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Mesoporous aluminophosphates from a single-source precursor

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Mesoporous aluminophosphates with a strict ratio of Al : P = 1 : 1 have been synthesised from a single-source molecular precursor.

The utilisation of self-assembled supramolecular arrays of organic amphiphiles as structure-directing agents[1] has become a widely explored synthesis method for nanoscopically structured materials, among them mesoporous aluminophosphates.[2–7] In light of the significance of their microporous analogues (crystalline '$AlPO_4$-*n*' with uniform pore diameters below 1 nm),[8] particularly in the field of size-selective heterogeneous catalysis,[9] there is an obvious demand for larger pores with an equally regular arrangement. Mesoporous aluminophosphates exhibit uniform pore diameters between 2 and 4 nm. However, they are not crystalline and vary in their relative Al : P ratios. Controlling their precise composition has turned out to be very difficult to achieve. Porous products with an exact 1 : 1 stoichiometry of Al and P have not been rationally prepared so far. The entire topic of ordered mesostructured aluminophosphates has recently been reviewed.[10]

In contrast to the well-established mesoporous silica materials, which usually require only one single reactant (such as tetraethyl orthosilicate), aluminophosphates have so far exclusively been prepared from separate sources of aluminium and phosphorus [*e.g.* $Al(OPr^i)_3$ and H_3PO_4]. Owing to the complexity of the synthesis it is generally difficult to control the reaction in a rational way. This problem can be overcome by the utilisation of single-source precursors which contain the elements for the inorganic network in a pre-defined stoichiometry and short-range structural order. This concept is widely established in various kinds of inorganic syntheses, such as (non-oxide) amorphous ceramic materials.[11–13] However, in the field of mesostructured materials, single-source syntheses have so far been reported only for silica phases (from a double four-ring $Si_8O_{20}^{8-}$ unit)[14] and for aluminosilicates (from an analogous $Si_4Al_4(OH)_8O_{12}^{4-}$ unit).[15]

Here we describe the first rational synthesis of ordered mesoporous aluminophosphates with strict 1 : 1 molar ratios of Al : P from an ethanol-soluble molecular single-source precursor,[16] which can be conveniently prepared in large quantities. The core unit of the precursor consists of a cube-like arrangement of alternating aluminium and phosphorus atoms connected with each other by oxygen atoms. The empirical formula is $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$ (Fig. 1). The synthesis of mesoporous aluminophosphates from this precursor requires non-aqueous conditions, since the compound is not stable in the presence of water; we have recently shown that ethanol is a suitable solvent for such syntheses.[7,17]

In a typical synthesis of mesoporous aluminophosphates from the precursor a solution of 4.8 g *n*-hexadecylamine ($C_{16}H_{33}NH_2$) in 10 g ethanol (99.8%) was added to a solution of 13.8 g of the precursor in 50 g ethanol (99.8%), corresponding to an approximate molar ratio in the synthesis mixture of Al : P : surfactant : ethanol = 1 : 1 : 0.5 : 32. After stirring at room temperature for 30 min the slurry was kept at 363 K for 48 h in a Teflon-lined autoclave without agitation. The product was filtered off, washed with ethanol and dried. (*n*-Tetradecylamine and *n*-dodecylamine were also used.) For the extraction of the surfactant, 5 g of the sample were dispersed in a solution of 20 g methanol and 5 g aqueous hydrogen chloride (1 mol l^{-1}). The mixture was stirred at room temperature for 15 min, filtered off, and washed with methanol. This process was repeated three times.

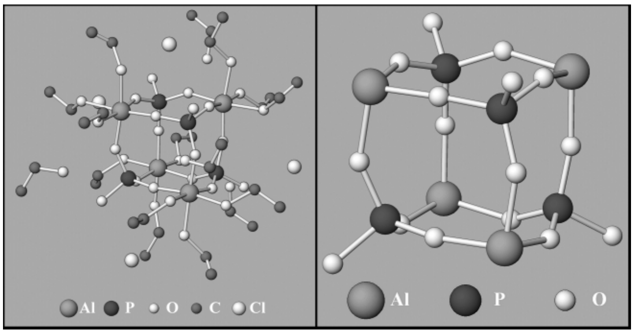

Fig. 1 Left: schematic representation of the molecular structure of the precursor $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$. Right: the same view without the ethanol and Cl ligands clarifies the cube-like structure of the core unit (drawing based on crystal data from ref. 16; H atoms not shown).

Elemental analysis shows that the molar ratio of Al : P : surfactant is 1 : 1 : ~0.5 in all products (Table 1). The molar composition suggests that the core unit of the precursor may remain intact during the synthesis, thus serving as a building block for the inorganic network. Otherwise, an Al : P ratio different from unity would have to be expected. As we have recently shown, the 'conventional' synthesis from separate sources of Al and P under otherwise very similar conditions leads to products with an excess in Al of at least 12%.[7]

Table 1 Relative molar ratios of Al, P, C, and N in three representative mesostructured aluminophosphates synthesised from the molecular precursor $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$

	Relative molar amount[a]					
Surfactant	Al	P	C	N	Al : P	C_n-NH_2 : P
C_{12}-NH_2	0.117	0.118	0.710	0.057	0.99	0.50
C_{14}-NH_2	0.100	0.101	0.752	0.052	1.00	0.53
C_{16}-NH_2	0.099	0.099	0.754	0.048	1.00	0.48

[a] By elemental analysis.

The powder X-ray diffraction diagrams of a representative sample (as-synthesised and after surfactant removal, Fig. 2) show a single broad reflection (and another very weak reflection at approximately double the diffraction angle) as typical of randomly ordered tubular mesostructures; this is also confirmed by transmission electron microscopy (not shown). The *d* value in the as-synthesised sample (prepared with *n*-hexadecylamine) is 3.74 nm. A slight decrease to 3.42 nm occurs after surfactant extraction; such shrinkage upon removal of the structure-directing species is frequently observed for mesoporous materials.

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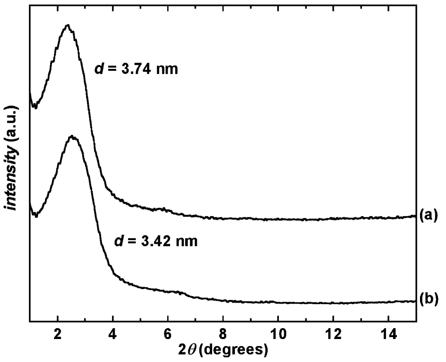

Fig. 2 Powder X-ray diffraction diagram (Bruker AXS D8, CuKα) of a mesoporous aluminophosphate prepared from the molecular precursor $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$: (a) as-synthesised; (b) after removal of the surfactant (*n*-hexadecylamine).

Nitrogen physisorption (Fig. 3) confirms the mesoporous nature of the samples: The adsorption–desorption isotherms are of type IV with a well-defined step at $p/p_0 \approx 0.35$–0.45, indicating capillary condensation. The pore size (diameter) distribution (calculated by the BJH method from the desorption branch) has its maximum at *ca.* 3.3 nm; the specific surface area (calculated by the BET equation for $p/p_0 \approx 0.05$–0.2) is 410 $m^2\ g^{-1}$. Hysteresis is attributable to textural porosity.[18,19] The quantitative removal of the surfactant is confirmed by elemental analysis and IR spectroscopy (not shown).

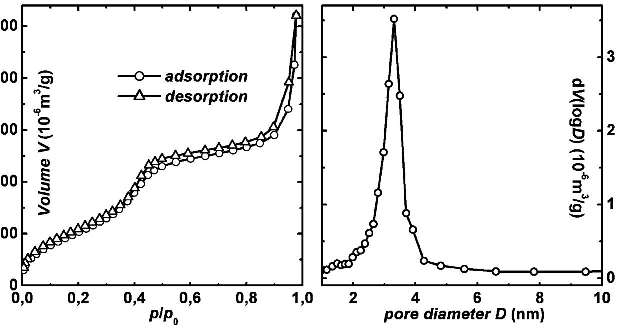

Fig. 3 Left: nitrogen adsorption–desorption isotherms (Quantachrome Autosorb 1; $T = 77$ K) of a mesoporous aluminophosphate prepared from the molecular precursor $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$. The isotherms are of type IV; the specific BET surface area is 410 $m^2\ g^{-1}$. Right: pore size (diameter) distribution (calculated by the BJH method).

Solid-state MAS NMR spectroscopy confirms that the inorganic network consists of Al–O–P linkages. The ^{27}Al spectra of a representative sample (as-synthesised and after surfactant removal, Fig. 4, left) exhibit two resonances, at *ca.* 42 and 8 ppm, corresponding to tetrahedral $Al(OP)_4$ and octahedral $Al(OP)_4(H_2O)_2$, respectively.[20] In the porous sample a slightly higher relative intensity of the octahedral resonance is observed than in the as-synthesised material, which can be explained by additional water ligands coordinating to Al after the (partly aqueous) extraction of the surfactant. The ^{31}P spectra (Fig. 4, right) show one broad line between 0 and 30 ppm in both the as-synthesised and the porous samples, attributable to four-fold coordinated P with O–Al (tetrahedral and/or octahedral Al) and various amounts of H_2O or OH groups, *i.e.* $P(OAl)_x(H_2O)_{(4-x)}$.[21]

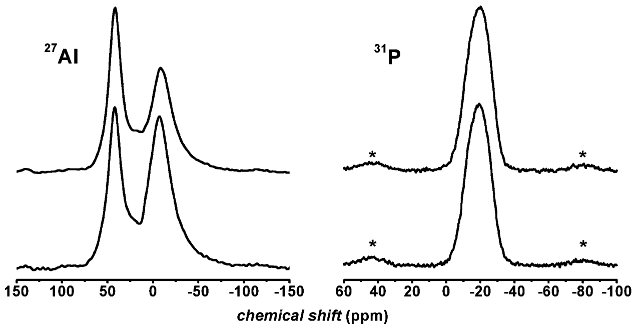

Fig. 4 ^{27}Al (left) and ^{31}P (right) solid-state MAS NMR spectra (Bruker AXS 400; ^{27}Al, 102 MHz; ^{31}P, 161 MHz) of a mesoporous aluminophosphate prepared from the molecular precursor $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$ before (top) and after (bottom) removal of the surfactant (*n*-hexadecylamine). The assignment of the resonances is made in the text. (* = spinning side bands.)

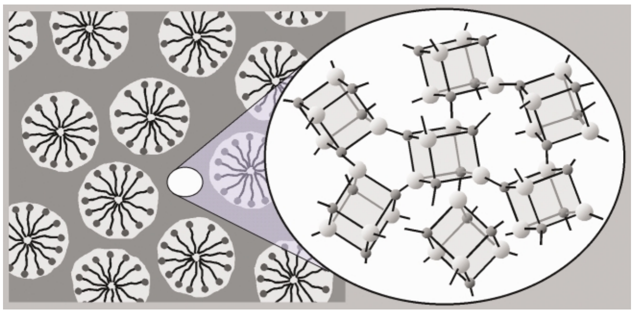

Fig. 5 Schematic representation of the proposed structural properties of a mesostructured aluminophosphate prepared from the single-source molecular precursor $[Al(PO_4)(HCl)(C_2H_5OH)_4]_4$. The stoichiometry of Al : P = 1 in all products suggests that the inorganic matrix consists of cube-like $Al_4P_4O_{12}$ core units connected with each other by oxygen bridges; for clarity, oxygen atoms (*cf.* Fig. 1) are not shown.

The successful utilisation of a single-source molecular precursor for mesoporous aluminophosphates (Fig. 5) opens new perspectives for future syntheses. Modification of the precursor, especially the incorporation of transition metals, may lead to tailor-made catalyst materials.

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Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 Z. Luan, D. Zhao, H. He, J. Klinowski and L. Kevan, *J. Phys. Chem. B*, 1998, **102**, 1250.
3 T. Kimura, Y. Sugahara and K. Kuroda, *Microporous Mesoporous Mater.*, 1998, **22**, 115.
4 B. T. Holland, P. K. Isbester, C. F. Blanford, E. J. Munson and A. Stein, *J. Am. Chem. Soc.*, 1997, **119**, 6796.
5 S. Cabrera, J. E. Haskouri, C. Guillem, A. Beltrán-Porter, D. Beltrán-Porter, S. Mendioroz, M. D. Marcos and P. Amorós, *Chem. Commun.*, 1999, 333.
6 Y. Z. Khimyak and J. Klinowski, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5275.
7 M. Tiemann, M. Schulz, C. Jäger and M. Fröba, *Chem. Mater.*, 2001, **13**, 2885.
8 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
9 For review see, for example: M. Hartmann and L. Kevan, *Chem. Rev.*, 1999, **99**, 635.
10 M. Tiemann and M. Fröba, *Chem. Mater.*, 2001, **13**, 3211.
11 M. Birot, J.-P. Pillot and J. Dunogues, *Chem. Rev.*, 1995, **95**, 1443.
12 J. Bill and F. Aldinger, *Adv. Mater.*, 1995, **7**, 775.
13 H.-P. Baldus and M. Jansen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 328.
14 C. A. Fyfe and G. Fu, *J. Am. Chem. Soc.*, 1995, **117**, 9709.
15 G. Fu, C. A. Fyfe, W. Schwieger and G. T. Kokotailo, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1499.
16 J. E. Cassidy, J. A. J. Jarvis and R. N. J. Rothon, *J. Chem. Soc., Dalton Trans.*, 1975, 1497.
17 M. Tiemann, M. Fröba, G. Rapp and S. S. Funari, *Chem. Mater.*, 2000, **12**, 1342.
18 Y. Long, T. Xu, Y. Sun and W. Dong, *Langmuir*, 1998, **14**, 6173.
19 C. G. Sonwane and S. K. Bhatia, *Langmuir*, 1999, **15**, 2809.
20 M. Schulz, M. Tiemann, M. Fröba and C. Jäger, *J. Phys. Chem. B*, 2000, **104**, 10 473.
21 A. Sayari, I. Moudrakovski, J. S. Reddy, C. I. Ratcliffe, J. A. Ripmeester and K. F. Preston, *Chem. Mater.*, 1996, **8**, 2080.