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Preparation of Stoichiometric Aluminum Phosphate

Two recent publications (*1, 2*) discuss the catalytic properties of stoichiometric phosphates, in particular aluminum phosphate. In both reports, the preparation technique yields an aluminum phosphate with reasonably high surface area and in the analogous case of iron phosphate, Gallace and Moffat found that both high and low surface area materials could be prepared depending upon the procedure used for preparation.

We have observed great variation in the surface properties of aluminum phosphate precipitates when prepared from aqueous media at varying pH. Careful addition of separate solutions of aluminum nitrate and ammonium phosphate to a well-mixed precipitation vessel while maintaining a pH of less than 4.0 will result in the formation of a pure aluminum phosphate, which upon calcination yields a well-crystallized compound with the characteristic X-ray pattern shown in Fig. 1A. When a similar preparation is carried out using separate solutions

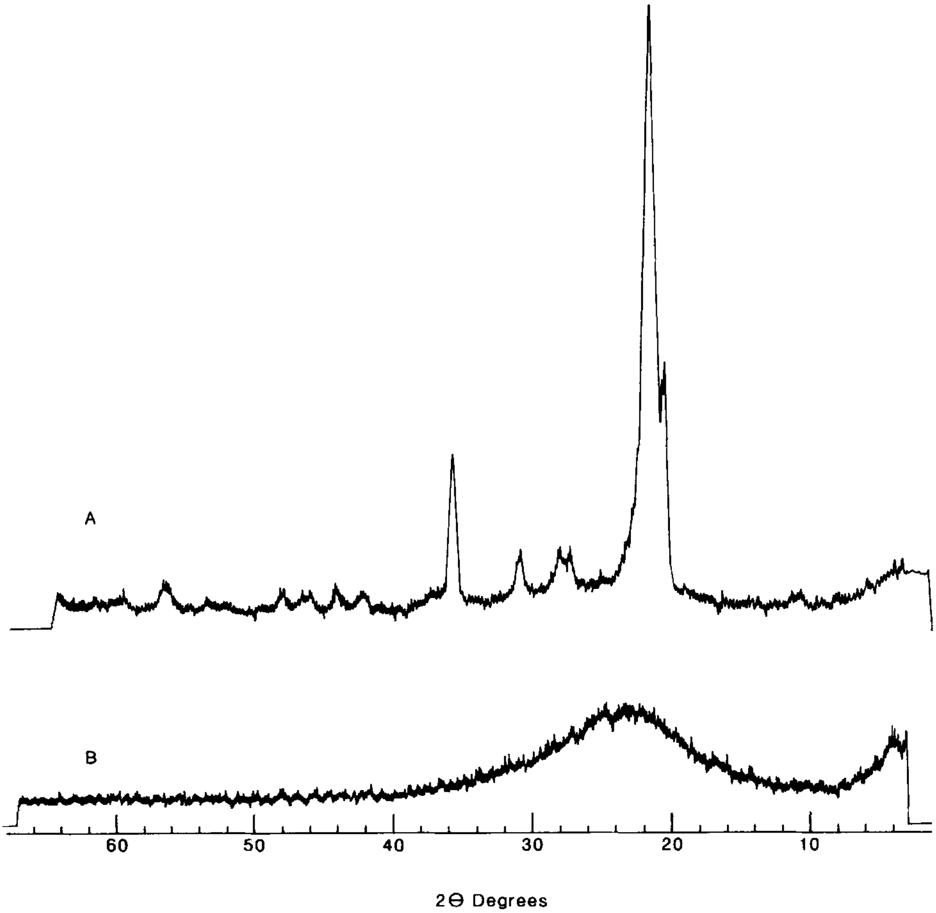

FIG. 1. X-Ray diffraction pattern of "$AlPO_4$" precipitated at (A) pH 2.5 and (B) pH 8.5.

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TABLE 1

Surface Properties of Aluminum Phosphate as a Function of Precipitation pH

pH	Median pore radius (Å)	Pore volume (cm^3/g)	Surface area (m^2/g)
2.5	200	0.03	4
8.5	165	0.29	63

of aluminum nitrate containing a stoichiometric amount of phosphoric acid, and ammonium hydroxide at a constant pH of 8.5, the resulting precipitate after calcination shows an amorphous X-ray pattern, quite different from that of pure $AlPO_4$, as shown in Fig. 1B. Comparison of the surface properties of the calcined materials prepared at low and high pH, shown in Table 1, reveals significant differences in characteristics, and in fact measurements of the properties of the low pH product were beyond the scope of the method. It is clear that the exact pH greatly influences the nature of the precipitate.

It is well known that precipitation of alumina precursor species occurs readily above a pH of 4 (*3*). For this reason we believe that preparation under more basic conditions or with poor pH control will result in a mixed precipitate of alumina–aluminum phosphate (AAP). The AAP family is known to consist of amorphous composites which exhibit high surface area even at low percentages of alumina (*4*, *5*).

As further evidence for the formation of mixed AAP phases during preparation at the higher pH (i.e., 8.5), qualitative tests were performed on the filtrate for each of the ions of interest. These tests revealed the presence of phosphate ion but no aluminum ion, demonstrating that a portion of the aluminum was removed from solution by hydroxide. Quantitative analysis of a portion of the filtrate indicated that approximately 6% of the phosphate was not precipitated and therefore the corresponding portion of the aluminum must be present as the oxide.

The variation in the surface area of the different "stoichiometric" phosphates observed by Gallace and Moffatt may simply be an indication of the presence or absence of such an oxide–phosphate composite, with true stoichiometric materials exhibiting low surface areas similar to aluminum phosphate. For example, Ni and Co phosphates, where hydroxide precipitation only occurs at $pH > 6$, invariably exhibited low surface areas. On the other hand, the iron phosphates can be easily contaminated with $Fe(OH)_3$ which begins to precipitate at a pH of about 2, yielding the larger surface areas. The discrepancy in surface area between the two Fe phosphates may simply be due to the amount of the oxide present.

We wish to warn other investigators of this pitfall in the preparation of stoichiometric phosphates and recommend that care be taken to exclude the possible formation of AAP during studies aimed at the determination of properties of aluminum phosphate.

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