Functionalization of Aluminophosphate $AlPO_4$-H1 (VPI-5) with Phenylphosphonic Acid

Wenfu Yan, Edward W. Hagaman,* and Sheng Dai*

Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008,
Oak Ridge, Tennessee 37831-6201

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Zeolites and related substances, such as aluminophosphates with periodic three-dimensional framework structures which contain pores, have attracted much scientific interest for applications in chemical separation, shape-selective catalysis, host/guest chemistry, and low dielectric constant (low-κ) materials preparation, etc. The recent interest in organically functionalized mesoporous and microporous inorganic materials arises from the advantages that the disparate moieties bring to the system. Although the synthesis of organically functionalized periodic mesoporous organosilicas has been extensively reported, there has been limited success in the functionalization of microporous materials. Herein, we describe the preparation of phenyl-functionalized $AlPO_4$-H1 (VPI-5). The functionalization of $AlPO_4$-H1 with phenylphosphonic acid was investigated by solid state ^{13}C and ^{31}P NMR, BET, XRD, FTIR, EDX, and TGA.

Introduction

Zeolites and related compounds, such as aluminophosphates with periodic three-dimensional framework structures which contain pores,[1,2,3,4] have attracted much scientific interest for applications in chemical separation, shape-selective catalysis, host/guest chemistry, and low dielectric constant (low-κ) materials preparation, etc.[5,6,7] Microporous aluminophosphates $AlPO_4$-*n* (*n* denotes a structure type) is a new class of molecular sieves first discovered by Wilson and coworkers in 1982.[8] The typical structure is built up from strict alternation of AlO_4 and PO_4 tetrahedra through corner sharing to form a neutral open-framework. Owing to the rich variety of structural chemistry of oxides of Al and P in aluminophosphates (i.e., Al atoms in aluminophosphates can adopt four, five, and/or six coordination and the tetrahedral P atoms can share their one, two, three, or four oxygen atoms with adjacent Al atoms), these compounds display a rich variety of structures and stoichiometries.[9−12]

Among microporous aluminophosphates, $AlPO_4$-H1 (VPI-5), **1**, was first identified as a microporous framework with an 18-membered-ring channel.[13] The wide channels of VPI-5 serve as effective catalyst supports and can adsorb molecules as large as triisopropyl benzene (diameter 13 Å). It is known that VPI-5 is isostructural with $AlPO_4$-H1, which was prepared about 40 years ago by d'Yvoire.[14,15] In contrast to the synthesis of VPI-5, $AlPO_4$-H1 was synthesized conveniently without any organic template via a microwave process.[16] Accordingly, the latter synthesis can be more easily adapted to introduce functional groups into zeolitic frameworks.

Recent interest in organically functionalized mesoporous and microporous inorganic materials arises from the advantages that the disparate moieties bring to the system.[17,18] The inorganic components can provide mechanical, thermal, or structural stability, while the organic features are often more readily modified for specific applications in catalysis, separation, or sensing.[19] Organically functionalized mesoporous organosilicas with organic groups uniformly distributed in ordered inorganic frameworks have been extensively investigated.[20−27] However, there are fewer reports on

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* Corresponding author. E-mail: dais@ornl.gov.

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the functionalization of microporous crystalline zeolitic materials. Notably, Corma et al. first reported zeolites functionalized with organic groups by grafting organosilanes principally onto the external region of USY (ultrastable Y) zeolites.[28] Later, Cauvel et al. also investigated the grafting of organosilanes onto a series of Y zeolites with varying mesopore content introduced via steaming.[29] Recently, Jones et al. reported the first co-synthesis of crystalline, microporous silicates with organic functionalities covalently tethered within the micropores of pure-silica zeolite beta.[30] We have developed an imprinting methodology to functionalize internal micropores of zeolite L.[31] Very recently, Tatsumi and co-workers successfully synthesized a hybrid zeolitic material containing carbon in the framework by partial replacement of a lattice oxygen atom by a methylene group.[32] Haw and co-workers successfully functionalized the cage cavity of zeolite H-SAPO-34 (chabazite structure) through a ship-in-a-bottle route starting with PH$_3$, which achieved 95% conversion and an impressive ethylene selectivity of 44% in the catalytic conversion of methanol into olefins.[33]

Because of the rich structural chemistry of phosporus related to its ability to share less than four oxygen atoms with adjacent Al atoms, it is possible to introduce organic functionality attached to phosphorus through co-synthesis. In 1994, Maeda et al. successfully synthesized two isomeric organic-functionalized microporous aluminophosphates, AlMepO-α and -β, which have the same composition, Al$_2$(O$_3$PCH$_3$)$_3$, and one-dimensional channels lined with methyl groups along the *c*-axis.[34] The organic functionality was introduced by using methylphosphonic acid in the synthesis. To our knowledge, no other organic functional groups have been introduced into the neutral frameworks of microporous phosphate zeolites. Herein, we describe the preparation of functionalized AlPO$_4$-H1 (VPI-5) using phenylphosphonic acid. Phenyl groups, nonstoichiometrically bonded to phosphorus, were incorporated into the framework.

Experimental Section

In a typical synthesis of AlPO$_4$-H1, **1**, aluminum hydroxide (Aldrich, 50−57% Al$_2$O$_3$, 5.0 g, 64.1 mmol) was dissolved in 24 mL of deionized water and the resulting mixture was stirred for 1 h. Phosphoric acid (Aldrich, 85 wt % in water, 2.92 mL, 43.1 mmol) was added dropwise over 2 min. Concentrated hydrochloric acid (Aldrich, 37 wt % in water, 2.69 mL, 32.3 mmol) was added dropwise over 2 min and the mixture was stirred for an additional hour. The homogeneous mixture was sealed in a 90-mL Teflon-lined autoclave and heated under autogenous pressure at 125 °C for 70 min in a microwave oven (Milestone Microwave Laboratory System, Milestone Inc, 1000 W, heating rate, 1 °C/sec). The product was separated by centrifugation, washed with deionized water, and dried overnight at room temperature. The synthesis of functionalized AlPO$_4$-H1 [denoted (AlPO$_4$)$_{1-x}$(AlPhPOH$_3$)$_x$-H1, **2**] used the same procedure and concentrations as those for the synthesis of AlPO$_4$-H1, with the exception that phenylphosphonic acid (ACROS, 98%, 0.595 g, 3.7 mmol) was added to the mixture after the addition of concentrated hydrochloric acid. The mole ratio of phenylphosphonic acid to phosphoric acid was 0.09: 1.00.

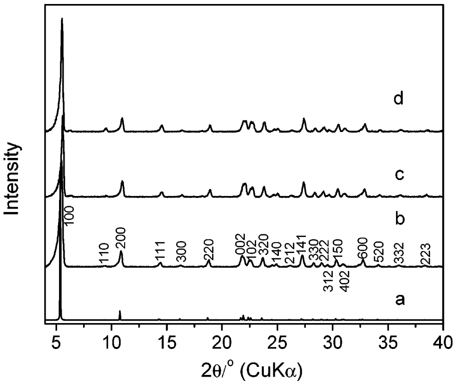

Figure 1. Simulated XRD patterns of AlPO$_4$-H1 (a) and the experimental XRD patterns of AlPO$_4$-H1(b), (AlPO$_4$)$_{1-x}$(AlPhPO$_3$)$_x$-H1 [at room temperature (c) and at 150 °C (d)].

Powder XRD data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Adsorption isotherms were recorded on an Autosorb-1 adsorptioner manufactured by Quantachrome Instrument, Inc. The FT-IR spectra of **1** and **2** were recorded on a Digilab FTS 7000 spectrometer equipped with a Harrick diffuse reflectance accessory (DRIFTS). The samples were run neat with a total of 128 scans and a resolution of 8 cm^{-1}. An HD-2000 STEM (probe size ≈0.8 nm) operating at 200 kV was used to carry out the energy-dispersive X-ray (EDX) analysis. A TGA 2950HR V5.4A unit (TA Instruments, Inc.) was used to carry out the thermogravimetric analysis (TGA) in nitrogen with a heating rate of 20 °C/min.^{13}C NMR analyses were performed on a Chemagnetics Infinty NMR spectrometer operating at 2.42 T using standard cross polarization and magic angle spinning techniques and the following parameters: ^{1}H frequency, 102.959 MHz; ^{13}C frequency, 25.891 MHz; ^{1}H rf amplitude, 81 kHz (3.1 μs, 90° pulse), held constant for ^{1}H excitation, cross polarization, and dipolar decoupling; 1.0 ms cross polarization contact time; 1 s recycle delay; MAS = 4500 ± 2 Hz. Chemical shifts are reported with respect to TMS (δ = 0 ppm) using the methyl resonance of hexamethylbenzene as secondary standard (δ = 17.3 ppm). ^{31}P MAS and ^{1}H-^{31}P CP/MAS ^{31}P NMR spectra were recorded on a Bruker 400 Avance spectrometer operating at 9.4 T, using the following parameters: ^{1}H frequency, 400.132 MHz: ^{31}P frequency, 161.983 MHz; MAS = 8000 ± 100 Hz. For single pulse excitation: ^{31}P rf amplitude, 83.3 kHz (3.0 μs, 90° pulse); 4.0 or 30.0 s recycle delays. For CP: ^{1}H rf amplitude, 50 kHz (5.0 μs, 90° pulse) held constant for ^{1}H excitation, cross polarization, and dipolar decoupling; 1.0 ms cross polarization contact time; 4 s recycle delay. Chemical shifts are reported with respect to H$_3$PO$_4$ (δ = 0 ppm), by substitution.

Results and Discussion

The powder X-ray diffraction pattern of the as-synthesized organic-functionalized AlPO$_4$-H1 shown in Figure 1 is consistent with the crystalline VPI structure, and all peaks of the XRD pattern can be indexed according to VFI structure. After degassing in a vacuum at 150 °C for 3 h, **2** gives the multipoint BET surface area of 306 m^2/g, which is slightly smaller than that of pure AlPO$_4$-H1 of 355 m^2/g. However, the pore size with

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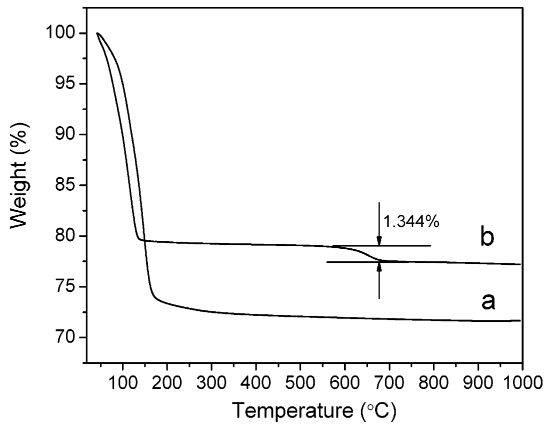

Figure 2. TGA curves of $AlPO_4$-H1 (a) and $(AlPO_4)_{1-x}$-$(AlPhPO_3)_x$-H1 (b).

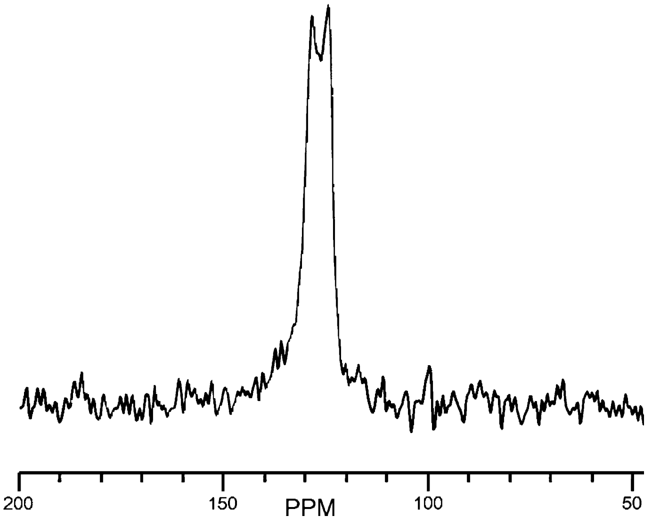

Figure 3. ^1H-^{13}C CP ^{13}C MAS NMR spectrum of $(AlPO_4)_{1-x}$-$(AlPhPO_3)_x$-H1.

and without organic-functionalization is similar, which indicates that the incorporation of the phosphor atoms with aryl group is very small. (For isothermal plot and pore size distribution curves of pure $AlPO_4$-H1 and organic-functionalized $AlPO_4$-H1, see Supporting Information, Figure s1). XRD measurement indicates that the framework of **2** is retained during degassing.

EDX analysis (see Supporting Information, Figure s2) indicates the existence of carbon in **2**. More direct proof of the existence of organic species in **2** comes from the TGA analyses. As shown in Figure 2b, **2** has a weight loss of 1.3% from 580 to 700 °C, which is not observed in the TGA curve of **1** (Figure 2a). Further support for the successful incorporation of the functional group comes from the FR−IR investigation, which shows the existence of C−H vibrational bands around 3060 cm^{-1} for sample **2** but not for sample **1** (see the Supporting Information, Figure s3).

The ^{13}C CP/MAS NMR spectrum of **2** shown in Figure 3 displays partially resolved aromatic resonances at 125.0 and 129.0 ppm, representing the phenyl group and indicating that the organic residue is in the final product. Relative to the ^{13}C NMR spectrum of phenylphosphonic acid in acetone (*ipso*, 129.9; *ortho*, 130.0; *meta*, 128.2; *para*, 131.9 ppm) the resonances are consistent with a loss in conjugation of the phosphonyl group with the ring and an increase in steric bulk at the *ortho* carbon sites, shifts compatible with the notion that the phenyl group is attached to a phosphorus atom of tetrahedral hybridization.

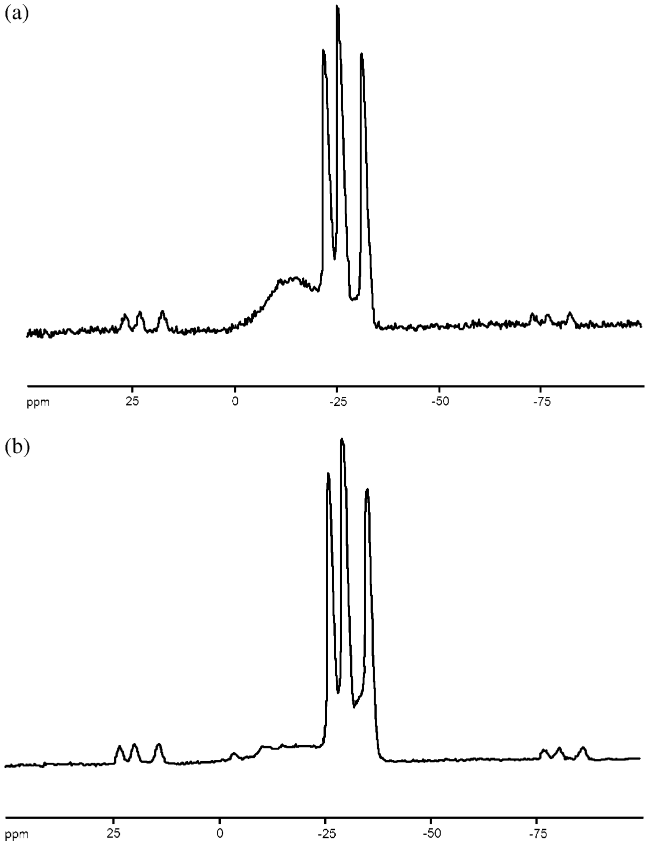

Figure 4. ^{31}P MAS NMR of $AlPO_4$-H1 (a) and $(AlPO_4)_{1-x}$-$(AlPhPO_3)_x$-H1 (b).

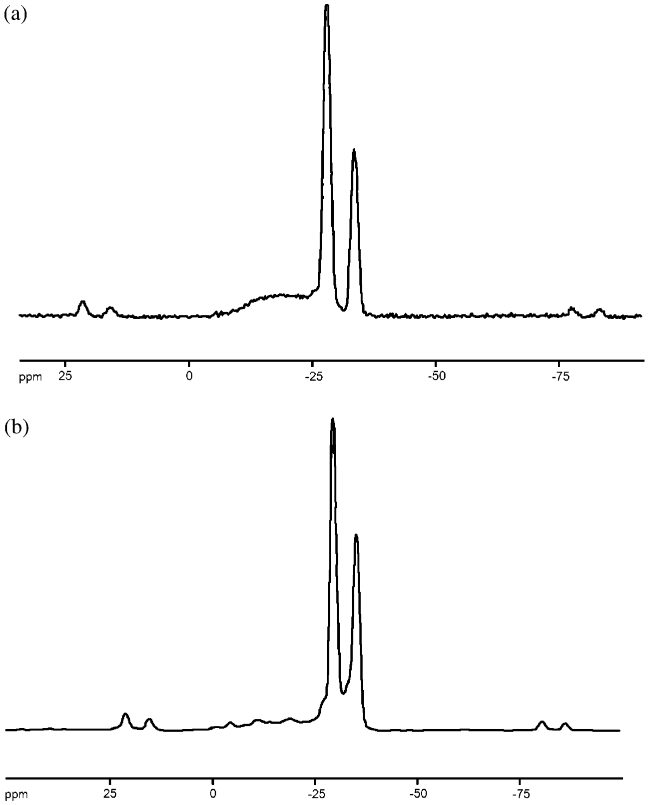

Figure 5. ^{31}P MAS NMR of $AlPO_4$-H1 (a) and $(AlPO_4)_{1-x}$-$(AlPhPO_3)_x$-H1 (b) recorded at elevated temperature.

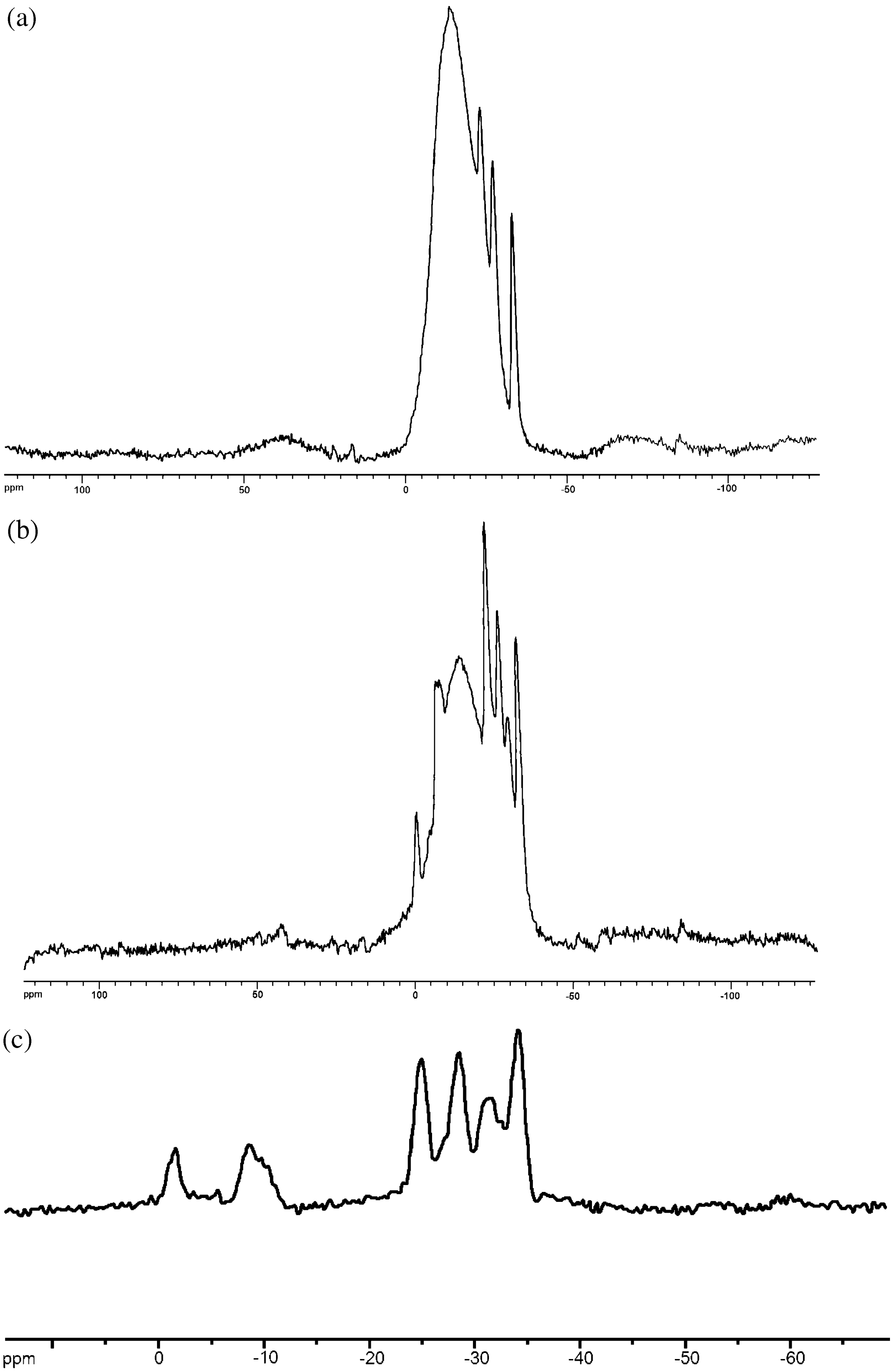

Figure 6. ^{1}H-^{31}P CP ^{31}P MAS spectrum of AlPO$_4$-H1 (a) and (AlPO$_4$)$_{1-x}$(AlPhPO$_3$)$_x$-H1 (b) recorded at room temperature. (c) Difference spectrum between the room-temperature CP spectra of AlPO$_4$-H1 and (AlPO$_4$)$_{1-x}$(AlPhPO$_3$)$_x$-H1.

The ^{31}P MAS NMR of **1** shown in Figure 4a is the same as that reported in the literature for VPI-5.[35,36] The spectrum consists of three resonances in 1:1:1 ratio at −32.9, −27.2, and −23.8 ppm for the crystalline framework and a broad low field resonance centered at −15.9 ppm which has been assigned to P−OH,[37] presumably at the terminus of crystalline faces. The ^{31}P MAS NMR spectrum of **2** shown in Figure 4b differs significantly from that of pure **1**. In the room-temper-

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ature spectrum, three new low-intensity resonances appear in the spectrum in addition to the four major resonances discussed above for **1**. The three new resonances have line widths comparable to the sharp $AlPO_4$-H1 framework phosphorus resonances, and therefore represent unique sites in the network. Two of these appear on the low field shoulder of the broad P−OH resonance at −0.4 and −7.4 ppm, with the latter peak displaying ca. twice the half-width and intensity of the −0.4 ppm resonance, as well as an asymmetric line shape that suggests the resonance represents two sites. These resonances display chemical shifts intermediate between those of the framework phosphorus and the resonance of phenylphosphonic acid (+16.7 ppm) and are assigned to the phosphorus sites bearing a phenyl group. The third resonance appears as a poorly resolved shoulder on the low field side of the −32.9 ppm framework resonance. This peak may arise from a chemical shift perturbation of one of the framework resonances resulting from a local structure distortion near the site of the organic residue in the matrix.

The room-temperature spectrum of **1** becomes a two-resonance spectrum with relative intensities of 2:1 (−28.2 and −33.7 ppm, respectively) at elevated temperature (shown in Figure 5a), a transition well documented in the literature, corresponding to a crystalline symmetry change from $P6_3$ at room temperature to $P6_3cm$ upon heating.[38] This symmetry transition induced by hydration of an aluminum site is fully reversible. The symmetry and underlying structural change described in pure $AlPO_4$-H1 also occurs in **2** upon heating (Figure 5b). In addition to the shifted framework phosphorus resonances, three low intensity resonances appear at −17.6, −8.9, and −2.1 ppm, with relative intensity of 1:1:1, riding on the broad P−OH peak. These resonances, attributed to organophosphorus resonances, are sensitive to the symmetry transition in this material.

The ^1H-^{31}P CP/MAS ^{31}P NMR spectra of **1** and **2** are shown in Figure 6. Figure 6a displays enhanced signal intensity for the P−OH resonances of **1** which have faster cross polarization rates than the framework phosphorus resonances. The faster rate is the result of closer proximity of the phosphorus atoms of the POH moieties to the cross polarization source, the acid protons of the POH group itself. The spectrum of **2** (Figure 6b) displays enhanced signals from the POH sites *and* the newly created sites assigned to organophosphorus species, relative to the framework phosphorus resonances. This assignment is consistent with the notion that these resonances arise from phosphorus sites attached to phenyl groups and consequently carry an efficient internal cross polarization source, the *ortho* protons of the phenyl ring. The nominal intramolecular three-bond separation between the nearest hydrogen and the phosphorus atom in an arylphosphorus moiety is, by virtue of configurational constraints in the molecule, similar in ^1H-^{31}P internuclear distance, and hence cross polarization rate, to the two-bond separation in the POH residues. The difference spectrum between the CP spectra of **1** and **2** taken at room temperature (Figure 6c) clearly depicts the low field resonances at −0.4 and −7.4 ppm, as well as the −30.2 ppm resonance.

The collective ^{13}C and ^{31}P chemical shift data and relative cross polarization rate data show that aryl moieties have been incorporated into the $AlPO_4$-H1 framework. Using the ^{31}P MAS NMR spectrum taken with a 30.0 s recycle delay and the integral of the −0.4 ppm resonance and the −32.9 ppm resonance for comparison, the total incorporation of the aryl group is estimated as 2 per 100 P and will result in a calculated 1.3% weight loss when the organic ligand is burned out, consistent with the TGA analysis weight loss of 1.3%.

Conclusions

The successful functionalization of $AlPO_4$-H1 with phenylphosphonic acid has been accomplished by a cosynthesis method. Unlike the synthesis of functionalized microporous zeolitic materials reported previously,[30,32] no organic template was used in the synthesis of the phosphate-based microporous materials so that the functional groups incorporated into the microporous frameworks are expected to be fully accessible. Functional group concentration as high as 2 mol % has been achieved. Research is currently underway to introduce active acidic sites into $AlPO_4$-H1 through sulfonic acid functionalization of the phenyl groups.

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Supporting Information Available: Adsorption isothermal plots, pore size distribution curves, EDX analysis, and FT-IR spectra (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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