Organosilane surfactant-directed synthesis of mesoporous aluminophosphates constructed with crystalline microporous frameworks†

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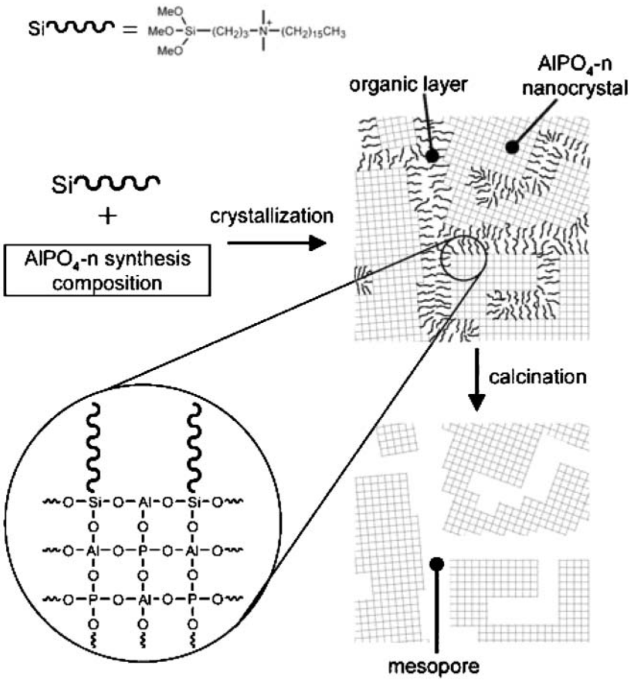
A direct hydrothermal assembly process was developed to synthesize mesoporous aluminophosphates that are constructed with crystalline microporous frameworks, by the addition of organosilane surfactants into the conventional synthesis composition for crystalline microporous aluminophosphates.

Zeolite-type microporous materials have attracted much scientific attention in adsorption and catalysis.[1] Traditionally, definition of the zeolite-type materials was restricted to crystalline aluminosilicate materials constructed with SiO_4 and AlO_4 tetrahedra. In 1982, Wilson and co-workers developed a new class of zeolite-like inorganic crystals denoted as $AlPO_4$-*n* (*n* indicates a structural type), whose structures are constructed with AlO_4 and PO_4.[2–4] The beauty of these materials is that part of the Al can be substituted with diverse metal species including Si, Mg, Ti, V, Cr, Mn, Fe, Co, *etc.*, which allows the introduction of various catalytic functions.[3] For example, Si-containing aluminophosphates (SAPOs) possessing Brønsted-acid sites have been extensively studied as catalysts for methanol-to-olefin (MTO) transformation.[3,5] Plant construction for SAPO-34-based MTO process is under way in Lagos, Nigeria by UOP/Eurochem Technologies. Ethylene and propylene obtained from this plant should result in the production of 400000 metric tons per year of high-density polypropylene and polyethylene.[3] Transition metal-containing aluminophosphates are attractive as a catalyst for redox reactions.[3] Another remarkable feature of the aluminophosphates is the rich variety of microporous structures: 53 structures including 18 analogues of zeolite. Some of the structures possess extra-large pore entrances composed of more than 12 T atoms.[3,4]

After discovery of the MCM-41-type mesoporous ($2 <$ diameter < 50 nm) silicates,[6,7] extensive efforts were devoted to the synthesis of such ordered mesoporous analogues of various compositions *via* the supramolecular templating route using surfactant micelles.[8–12] As compared with zeolite-type microporous materials, the large pores showed good potential for application as catalysts and adsorbents requiring facile diffusion of large molecules. So far, several aluminophosphate materials with such mesoporous structures have been reported, including lamellar[8,9] and 2-dimensional hexagonal.[9,10] However, the mesopore walls were built with incompletely cross-linked, non-crystalline aluminophosphate frameworks showing no significant microporosity. With this regard, it is challenging to synthesize mesoporous aluminophosphate materials that are built with crystalline microporous frameworks. The rich structural variety of conventional $AlPO_4$-*n* with a molecular sieving effect and their transition metal incorporation would then be synergistically combined with the advantage of a mesoporous structure. Indeed, in the case of zeolite, it has been reported that mesoporous materials built with microporous frameworks can exhibit remarkably high resistance to catalyst deactivation in various organic reactions.[13] The zeolites having such mesoporous–microporous hierarchical structures were synthesized through a one-step hydrothermal crystallization, wherein a rationally designed organosilane surfactant was added as a mesopore director into conventional zeolite synthesis composition.[14]

Here, we demonstrate that the synthesis strategy using organosilane surfactants as a mesopore director can be successfully extended to aluminophosphate compositions. The resultant aluminophosphates exhibited mesoporous structures. The mesopore walls were constructed with crystalline microporous $AlPO_4$-*n*.



Scheme 1 Proposed synthesis mechanism for the hierarchically porous aluminophosphates (HP-AlPO-*n*).

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† Electronic supplementary information (ESI) available: Synthesis details, ^{27}Al and ^{31}P MAS NMR, NH_3-TPD profiles. See DOI: 10.1039/b612265e

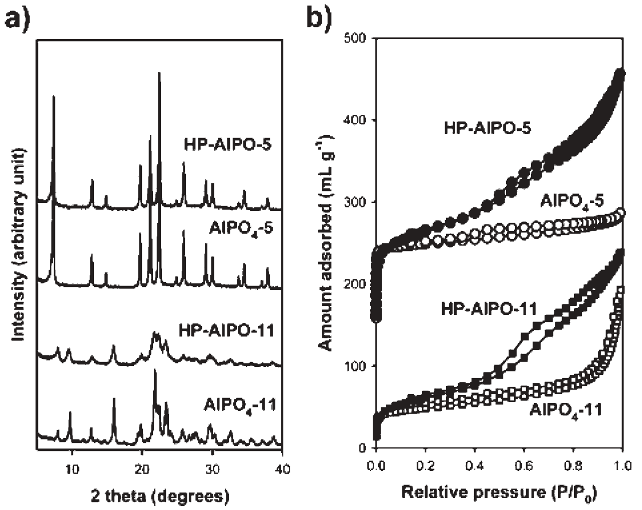

Fig. 1 (a) XRD patterns and (b) argon adsorption isotherms of $AlPO_4$-*n* and HP-AlPO-*n* samples. Isotherms for $AlPO_4$-5 and HP-AlPO-5 are vertically offset by 150 mL g^{-1}.

Like the case of zeolite synthesis, we propose that the organic tail of the surfactant directs the mesoporous structure while the silica moiety is incorporated in the resultant aluminophosphate frameworks (Scheme 1).

In a typical synthesis of such hierarchically porous aluminophosphates (denoted as HP-AlPO-*n*), 3-(trimethoxysilyl)propyl] hexadecyldimethylammonium chloride ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{16}H_{33}]Cl$, TPHAC) was added into a synthesis composition for the corresponding $AlPO_4$-*n*[15] (see the synthesis details in the ESI†). A hydrothermal reaction at 200 °C was employed for crystallization. For comparative purposes, conventional $AlPO_4$-*n* samples were also synthesized without the addition of TPHAC. Products were analyzed by mutually complementary techniques including powder X-ray diffraction (XRD), magic angle spinning (MAS) NMR, scanning electron microscopy, and argon adsorption.

The HP-AlPO-5 and HP-AlPO-11 products exhibited wide-angle XRD patterns that are characteristic of the corresponding $AlPO_4$-*n* structures with high phase purity (Fig. 1a). ^{27}Al and ^{31}P MAS NMR showed that HP-AlPO-*n* possessed fully condensed crystalline frameworks as in the case of conventional $AlPO_4$-*n* crystals (see ESI). In the ^{27}Al MAS NMR spectrum, an intense NMR peak at 37 ppm was assigned to the tetrahedral aluminium in the crystalline aluminophosphate framework. Less intense peaks at -16 and 8 ppm were assigned to the octahedral and five-coordinated Al species, respectively. These peaks can be attributed to partial hydration of the tetrahedral Al sites.[16] The ^{31}P NMR spectrum of HP-AlPO-*n* exhibited a single resonance at -28 ppm, which can be assigned to the fully condensed tetrahedral phosphorus environment, *i.e.*, P atom connected to four Al atoms *via* bridging oxygen. These NMR data are markedly different from those for ordered mesoporous aluminophosphates having non-crystalline frameworks, which exhibited a number of NMR peaks corresponding to less condensed framework species.[9–11]

Scanning electron microscopic (SEM) investigations (Fig. 2) revealed that the HP-AlPO-*n* particles were composed of 20–50 nm nanocrystals, while the conventional $AlPO_4$-*n* particles were composed of 200–1000 nm crystals. As shown in Fig. 1, the XRD patterns for HP-AlPO-*n* exhibited much broader diffractions, in good agreement with the smaller crystalline domains. Argon adsorption study revealed that the HP-AlPO-*n* samples possessed higher BET specific surface area and mesopore volume than conventional $AlPO_4$-*n* materials, while the micropore volume did not change significantly (Fig. 1b and Table 1). Notably, the argon adsorption isotherms of HP-AlPO-*n* corresponded to the type-IV isotherm, which is characteristic of materials having mesoporosity. The major difference in the isotherms between HP-AlPO-*n* and ordinary $AlPO_4$-*n* materials is a distinct increase in the adsorption quantity in the region $0.4 < P/P_o < 0.9$. This increase is interpreted as capillary condensation in the mesopores. As revealed by the SEM images, the presence of the mesoporosity can be ascribed to the intercrystalline void space between nanosized crystallite domains within a particle.

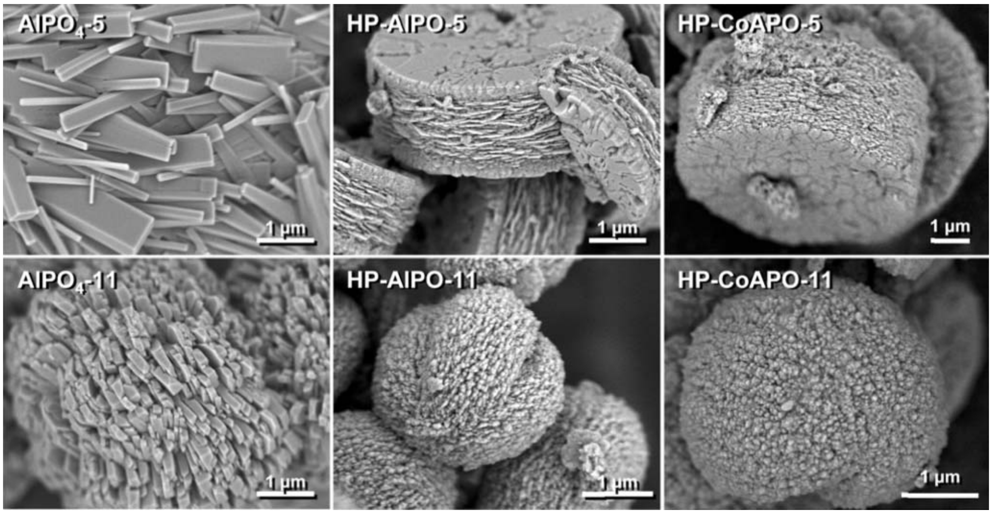

Fig. 2 Scanning electron micrographs of $AlPO_4$-*n*, hierarchically porous aluminophosphates (HP-AlPO-*n*) and hierarchically porous Co-containing aluminophosphates (HP-CoAPO-*n*).

Table 1 Composition and pore structural properties of the aluminophosphate materials

Sample	Molar composition	$S_{\mathrm{BET}}{}^{a}$/ $\mathrm{m^2\ g^{-1}}$	$V_{\mathrm{micro}}{}^{b}$/ $\mathrm{mL\ g^{-1}}$	$V_{\mathrm{meso}}{}^{b}$/ $\mathrm{mL\ g^{-1}}$
$AlPO_4$-5	$Al_{0.50}P_{0.50}O_2$	206	0.093	0.05
HP-AlPO-5	$Al_{0.50}P_{0.45}Si_{0.05}O_2$	280	0.089	0.26
HP-SAPO-5	$Al_{0.50}P_{0.14}Si_{0.36}O_2$	265	0.087	0.26
HP-CoAPO-5	$Al_{0.46}P_{0.46}Si_{0.05}Co_{0.03}O_2$	254	0.085	0.24
$AlPO_4$-11	$Al_{0.52}P_{0.48}O_2$	112	0.038	0.16
HP-AlPO-11	$Al_{0.49}P_{0.45}Si_{0.06}O_2$	174	0.041	0.25

[a] S_{BET} is BET surface area. [b] V_{micro} is micropore volume calculated from Saito–Foley analysis. V_{meso} is mesopore volume (total pore volume $-$ V_{micro}).

Elemental analysis using inductively coupled plasma (ICP) spectroscopy (Table 1) showed that the HP-AlPO-*n* products had compositions close to $Al_{0.50}P_{0.45}Si_{0.05}O_2$. The Si content corresponded to the total amount of Si present in the organosilane surfactant. The sum of the Si and P content was almost equal to the Al content. Based on the elemental analysis, we believe that the Si atoms selectively substituted P atoms as in the case of crystalline microporous silicoaluminophosphate (SAPO) materials.[3,17] We have used temperature programmed desorption (TPD) of ammonia to confirm the framework acidity due to Si incorporation. The result showed significantly higher acidity of HP-AlPO-*n* than ordinary $AlPO_4$-*n* (see NH_3-TPD profiles in the ESI).

The HP-AlPO-*n* synthesis conditions can be modified so that the products can contain more Si, and also transition metal elements such as Co and Mn. For instance, addition of tetraethyl orthosilicate into the HP-AlPO-*n* synthesis composition resulted in the formation of highly siliceous aluminophosphates (HP-SAPO-*n*, Table 1), which exhibited remarkably increased framework acidity (see ESI). The addition of $Co(OAc)_2$ resulted in the substitution of Al with Co (HP-CoAPO-*n*, Table 1). The blue colour of the sample, as synthesized and also after calcination, can be attributed to the framework tetrahedral Co(II) species.[18] Further work would be necessary for more detailed characterization of the Co chemical states and their catalytic functions.

In summary, we have demonstrated that the synthesis strategy using organosilane surfactants as a mesopore director can be generalized to aluminophosphate compositions. It would be possible to obtain such materials with rich compositional and framework structural variations. It is expected that the synthesis strategy would provide many opportunities for the synthesis, characterization, modification, and application of crystalline aluminophosphate materials with micro-/mesoporous structural hierarchy.

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