Acid-soluble mixed-metal phosphates

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Mixed-metal phosphites can be obtained by refluxing mixtures of single-metal phosphates in phosphoric acid until they dissolve; the new mixed phosphates are slightly soluble in aqueous sulfuric acid and have a greatly increased surface area relative to their precursors.

Mixed zirconium–titanium phosphates have been prepared by coprecipitation of a phosphate mixture, followed by refluxing for 300 h in phosphoric acid.[1] The authors concluded that the two layered metal phosphates formed layered solid solutions of variable composition. Mixed zirconium–germanium phosphates[2] and zirconium–tin phosphates[3] have been prepared similarly. They appear to exist as solid solutions of infinitely variable composition.

We have prepared mixed-metal phosphates by refluxing much smaller amounts of mixtures of single-metal phosphates in phosphoric acid; under these conditions, the metal phosphates dissolve, usually over a period of several days. The method has been applied successfully to a wide range of metal(IV) phosphates. On cooling, the products occasionally crystallised, but were usually recovered from solution by neutralisation. We have extended the method to combine metal(III) and metal(IV) phosphates. Yttrium(III) phosphate is readily soluble in phosphoric acid, and the solution dissolves metal(IV) phosphates quite rapidly. Niobium(V) phosphate dissolves only slowly in phosphoric acid when mixed with a metal(IV) phosphate. These mixed-metal phosphates show slight solubility in aqueous sulfuric acid, similar to that of mixed metal(IV) phosphates. The yttrium phosphate cannot be dissolved out alone in acid. We have also prepared a mixed yttrium–niobium phosphate, whose X-ray diffraction spectrum shows a spacing of 7.6 Å similar to the interlayer spacing of metal(IV) phosphates, suggesting a possible layered structure. A triple-metal phosphate has been prepared by refluxing equal amounts of yttrium, zirconium and niobium phosphates in phosphoric acid. Zirconium phosphate even dissolves in a solution of copper(II) hydroxide in phosphoric acid, but neutralisation yielded only a mixture of the hydroxides of zirconium and copper.

We typically prepared a sample of a mixed zirconium–titanium phosphate by refluxing zirconium phosphate (1.0 g) and titanium phosphate (1.0 g) in 11 mol dm^{-3} phosphoric acid (400 ml). Complete solution of both phosphates occurred over a period of 5–6 days. On cooling the solution, a small quantity of feathery crystals was formed; these were separated off. Neutralisation of the rest of the solution with sodium carbonate produced a gel, which was separated and dried. Formation of mixed zirconium–titanium phosphates does not require equal amounts of the component phosphates, but when we refluxed zirconium phosphate (3.0 g) with titanium phosphate (1.6 g) in 1 1 mol dm^{-3} phosphoric acid (400 ml), complete solution took 19 days.

Our product showed similarities and differences from a material of similar composition prepared by Clearfield's method.[1] Both samples were moderately soluble in dilute (5 mol dm^{-3}) aqueous sulfuric acid on warming, conditions under which single metal(IV) phosphates show no detectable solubility. The solutions can be made sufficiently concentrated to permit measurement of ^{31}P NMR spectra. The crystalline material gave a single peak at δ −3.47, while the residual amorphous material gave a single peak at δ −2.92 [rel. to aq. 85% (*v*/*v*) phosphoric acid].

The materials prepared by different routes show important differences in surface area. Our method yielded materials with unexpectedly large surface areas. A sample of a 1 : 1 ratio of zirconium–titanium phosphate had a surface area, measured by the BET method, of 338.0 m^2 g^{-1}, compared to a sample of similar composition prepared by Clearfield's method, which had a surface area of 17.7 m^2 g^{-1}, and a sample of coprecipitated but not refluxed material which had a surface area of 2.19 m^2 g^{-1}. The results for a wider range of samples are summarised in Table 1.

The mixed-metal phosphates prepared by different routes also gave different X-ray diffraction spectra, as reported in Table 2. Our results refer to the 'feathery crystals'; the precipitated gel did not give an X-ray diffraction spectrum.

Table 1 Surface areas and ^{31}P NMR spectra of mixed-metal phosphates

Polymer	Method of preparation[a]	BET surface area/m^2 g^{-1}	^{31}P NMR signal, δ[b]
Zr/Ti	1	2.19	—
Zr/Ti	2	338.0	−2.92
Zr/Ti	3	17.71	—
Zr/Y	1	133.6	—
Zr/Y	2	338.2	−3.37
Zr/Nb	1	2.60	—
Zr/Nb	2	58.40	—
Nb/Y	1	97.24	—
Nb/Y	2	152.8	−2.81
Zr/Nb/Y	2	—	−3.48

[a] (1) Coprecipitation of mixture of chlorides; (2) refluxing a 1 : 1 mixture of individual phosphates in phosphoric acid until dissolved, then neutralising; (3) ref. 1. [b] Peak position is given relative to an aq. 85% (*v*/*v*) phosphoric acid standard. (The actual reference used was 10% trimethylphosphite, at δ 140.5.)

Table 2 X-Ray diffraction spectra of mixed-metal phosphates

Zirconium phosphate		2 : 1 Zirconium–titanium phosphate[a]		1 : 1 Zirconium–titanium phosphate[b]		Titanium phosphate	
d/Å	*I*/*I*$_0$	*d*/Å	*I*/*I*$_0$	*d*/Å	*I*/*I*$_0$	*d*/Å	*I*/*I*$_0$
7.50	71	7.55	90	10.09	20	7.65	100
4.48	38	4.40	20	9.64	16	4.27	10
3.56	100	4.37	25	7.52	78	3.50	84
2.65	22	4.31	15	4.43	69	3.42	31
2.62	27	3.52	100	4.07	21	2.54	10
		3.49	80	3.89	59	2.50	13
		2.63	13	3.50	100		
		2.61	15	3.25	26		
		2.59	17	3.12	13		
		2.58	15	3.08	10		
		2.54	10	2.62	33		
		2.39	12	2.41	11		
		1.88	10	2.38	12		
				2.30	11		
				2.21	12		

[a] Data from ref. 1. [b] Prepared as described in this paper.

Metal(IV) phosphates are known to be very slightly soluble in refluxing phosphoric acid, since they can be crystallised by refluxing in phosphoric acid. If two phosphates are refluxed together, they interact when both are in solution, and probably form a disrupted lattice which remains in solution. Dissolving the phosphates together thus achieves instantly a level of intimate mixing which is approached only slowly by refluxing together greater amounts of the solids. In either case, a solid solution of the phosphates is achieved; it appears that solid solutions may vary in arrangements of atoms as well as in composition.

On the basis of the present evidence, we cannot assign structures to the mixed-metal phosphates. Clearfield *et al.*[4] assign the X-ray observed spacing of 7.55 Å in the zirconium phosphate crystal to the interlayer distance; the mixed-metal phosphates also show a strong peak corresponding to a spacing of *ca.* 7.5 Å, suggesting that they have a layered structure. This evidence is all consistent with the view[1] that mixed-metal phosphates are solid solutions, but it is not clear whether mixing occurs within layers, whether layers of different metals exist, or whether fragments of the individual layered structures are bonded together.

Since our material could be obtained by dissolving two or more metal phosphates in phosphoric acid we attempted to prepare a mixed-metal phosphate from equal amounts of zirconium and titanium phosphates by dissolving the mixture in hydrofluoric acid and recrystallising by the conventional method.[5] This was not successful; we obtained an amorphous solid with a BET surface area of 4.6 $m^2 g^{-1}$. Clearly, association with HF affects the ability of the polymers to form a solid solution.

Earlier preparations of mixed-metal phosphate polymers show enhanced activity in catalysis of cyclohexanol dehydration.[6] Our materials have shown a high degree of activity as catalysts for the dehydration of 2-methylcyclohexanol, with zirconium–niobium–yttrium phosphate being particularly active, and as catalysts for diol cyclisation and alkene hydration and rearrangement.

References

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