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Sol–Gel Synthesis of High Surface Area Aluminum Phosphate: A Thermally Reversible Sol–Gel System

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Over the past few years there has been considerable interest in the area of sol–gel chemistry.[1–3] Much of this effort has been directed toward silica-based systems.[2,3] In the area of catalysis, work has been reported on the synthesis of high surface area aluminum phosphate for use both as a catalyst[4–9] and as an alternate support material.[10–12] Most of the reported routes are based upon reaction of aluminum nitrate with a variety of phosphate sources.[4–12] As pointed out by Glemza et al.[4] the main problem with this approach has been related to the difficulty in synthesizing the stoichiometric compound with a P/Al ratio of unity. Often mixed phases of $AlPO_4$, Al_2O_3, and P_2O_5 result. For an P/Al ratio of unity, surface areas are obtained typically in the range 250–350 m^2/g and as high as 523 m^2/g when 5 wt % excess alumina was employed.[5] In this paper we describe a novel reaction, based upon sol–gel chemistry using alkoxides, to produce a high surface area aluminum phosphate (P/Al = 1), in excess of 550 m^2/g. We also find that the sol–gel reaction displays a thermally reversible sol–gelation step.

The sol–gel preparation of aluminum phosphate using alkoxides has been described[13] based upon the reaction of aluminum (bisisobutoxide)ethylacetoacetate with phosphoric acid. Using the literature procedure however leads to immediate gelation (taking place before the complete addition of the phosphoric acid) making it difficult to prepare homogeneous mixtures. Some of the potential applications of aluminum phosphate (for example as an inert coating material)[14,15] would be limited since a free-flowing solution is required. We found that adding small amounts of HCl to the precursor solutions gives rise to a more controllable sol–gelation step and radically changes the crystallization behavior. An extremely interesting sol–gel reaction occurs which could have wide applications in the area of catalysis, coatings, as well as a glass matrix for the formation of nanocomposites.[16]

The sol–gel synthesis of $AlPO_4$ has been developed using a modification of the literature procedure.[13] In a typical preparation, 38% HCl (in water), is added to a solution of aluminum (bisisobutoxide)ethylacetoacetate (5 g in 15 mL of isopropyl alcohol), and the resulting solution is stirred at room temperature (15 min). The amount of HCl was varied from 0.2 to 2.0 mol/mol of aluminum. A stoichiometric amount of solid orthophosphoric acid (per aluminum), dissolved in isopropyl

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alcohol (2.5 mL), is then added. The gelation depends upon the amount of HCl added. In the case of HCl additions, which contain about 0.3 mol of HCl/aluminum or less, gels form instantly whereas with higher amounts clear solutions result. The solutions can be gelled by heating sealed vessels in an oven for times ranging from a few minutes to a few hours depending upon the HCl concentration. In the case of 0.5 mol of HCl (per aluminum), completely clear and homogeneous gels formed within about 5–10 min at 70 °C. Upon drying, monolithic bodies are obtained although after calcination cracking occurs. Nitric acid had the same effect as HCl although 1 mol of acid/mol of aluminum was required to prevent immediate gelation. Formic and acetic acid did not give rise to homogeneous gels (very rapid gelation was observed). Chloride ion is not important but rather stronger acids appear to effect the sol–gel transformation.

Interestingly we found that within the concentration range of about 0.4–0.6 mol of HCl/mol of Al, the gelation step appeared thermally reversible. Thus, a gel could be formed by heating the precursor sol at 70 °C for 10 min, and if the gel was immediately removed from the oven and left to cool to room temperature, a free flowing sol would reform after 30–40 min. This process could be repeated, i.e., the free-flowing solution could be again heated to 70 °C and a solid gel would result which if cooled became a sol again. Extended heating at 70 °C (>1 h) however led to irreversible gelation.

The role of the acid on the sol–gelation chemistry was investigated using quasi-elastic light scattering (QLS). The QLS at room temperature of the solution phase, at different acid concentrations showed for the 0.5 M HCl sample a hydrodynamic diameter of about 24 nm, the 1.0 M HCl a value of about 13 nm with a much weaker signal, and the 2.0 M HCl had no measurable signal. These data show that higher acid concentration reduces the size of the sol particles and imply that the higher acidity prevents extensive condensation, due to the competing water hydrolysis reaction (at low pH).

Both the solution chemistry and the solid state chemistry were investigated by ^{27}Al NMR. A detailed description of the results will be published separately. Here we show some of the spectra which were obtained with a single 90° excitation pulse. These spectra represent the relatively narrow peaks of the rapidly rotating dissolved aluminum complexes, but not the broad signals of the gelled aluminum species. Figure 1a shows the spectrum of the complex with 0.5 mol of HCl/water added. The peak at 4 ppm is consistent with an octahedral Al environment where some of the aluminum is coordinated with water (or hydroxide). Upon addition of phosphoric acid, two peaks result at −12 and +40 ppm, respectively (Figure 1b). The exact assignment of these is not clear at this stage but presumably reflects octahedral and tetrahedral aluminum complexed to phosphate groups.[13] Figure 1c,d depicts the thermally reversible sol–gelation step. In the gelled state after heating (c) a large reduction in signal is observed (due to line broadening of the less mobile Al centers). Upon cooling (d) the two peaks then reappear as the solid gel transforms back to the sol. Solid-type spectra (not shown) were obtained with a 30°–τ–60° echo sequence. The spectra of the gel and calcined material are almost identical, indicating that the aluminum environment in the gel is essentially the same as in $AlPO_4$. Figure 1e shows the magic-angle-spinning spectrum of the calcined glass. The peak is at +33 ppm, which falls within the range 23–40 ppm

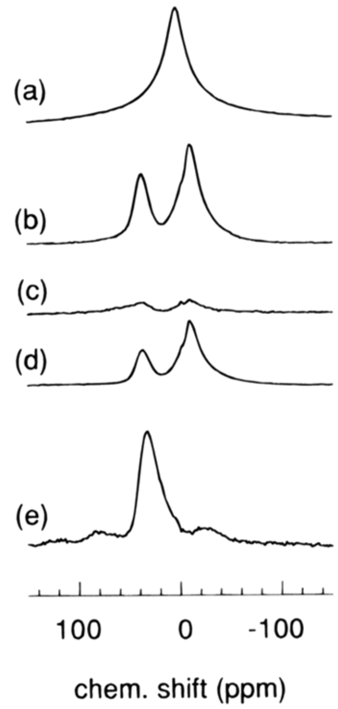

Figure 1. ^{27}Al NMR solution spectra showing (a) Al complex in isopropyl alcohol with 0.5 mol of HCl (water), (b) Al complex, isopropyl alcohol, HCl (water) and phosphoric acid at room temperature, (c) solution (b) heated to a solid gel for 10 min at 70 °C and (d) the heat-aged material after cooling at room temperature for 24 h with the conversion of the solid gel back to a free-flowing sol. (e) ^{27}Al magic-angle-spinning solid-state NMR of the aluminum phosphate calcined at 750 °C.

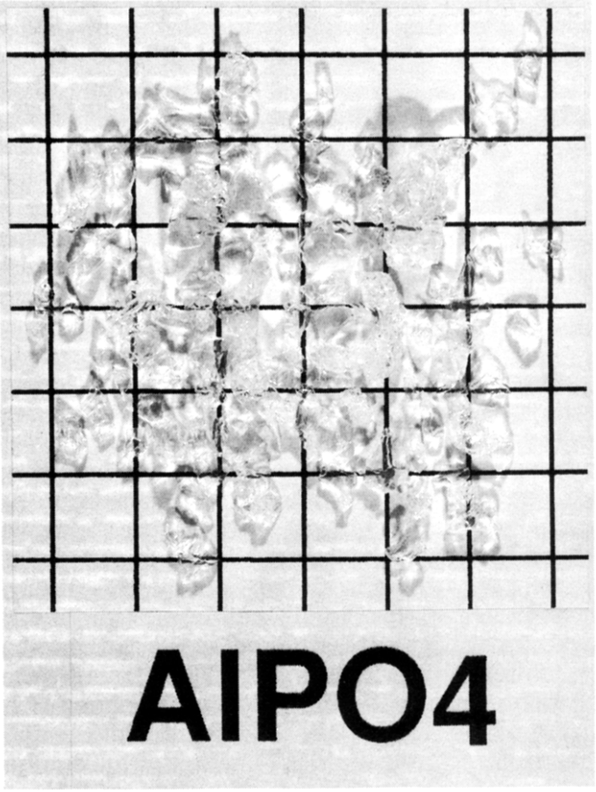

Figure 2. High surface area aluminum phosphate, calcined to 800 °C, prepared via the sol–gel process (1 bar = 1 cm).

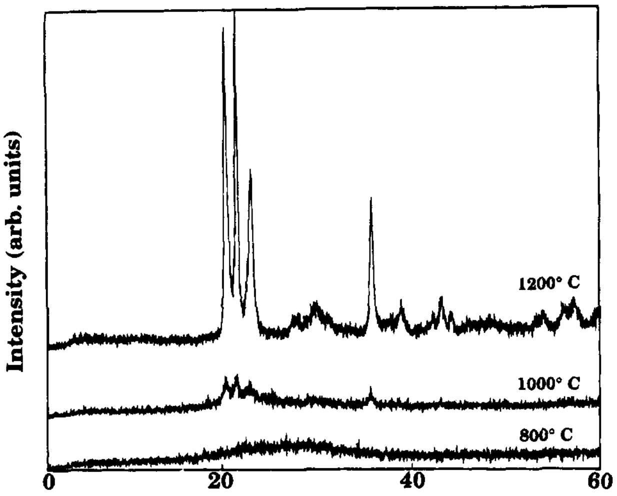

Figure 3. X-ray diffraction pattern of aluminum phosphate calcined at (a) 800, (b) 1000, and (c) 1200 °C showing the conversion to the tridymite phase.

observed for crystalline $AlPO_4$ structures.[13]

High surface area aluminum phosphate glass is produced by heating the dried gels in air to 600–800 °C. Typical conversion yields from the dried gel to the calcined $AlPO_4$ glass are 85 wt %. Analytical data, both C and Cl analysis, coupled with infrared data, show that some of the ethyl acetoacetate, water, and chloride ion is trapped in the gel after drying (100 °C for 24 h) but these are removed upon calcination in air leaving $AlPO_4$ with an P/Al ratio of unity. The overall stoichiometric reaction is shown in eq 1. The $AlPO_4$ glass is clear and colorless (Figure 2).

$$Al(OC_4H_9)_2(O_3C_6H_9) + H_3PO_4 \xrightarrow[\text{heat}]{\text{HCl/solvent}} AlPO_4 + 2C_4H_9OH + C_6H_9O_3H \quad (1)$$

Surface areas obtained for the glass calcined at 600 and 800 °C were 565 and 425 m^2/g, respectively (at higher calcination temperature, 1000 °C, the surface area drops off dramatically with values of about 1 m^2/g). Typical pore volumes are 0.63 cm^3/g with an average pore diameter of 4.2 nm. These values are higher than obtained using aqueous based routes which are typically in the range 250–350 m^2/g.[4–12] The porous $AlPO_4$ glass is very similar in character to typical high surface area silica's.

It is interesting to compare the crystallization of the $AlPO_4$ prepared using the method above with that previously described in the literature.[13] In the absence of HCl/water in the precursor stage, upon heating the dried gel, crystallization occurs as low as 180 °C, forming cristobalite, berlinite, and tridymite. At 1000 °C, the berlinite phase disappears and the tridymite phase transforms into cristobalite.[13] We find however that in the presence of HCl in the precursor stage, completely X-ray amorphous glasses are obtained. The aluminum phosphate remains X-ray amorphous up to at least 800 °C. Crystallization begins in the range of 900 °C with complete crystallization to the tridymite phase in the region of 1200 °C, Figure 3. This is a striking example of where an apparent small change in the precursor chemistry dramatically alters the crystallization behavior, inhibiting crystallization for several hundred degrees.

In summary, we have found a novel route to high surface area $AlPO_4$ which maintains a P/Al ratio of unity. Small variations of the precursor chemistry (for example, in the presence or absence of HCl/water) give rise to large changes in both the sol–gel reaction and also the crystallization. The size of the sol particles can be controlled by altering the acidity which in turns allows control of the gelation rate. We have also discovered a very interesting and rare thermally reversible sol–gelation step.