

Growth of AlPO_4 -5 and CoAPO -5 films from amorphous seeds

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Abstract

The growth of aluminophosphate AlPO_4 -5 (AFI structure with one-dimensional parallel and straight channels of 7.3 Å in cross section) and cobalt-substituted AlPO_4 -5 (CoAPO -5) films by hydrothermal treatment is investigated. In situ growth on bare (unmodified) silicon substrates using different growth temperatures, times, and precursor mixture compositions was carried out first and yielded films that exhibited either preferred orientation and poor coverage or good coverage but random orientation. Introducing seeded growth, which involved functionalization and seeding of the substrate with the amorphous fraction of an AlPO_4 -5-containing powder followed by hydrothermal seed growth, *c*-oriented, well-intergrown films were obtained with a variety of morphologies depending on the synthesis mixture composition and growth conditions. The effect of two different structure directing agents (SDAs), namely triethylamine and tripropylamine, was also examined. Controlled experiments by systematically varying secondary growth duration were performed in order to find the optimal growth time that yields complete coverage while minimizing the degree of misorientation. Seeded growth using dilute precursor mixtures favors *c*-out-of-plane growth yielding films with a thickness of several micrometers, while reducing the water/ Al_2O_3 molar ratio and executing secondary growth under the appropriate hydrothermal conditions favored in-plane growth yielding well-intergrown films with sub-micron thickness. SEM, XRD, and UV–vis spectroscopy were used to characterize the synthesized AlPO_4 -5 and CoAPO -5 films.

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1. Introduction

The class of crystalline, microporous, aluminophosphates (AlPO_4 -n) is the first family of framework oxide molecular sieves synthesized without silica, and was discovered in 1982 by Wilson et al. [1]. Since then, extensive research has focused on developing novel synthetic strategies to yield various crystal morphologies and characteristics of aluminophosphates [2–9] and metal-substituted aluminophosphates [10–14], as well as techniques for incorporating them in emerging applications such as demanding

separations, catalysis, sensors, optics, and host–guest assemblies [2,3,15–22].

Important findings concerning synthesis parameters and conditions and how these affect the properties and quality of the obtained APO products have been reported. Finger et al. [4] investigated how the synthesis conditions affect crystal dimensions and observed that dilution of the synthesis mixture results in growth of larger crystals but at the same time increases the content of byproducts. The largest crystals (up to 750 μm) were obtained by using a gel composition of $1\text{Al}_2\text{O}_3:1\text{P}_2\text{O}_5:1.55\text{TEA}:1000\text{H}_2\text{O}$ (see Fig. 1), though the yield was limited to approximately 60%. Rising the SDA content, forces the system to form the AFI phase by accelerating the nucleation rate. However, an excess of SDA favors the growth of aggregates and/or disordered crystals (compositions $1\text{Al}_2\text{O}_3:1\text{P}_2\text{O}_5:3.1\text{TEA}:300$,

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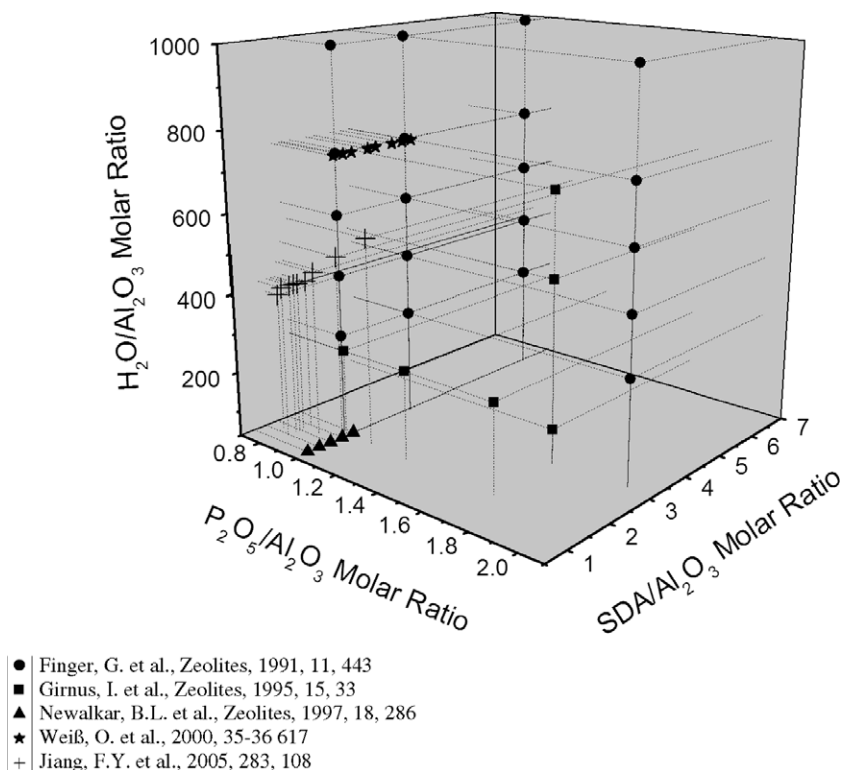


Fig. 1. Synthesis mixture compositions used in the literature to investigate the effect of synthesis parameters on the quality of products for AlPO₄₋₅ crystal synthesis.

450H₂O and 1Al₂O₃:1P₂O₅:6.2TEA:300, 450, 600, 750H₂O). Diluting the system further is counteracting this effect by lowering the reaction rate, and the growth of better formed hexagonal prisms is possible. A similar but stronger effect is caused by increasing the P₂O₅ content. Polycrystalline sphere-like aggregates were formed by using compositions of 1Al₂O₃:2P₂O₅:3.1TEA:300, 450H₂O, while the system did not yield any byproducts. Further diluting the system again recovers its ability to form well-defined hexagonal prisms. Jahn et al. [23] investigated the possibility that formation and stabilization of tetrahedral Al is necessary for the synthesis of a pure AlPO₄₋₅ phase in relation to the preparation of the reaction mixtures, and concluded that the role of the template (triethylamine) in the formation of AlPO₄₋₅ is to stabilize the newly created tetrahedral Al and to prevent conversion to octahedral Al by shielding from attack by water.

Girnus et al. [5] applied for the first time microwave heating in AlPO₄₋₅ synthesis and were able to achieve crystallization within as fast as 60 s. The fast crystallization was attributed to a combination of mechanisms, among them the assumptions that microwave radiation destroys H-bridges causing fast gel dissolution and formation of Al–O–P bonding, that the gel contains self-assembled microarrays which transform directly into the AFI structure, and that the heating is not disturbed by convection. Parametric analysis showed that under microwave heating, dilution of the synthesis gel yields smaller crystals when the water is given to the starting gel in one step (see composi-

tions 1Al₂O₃:1.7P₂O₅:3TEA:125, 490, 700H₂O in Fig. 1), which seems to contradict the results obtained by using conventional heating. Larger crystals can be obtained however, if the water is added dropwise and the gel is stirred for several hours before crystallization. Increasing the P₂O₅ content gives larger crystals (compositions 1Al₂O₃:1.1.3P₂O₅:1.6TEA:260H₂O), similarly to conventional heating. A further increase in P₂O₅ content however, without simultaneous increasing the amine concentration (composition 1Al₂O₃:1.7P₂O₅:1.6TEA:260H₂O), lowers the pH of the gel and gives dense byproducts. It should be noted that the crystallization was facilitated by adding HF in the synthesis gel. Addition of F⁻ anions to AlPO₄₋₅ synthesis mixture was first established by Qiu et al. [24] as it is believed to shorten the crystallization time, give larger crystals with a more perfect habit, and enable the isomorphous framework substitution. Kodaira et al. [25] improvised the microwave synthesis technique by modifying the preparation process and they were able to further limit the byproducts and produce high quality crystals. If the desired outcome of the synthesis is a small crystal size, Du et al. [26] proved that microwave treatment is more efficient than conventional heating in producing AlPO₄₋₅ crystals with dimensions as small as a few tens of nanometers.

The effect of pH of the synthesis gel on the kinetics of crystallization was investigated by Newalkar et al. [27] by studying a series of compositions with different SDA contents and a low dilution rate. They concluded that the time required for the complete synthesis of a pure AlPO₄₋₅

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