Synthesis of mesostructured lamellar aluminophosphates

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The liquid-crystal templating approach used for the synthesis of M41S mesostructured materials is extended to aluminophosphates; a variety of lamellar $AlPO_4$ phases with *d*-spacings in the nanometre range are prepared in the presence of long-chain alkyl- or dimethylalkyl-amines.

Aluminophosphates ($AlPO_4$) are a well known family of crystalline microporous materials.[1] Here, we extended for the first time the liquid-crystal templating approach[2] to the preparation of lamellar aluminophosphates with *d*-spacings in the range of 2 to 4 nm. This technique was first used by Kresge *et al.*[3] to synthesize the so-called M41S family of silica-based mesoporous molecular sieves, and was further applied by Huo *et al.*[4] and others[5,6] to the synthesis of a large number of oxides and to metal-cation modified mesoporous silicates. Unlike most crystalline mesoporous silicates which were prepared using ionic surfactants, our $AlPO_4$ phases were synthesised in the presence of long-chain alkyl- or dimethylalkyl-amines.

In a typical synthesis, pseudoboehmite alumina (Catapal B, 74% from Vista) was added to a dilute phosphoric acid solution under vigorous stirring. After 1 h, the template was added to this mixture and stirred for an additional 3 h. The gel was then typically heated at 373 K for 24 h with no stirring. The molar gel composition was $x\,P_2O_5 : y\,Al_2O_3 : z\,C_nH_{2n+1}NR_2 : w\,H_2O$, with R = H or Me. For $n = 12$ and R = H, we used $x = 1$, (or 0 for a P-free sample), $y = 0$–2; $z = 0.125$–2; and $w = 60$–300. This communication deals only with samples prepared in the presence of dodecylamine with $x = 1$, $y = 0$–2, $z = 1$ and $w = 60$.

^{31}P MAS NMR spectra were recorded using either a Bruker AMX-300 instrument (Larmor frequency 121.47 MHz, speed of rotation 10–12 kHz, delay time 60 s) or a Bruker AMX-600 instrument at a frequency of 242.95 MHz. ^{27}Al MAS NMR spectra were obtained on AMX-300 and AMX-600 instruments at frequencies of 78.18 and 156.36 MHz, respectively [speed of rotation 10–15 kHz, delay time 300 ms; radiofrequency pulse: 0.5 μs (π/20)]. Phosphoric acid (85%) and 1 mol dm^{-3} aluminium nitrate were used as external references.

The pHs of the gels were quite low, *ca.* 2.5–3.5, and as a consequence ^{15}N as well as ^{13}C NMR data showed that in the final product the template was protonated.[7] As shown by XRD (Fig. 1), all samples exhibit only 00*l* peaks indicative of the occurrence of lamellar structures. TEM (Fig. 2) provides direct evidence of the presence of layered materials. Additional TEM and electron diffraction data may be found in the following paper.[8]

Figs. 3 and 4 show the ^{31}P and ^{27}Al NMR spectra for samples with $y = 0$–2. The alumina-free sample ($y = 0$) exhibited two overlapped ^{31}P NMR peaks at δ 2.3 and 0.6 with relative intensities of 40 and 60%, respectively. On the basis of the isotropic chemical shifts and the parameters of anisotropy (75 ± 5 ppm), these peaks were assigned to two non-equivalent isolated $PO_2(OH)_2$ groups[9] present in the inorganic layers of the template–phosphate complex. As the ratio of A : P increased to 0.4 : 1, in addition to the two ^{31}P peaks already mentioned, a new peak at δ −19.3 developed. This peak, attributable to P with at least two Al next-neighbours,[10,11] corresponds most probably to the formation of an additional layered $AlPO_4$ phase. In this composition range, ^{27}Al NMR gave only one narrow line at δ −10.3 (Fig. 4) corresponding to six-coordinate Al species $Al(OP)_{6-n}(H_2O)_n$, where $n = 2$ or 3.[10,12]

As seen in Fig. 1, at an Al : P ratio of 0.6 : 1 , major changes in the crystalline structure occur. Furthermore, in addition to the two ^{31}P NMR peaks at δ 2.3 and 0.6 associated with the layered phase formed by interaction between phosphoric acid and the surfactant, a series of new signals ranging from δ −4 to −26 were observed. Two minor (14%) tetrahedral Al species at δ *ca.* 45, and two major (86%) octahedral Al species at δ *ca.* −10.5 were also formed. All these species corresponded to a unique lamellar $AlPO_4$ phase with a *d*-spacing of *ca.* 32 Å.

Samples with Al : P ratios in the range 0.8–1.6 : 1 exhibited the same XRD pattern (Fig. 1) consisting of a series of 00*l* peaks which correspond to a layered structure with a *d*-spacing of

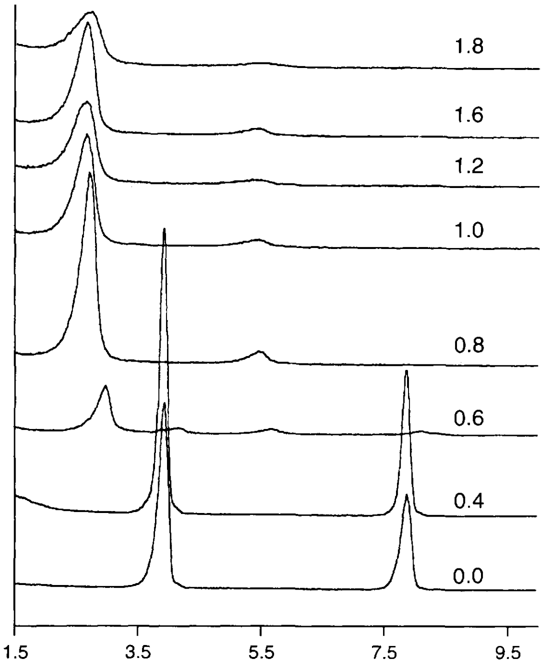

Fig. 1 X-Ray diffraction patterns of $AlPO_4$ mesophases with the gel molar composition of $P_2O_5 : y\,Al_2O_3 : C_{12}H_{25}NH_2 : 60\,H_2O$. The values of *y* are shown on the right hand side.

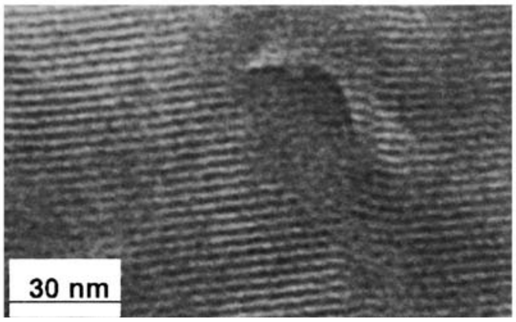

Fig. 2 Transmission electron micrograph of the sample with $x = 1$, $y = 0.8$, $z = 1$ and $w = 60$ ($d = 32.5$ Å)

32 Å. The micrograph of the sample with $y = 0.8$ shown in Fig. 2 also gives $d = 32.5$ Å. The crystallinity of these samples went through a maximum at a gel Al : P ratio of *ca.* 0.8 : 1. All ^{31}P NMR spectra of these samples consisted of only one broad peak centred at δ *ca.* −13. The broadening of the spectrum stems from a distribution of chemical shifts that results from a distribution in the local coordination of phosphorus. As shown in Fig. 3 the peak shape is preserved at higher field (14.1 T), thus confirming that the lineshape is dominated by the distribution in the chemical shifts. The first derivative of the ^{31}P NMR signals showed the presence of at least five components (Fig. 3, inset); however, the overall broadening of the signals did not allow us to draw definite assignments of the various phosphorus environments. Nevertheless, the range of the observed chemical shifts excludes the presence of P–O–P species.[9,13] ^{27}Al NMR spectra (Fig. 4) were comprised of one tetrahedral species at δ 45 and two octahedral species at δ 9 and −10. The species at δ 9 was assigned to extraframework alumina. Indeed, a P-free sample prepared under similar conditions was amorphous and had only one ^{27}Al NMR peak at δ 9. It should be noted that as the total Al content of the sample increased, the relative intensity of the peak at δ 9 also increased while those of the other two peaks decreased. Chemical analysis showed that for all these samples, the ratio of framework Al species, with NMR signals at δ 45 and −10, to P was constant and close to 0.9 : 1. This indicates that both Al species belong to the same lamellar $AlPO_4$ mesophase. This conclusion was further supported by the fact that treatment of the samples under vacuum brought about a significant decrease in the δ −10 peak intensity in favour of the δ 45 peak, indicating again that both species are related to each other and that at least two ligands of the octahedral species are water molecules.[7] As mentioned above, the $AlPO_4$ mesophase had an Al : P ratio of less than unity. Since there were no P–O–P species, it was inferred that some of the second-neighbours of P were protons or most likely alkylammonium species. In conclusion, for $0.8 < y < 1.6$, in addition to variable amounts of excess amorphous alumina there was mainly one lamellar $AlPO_4$–surfactant mesosphase with $d = 32$ Å and Al : P = 0.9 : 1.

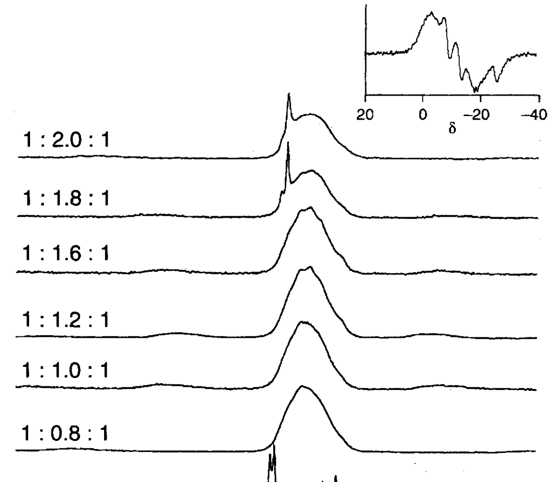

Fig. 3 ^{31}P NMR spectra of $AlPO_4$ samples with the gel molar composition of $P_2O_5 : y\ Al_2O_3 : C_{12}H_{25}NH_2 : 60\ H_2O$. The values of *y* are shown on the left hand side. Spectra of samples with $y = 0.6$, 1.0, 1.2, 1.6 and 1.8 were recorded at high frequency (14.1 T). *Inset*: first derivative of the spectrum of the sample with $y = 1.2$.

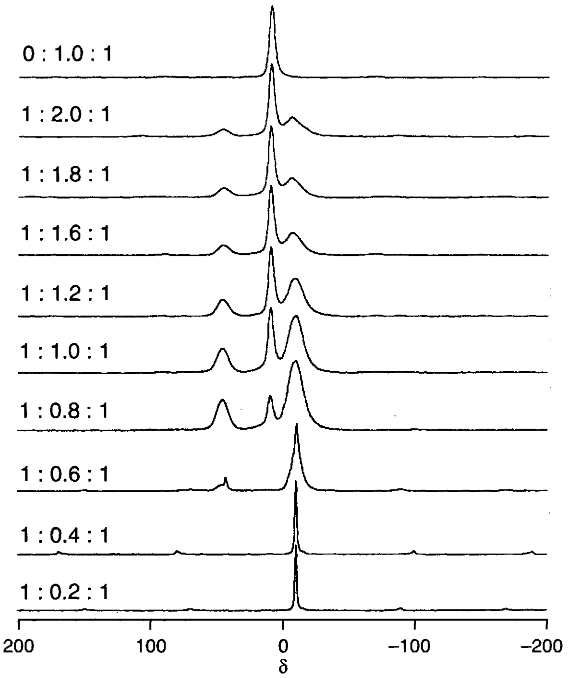

Fig. 4 ^{27}Al NMR spectra of $AlPO_4$ samples with the gel molar composition of $P_2O_5 : y\ Al_2O_3 : C_{12}H_{25}NH_2 : 60\ H_2O$. The values of *y* are shown on the left hand side.

At higher Al content (Al : P > 1.6 : 1), the shape of the ^{31}P NMR signal remained essentially the same, except that a sharp and low intensity line developed at δ −3.7. Since the total integral intensity of this line was well below 5%, it was ascribed to impurities.

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