Synthesis of the LTA-type $AlPO_4$ in the presence of the diazapolyoxa macrocycle 'Kryptofix 222'

L. Schreyeck, F. D'agosto, J. Stumbe, P. Caullet* and J. C. Mougenel

Laboratoire de Matériaux Minéraux-ENSCMu-URA 428, 3, rue Alfred Werner, 68093 Mulhouse Cedex, France

The LTA-type aluminophosphate can be synthesized from aqueous mixtures in the presence of a single structuring agent, hexaoxa-4,7,13,16,21,24-diaza-1,10-bicyclo[8,8,8]-hexacosane (possibly associated with F^- ion as optional co-template) and is characterized through XRD, SEM, chemical analysis, thermal analysis and solid-state NMR spectroscopy.

Microporous materials with the LTA structure were first synthesized in their aluminosilicate forms with Na^+ and possibly NMe_4^+ as templates.[1–4] Low phosphorus-substituted LTA-type aluminosilicates [with P/(P + Si + Al) molar ratios ranging from *ca.* 0.01 to 0.04] were then prepared by Kühl[5] and Lok *et al.*[6] from alkaline media in the presence of the same templates. During the 1990s, microporous LTA-type metallophosphates could be synthesized from near-neutral reaction mixtures but only in the presence of F^- ions which act as co-template by structuring the D4R units of the framework. The synthesis of the gallophosphate was thus achieved in 1992[7] with the dipropylamine as the organic template, this species being incorporated in the large α cage of the structure. In 1994, Sierra *et al.*[8] prepared the aluminophosphate in the presence of two organic structuring agents, namely diethanolamine and tetramethylammonium cation, these species being occluded in the α cage and the sodalite cage respectively.

In this work, the LTA-type aluminophosphate was prepared with the hexaoxa-4,7,13,16,21,24-diaza-1,10-bicyclo[8,8,8]-hexacosane ('Kryptofix 222', hereafter K222) as the only organic template. In opposition to the previous experimental observations concerning the LTA-type metallophosphates, the presence of the co-templating F^- ions is here only optional.

The molar composition of the used gels was $0.5\ Al_2O_3 : 0.5\ P_2O_5 : 0.25$ K222 : 0.25 or 0 HF : 40 H_2O. These gels were prepared by first mixing the phosphoric acid aqueous solution (85 mass% H_3PO_4, Prolabo, Normapur) with the aluminium source [pseudoboehmite (Catapal B, 69 mass% Al_2O_3–31 mass% H_2O, Vista Chemical Co.) or aluminium triisopropoxide (Fluka)] and the required amount of distilled water; this mixture was stirred for 30 min at room temp. before the successive addition of the (optional) HF aqueous solution [40 mass% HF (Prolabo, Normapur)] and K222 (Merck, $> 99\%$). After stirring for 1 or 14 h (depending on whether aluminium triisopropoxide or pseudoboehmite is used, respectively), the gel was finally transferred into a Teflon-lined stainless-steel autoclave which was then heated at 170 °C without agitation in an oil-bath (the time required to reach this temperature is < 5 min). After reaction, the solids were recovered by filtration, washed with distilled water, dried at 60 °C overnight and rehydrated at room temp. for one day at 80% relative humidity. As an example, the recovered mass of solid is *ca.* 120 mg when the gel is prepared with 163 mg of aluminium triisopropoxide, 92 mg of H_3PO_4 solution, 10 mg of HF solution, 75 mg of K222 and 560 mg of water. The volume of the autoclave used was *ca.* 20 cm^3.

In the presence of HF, fully crystallized samples of LTA-type $AlPO_4$ could be easily synthesized from either aluminium source used. For instance, in the presence of aluminium triisopropoxide, crystallization was already achieved after 6 h of reaction at 170 °C, whereas a large proportion of the recovered product remains amorphous after 1 h of heating.

On the other hand, from fluoride-free reaction mixtures, the formation of pure samples of LTA-type $AlPO_4$ was only possible when pseudoboehmite was used as the aluminium source (after 5 days of heating). When aluminium triisopropoxide was employed, a mixture of the LTA-type $AlPO_4$ and of an unidentified impurity was obtained after 5 days of reaction (this impurity could correspond to a layered compound according to the XRD data and the micrographs), whereas for shorter crystallization times (one or two days) only a partial transformation of the gel into the LTA-type $AlPO_4$ occurred. The reason for this strong influence of the nature of the aluminium source is questionable, but could be related to the difference observed between the initial pH values, *i.e.* close to 3 or 7 according to whether pseudoboehmite or aluminium triisopropoxide were used, respectively (the final pH was systematically close to 7–8).

The crystals prepared from fluoride-free or fluoride-containing mixtures display the same usual cubic shape already found for the other LTA-type materials (Fig. 1). The cubes are more or less truncated, their sizes ranging from < 1 μm to *ca.* 20 μm depending on the synthesis conditions used.

X-Ray diffraction patterns [STOE STADI-P diffractometer, equipped with a curved germanium (111) primary monochromator, Cu-Kα_1 radiation] of all samples (Fig. 2) are very similar to the pattern characteristic of the cubic LTA structure (space group *Fm*3*c*). Only small differences in the relative intensities are visible between the patterns of the fluoride-containing [Fig. 2(*a*)] and fluoride-free samples [Fig. 2(*b*)], the value of the *a* parameter for the latter being slightly smaller. Both parameter values are close to the value found by Sierra *et al.*[8] for a LTA-type structure aluminophosphate (Table 1).

Only the presence of the original template K222 is detected by solution ^1H NMR spectroscopy (Bruker AC250 spectrometer) on samples dissolved in 6 M HCl aqueous solution

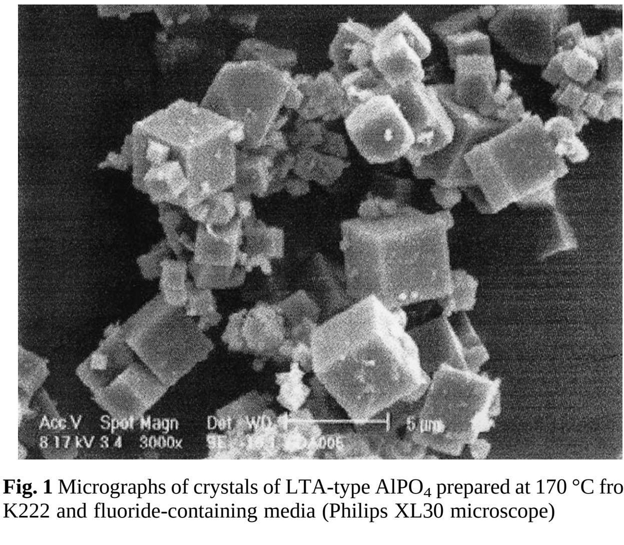

Fig. 1 Micrographs of crystals of LTA-type $AlPO_4$ prepared at 170 °C from K222 and fluoride-containing media (Philips XL30 microscope)

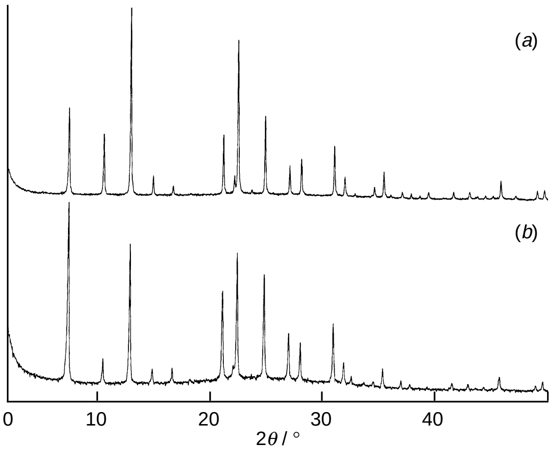

Fig. 2 XRD patterns of the LTA-type $AlPO_4$ materials prepared in the presence of K222 from fluoride-containing (*a*) or fluoride-free media (*b*)

Table 1 Values of the *a* parameter for as-made LTA-type $AlPO_4$ samples

Template(s) occluded	*a*/Å
Kryptofix 222 + F^-	23.867(2)
Kryptofix 222	23.773(3)
Diethanolamine + NMe_4^+ + F^-[8]	24.063(3)

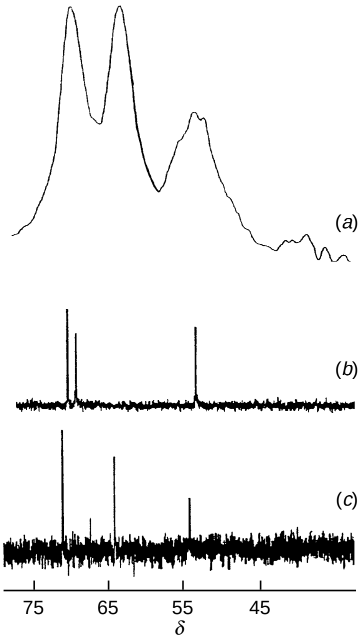

Fig. 3 ^{13}C CP MAS NMR spectrum of an LTA-type $AlPO_4$ sample (*a*) and ^{13}C solution NMR spectra of K222 in basic (*b*) or acid (*c*) aqueous solution

(with dioxane as the internal standard). The content of K222 is close to 19 mass%, which corresponds to the incorporation of one K222 molecule per pseudocell (most probably in the large α cage). Samples prepared in the presence or absence of F^- ions display the same ^{13}C CP MAS NMR spectrum (Bruker MSL 300 spectrometer) with three peaks at δ *ca.* 71, 65 and 55 (ref. TMS) [Fig. 3(*a*)]. These chemical shift values match more closely with those found for an acidic (pH *ca.* 3) aqueous solution of K222 [Fig. 3(*c*)] than with those measured for a basic (pH *ca.* 11) aqueous solution of K222 [Fig. 3(*b*)]. The K222 is thus probably incorporated in a diprotonated form.

According to the solution ^{19}F NMR spectroscopy (performed on samples dissolved in 6 M HCl solution with CF_3CO_2H as the internal standard), the amount of fluoride is close to 1.8 mass% in the samples prepared from fluoride-containing mixtures, whereas, as expected, no fluoride is detectable in samples synthesized from fluoride-free media. Besides, the ^{19}F MAS NMR spectrum (not shown) of the fluoride-containing samples displays a unique signal (with sidebands) located at δ *ca.* −95 (relative to $CFCl_3$). Such a chemical shift value is characteristic of F^- ions trapped in the D4R units of the structure of microporous aluminophosphates as previously found by Sierra *et al.*[8] (LTA-type $AlPO_4$) and Schott-Darie *et al.*[9] (AST-type $AlPO_4$). In each pseudocell, the two charges of the organic cation are compensated by two F^- ions, which corresponds to the occupation of two thirds of the D4R units of the structure. In samples containing no fluoride, the positive charges of the organic species might be compensated by OH^- ions.

The TG and DSC curves recorded under air (not shown) on a Setaram TG/DSC11 thermoanalyser are very similar for all samples. The first mass loss observed between 20 and 200 °C is close to 8% and can be probably attributed to the elimination of water, an endothermic signal occurring in this temperature range on the DSC curve. The remainder of the mass loss takes place between 200 and 700 °C (in two steps corresponding to two exothermic peaks at *ca.* 400 and 600 °C on the DSC curve) and amounts to *ca.* 20% which is in good agreement with the organic content determined previously from ^1H NMR experiments.

According to X-ray diffraction, on completion of the thermal treatment (*ca.* 750 °C) a partial amorphization occurs together with a partial conversion into tridymite. Even for calcination at lower temperatures, *e.g.* 550 °C for 4 h, a partial collapse of the structure occurs.

Finally from the experimental results above the idealized chemical formula of the unit cell can be written as

$$8\{(Al_{12}P_{12}O_{48})(X^-)_2(K222^{++})(H_2O)_8\}$$
$$\text{where } X^- = F^- \text{ or } OH^-$$

LTA-type $AlPO_4$ was previously obtained in the presence of three templates, *i.e.* diethanolamine, F^- and NMe_4^+, each of them structuring one of the three polyhedra present, *i.e.* the α cage, the D4R unit and the sodalite cage, respectively. In this work, the LTA-type $AlPO_4$ was synthesized in the presence of Kryptofix 222 alone. This species, which is probably incorporated in the α cage, appears thus very well suited to preparation of this material. Although the presence of F^- is clearly optional, the crystallization appears easier when these ions are present in the reaction mixtures. In this case F^- ions are incorporated in the D4R units of the structure as co-templates.

Other organic templates of the same family are currently being tested in synthesis, possibly in association with F^- ions but also with NMe_4^+ ions as potential co-templates.

References

1 T. B. Reed and D. W. Breck, *J. Am. Chem. Soc.*, 1956, **78**, 5972.
2 R. M. Barrer and P. J. Denny, *J. Chem. Soc.*, 1961, 971.
3 G. T. Kerr, *Inorg. Chem.*, 1966, **5**, 1537.
4 R. L. Wadlinger, E. J. Rosinski and C. J. Planck, *US Pat.*, 3375205, 1968.
5 G. H. Kühl, *Inorg. Chem.*, 1971, **10**, 2488.
6 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and E. M. Flanigen, *US Pat.*, 4440871, 1984.
7 A. Merrouche, J. Patarin, M. Soulard, H. Kessler and D. Anglerot, *Molecular Sieves—Synthesis of Microporous Inorganic Materials*, Van Nostrand Reinhold, New York, vol. 1, 1992, p. 384.
8 L. Sierra, C. Deroche, H. Gies and J. L. Guth, *Microporous Mater.*, 1994, **3**, 29.
8 C. Schott-Darie, J. Patarin, P. Y. Le Goff, H. Kessler and E. Benazzi, *Microporous Mater.*, 1994, **3**, 123.

Received in Cambridge, UK, 2nd April 1997; Com. 7/02209C