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ChemComm www.rsc.org/chemcomm

Synthesis of amorphous mesoporous aluminophosphate materials with high thermal stability using a citric acid route

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Received (in Cambridge, UK) 21st April 2004, Accepted 18th May 2004
First published as an Advance Article on the web 15th June 2004

Amorphous mesoporous aluminophosphate materials synthesized from precursors of $Al(NO_3)_3/H_3PO_4/NH_4OH$ in the presence of citric acid, exhibit high specific surface areas, narrow pore size distributions and excellent thermal stabilities.

Metal phosphates are active solid catalysts that can be used in various acid–base catalysis, redox catalysis and photocatalytic processes.[1] Recently, much work has been devoted to the synthesis of mesoporous metal phosphate materials,[2,3] since the characteristics of mesoporous materials are of high relevance for the catalytic application to the direct activation of large organic molecules, and they are also suitable for supporting catalytically active sites bearing large organic functionalities.[4]

Mesostructured metal phosphates with lamellar or hexagonal structures can be obtained by a liquid-crystal templating route, which is an extension of the synthesis of mesostructured silica. However, most of these materials are thermally unstable and therefore collapse upon removal of the surfactants by calcination.[2a,2b] So far only a few examples of relatively stable mesoporous metal phosphates of Al, Sn, Zr and Ti *etc.* were reported; these are usually required to strictly control the synthesis conditions and/or to carry out complicated post-synthesis treatments.[3] Recently, Campelo *et al.*[5] described an alternative way for synthesizing thermally stable mesoporous aluminophosphates by a sol–gel precipitation method in the presence of organic additives like 1,2-ethanediol. These materials possess relatively broad pore size distribution in the mesoporous range from 5 to 50 nm. The approach they adopted should be derived from the sol–gel method by using an organic additives route for synthesizing porous silica or other metal oxides.[6]

Citric acid has shown special abilities for creating amorphous mesoporous materials (*e.g.* mesoporous Ni–MgO[7a] and silica[7b]) as organic additives in the sol–gel process. Here, by extending this strategy to the aluminophosphate system, we obtained amorphous mesoporous aluminophosphate materials (AlPO) with relatively high specific surface areas, narrow pore size distributions and excellent thermally stabilities.

The amorphous mesoporous AlPO (P/Al = 1) was prepared using the following procedure: 48 g of $Al(NO_3)_3{\cdot}9H_2O$ and 27 g of citric acid were dissolved in 200 mL of distilled water, the resulting solution was stirred at ambient temperature for 30 min. Then 8.7 mL of H_3PO_4 (85 wt%) was dropped into the solution under vigorous stirring. After that, a diluted aqueous ammonia (10 wt%) solution was added dropwise until pH 5.0 was achieved. After standing for 5 h, the mixture was heated at 363 K in open air with continuous stirring to remove water and all other volatiles. The resulting white solid was then calcined at 873 K or 1073 K for 3 h, denoted as AlPO-873 and AlPO-1073, respectively.

The mesoporous structure of the AlPO materials can be confirmed by N_2-adsorption/desorption isotherms (Fig. 1). Both samples present type IV isotherms (definition by IUPAC),[8] which is characteristic of mesoporous materials. The appearance of hysteresis loops in the isotherms may indicate the presence of "ink-bottle" type pores in the AlPO materials.[7b] The specific surface area decreased from 546 m^2g^{-1} to 303 m^2g^{-1} when the calcination temperature changed from 873 K to 1073 K. However, both AlPO materials exhibit similar pore size distributions (calculated from the desorption branch) over a relatively narrow range from 1.5 to 4.0 nm. These results suggest that the mesopore structure of these AlPO materials do not collapse at such high calcination temperatures.

Powder X-ray diffraction (XRD) patterns of two calcined AlPO samples exhibit only a very broad band centred at 22° (2θ), which is a characteristic of amorphous aluminophosphates.[5] No crystallized $AlPO_4$ phase appears even after calcination at 1073 K. The absence of a low angle peak in the 2θ range from 1.0° to 3°, which is characteristic of ordered mesoporous materials, indicates that there is no long-range order in these mesoporous AlPO materials.

The ^{27}Al MAS NMR spectra of two AlPO samples were measured to obtain the information on the short-range coordination environment of aluminium (Fig. 2A). AlPO-873 shows two major signals at 38 and −13 ppm, which can be assigned to tetrahedral $Al(OP)_4$ groups, and octahedrally coordinated Al species, *i.e.* $Al(OP)_x(H_2O)_{6-x}$, respectively.[2b] In the case of AlPO-1073, the resonances corresponding to the octahedral Al species is nearly undetectable; indicating that the condensation reaction of surface hydroxyls is nearly complete at such a high calcination temperature.

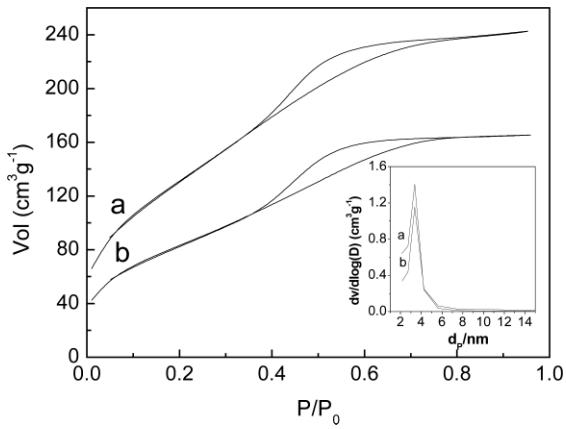

Fig. 1 N_2 adsorption/desorption isotherms at 77 K and pore size distribution profiles (inset) of (a) AlPO-873 and (b) AlPO-1073.

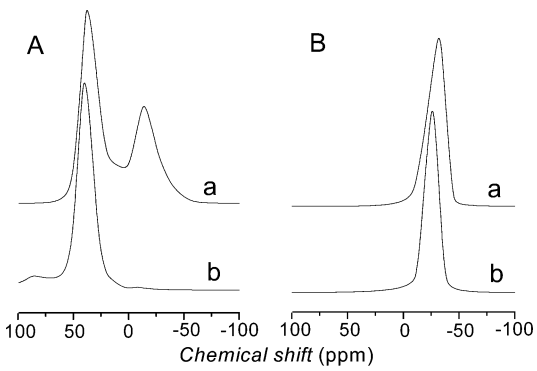

Fig. 2 (A) Solid-state ^{27}Al MAS NMR spectra of (a) AlPO-873 and (b) AlPO-1073. (B) Solid-state ^{31}P MAS NMR spectra of (a) AlPO-873 and (b) AlPO-1073.

DOI: 10.1039/b406013j

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The ^{31}P MAS NMR spectra of both AlPO materials exhibit a sole single component at around −30 ppm, which can be mainly attributed to a P atom in tetrahedral coordination with O–Al bands.[2b] The relatively broad resonance may be due to the presence of a small amount of a phosphorous species, coordinating partly with H_2O or OH groups, *i.e.* $P(OAl)_x(HO)_{4-x}$.[2b] Additionally, FT-IR spectra of these AlPO materials confirmed the presence of P–OH groups (3670 cm^{-1}), which can normally be assigned to the weak Brønsted acid sites.

Thermal gravimetry and differential thermal analysis (TG-DTA) profiles of pure citric acid showed three main endothermic peaks at 329, 427, and 483 K (Fig. 3), which can be ascribed to the elimination of water of crystallization, the melting of the citric acid crystal, and the decomposition of citric acid, respectively.[7b] The strong exothermic peak around 778 K can be attributed to the burning of carbon formed by the decomposition of citric acid.

For the as-synthesized AlPO precursor (Fig. 3), the TG profile indicates a *ca.* 83% loss of mass from room temperature to 1073 K. The endothermic peak around 500 K corresponding to the decomposition of citric acid, shifted slightly to higher temperatures in comparison with that of pure citric acid, indicating that there is no strong interaction between citric acid and the AlPO network. The existence of a very strong exothermic peak at 530 K may be caused mainly by the decomposition of some nitrates, like ammonium nitrates. The slightly gradual weight loss in the range from 540 to 873 K should be due to the continued condensation reaction of surface hydroxyls. No obvious exothermic peaks can be observed in the temperature range from 873 to 1173 K, indicating that no phase transformation (from amorphous AlPO to any kind of crystalline $AlPO_4$) occurs at such high temperatures.

It should be pointed out that the presence of citric acid in the precursor of AlPO is critical for the formation of the mesoporous structure, since no such relatively uniform pores can be obtained in a reference sample prepared by the same process without the addition of citric acid. Another point we need to emphasize here is that no gelation or precipitation occurred in the wide pH range from 2 to 12 when citric acid was used in the preparation process, which is quite different from the general sol–gel and/or precipitation routes in the presence of organic additives for obtaining mesoporous materials.[5,7] This might be due to the fact that citric acid can bind with Al^{3+} to form a stable complex in aqueous solution.[9] Thus,

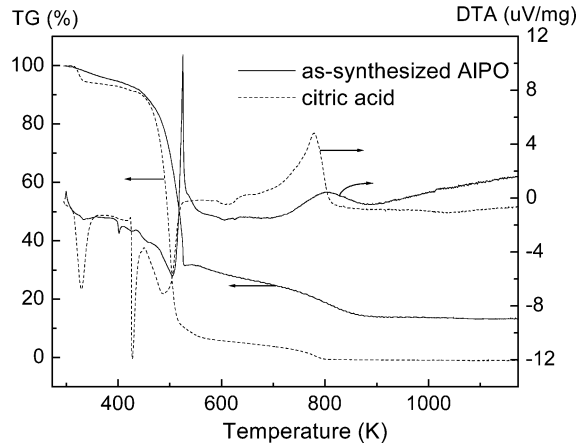

Fig. 3 TG-DTA profiles of as-synthesized AlPO (solid lines) and pure citric acid (dash lines).

in our case, the solid products could only be obtained by evaporating water as described in the experimental part. The pore formation mechanism in this process might be similar to that in an aero gel prepared by supercritical drying, as suggested by Takahashi *et al.*[7b] according to their studies on the mesoporous silica obtained by a sol–gel process in the presence of citric acid. Therefore, citric acid can be regarded as a structure-template for providing mesopores of the AlPO material. However, the concrete role of citric acid in the pore formation process remains unclear, which is our future task to be carried out.

In summary, our work presents a simple and efficient way to synthesize amorphous mesoporous aluminophosphates with high thermal stability. This method may be extended to the synthesis of other kinds of metal phosphates. We believe that the outstanding properties of such materials will provide numerous opportunities for the application in the field of catalysis and material science.

We wish to thank for financial support the Development Project of Science and Technology of Jilin Province (No. 990546) and the Innovation Foundation of Jilin University (No. 2002CX092).

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