A New Route for the Synthesis of Molecular Sieves: Crystallization of APO-5 at High Temperature

Qisheng Huo and Ruren Xu*

Department of Chemistry, Jilin University, Changchun, P.R. China

A new route for the synthesis of molecular sieves is described: a sol or hydrogel of the reactive precursor mixture was heated at high temperature for a short time, and APO-5 crystallized.

Aluminophosphate molecular sieves (designated APO-*n*), which have three-dimensional microporous crystal frameworks consisting of alternate PO_4 and AlO_4 tetrahedral units, were developed in 1982.[1,2] The current technique for preparing aluminophosphate molecular sieves involves hydrothermal crystallization of a hydrous gel which is composed of reactive phosphorus and aluminium oxides (*e.g.* phosphoric acid and aluminium hydroxide) and organic bases (*e.g.* quaternary ammonium ions and different type of amines). For example, APO-5 could be synthesized by crystallization of a reactive aluminophosphate gel in the presence of templates, including various primary, secondary, tertiary, and cyclic amines, alkanolamines and quaternary ammonium species at 150–200 °C under autogenous pressure conditions.[3] In an alternative approach, we have recently synthesized aluminophosphate molecular sieves (*e.g.* APO-5, APO-11 and APO-21)[4] from alcoholic systems. Both methods have the identical steps of conducting the crystallization of amorphous gels with the solvent under autogenous pressure conditions for several hours to some days and separation of the final products from the mother liquor by filtration or centrifugation followed by calcination. In order to improve the synthetic procedure, we now report a new method for synthesizing molecular sieves, *via* the direct heating of reactive mixtures at high temperatures, which could simplify synthetic procedures. Using this method APO-5 has been prepared.

The reaction mixtures we used contained phosphoric acid (H_3PO_4, 85 wt.%), aluminium isopropoxide, triethylamine and solvent (*e.g.* di-, tri- or tetra-ethylene glycol). A typical procedure involved the following steps: (*i*) an aluminium isopropoxide–solvent slurry is formed; (*ii*) the amine is added to the slurry, after stirring for 10 min, H_3PO_4 is slowly dropped into the mixture; (*iii*) the precursor mixture is aged under ambient conditions with agitation; (*iv*) the reactive mixture is heated at a high temperature for several minutes; (*v*) the product is characterized by X-ray powder diffraction (XRD). Here we illustrate a reproducible procedure with triethylene glycol as solvent as an example. The reaction mixture consisted of aluminium isopropoxide (5 g), triethylamine (8 ml), 85 wt.% H_3PO_4 (3 ml) and triethylene glycol (30 ml). The reactive sol mixture (10 ml) was heated at 600 °C for 5–10 min in ambient air; the final product was identified as APO-5 from its powder XRD pattern.[3,5]

Our synthetic route is simple: the crystallization of the reactive aluminophosphate gel under autogenous pressure and the separation of the product from the mother liquor were omitted and a good yield of APO-5 was obtained. It is apparent that the new procedure is not only an improvement, it is also helpful to our understanding of some features of, and the mechanism of formation of, aluminophosphate molecular sieves. The results lead us to believe that certain species, which are precursors of the APO-5 structure and can result in the formation of APO-5 in a particular way at high temperatures in a short time, exist in the reactive mixture. The product which crystallizes using the direct heating method is dependent on the composition of the reaction mixture; another crystal phase was obtained by using other solvents and organic bases (*e.g.* $AlPO_4$–tridymite crystallized by using ethylene glycol and dipropylamine).

As further evidence, an aluminophosphate gel containing triethylamine and ethylene glycol could be crystallized to APO-5 under hydrothermal condition; if a part of the gel was removed in the induction period and heated at high temperature for short time, high purity APO-5 was also obtained. Further synthetic investigations and studies of the mechanism of formation of microporous aluminophosphates at high temperature are in progress.

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