

Syntheses of $\text{AlPO}_4\text{-5}$, $\text{AlPO}_4\text{-11}$, and $\text{AlPO}_4\text{-21}$ from Non-aqueous Systems

Huo Qisheng and Xu Ruren

Department of Chemistry, Jilin University, Changchun, People's Republic of China

Several aluminophosphate molecular sieves ($\text{AlPO}_4\text{-5}$, $\text{AlPO}_4\text{-11}$, and $\text{AlPO}_4\text{-21}$) have been synthesized from non-aqueous systems in the presence of organic amine templating agents.

Recently, scientists at Union Carbide Corporation have synthesized a series of aluminophosphates ($\text{AlPO}_4\text{-}n$)¹ and element-substituted aluminophosphate² molecular sieves such as silicon substituted (SAPO) and metal substituted (MAPO) examples. $\text{AlPO}_4\text{-}n$ are generally prepared from aqueous

hydrothermal systems through crystallization of an active aluminophosphate gel containing organic amine or quaternary ammonium templating agents.¹⁻³ While some zeolites can be synthesized⁴⁻⁶ from organic or mixed solvent systems in which water is a minor component, there have been no

Table 1. The typical reactant compositions, crystallizations, and products.

Run	Reactants (moles)			Crystallization		
	Al ₂ O ₃	P ₂ O ₅	Solvent	Template	t ^a /days	Product
1	1.0	2.5	60 EG	9.8 Et ₃ N	30	AlPO ₄ -5
2	1.0	1.8	45 PG	5.9 Et ₃ N	20	AlPO ₄ -5
3	1.0	1.8	25 HexOH	4.3 TEA	20	AlPO ₄ -5
4	1.0	1.8	60 EG	5.0 Pr ₂ NH	15	AlPO ₄ -11
5	1.0	1.8	45 EG	2.4 Bu ₂ NH	30	AlPO ₄ -11
6	1.0	1.8	45 EG	2.7 Me ₂ NH	10	AlPO ₄ -21
7	1.0	1.8	30 Bu ^s OH	2.7 Me ₂ NH	10	AlPO ₄ -21
8	1.0	1.8	45 EG	5.2 EtNH ₂	15	AlPO ₄ -21
9	1.0	1.8	30 Bu ^s OH	5.2 EtNH ₂	10	AlPO ₄ -21

^a Crystallization temperature 180 °C.

reports, to date, of the synthesis of aluminophosphate-based molecular sieves from non-aqueous systems. Here, we report the syntheses of AlPO₄-5, AlPO₄-11, and AlPO₄-21 from non-aqueous media in the presence of different amine templating agents.

Aluminium tri-isopropoxide and 85 wt% phosphoric acid were used as starting materials. A typical experimental procedure involved the following steps: aluminium tri-isopropoxide was first added in organic solvent, then amine was added with stirring. H₃PO₄ was slowly dropped into the mixture. A thick gel resulted, which after continued stirring for a few minutes thinned to a smooth, even consistency. The gel formed after 30 min stirring was used for all subsequent work. The crystallization of the reactive aluminophosphate gel was carried out in a stainless steel autoclave with a polytetrafluoroethylene liner under autogenous pressure at 180 °C. The crystalline product was filtered, washed with distilled water, and dried at ambient temperature. The products were characterized by X-ray powder diffraction. The typical reactant compositions, crystallization conditions, and products are shown in Table 1.

Our method of synthesis of AlPO₄-*n* is unusual in that the solvent system is essentially non-aqueous.⁷ The water comes from H₃PO₄ and other reactants but does not seem to be essential as some can be distilled off at the mixing of the reactants. We believe that this small quantity of water did not play the role of solvent and did not affect the non-aqueous nature of the media.

The AlPO₄-5 was synthesized using ethylene glycol (EG) as solvent. The X-ray powder diffraction pattern of our AlPO₄-5 and of conventionally prepared AlPO₄-5⁸ show no significant difference. Besides triethylamine (run 1), the templates for formation of AlPO₄-5 in the solvent system may be tripropylamine, tributylamine, diethanolamine, triethanolamine, diethylamine, or cyclohexylamine. AlPO₄-5 was also synthesized from propane-1,3-diol (PG) (run 2) and hexanol (HexOH) (run 3) solvent systems in the presence of triethylamine (Et₃N) and triethanolamine (TEA) templating agents, respectively.

The X-ray powder diffraction pattern of the AlPO₄-11 obtained was very similar to that of AlPO₄-11 from an aqueous hydrothermal synthetic system.⁸ A gum-like material appeared if di-isopropylamine was used instead of dipropylamine as templating agent under the same crystallization conditions; this may result from a chemical reaction between the reactants. Initial attempts to prepare AlPO₄-11 from other solvent media (e.g., HexOH) were not successful.

We have found dimethylamine (Me₂NH) 33 wt% and ethylamine (EtNH₂) 70 wt% aqueous solution to be quite successful for AlPO₄-21⁹ synthesis (runs 6–9) in ethylene

glycol and *s*-butyl alcohol solvent systems. Me₂NH has recently been reported as a templating agent for AlPO₄-21.¹⁰ EtNH₂ has not previously been reported as a templating agent. This result suggests that other suitable templating agents for the various AlPO₄-*n* structures in non-aqueous media may still be found.

In contrast to the acidic media required for aqueous hydrothermal systems, the near neutral or slightly basic media of non-aqueous synthetic systems is suitable for the formation of AlPO₄-*n*, and the apparent pH precursor mixture is not critical to the synthesis. Not all templating agents, which are effective in aqueous solution, can be used in non-aqueous systems (e.g., ethylenediamine).

Although this method itself has little commercial importance, it will contribute substantially to our understanding of the nature and chemistry of AlPO₄-*n* and other related microporous solids.

Several amines can act as templating agents for the formation of AlPO₄-5 in ethylene glycol. In the presence of effective templating agents, AlPO₄-5, AlPO₄-11, and AlPO₄-21 can be synthesized from non-aqueous systems. Our recent experimental results imply that a rich area of crystallization chemistry of microporous aluminophosphate solids in non-aqueous systems awaits further study.

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