

³¹P Magic-Angle-Turning NMR Studies of the Chemical and Electronic Nature of Phosphorus in Magnesium Aluminophosphate MgAPO-20

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The chemical and electronic nature of the various phosphorus environments in the microporous magnesium aluminophosphate MgAPO-20 has been investigated by ³¹P magic-angle-turning NMR. Although the P(4Al) unit is highly symmetric, Mg incorporation into the lattice distorts this symmetry by altering the three ³¹P shielding tensors unevenly and thus producing chemical shift anisotropy (CSA) patterns. The P(3Al, 1Mg) unit is close to axial symmetry whereas P(2Al, 2Mg) is highly asymmetric. The dramatic change in the electronic nature of phosphorus by magnesium substitution correlates with the number of magnesium atoms adjacent to phosphorus. These experimental findings not only reveal a wealth of information on the electronic nature of phosphorus in MgAPO-20 but also constitute strong evidence as to the magnesium incorporation into the AlPO-20 lattice. In like manner, this contribution may extend to a new strategy for the understanding of isomorphous substitutions in microporous materials.

Introduction

The synthesis of microporous aluminophosphates (AlPO₄) with a plethora of structures, followed by Si incorporation and thus the formation of silicoaluminophosphate solids (SAPO), has long been reported.^{1,2} Furthermore, various metals such as Mg, Mn, Fe, Co, or Zn have later been reported to incorporate into the AlPO₄ and SAPO frameworks resulting in the MeAPO and MeAPSO molecular sieves, respectively.^{3,4} The wealth of various chemical and structural properties of these solids has stimulated a huge amount of research.^{4–16}

Magic-angle-spinning nuclear magnetic resonance (MAS NMR) experiments on solids yield spectra depicting isotropic chemical shifts, which probe chemical structure. This technique has been widely used to characterize the various P, Al, and Si chemical environments of these novel inorganic materials.^{5–7,9–12} However, isotropic chemical shifts in MAS NMR spectra are obtained at the expense of chemical shift anisotropy (CSA) principal tensors which in turn provide a great deal of information on the local electronic environment of nuclei. Both isotropic and CSA values for solids can be obtained by the application of magic-angle-turning NMR (MAT NMR),^{17–19} and the potential of this novel technique in the area of microporous materials is illustrated in this contribution. The chemical and electronic nature of the different local phosphorus environments in MgAPO-20 is investigated by means of ³¹P MAT NMR.

Experimental Section

Sample Preparation. The MgAPO-20 sample was synthesized following the procedure reported in the literature.³ This material was fully characterized by powder X-ray diffraction, SEM (scanning electron microscopy), EDAX (electron dispersive analysis of X-rays), and ³¹P and ²⁷Al MAS NMR.

Solid-State NMR. The NMR spectra shown in this contribution were recorded on a Bruker 400 MSL. The MAS NMR

experiments were carried out by means of single pulse direct excitation using a Bruker 4 mm probe. Pulse delays of 80 s were found adequate to yield quantitatively reliable ³¹P spectra and chemical shifts are referenced to external phosphoric acid. For the ²⁷Al MAS NMR spectra, pulse delays of 0.5 s were used and the chemical shifts are referenced to external [Al(H₂O)₆]³⁺.

The MAT NMR experiments were recorded using the PHORMAT pulse sequence^{18,19} and a Chemagnetics pencil probe. A Chemagnetics pencil rotor containing the solid material was spun at 30 ± 0.2 Hz and the spinning rate was constantly controlled by a modified Bruker MAS control unit to ensure stable spinning over long time periods. A total of 45 complex blocks of data with a 2.7 ms acquisition time in the F1 dimension have produced the 2D spectra shown in this report. The repetition delay was 80 s and each block was the result of 32 transients. The raw data were manipulated following the routine reported¹⁹ by Hu et al. and using NMR software written by P. J. Grandinetti (RMN FAT 1996).

Results and Discussion

Characterization of MgAPO-20. The powder X-ray diffractogram of the as-synthesized MgAPO-20 is shown in Figure 1 indicating a highly crystalline and pure material. The scanning electron micrograph of this material (not shown) illustrates cubic crystallites of ca. 40 μm in size. The P/Al and P/Mg ratios found by EDAX are 1.8 and 2.7, respectively. The ²⁷Al MAS NMR spectrum of this solid (see Figure 2a) shows a strong line at ca. 35 ppm assigned to framework tetrahedral Al(4P) environment and a small signal at ca. 7 ppm attributed to framework Al with a coordination higher than four. An interaction between framework Al and template hydroxyl groups or water may increase the coordination number of framework Al and thus give rise⁵ to the line at 7 ppm. Furthermore, magnesium as a second coordination T-site neighbor indirectly changes the chemistry of Al(4P) tetrahedron and such an alteration may account for the small shoulder on the left of the strong signal.

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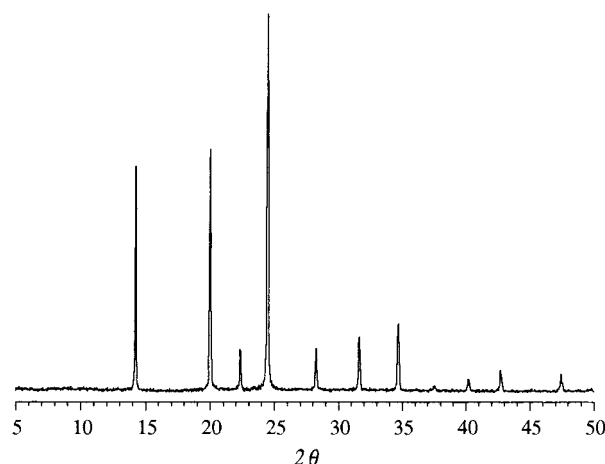


Figure 1. Powder X-ray diffraction pattern of the as-synthesized MgAPO-20.

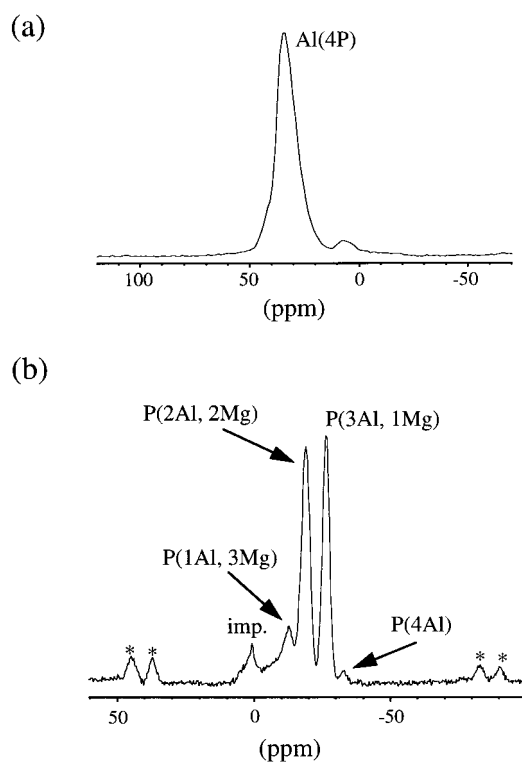


Figure 2. (a) ^{27}Al MAS NMR spectrum of MgAPO-20 and (b) ^{31}P MAS NMR spectrum of MgAPO-20; asterisks denote spinning sidebands and imp. = impurity.

The single Al(4P) chemical environment coupled with the chemical composition of these inorganic materials (50% of the framework is made up of P) indicates that Mg substitutes exclusively Al sites in the corresponding AlPO_4 structure. This leads to various P environments arising from the different compositions of the P second coordination sphere, i.e., P(4Al), P(3Al, 1Mg), P(2Al, 2Mg), etc. These P chemical environments are manifested in the ^{31}P MAS NMR spectra of these materials and may also be quantified to give P/Al and P/Mg ratios.⁵

The ^{31}P MAS NMR spectrum of MgAPO-20 (see Figure 2b) exhibits two strong peaks at -28.2 and -22.0 ppm assigned to P(3Al, 1Mg) and P(2Al, 2Mg) units, and two weak lines at -34.5 and -13.7 ppm attributed to P(4Al) and P(1Al, 3Mg), respectively. The weak signal at ca. 0 ppm, which accounts for 2.0% of the spectrum, is assigned to either unreacted

orthophosphoric acid (P source) or extraframework phosphate species. Furthermore, there is a weak broad signal at ca. -12.0 ppm accounting for ca. 6.0% of the spectrum which one may argue that it results from an amorphous phase. However, there is no indication of an amorphous phase in either the X-ray diffractogram or the scanning electron micrograph of the material. This suggests that the line at -12.0 ppm must relate to structural defect sites occupied by phosphorus atoms. Based on the method developed by Barrie and Klinowski,⁵ one may deconvolute and quantify this spectrum and thus calculate framework P/Al and P/Mg ratios of this magnesium aluminophosphate. The framework P/Al and P/Mg ratios were found to be 1.7 and 2.5, respectively, and though these values are in close agreement with EDAX results, do not include P in defect sites.

Application of MAT NMR. Ostensibly, the ^{31}P MAS NMR spectra of these solids give the chemist a wealth of information as to the chemical nature of the various P environments in these microporous solids. Moreover, the MAS NMR experiment is designed to average the three CSA shielding tensors which define the electronic structure of a nucleus. Therefore, the CSA character of these signals is overlooked in the MAS NMR spectra and may only be obtained from spectra recorded either statically or at slow MAS conditions²⁰ (Herzfeld and Berger method). Due to the small chemical shift differences among these peaks, the ^{31}P static NMR spectrum of this sample exhibits a broad featureless line which is the composite of five individual static lines. This is a nontrivial problem and makes the extraction of CSA values from the static spectrum impossible. Furthermore, the application of Herzfeld and Berger method²⁰ to these systems is rather problematic and entails a large error.

All these constraints may be overcome by the application of MAT NMR^{18,19} and Figure 3 shows the ^{31}P MAT NMR spectrum of MgAPO-20. This 2D spectrum depicts the isotropic spectrum along F1 with CSA slices along F2 at the various isotropic positions. As shown in this figure, five slices were taken at -34.5 , -28.2 , -22.0 , -13.7 , and 0 ppm along F1. In order to obtain the CSA values, these spectra must be simulated and thus the ^{31}P shielding tensors are extracted from the simulated spectra. In the simulation process the isotropic position is kept constant and the rest of the CSA values are optimized to give the best fit. The line at -13.7 ppm could not be simulated because of the heavy contribution from the neighboring signal at -12.0 ppm. Such an overlap coupled with the weakness of this signal leads to a large error in the simulation process. Furthermore, the impurity signal (0 ppm) exhibits an isotropic line shape and, therefore, no simulation was needed in that case. The weak broad line shown in this slice (0 ppm) is the contribution of the neighboring signals.

Figure 4 illustrates three spectra with their simulated best fits superimposed. As discussed above, the signal at -34.5 ppm is assigned to the P(4Al) environment, and as shown in Figure 4a, exhibits an isotropic line shape. The isotropic character of this signal is due to the high symmetry of this P chemical environment. This interpretation, however feasible, is questioned by the low intensity of this signal (see Figure 2b) which makes the simulation results disputable. To address this problem, the ^{31}P MAT NMR spectrum of AlPO_4 -20 (not shown) was also recorded. Figure 5 illustrates the slice of this 2D spectrum obtained at -34 ppm which is attributed to P(4Al) in the AlPO_4 -20 structure. The isotropic character of this line is obvious, and it is therefore deduced that the P(Al) unit in these materials is highly symmetric, and this symmetry is retained after magnesium incorporation into the lattice. Based on the deconvolution of the ^{31}P MAS NMR spectrum (Figure 2b), 40%

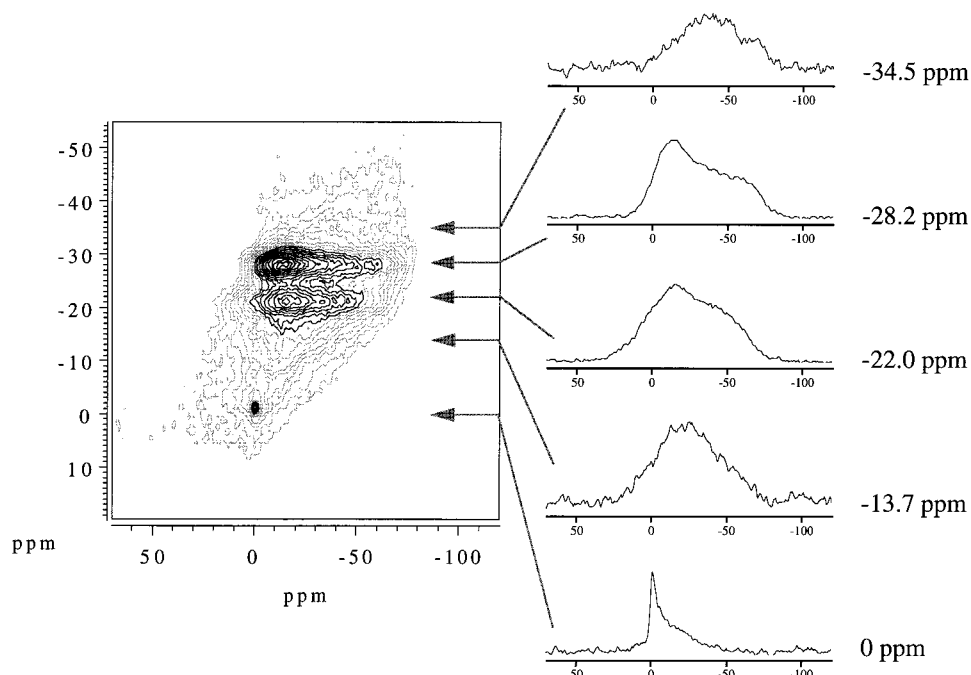


Figure 3. ^{31}P MAT NMR spectrum of MgAPO-20 with the slices taken at the various isotropic positions along F1.

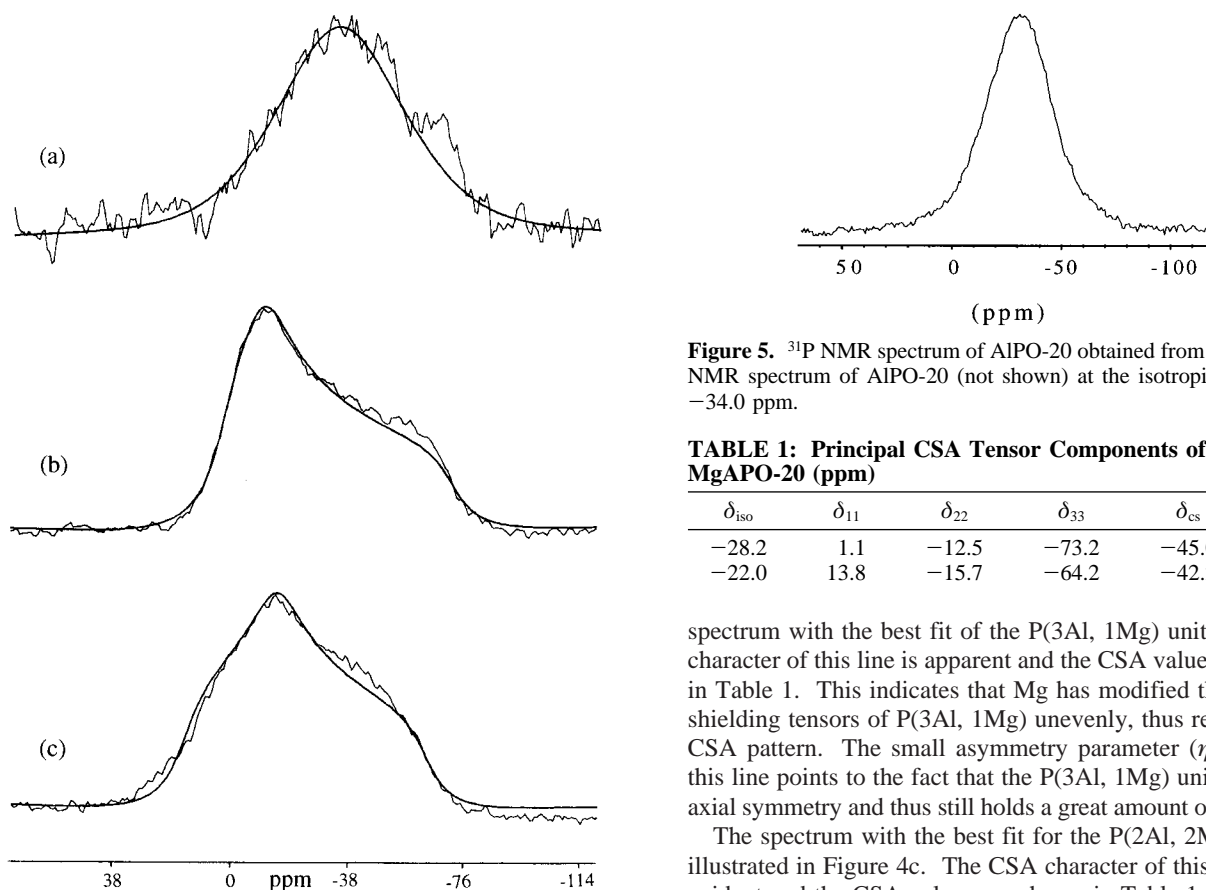


Figure 4. ^{31}P NMR spectra with the best fits (smooth lines) superimposed; these lines correspond to the signals at (a) -34.5 ppm, (b) -28.2 ppm, and (c) -22.0 ppm.

of the lattice Al has been replaced by Mg and thus there is only ca. 3% of P(4Al) in MgAPO-20. Evidently, the isomorphous substitution of Mg in AlPO-20, however extensive, fails to alter the symmetry of P(4Al), an intrinsic property of this unit.

The symmetry of the other P environments in MgAPO-20 is now a question to be addressed. Figure 4b illustrates the

Figure 5. ^{31}P NMR spectrum of AlPO-20 obtained from the ^{31}P MAT NMR spectrum of AlPO-20 (not shown) at the isotropic position of -34.0 ppm.

TABLE 1: Principal CSA Tensor Components of ^{31}P in MgAPO-20 (ppm)

δ_{iso}	δ_{11}	δ_{22}	δ_{33}	δ_{cs}	η_{cs}
-28.2	1.1	-12.5	-73.2	-45.0	0.3
-22.0	13.8	-15.7	-64.2	-42.2	0.7

spectrum with the best fit of the P(3Al, 1Mg) unit. The CSA character of this line is apparent and the CSA values are shown in Table 1. This indicates that Mg has modified the three ^{31}P shielding tensors of P(3Al, 1Mg) unevenly, thus resulting in a CSA pattern. The small asymmetry parameter ($\eta_{\text{cs}} = 0.3$) of this line points to the fact that the P(3Al, 1Mg) unit is close to axial symmetry and thus still holds a great amount of symmetry.

The spectrum with the best fit for the P(2Al, 2Mg) unit are illustrated in Figure 4c. The CSA character of this line is also evident and the CSA values are shown in Table 1. The rather large asymmetry parameter ($\eta_{\text{cs}} = 0.7$) is the result of a very asymmetric unit. Thus, contrary to one magnesium, two magnesium atoms have strongly altered the local electronic structure of P forming a very asymmetric P(2Al, 2Mg) environment.

Although the CSA values of P(1Al, 3Mg) could not be derived from these studies, this unit is suggested to be more symmetric than P(2Al, 2Mg). This assumption is based on a correlation between the symmetries of P(3Al, 1Mg) and P(1Al,

3Mg) units, both of which assemble a P(3X, 1Y) character where X and Y may be either Al or Mg.

Conclusion

The chemical and electronic nature of the various P environments in MgAPO-20 has been investigated by ^{31}P MAT NMR. The P(4Al) was found highly symmetric and this symmetry yields isotropic line shapes. Mg incorporation into the lattice distorts this symmetry by altering the three ^{31}P shielding tensors unevenly and thus producing CSA patterns. The P(3Al, 1Mg) unit is close to axial symmetry and thus still holds a great amount of symmetry whereas P(2Al, 2Mg) is highly asymmetric. The P(1Al, 3Mg) is proposed to regain symmetry on grounds of the P(3X, 1Y) character, as observed for the P(3Al, 1Mg) unit. Finally, the dramatic change in the electronic nature of P by Mg substitution constitutes sound evidence as to the Mg incorporation into the AlPO-20 lattice. The implications of such an observation in the area of microporous materials are of great significance. That is to say that these experimental findings provide a new approach as to the investigation of isomorphous substitutions in framework materials.

References and Notes

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