Boron Phosphate and Aluminum Phosphate Aerogels

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Abstract

Anhydrous sol-gel condensation of triethyl phosphate $[(CH_3CH_2O)_3PO]$ with boron trichloride (BCL_3) or triethyl aluminum $[(CH_3CH_2)_3Al]$ in organic solvents, led to formation of metallophosphate gels. The pore fluid of the gels was removed under supercritical conditions in a pressurized vessel to form aerogels. The aerogels were then calcined at progressively higher temperatures to produce high surface area phosphates. Since the initial gel reagent mixtures contained several NMR active nuclei, the condensation chemistry prior to the gel point was monitored by solution $^1H, ^{13}C, ^{31}P,$ and ^{11}B NMR. The surface areas, distribution of pore sizes, and total pore volumes of the aerogel products were determined using nitrogen gas physisorption methods.

Introduction

The orthophosphate (MPO_4) compounds of boron, aluminum, and iron(III) may be described as covalent network solids of oxygen bridging alternating PO_4 and MO_4 tetrahedra (Van Wazer, 1958). These phosphates are consequently structurally isomorphous with one or more of the various forms of silica (SiO_2) and also share similar chemical and physical properties with silica. The formation of silica by sol-gel routes has been intensively studied for various applications such as coatings and formation of high surface area materials (Brinker and Scherer, 1990), but comparatively little has been written on the sol-gel preparation of covalent phosphates (Gerrard and Griffey, 1961; Kearby, 1967; Glenz et al., 1991; Rebenstorf et al., 1991).

Phosphate gels of aluminum and boron were prepared in this work; iron phosphate $(FePO_4)$ will be described in future studies. Since phosphates of acidic metal cations have useful solid acid catalytic properties, it was desirable to prepare them with a high surface area. Aerogels have high surface areas since the liquid in the gels is removed under supercritical conditions, and collapse of the pore structure, which can be problematic for evaporatively dried gels, is greatly reduced. We chose to prepare gels under nonaqueous conditions because most organic solvents have a considerably lower critical temperature than water. A second rationale for anhydrous conditions is the difficulty in making stoichiometric phosphate compositions from aqueous solutions. In water solutions one may obtain some metal oxide phase in addition to the desired phosphate due to competing hydrolysis reactions.

Materials and Methods

Gel Syntheses and Aerogel Processing.--All solvents were dried under a dry nitrogen atmosphere by distillation from P_2O_5 in the case of chlorobenzene, potassium carbonate for acetone, and sodium benzophenone ketyl for pentane. The triethyl phosphate was also freshly distilled and all gel syntheses conducted under a dry nitrogen atmosphere using Schlenk techniques.

The boron phosphate gels in this work were synthesized using the method of Gerrard and Griffey (1959) by reaction of triethyl phosphate with boron trichloride to yield boron phosphate and ethyl chloride as a byproduct. To prepare the boron phosphate gels, 8 mL (46 mmol) of triethyl phosphate $(CH_3CH_2O)_3PO$ was dissolved in 18 mL of chlorobenzene. The solution was cooled in an ice bath and a flask containing 4 mL (46 mmol) of boron trichloride (BCL_3) was mated to the triethyl phosphate solution flask to allow condensation of the BCL_3 vapor into the stirring phosphate solution over a period of about three hours. During this time, the flasks were closed off from nitrogen purge so that no BCL_3 was lost from the system. The resulting solution of adduct was then aged at 60°C for 8 hours. During this time, the flask was periodically vented to allow for escape of the ethyl chloride byproduct. The gel point occurred, on average, 1 hour after beginning heating at 60°C. The gel was then allowed to age in a sealed flask at room temperature for two days.

The $AlPO_4$ gel was prepared by a novel method using triethyl aluminum instead of the chloride compound due to the low solubility of aluminum chloride in organic solvents. In a flask equipped with a water condenser, a neat

mixture of 10 mL (73 mmol) of $(CH_3CH_2)_3AL$ and 12.4 mL of $(CH_3CH_2O)_3PO$ (73 mmol) were heated to 175°C in an oil bath on a hot plate stirrer overnight. This formed an oligomeric oil. The oligomer (2 mL) was then dissolved in 24 mL of acetone and the solution cooled in a salt ice bath (-40°C). Anhydrous NH_3 was then bubbled vigorously through the solution with a syringe needle. After a few minutes the mixture gelled with a concomitant evolution of gas. The gel was then allowed to stand in a sealed flask at room temperature for two days.

The aged gels then were transferred to a soxhlet apparatus and the chlorobenzene or acetone exchanged for pentane by reflux overnight (15 hr). While in the soxhlet, the gels were kept in an open top glass container so that fresh refluxing pentane could condense and pour off the top of the gels without draining the pore liquid from the gels during each emptying cycle of the soxhlet. The solvent exchange through the gels could be monitored visually because the translucent gels became more opaque upon substitution of the pentane for chlorobenzene or acetone.

The pentane solvent exchanged gels were transferred to a one liter bomb (Parr® Instrument Co. Model 4500) along with an additional 100 mL of dry pentane. The vessel was then pressurized with nitrogen gas to 400 psi, heated over a period of one hour to 210°C, and held at this temperature under supercritical conditions for 0.5 hour. During heating, the vessel attained a maximum pressure of approximately 1000 psi; the critical point of pentane is 196°C and 480 psi. The supercritical pentane then was vented from the bomb while maintaining the temperature at 210°C. Portions of the prepared aerogels were subsequently heated in air in a muffle furnace at elevated temperatures of 200°C, 500°C and 800°C for one hour at each temperature. This heating was done in order to determine the effects of progressive calcining on the microstructure of the gels.

Characterization Methods.--The early stages of the condensation chemistry prior to the gel point could be monitored by multinuclear solution NMR. In the case of boron phosphate, the freshly prepared chlorobenzene adduct solution was examined by ^1H, ^{13}C, ^{31}P, and ^{11}B.

FT-NMR (Bruker Instruments 250 MHz FT-NMR). The NMR spectra were collected from samples in vacuum sealed NMR tubes containing $CDCl_3$ lock solvent. NMR spectra were also collected from heated and aged samples. Infrared spectra of aerogels were obtained as Nujol mulls. The instrument used was a Perkin Elmer Model 1600 FTIR. Surface characterization of solids by nitrogen physisorption, including isothermal desorption, multipoint Brunauer-Emmett-Teller (BET) surface area, total pore volume, and average pore radius were determined using a Quantachrome® Model NOVA 1000 instrument. Samples were outgassed at 200°C overnight under oil

pump vacuum prior to physisorption measurements. Multipoint BET data were collected using a 4 point adsorption isotherm (P/P_0=0.05, 0.15, 0.25, and 0.35). The total pore volume was determined based on the quantity of N_2 adsorbed onto the sample at a relative pressure P/P_0=0.99. The average pore reaius in the gels was calculated by dividing twice the pore volume by the surface area. This method of calculating the value of the average pore radius assumes that the pores have a cylindrical geometry.

Results and Discussion

Polymerization of the boron phosphate gel proceeded by a condensation of B-O-P bonds with concomitant elimination of chloroethane (Gerrard and Griffey, 1959). Freshly prepared solutions of the metal chlorides and triethyl phosphate showed sharp NMR resonances attributable to a 1:1 adduct $[(CH_3CH_2O)_3P=O:BCl_3]$. The NMR characterization data for the $(CH_3CH_2O)_3P=O:BCl_3$ adduct in chlorobenzene solution with $CDCl_3$ lock solvent are as follows: ^1H δ 4.57 multiplet (CH_2 intensity 1.5), 1.58 multiplet (CH_3 intensity 1.0); $^{11}B(BF_3 \cdot Et_2O)$ δ 5.4 (h/2~13 Hz): ^{13}C δ 63.6 (CH_2), δ 15.0 (CH_3); ^{31}P (85% H_3PO_4) δ -11.6. The ^{11}B resonance of the adduct was narrow due to the tetrahedral coordination of boron. NMR spectra collected after heating the sample at 50°C in water for 5 minutes, exhibited the emergence of peaks ascribed to ethyl chloride and a concomitant diminution of adduct peaks as condensation began. The ^{31}P spectrum of the heated sample also showed an additional resonance at -20 ppm pertaining to formation of $(CH_3CH_2O)_2P(O)OBCl_2$ by elimination of one equivalent of ethyl chloride from the adduct. After an additional two days of aging at room temperature only ethyl chloride could be seen in the NMR spectra since the boron and phosphorus had become incorporated into the cross-linked gel.

The structure of the oligomer formed by heating the neat mixture of $CH_3CH_2)_3Al$ and $(CH_3CH_2O)_3PO$ is not yet understood. The NMR data indicate that ethyl groups remain on both aluminum and phosphorus atoms. The proton NMR characterization data for the aluminum phosphate oligomer in $CDCl_3$ are as follows: 1H δ 4.05 multiplet [CH_2-(P) intensity 1.0), δ 1.35 triplet [CH_3-(Al) intensity 1.8]. δ 0.96 triplet [CH_3-(P) intensity 1.3], δ -0.23 quartet [CH_2-(Al) intensity 1.3]. Integration of the ^1H resonances indicated that there were more ethyl groups on aluminum that on phosphorus (4:3 ratio) instead of the expected 1:1 ratio. We are currently investigating the chemistry of this system to better understand it. Regardless of the chemistry which led to formation of the $AlPO_4$ gel, the aerogel product nonetheless had favor-

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able properties as evidenced by its high surface area and the thermal stability of its microstructure.

Figures 1 and 2 illustrate the desorption isotherm data from the NOVA 1000 instrument for the three calcined BPO_4 aerogels and the three calcined $AlPO_4$ aerogels respectively. The 200°C BPO_4 aerogel and all three of the $AlPO_4$ samples exhibited Type IV isotherms (Brunauer et al., 1940). The adsorption of N_2 at both low and high relative pressures in these samples is indicative of materials with a distribution of pore radii, from micropores (r<15Å) to macropores (r≈1000Å). However, the 500°C and 800°C BPO_4 showed almost no desorption at low relative pressures illustrating a lack of microporosity. The 800°C BPO_4 sample was lacking in macroporosity as well. It is clearly evident in comparing Figs. 1 and 2 that the BPO_4 becomes increasingly dense and nonporous with increased heating, whereas the $AlPO_4$ largely maintains its original microstructure.

Fig. 2. N_2 desorption isotherm curves for $AlPO_4$ aerogel heated to 200°C, 500°C, and 800°C.
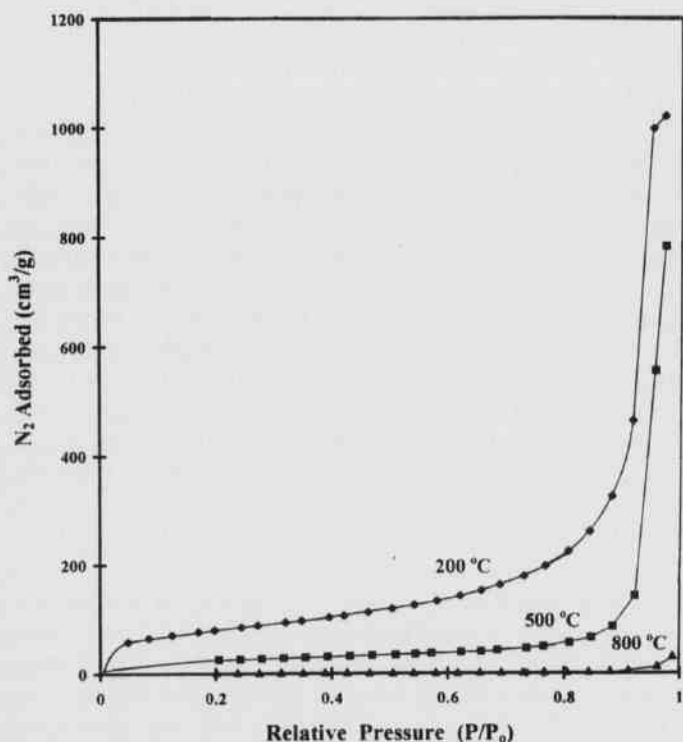

Fig. 1. N_2 desorption isotherm curves for BPO_4 aerogel heated to 200°C, 500°C, and 800°C.

There is an anomalous feature in Fig. 2; the 200°C isotherm is less than that of the 500°C sample. This might be explained as adsorbed water in the pore structure not removed during the 200°C outgassing procedure prior to the isotherm measurements. The presence of water
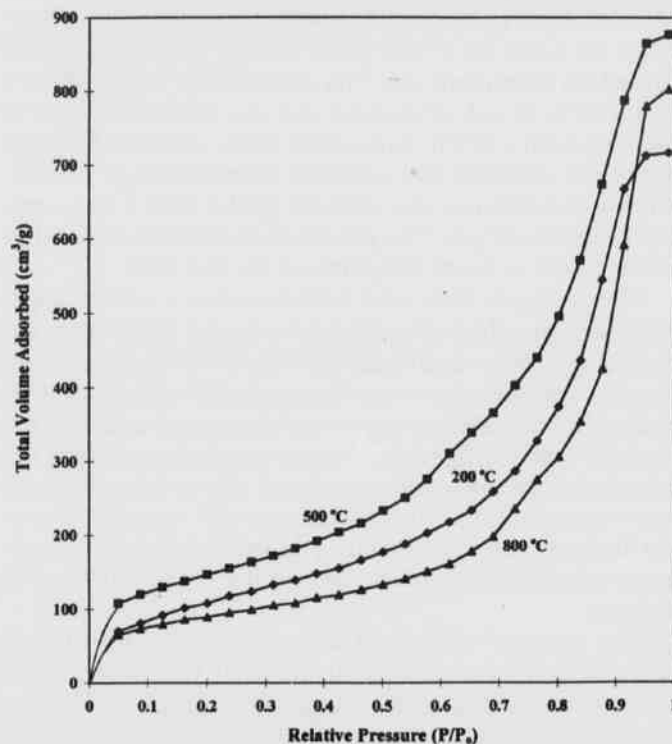
trapped in the micropores at temperatures below 500°C is reasonable since such high surface area materials make very good desiccants.

Table 1 is a compilation of the calculated specific surface area, total pore volume, and average pore radius for each of the heated aerogels. The microstructure becomes more course and the small pores are vanquished with increasing temperature. This is manifested as a decrease in total surface area and an increase in the average pore radius at higher temperatures and is a general phenomenon of sintering. There is not reported value for the average pore radius of the 800°C BPO_4 sample since the only "porosity" remaining would be the free space between the aerogel sample pieces which have already densified. The relatively constant total pore volume for the $AlPO_4$ aerogels reflects the stability of this material's microstructure.

Now that we have some basic understanding of these materials, we are currently working on developing applications for these phosphates. These applications include micro filtration membranes and catalytic membranes. In addition we hope to develop new types of crystalline catalysts by processing the solvent containing gels under similar conditions as those used to manufacture zeolites.

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Table 1. Aerogel microstructural changes with increasing temperature.

AIPO$_4$	200°C	500°C	800°C
Surface Area (m^2/g)	410	530	320
Total Pore Volume (cm^3/g)	1.1	1.4	1.3
Average Pore Radius (Å)	54	51	77

BPO$_4$	200°C	500°C	800°C
Surface Area (m^2/g)	230	86	12
Total Pore Volume (cm^3/g)	1.7	1.0	0.05
Average Pore Radius (Å)	150	240	

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