Incorporation of Zinc in an Aluminophosphate Microporous Phase

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A new molecular sieve with formula $Zn_{0.06}Al_{0.96}PO_4$ has been prepared, which has a structure similar to that of the aluminophosphate ALPO-5; considerable difficulty has been encountered in the complete removal of the templating molecule from both ALPO-5 and its zinc containing analogue.

The family of aluminophosphate molecular sieves (ALPO-*n*) which has recently been developed by Union Carbide[1—3] comprises a range of structural types, some of which, notably the so-called ALPO-5, are similar to those encountered in zeolites.[4] Considerable interest has been shown in these microporous structures, which possess both Brönsted and Lewis acid sites and in some cases show some catalytic activity.[2] However, the concentration of the acid sites is less in ALPO-*n* than it is in zeolites. ALPO-*n*-phases, which are covalent and neutral, are more hydrophilic than their zeolitic analogues (*e.g.* silicalite) but less so than aluminous zeolites.

There is considerable scope for improving the catalytic activity of the aluminophosphates. In the present paper we report one possible way in which this may be brought about, namely the synthesis of new ALPO-*n*-phases, by introducing heteroatoms into the structure without disrupting the microporous framework. One such family has already been reported, with the formula $Si_xAl_yP_zO_2$, where some phosphorus atoms have been replaced by silicon.[5] We hoped that by introducing metallic heteroatoms, aluminium atoms would be replaced rather than phosphorus, thus increasing the surface acidity.

Zinc containing ALPO-5 (designated as ZAPO-5) has been prepared from a reaction mixture containing alumina (boehmite) and zinc oxide in aqueous ortho-phosphoric acid and triethylamine (the templating molecule), in the following ratios: 1.00 Al_2O_3 : 1.04 P_2O_5 : 0.105 ZnO : 36.9 H_2O : 1.5 Et_3N. Powder *X*-ray diffraction of the resulting white solid has shown that the cell dimensions of ZAPO-5 were similar to those of ALPO-5, although, as expected, changes in peak intensity have been observed. No significant extra peaks have been observed in ZAPO-5. Chemical analysis (by atomic absorption spectroscopy) gave the formula $Zn_{0.06}Al_{0.96}PO_4$, which has been confirmed by *X*-ray fluorescence analysis. Comparison of scanning electron micrographs for ALPO-5 and ZAPO-5 showed changes in morphology. Whereas ALPO-5 consisted of spheroidal aggregates of small platelets, ZAPO-5 consisted of two types of particles, *viz.*, spheroidal aggregates with ill-defined platelets, and large prismatic single crystals. *X*-Ray analysis in the scanning electron microscope (SEM) gave the same analysis for both these types of particle in ZAPO-5.

The nitrogen adsorption isotherms (Figure 1) for ALPO-5 (both samples prepared in this laboratory and supplied by Union Carbide) and ZAPO-5 were essentially of Type I and show a high degree of rectangularity at low pressures, typical of microporous solids, with apparent surface areas of the order of 250 m^2 g^{-1}. Some hysteresis was observed over the complete range of the isotherm, for both ALPO-5 and

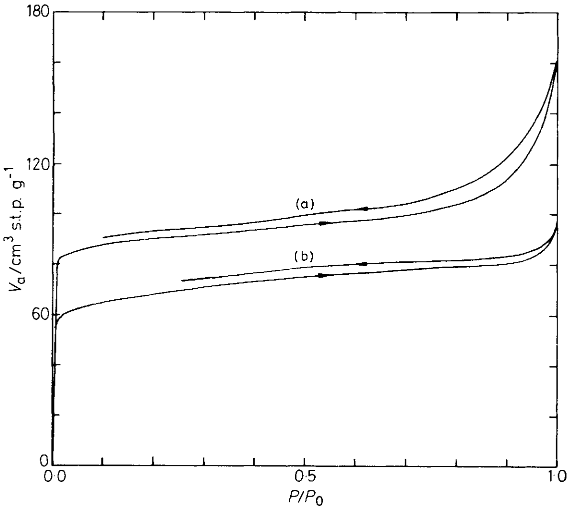

Figure 1. N_2 adsorption isotherms (77 K) for (a) ALPO-5 and (b) ZAPO-5.

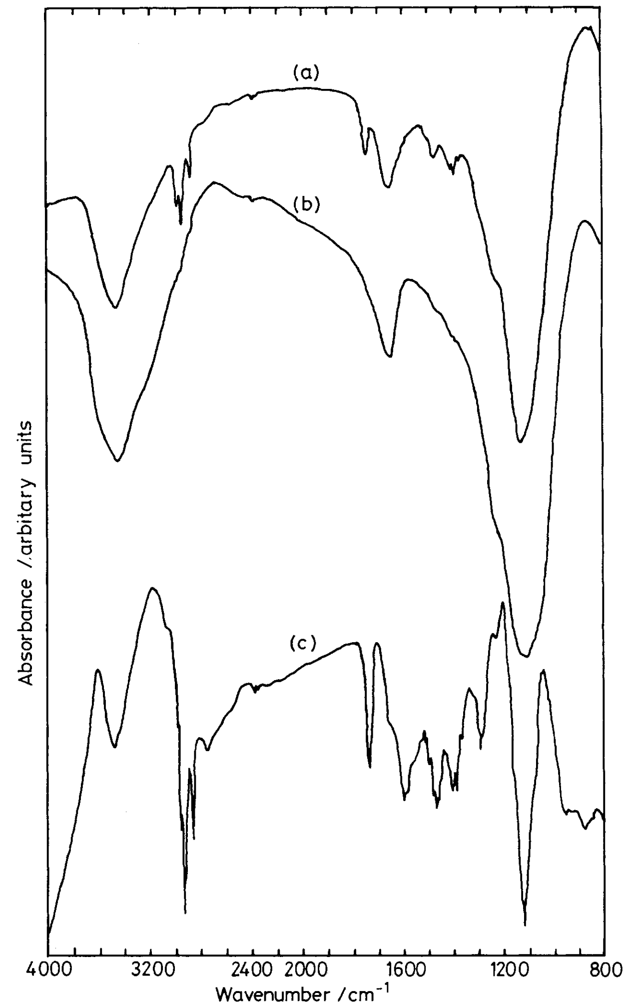

Figure 2. FTIR spectra of (a) ZAPO-5, (b) ZAPO-5 activated in air, and (c) difference spectrum (a − b) which contains bands owing to the templating molecules from spectrum (a), and of the degradation products from spectrum (b).

ZAPO-5; this has been assigned to adsorption between the platelets in the spheroidal aggregates. The hysteresis was significantly less marked for ZAPO-5, where the platelets were less well formed. EDA (energy dispersive *X*-ray analysis) mapping in the SEM for Al and Zn in ZAPO-5 showed that both these elements were randomly distributed, indicating that to a large extent Zn has been incorporated into the ALPO-5 lattice and has not formed a separate phase.

The removal of the templating molecules and the desorption of zeolitic water was carried out in air and under vacuum. Under both these conditions, heating of ZAPO-5 resulted in discoloration of the samples, to brown in air and grey under vacuum. FTIR (Fourier transform i.r. spectroscopy) showed that most of the templating molecules have been removed, leaving degradation products behind in the inorganic matrix (Figure 2). These products are different in the two cases. For ALPO-5, it was found that heating in air led to discoloration, but heating under vacuum led to the clean desorption of triethylamine, indicating that the difficulties encountered in desorbing the amine were due to strong adsorption and not to blocked access to the external surface. Comparison of the i.r. spectra of ZAPO-5 and ALPO-5 showed considerable differences, especially in the bonded –OH stretching bands normally associated with Brönsted acid sites.

I.r. evidence indicates that triethylamine is attached to surface acid sites, confirming their existence in both ZAPO-5 and ALPO-5. Even activated white samples of ALPO-5 contained easily detectable amounts of the template, indicating that the limited catalytic activity of these solids may, in part, be due to the blocking of the active sites.

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