Synthesis of thermally stable mesoporous hexagonal aluminophosphate molecular sieves

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Thermally stable mesoporous hexagonal aluminophosphates (UHM-1) and silicoaluminophosphates (UHM-3) are synthesized based on ion-pair interactions of aluminophosphate species in the presence of tetramethylammonium hydroxide with a cationic surfactant [$C_{16}H_{33}NMe_3Cl$].

Aluminophosphate materials (AlPO-*n*) are recently developed crystalline microporous materials of potential use in catalysis.[1,2] For catalytic processing of larger micelles, mesoporous AlPO-*n* materials are desirable. Lamellar mesostructures of aluminophosphate have been synthesized by using an amphiphilic alkylamine ($C_{10}H_{21}NH_2$) in tetraethylene glycol[3] and by using dimethylalkylamines with C_8–C_{16} alkyl groups in water,[4] but these materials are thermally unstable as are lamellar mesostructures of M41S silicates.[5]

The M41S family of silica-based mesoporous molecular sieves is formed by a self-assembly process involving electrostatic interactions between positively charged quaternary ammonium surfactants (S^+) and inorganic anions (I^-).[5] This process can form hexagonal MCM-41 silica tubes. The electrostatic assembly method has been generalized.[6] A neutral precursor assembly method involving hydrogen bonding between neutral amine surfactants (S^0) and neutral silica precursors (I^0) in alcohol–water solvent has also been demonstrated.[7]

Here we report the synthesis of thermally stable mesoporous hexagonal aluminophosphate and silicoaluminophosphate molecular sieves by a S^+I^- route. Our approach is based on self-assembly between a cationic surfactant (S^+) and an aluminophosphate precursor (I^-) in the presence of alkylammonium hydroxide. This method produces stable hexagonal mesostructures of aluminophosphate (UHM-1) and silicoaluminophosphate (UHM-3).

Mesoporous aluminophosphate and silicoaluminophosphate were prepared using cetyltrimethylammonium chloride (CTAC, Aldrich, 25% in water) as a surfactant and the following gel composition: $Al_2O_3 : xP_2O_5 : ySiO_2 : \mu CTAC : \nu NR_4OH : \omega H_2O$, where R = Me, Et, Bu^n; x = 0.6–3.4, y = 0–0.6, μ = 0.24–0.50, ν = 8.5–47 and ω = 200–642. In a typical preparation of aluminophosphate, 3.53 g dried aluminium hydroxide (USP Pfaltz & Bauer Inc.) was slowly added to a solution of 4.2 g phosphoric acid (85 mass%, EM Industries) in 15 g water under vigorous stirring. The mixture was added to a solution of 11.6 g CTAC (25 mass%) in 100 g water with stirring. After 0.5 h, 17.3 g tetramethylammonium hydroxide (TMAOH, Aldrich, 25 mass% in water) was slowly added dropwise into the above mixture until pH 9.5 was achieved. In a typical silicoaluminophosphate preparation, an aluminophosphate gel prepared according to the above procedure and 0.79 g tetraethylorthosilicate (TEOS, Aldrich) was added to 11.6 g CTAC in 100 g water with stirring for 3 h. Then 19.0 g TMAOH was added dropwise to obtain pH 9.5. The gels obtained using these procedures were then stirred for 72 h at room temperature. The solid product was recovered, washed and air-dried at 70 °C. The template was removed by calcination at 500 °C for 1 h in flowing nitrogen, followed by 6 h in flowing oxygen.[5]

Powder X-ray diffraction (XRD) patterns of products were obtained on a Siemens D5000 diffractometer with a scan rate of 1° min^{-1} and Cu-Kα radiation (λ = 0.154 18 nm). Transmission electron micrographs (TEM) were measured on a JEOL 2000 FX microscope with an accelerating voltage of 100 kV. Electron probe microanalysis was performed on a JEOL JXA-8600 spectrometer. Thermogravimetric analysis (TGA) was performed on a DuPont 2100 thermal analyser with a heating rate of 10 °C min^{-1} in air. Surface areas of the samples were measured on a Monosorb (Quantachrome Corp.) surface area analyser by the single point method.

Powder X-ray diffraction patterns of as-synthesized and calcined UHM-1 and UHM-3 are shown in Fig. 1. The XRD patterns show a prominent peak corresponding to (100) reflections and much weaker but clearly present peaks corresponding to (110), (200) and (210) reflections in the as-synthesized material which can be indexed to a hexagonal lattice and which are similar to typical XRD patterns for siliceous hexagonal MCM-41 materials.[5,6] This shows that mesoporous hexagonal mesostructural aluminophosphate and

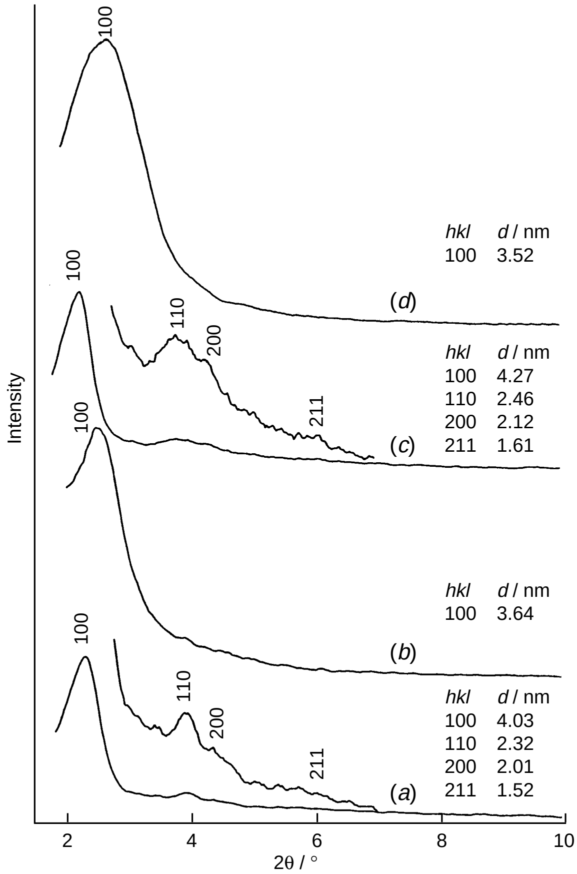

Fig. 1 Powder XRD patterns of (*a*) as-synthesized UHM-1 (P/Al = 2.0), (*b*) calcined UHM-1 (P/Al = 2.0), (*c*) as-synthesized UHM-3 (P/Al = 0.8, Si/P = 0.2) and (*d*) calcined UHM-3 (P/Al = 0.8, Si/P = 0.2)

silicoaluminophosphate have been synthesized. As-synthesized UHM-1 and UHM-3 show a *d*(100) spacing of 4.1 nm. All XRD patterns of calcined UHM-1 and UHM-3 are similar and exhibit a single broad diffraction peak corresponding to a *d*(100) spacing of 3.6 nm.

The broadening of the (100) reflection on calcination arises from less long-range crystallographic order.[7,8] The intensity of the *d*(100) reflection of calcined UHM-1 and calcined UHM-3 decreases in comparison with that of as-synthesized UHM-1 or UHM-3 as has been observed for hexagonal MCM-41.[5,6,9]

Transmission electron micrographs of as-synthesized UHM-1 (Fig. 2) show hexagonal-shaped pores of about 4 nm diameter which is in agreement with the value (4.1 nm) measured from XRD. These results are similar to, but show more disorder, than those of siliceous MCM-41 materials,[5,6,9] supporting that as-synthesized UHM-1 and UHM-3 essentially have long-range hexagonal packing but with some disorder.

Synthesis of mesoporous aluminophosphate (UHM-1) is successful with aluminium hydroxide but replacement of aluminium hydroxide by Capatal alumina produces only amorphous or lamellar aluminophosphate (designated UHM-2). UHM-2 with *d*(100) of 2.97 nm is similar to the lamellar aluminophosphate previously reported.[4] For the formation of silicoaluminophosphate, TEOS is used as the silica source.

UHM-1 can be formed over a range of P/Al mole ratios (3.4–0.6) in the gel which is different from a fixed P/Al ratio (*ca*. 1.0) required for synthesis of microporous aluminophosphates.[10] However, the P/Al ratio in the product is always less than unity and decreases with decreasing P/Al in the gel. This is perhaps why the products show better resolved XRD with higher P/Al gel ratios. The product P/Al ratio of <1 suggests that hydroxy aluminium species are involved in the mesoporous assembly process. Mesoporous aluminophosphate can be synthesized for a range of surfactant to alumina ratios of 0.24–0.50. At higher surfactant/Al_2O_3 ratios of 1–3 only amorphous material is formed.

Mesoporous hexagonal aluminophosphate can be synthesized at pH values from 7.5 to 9.5 at room temperature. At higher temperatures up to 100 °C formation of the hexagonal phase requires pH >8.5. Mesoporous hexagonal aluminophosphate is formed with cationic surfactants only in the presence of alkylammonium hydroxide, NR_4OH (R = Me, Et, Bu^n). Replacement of NR_4OH with 0.1 M NaOH led to no mesostructural materials.

The BET surface areas of calcined UHM-1 average 772 $m^2\ g^{-1}$ and of UHM-3 average 928 $m^2\ g^{-1}$ and are independent of the P/Al or Si/P gel ratios. These values reflect the thermal stability of UHM-1 and UHM-3 to calcination at 500 °C as do the TEM results.

Thermogravimetric analysis of UHM-1 shows a large mass loss of *ca*. 70% on heating to 700 °C. Three endothermic losses near 80 °C (15 mass%), 240 °C (30 mass%) and 340 °C (25 mass%) are observed. The 80 °C loss is assigned to water desorption. The 240 and 340 °C losses are assigned to desorption and decomposition of TMAOH and CTAC in either order.

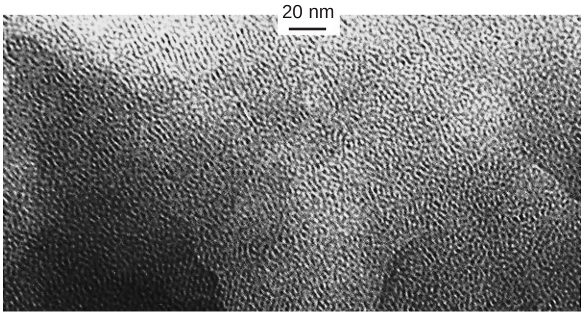

Fig. 2 Transmission electron micrograph (TEM) of as-synthesized UHM-1. TEMs for calcined UHM-1 and for UHM-3 are similar.

We postulate that the formation of UHM-1 and UHM-3 materials occurs by a modified S^+I^- ion-pair process. The inorganic precursors (I^-) are non-ideal aluminophosphate species of low polymerization degree with some hydroxy groups. When TMAOH is added, it reacts with the hydroxy group of these aluminophosphate species to produce a weak ion pair ($I^- \cdots TMA^+$) since the TMA^+ cation has a large ionic radius. These ion-pair species diffuse to the surfactant (S^+) assembly (micelle) interface and interact strongly with the cationic surfactant headgroups. The interaction of the aluminophosphate species with the cationic surfactant headgroups is stronger than that with TMA^+ cation. The micellar structure then organizes the condensation and polymerization of adjacent aluminophosphate species to form an ordered hexagonal mesostructure.[5,11]

The function of the organic ammonium cation from TMAOH seems to be to modify the strength of the electrostatic interaction between the aluminophosphate species and the cationic surfactant micelle assembly to form a $S^+I^- \cdots TMA^+$ ion pair. If NaOH is used the Na^+ cation with a smaller ionic radius than TMA^+ has a stronger ion-pair interaction with the aluminophosphate species and prevents sufficient interaction with the cationic surfactant assembly. Thus the assembly of mesostructural aluminophosphate fails. Aluminium hydroxide may form a less polymerized aluminophosphate with many hydroxy groups and favour the assembly of the mesostructure compared to Capatal alumina.

We conclude that mesoporous hexagonal aluminophosphate UHM-1 and silicoaluminophosphate UHM-3 molecular sieves can be synthesized *via* modified ion-pair interactions. The calcined materials are characterized by a hexagonal structure with *d*(100) *ca*. 4.0 nm and high surface area which reveals their thermal stability. These materials seem to have greater thermal stability than very large pore AlPO-*n* materials like VPI-5.

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Footnote

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