Synthesis of MnAPO-20 and CoAPO-20 using Tetrahedral Metal Species

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High substitution levels of manganese and cobalt in MnAPO-20 and CoAPO-20 are achieved using tetrahedral metal species.

The synthesis of the aluminophosphate family of molecular sieves ($AlPO_4$-*n* where *n* denotes structure type) was first reported in 1982.[1] The framework substituted analogues, SAPO-*n* and MAPO-*n* (where M = Mg, Mn, Co or Zn) were synthesised in 1984 and 1985, respectively.[2,3] Some of the aluminophosphates and substituted aluminophosphates are structural analogues of the aluminosilicates (zeolites), such as $AlPO_4$-34 (chabazite) and $AlPO_4$-20 (sodalite), whereas others are novel structures, *i.e.* $AlPO_4$-11 and VPI-5.

Tetramethylammonium ions (TMA^+) are used in the synthesis of the small pore sodalite-type aluminophosphate $AlPO_4$-20 and its substituted counterparts.[4] MgAPO-20[5], CoAPO-20[6] and ZnAPO-20[6] have all been successfully synthesised, as has a range of substituted silicoaluminophosphates.[4]

Metal species used in the synthesis of MAPO-*n*s are often those that are commercially available, the most common source of which is the metal(II) acetates. Here, we report the synthesis of CoAPO-20 and MnAPO-20 at higher substitution levels than previously reported using the species $[Me_4N]_2[CoCl_4]$ and $[Me_4N]_2[MnCl_4]$.

A typical experimental procedure is as follows: deionised water, 85 mass% orthophosphoric acid and pseudoboehmite were mixed together until a smooth paste was formed. TMACl was added and the resulting gel stirred until dissolved, when the $[Me_4N]_2[MCl_4]$ species was added. {$[Me_4N]_2[MCl_4]$ was synthesised by treating the appropriate M^{II} chloride with Me_4NCl in ethanolic solution.} The gel was stirred for 5 min until homogeneous. Sodium hydroxide pellets were dissolved in water and added to the gel with brisk stirring until the gel was smooth. Crystallisation was carried out in 30 cm^3 stainless steel reaction vessels with poly(tetrafluoroethylene) liners at 150 °C and autogeneous pressure. Samples were removed at regular intervals, centrifuged, washed with deionised water and dried, prior to characterisation. The molar reactant compositions of the gels are shown in Table 1.

Fully crystalline products were obtained in the MnAPO-20 system at all substitution levels except the 1.0 mol fraction substitution. Products synthesised using 0.2 and 0.4 mol fractions were pale green and grainy in texture; analysis by X-ray diffraction (XRD) suggests that framework substitution has taken place when comapred with an $AlPO_4$-20 standard prepared using the molar composition outlined by Union Carbide.[7] Unlike $AlPO_4$-20 and other MAPO-20s (M = Mg, Zn, Co), which have been indexed as having cubic symmetry,[5,6,8] MnAPO-20 appears to be triclinic. Hasha and coworkers[9] have also found difficulty in indexing their $AlPO_4$-20 and SAPO-20 materials to cubic symmetry. Examination of the morphology by scanning electron microscopy (SEM) shows crystals to be dendritic in appearance and very different to CoAPO-20 species previously reported.[6]

Table 1 Molar reactant compositions

	MO	Al_2O_3	P_2O_5	Na_2O	$(TMA)_2O$	H_2O
(i)	0.0	1.0	1.0	0.0	0.5	43
(ii)	0.4MO	0.8	1.0	1.0	1.0	36
(iii)	0.8MO	0.6	1.0	1.0	1.4	36
(iv)	1.0MO	0.5	1.0	1.0	1.6	36
(v)	1.2MO	0.4	1.0	1.0	1.8	36
(vi)	1.6MO	0.2	1.0	1.4	2.2	36
(vii)	2.0MO	0.0	1.0	1.8	2.6	36

At the higher substitution levels, 0.6 and 0.8 mol fraction, pale-green and pale-pink crystals are obtained, but there appears to be little variation in crystal morphology throughout the material, where 'blocky' cubes of *ca.* 0.1 mm diameter are seen by SEM. The presence of pink crystals indicates the presence of octahedral Mn^{2+}. It is possible, therefore, that at *ca.* 0.5 mol fraction increasing framework substitution no longer occurs as the strain on the structure is too great. It is likely that the manganese then becomes occluded in the channels, as octahedral species, as well as being framework sited. At 1.0 mol fraction, manganese phosphates are formed.

Fully crystalline CoAPO-20 was also obtained up to 0.8 mol fraction, and at all levels apart from 1.0 mol fraction was indexed as having cubic symmetry with a = 8.97–9.00 Å, which is comparable with that found by Rajic and coworkers,[6] and larger than that observed for $AlPO_4$-20[8] (a = 8.933 Å). Products obtained at lower substitution levels (0.2 and 0.4 mol fraction) were royal blue, indicating tetrahedral Co^{2+}, and XRD suggests cobalt is present in the framework as there is an increase in *d*-spacings. A similar morphology to that observed for MnAPO-20 at low substitution levels is observed by SEM.

At increased substitution levels it has been difficult to ascertain the position of the Co^{2+} species with certainty. Products were purple–blue, which indicates at least some of the cobalt is in a tetrahedral state, but that some may again be occluded in the channels as pink octahedral species. Longer synthesis times were also required to obtain the most crystalline products as substitution levels increased and at 0.8 mol fraction cobalt phosphate was formed as a precursor to CoAPO-20. Only cobalt phosphate was formed at the highest substitution level.

It appears that the inclusion of a suitable tetrahedral complex in an aluminophosphate gel ensures ready uptake of the M^{2+} species into the structure at higher substitution levels than previously reported.

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