (calcined)	$(Mg_{0.043}Al_{0.428}P_{0.529})O_2$	$(Mg_{0.044}Al_{0.455}P_{0.5})O_2$		0.10	0.097
B (as-syn)	$(Mg_{0.129}Al_{0.387}P_{0.483})O_2$	$(Mg_{0.127}Al_{0.373}P_{0.5})O_2$	0.5	0.333	0.340

[a] By chemical analysis. [b] By NMR (assuming $P = 0.5$).

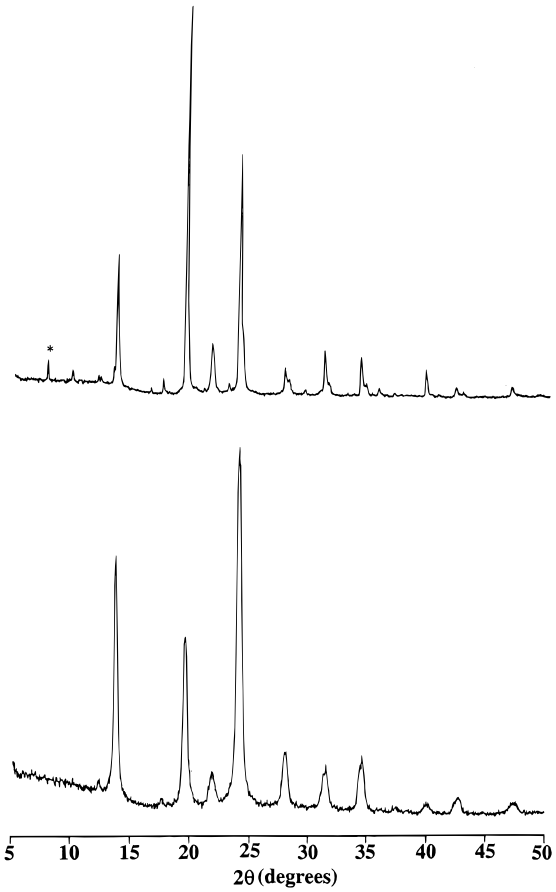

Figure 1. X-ray powder diffraction patterns of (bottom) sample A and (top) sample B. The most intense peak of the impurity phase in the sample B is marked.

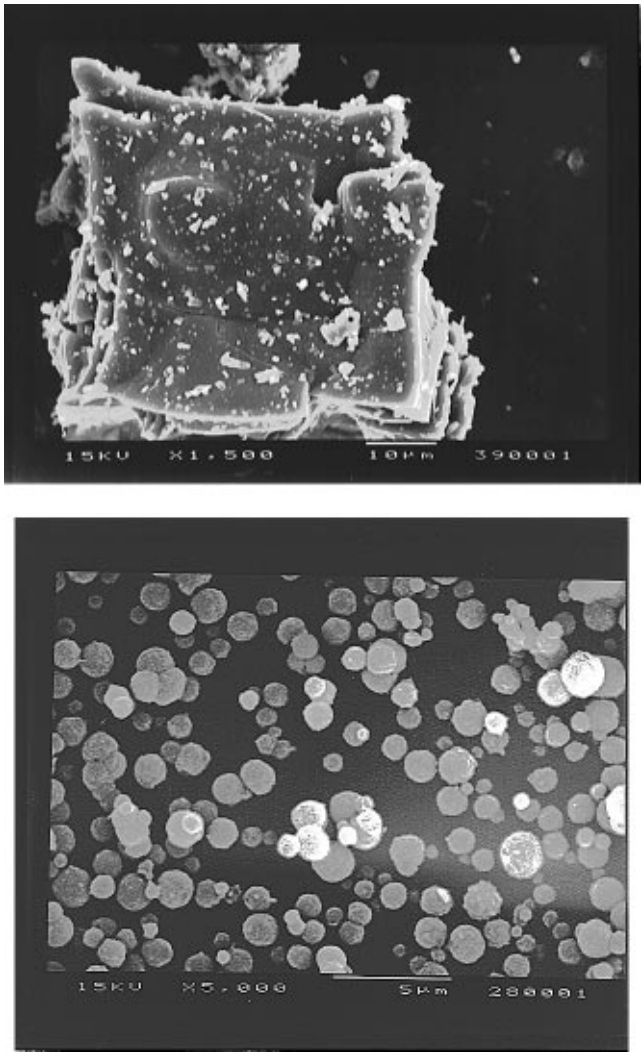

Figure 2. SEM photographs of (bottom) sample A and (top) sample B.

CoAPO-20 crystals depending on the amount of cobalt. Sample B contains a small amount of impurity (probably $AlPO_4$-15[7]).

The chemical compositions of both the samples in their as-synthesized forms determined by chemical analysis and NMR are given in Table 1. Chemical analysis data correspond to the elements present in the framework as well as the nonframework sites, while NMR data correspond to elements present in the framework only. For the sample A, the framework Mg content (derived from the decomposition of the ^{31}P spectrum) is almost double that of the bulk Mg content. However, there is a slight reduction in the framework Al as compared to the bulk. Thus in sample A, Al is present as nonframework species also (possibly unreacted boehmite). For sample B, the bulk chemical analysis data agree closely with the NMR data. The ^{27}Al NMR spectra of the samples show signals at 34, 5, and −9 ppm (Figure 3a,c). The major peak at 34 ppm is typical of Al in tetrahedral coordination. For the sample B, this line is split, and a sharp line appears at 40 ppm. The minor resonances are caused by secondary interaction of the framework Al sites with the template/water molecules. These signals are emphasized in the cross-polarization spectra (Figure 3b,d). It is also observed that the sharp resonance at 40 ppm in sample B disappears, indicative that these Al sites are inaccessible to the water/template molecules. The ^{27}Al MAS NMR spectrum of boehmite (not shown) displayed a broad peak centered at 6.1 ppm (fwhm = 1500 Hz). Therefore, we cannot rule out the possibility of the presence of a minor amount of unreacted boehmite contributing to the signal at 4 ppm in sample A.

^{31}P NMR spectra of $AlPO_4$ molecular sieves generally exhibit a single resonance at −30 ppm corresponding to P(4Al) sites in the framework.[8] The structural

(7) Szostak, R. *Molecular Sieves: Principles of Synthesis and Modification*; van Norstrand: New York, 1989; p 444.

(8) Blackwell, C. S.; Patton, R. L. *J. Phys. Chem.* **1984**, *88*, 6135−6139.

Table 2. ^{31}P Data for As-Synthesized (Samples A and B) and Calcined Dehydrated (Sample A) MAPO-20

	material type	peak 1	peak 2	peak 3	peak 4	peak 5
chemical shift (ppm)	as-syn (B)	−33.9	−28.0	−21.3	−14.8	absent
	as-syn (A)	−34.5	−28.3	−21.6	absent	−16.7
	calcined (A)	−34.5, −31.4	−27.7	−19.3	absent	absent
line width (Hz)	as-syn (B)	505.7	319.0	256.7	326.8	
	as-syn (A)	513.7	456.6	375.1		407.7
	calcined (A)	315.6, 226.8	754.5	397.5		
relative population (NMR)	as-syn (B)	19.8	59.6	19.7	0.76	
	as-syn (A)	34.7	48.6	9.87		6.8
	calcined (A)	59.9, 7.8	29.1	3.0		
relative population (binomial distribution)	as-syn (B)	31.7	42.3	21.6	4.9	
	as-syn (A)	44.5	40.0	13.5		
	calcined (A)	69.1	26.8	3.9		
structural unit		P(4Al)	P(3Al,1Mg)	P(2Al,2Mg)	P(1Al,3Mg)	nonframework

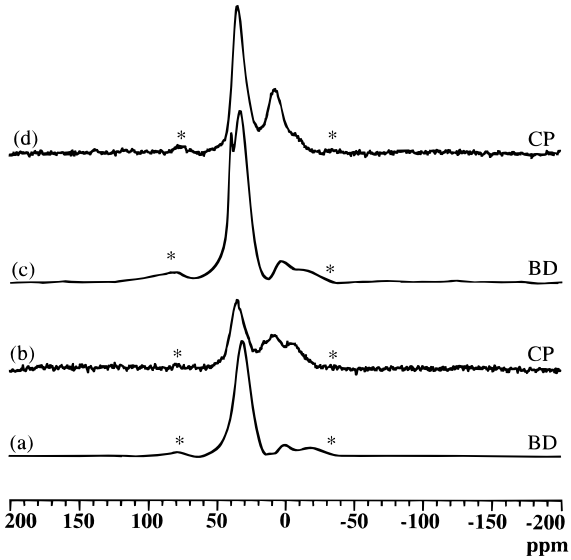

Figure 3. ^{27}Al Bloch decay (BD) and ^{1}H−^{27}Al cross polarization (CP) MAS NMR spectra of (a, b) sample A and (c, d) sample B in their as-synthesized forms.

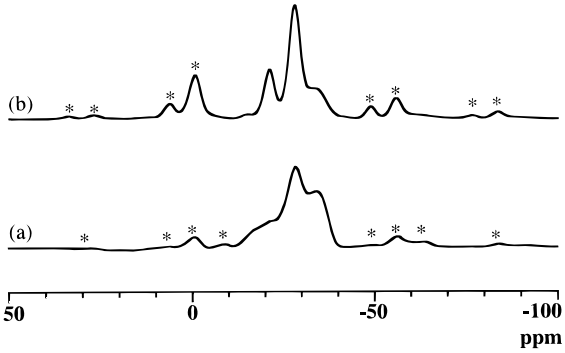

Figure 4. Proton-decoupled ^{31}P MAS NMR spectra of (a) sample A and (b) sample B in their as-synthesized forms.

characteristics of the P(4Al) sites (bond angle and bond length) have been found to influence the ^{31}P chemical shifts; the larger the Al−O−P angle, the more negative the ^{31}P chemical shift.[9] In $AlPO_4$-20 the ^{31}P resonance appeared further downward (34 ppm) due to the larger Al−O−P angle.[10] Occasionally, a minor shoulder appeared at −20 ppm that has been attributed to the interaction of template and/or water molecules with the P sites.[10] Klinowski[5] and others[11,12] have observed multiple resonances in the ^{31}P spectra of magnesium-substituted $AlPO_4$'s, indicating different P(*n*Al,*m*Mg) environments, where $n = 1-4$ and $m = 0-3$. For MAPO-5[12] and MAPO-34[12] the major ^{31}P resonance corresponding to P(4Al) appeared at −29 ppm. Depending on the Mg content, additional resonances appeared 6 ppm down field for P(3Al,1Mg) sites and further 6 ppm down field for P(2Al,2Mg) sites. For MAPO-20 (Figure 4), the major resonance for the P(3Al,1Mg) sites occurred at −28.3 ppm. For sample A, decomposition of the spectrum suggested additional resonances at −34.5 and −21.6 ppm corresponding to P(4Al) and P(2Al,2Mg) sites (Table 2), respectively. A minor resonance at −16.7 ppm contributing 6.8% appeared in the spectrum which disappeared upon calcination (vide infra). Thus we attribute this signal to precursor phosphate species (phosphorus nuclei bonded to Al monomers) that are not part of the framework and could possibly be the unreacted species from the gel.[13] The gel composition of our sample B resembles that of Barrie and Klinowski.[5] However, the relative amount of the different P(*n*Al,*m*Mg) sites vary in the edited ^{31}P spectra of the product. Unlike the sample A, the −16.7 ppm signal is absent, and additional signal of the P(1Al,3Mg) sites is seen at −14.8 ppm.

The distribution of P(*n*Al,*m*Mg) sites was calculated from the binomial theorem.[14] On the basis of this method, it has been observed that there is ordering of magnesium in MAPO-20,[5] while the distribution is random in MAPO-5 and MAPO-34.[12] We calculated the relative population of the different sites in our samples. For the as-synthesized materials, the calculated distribution varies significantly from the distribution observed by NMR (Table 2); hence the Mg is ordered in MAPO-20 regardless of the variation in the Mg content. The unit cell of $AlPO_4$-20 $\{(Al_6P_6)O_{24}\}$ consists of one sodalite (or β) cage. The ^{31}P spectra for the as-synthesized sample A correspond to approximately 1 magnesium atom/unit cell $(Mg_{1.1}Al_{4.9}P_6)O_{24}$. The observed $(Mg/Al)_{nmr}$ ratio in the product is *higher* than in the gel (Table 1). For the sample B, there are approximately 1.5 magnesium atoms per unit cell $(Mg_{1.52}Al_{4.48}P_6)O_{24}$. The observed $(Mg/Al)_{nmr}$ ratio in the product is *lower* than in the gel (Table 1). This apparent

(9) Muller, D.; Jahn, E.; Ladwig, G.; Haubenreisser, U. *Chem. Phys. Lett.* **1984**, *109*, 332−336.
(10) Hasha, D.; de Saldarriaga, L. S.; Saldarriaga, C.; Hathaway, P. E.; Cox, D. F.; Davis, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 2127−2135.
(11) Shea, W.-L.; Borade, R. B.; Clearfield, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3143−3149.
(12) Deng, F.; Yue, Y.; Xiao, T.; Du, Y.; Ye, C.; An, L.; Wang, H. *J. Phys. Chem.* **1995**, *99*, 6029−6035.
(13) Mortlock, R. F.; Bell, A. T.; Radke, C. J. *J. Phys. Chem.* **1993**, *97*, 767−775.
(14) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley and Sons: New York, 1987; Chapter 4, p 151.

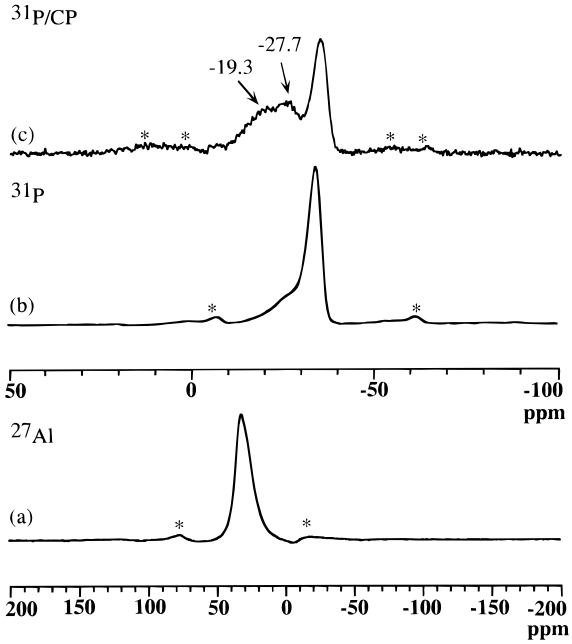

Figure 5. (a) ^{27}Al Bloch decay, (b) proton-decoupled ^{31}P Bloch decay and (c) ^{1}H−^{31}P cross-polarization (contact time 2 ms) MAS NMR spectra of calcined dehydrated sample A.

discrepancy in the $(Mg/Al)_{nmr}$ ratios of the samples probably arises in order to maintain ordering of Mg in the product.

Calcination of MAPO-20. The primary use of the Type 20 material would result once the occluded template is removed. We have attempted to undertake a study on the calcination behavior of this material. Sample A on calcination at 813 K for 12 h gave a white solid, while sample B gave a black product, indicating incomplete removal of the template. Repeated attempts at calcination for longer duration (24 h) or using a higher temperature (873 K for 6 h) failed to remove all the carbon. The results indicate a very strong interaction of the template with the MAPO-20 lattice when the magnesium content is high. Hence, further studies were restricted to sample A. The calcined sample was further dehydrated in vacuum up to a temperature of 673 K step by step and held at that temperature for 6 h before performing the NMR experiments.

The ^{27}Al MAS NMR spectrum of the dry sample shows only a single resonance attributed to tetrahedral Al (Figure 5a). In the ^{31}P spectrum, the peaks attributed to P(3Al,1Mg) and P(2Al,2Mg) sites were markedly reduced in intensity and the −16.7 ppm signal vanished

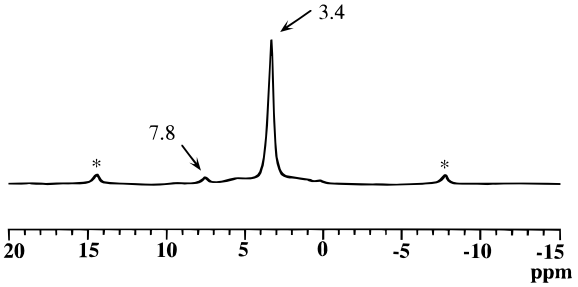

Figure 6. ^{1}H MAS NMR spectrum of calcined dehydrated sample A.

(Figure 5b). Table 1 shows that the framework composition of the calcined sample is different from that of the as-synthesized sample. The framework magnesium content is reduced by half (this corresponds to 0.5 Mg/unit cell). This process is similar to that of dealumination observed in zeolites, and we term it *demetalization*. Moreover, for the dry sample, the calculated distribution of the P(*n*Al,*m*Mg) sites match closely with observed NMR value (Table 2); here, the Mg is disordered. Thus the precise ordering of Mg is disturbed upon calcination of the sample. The substitution of Mg for Al results in an anionic framework. In the calcined form of the divalent metal-substituted $AlPO_4$'s the charge-balancing cation is a proton. Thus protons are expected to be located at the P−O−Mg bridging units of P(3Al,1Mg) (−27.7 ppm) and P(2Al,2Mg) (−19.3 ppm) sites in the ^{31}P spectrum. The ^{1}H−^{31}P CP spectrum (Figure 5c) shows considerable enhancement of the signals attributed to these sites supporting our assignment. Furthermore, the ^{1}H MAS spectrum shows a sharp (fwhm = 155 Hz) resonance at 3.4 ppm (Figure 6). There are no reports on the proton NMR spectra of metal−$AlPO_4$ systems. We assign this peak to Brønsted acid sites in our sample. Brønsted acid sites in silicon substituted $AlPO_4$'s (SAPO-5 and SAPO-11) appear at 3.8 ppm.[15] The minor resonance at 7.8 ppm is tentatively assigned to protons associated with residual amine groups.

Acknowledgment. This work was supported by the Basic Energy Sciences program of the U.S. Department of Energy (DE. FG03-93-ER14354).

CM950466U

(15) Pfiefer, H.; Ernst, H. *Annual Reports on NMR Spectroscopy*; Ando, I., Webb, G. A., Eds.; Academic Press: New York, 1994; Vol. 28, pp 91−176.