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Synthesis of large molecular sieve crystals with the AFI ($AlPO_4$-5) topology

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Abstract

Large crystals of the molecular sieves $AlPO_4$-5, SAPO-5, and MeAPO-5 (with Me=Cr, Fe, Mg, Zn) have been grown hydrothermally. MgAPO-5 crystals were obtained up to a length of 1700 μm. Starting from a standard synthesis procedure, the influence of seeding and addition of ethanol to the synthesis gel was investigated. ^{31}P MAS NMR spectra of the as-synthesized samples showed unusual peak intensities suggesting an effect of the template molecules on the phosphorus resonance. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of the family of crystalline microporous aluminophosphates in 1982 [1], much research work has been devoted to this new type of molecular sieve materials. As the framework of $AlPO_4$s is neutral, attempts have been made to partially substitute other elements for aluminum or phosphorus. This substitution usually introduces a negative charge into the framework which is counterbalanced by cations, e.g., protons, thereby creating Brønsted acid sites. The materials modified in this manner have a high potential both as catalysts in oxidation reactions and in acid catalyzed reactions.

Here, we report on the synthesis of large crystals of the $AlPO_4$-5 (AFI) topology and of various substituted derivatives. The incentives for growing large crystals are manifold: Firstly, large crystals are necessary for precise crystal structure determinations. Secondly, they are required for the study of transport mechanisms and diffusion. Further applications are especially related to molecular sieves with one-dimensional linear channels, e.g., AFI-type materials. Such crystals can be aligned and used for second harmonic generation, manufacture of molecular sieve membranes, or spectroscopic studies on guest molecules aligned in the channels of such microporous materials as hosts [2].

2. Experimental

The crystals were prepared by a modified method derived from the one described by Radaev et al. [3] for the synthesis of CrAPO-5. In a typical procedure, aluminum triisopropanolate was added to a solution of the metal salt in water. After refluxing for 2 h, a mixture of diluted phosphoric acid and the template triethylamine (TEtA) was added dropwise under vig-

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orous stirring at room temperature. After stirring for another 2 h, hydrofluoric acid was added. A typical molar composition of the gel was (for MgAPO-5 as an example):

$$0.15\,MgO : 0.9\,Al_2O_3 : P_2O_5 : 1.6\,TEtA : 0.8\,HF : 450\,H_2O.$$

Crystallization occurred in Teflon-lined stainless steel autoclaves within 5 d at 180°C without agitation. Thereafter, the product was diluted with water, and the crystals were separated from the amorphous by-products by decantation. Subsequently, the crystals were washed with a small amount of 1 M methanolic hydrochloric acid and afterwards with water. The dried product was calcined at 800°C in air.

The powder X-ray diffraction patterns were recorded with a Siemens D5000 diffractometer. The scanning electron micrographs (SEM) were taken on a CAM SCAN 44 electron microscope with equipment for EDX and WDX analysis. Elemental analysis was performed by ICP-AES on a Perkin Elmer Plasma 400 spectrometer. ^{27}Al and ^{31}P MAS NMR spectra were recorded on a Bruker MSL 400P spectrometer using single pulse excitation with standard 4 mm rotors. The resonance frequencies $\omega_0/2\pi$ were 104.31 and 161.96 MHz for ^{27}Al and ^{31}P, respectively. Aluminum nitrate in water and 85 wt% H_3PO_4 were employed as references.

3. Results and discussion

As the standard synthesis procedure given in Section 2 was actually derived from a method for the synthesis of CrAPO-5, we started with chromium nitrate as metal salt (concerning possible health hazards by the formation of nitrosamines in $AlPO_4$ syntheses, see e.g., [4]). In further syntheses we employed nitrates of other metals. Table 1 gives the molar compositions of the gels and the crystalline samples and the maximum length of the crystals obtained. Comparing the length of the crystals it is surprising that all samples synthesized in accordance with the standard procedure had a length of about 500 μm or less with the exception of the MgAPO-5 crystals which were obtained with a length of up to 1700 μm. Regarding the two upper scanning electron micrographs of Fig. 1 showing an MgAPO-5 crystal and a detail thereof, one notices that the crystal has a hexagonal prismatic shape which is typical for AFI-type materials. It appears that the surface of these large crystals is covered with holes. Possible reasons for this

Table 1
Details of synthesis and synthesis products

Sample	Metal (element) compound used	n_P:n_{Al}:n_{Me} in the gel	n_P:n_{Al}:n_{Me} in the as-synthesized sample	Maximum length of the crystals μm
$AlPO_4$-5[a]	$Al(NO_3)_3\cdot 9H_2O$[g]	1.00:1.00	1.00:1.01	300
SAPO-5-a[b]	TEOS[h]	1.00:0.98:0.07	–[i]	500
SAPO-5-b[c]	TEOS[h]	1.00:0.98:0.07	1.00:1.01:0.04	200
CrAPO-5[a]	$Cr(NO_3)_3\cdot 9H_2O$	1.00:0.90:0.06	1.00:0.98:(2×10^{-3})	180
FAPO-5[a]	$Fe(NO_3)_3\cdot 9H_2O$	1.00:0.90:0.06	1.00:0.97:0.01	180
MgAPO-5-a[a]	$Mg(NO_3)_2\cdot 6H_2O$	1.00:0.90:0.15	1.00:0.99:0.09	1700
MgAPO-5-b[d]	$Mg(NO_3)_2\cdot 6H_2O$	1.00:0.90:0.15	1.00:0.96:0.06	400
MgAPO-5-c[e]	$Mg(NO_3)_2\cdot 6H_2O$	1.00:0.90:0.15	1.00:0.95:0.06	1200
ZAPO-5-a[a]	$Zn(NO_3)_2\cdot 6H_2O$	1.00:0.90:0.15	–[i]	150
ZAPO-5-b[f]	$Zn(NO_3)_2\cdot 6H_2O$	1.00:0.80:0.25	–[i]	1300

[a] Synthesized according to the standard procedure.
[b] Synthesized according to the standard procedure with addition of TEOS[h] after refluxing for 1 h.
[c] Synthesized with less water in the gel.
[d] Synthesized with ethanol in the gel.
[e] Synthesized with addition of a nucleation gel.
[f] Synthesized with higher Zn content.
[g] Synthesis with two different alumina sources.
[h] Tetraethoxysilane.
[i] Analysis of mixed products not appropriate.

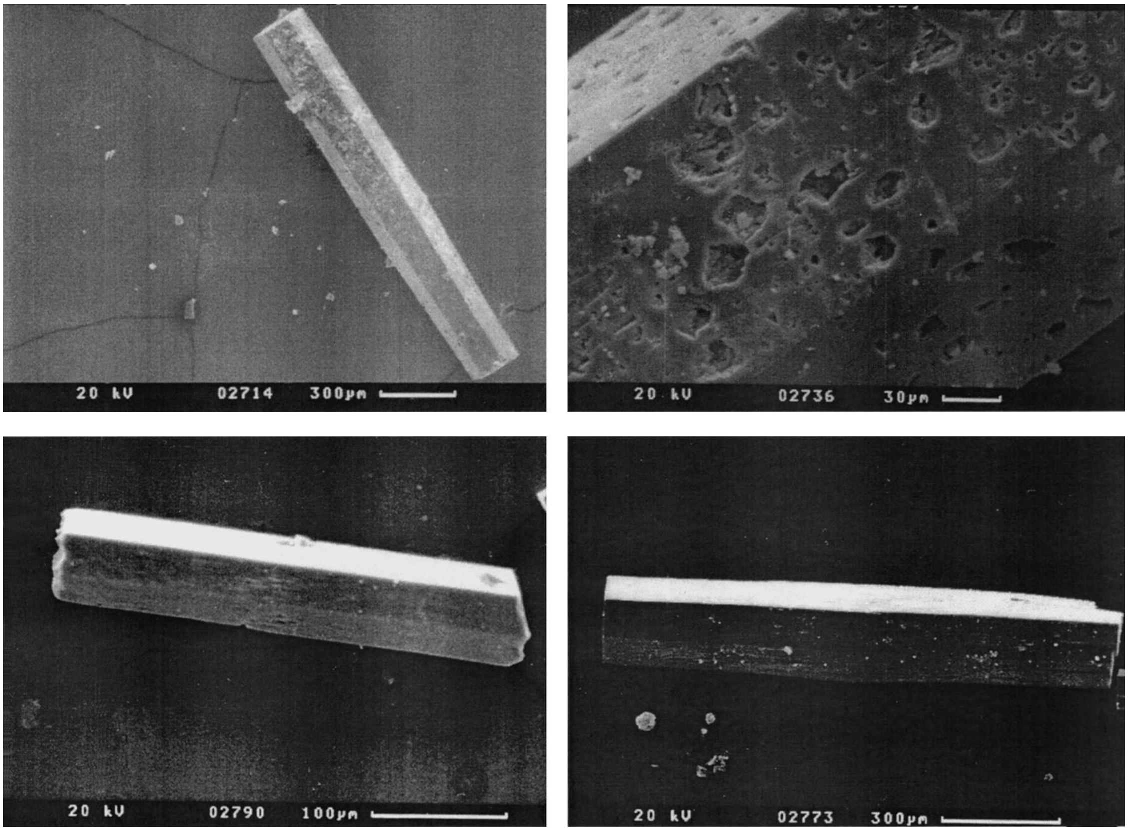

Fig. 1. Scanning electron micrographs of MgAPO-5-a (top left and top right (detail)), MgAPO-5-b (bottom left), and MgAPO-5-c (bottom right).

pitted surface are stacking faults occurring during the relatively fast growth or a starting (re-)dissolution of the crystals due to the attack of the mother liquor. However, more work is needed to understand in sufficient detail the formation of this uneven surface.

With the aim to obtain crystals of better quality, the standard synthesis procedure was modified. Three different strategies were applied, viz. (i) partial replacement of water by ethanol, (ii) seeding, and (iii) reduction of the water content.

Replacing one third of the water in a gel for the synthesis of MgAPO-5 with ethanol, after a crystallization time of 6 d (instead of 5 d as normally) crystals with a length of only 400 μm were obtained with slightly improved quality (see SEM in Fig. 1, bottom left). These findings are consistent with the results of Dutta et al. [5], that medium concentrations of ethanol in the synthesis gel improve the quality of the synthesized crystals.

For testing the effects of a seeding procedure on the synthesis of MgAPO-5, about one tenth of the prepared synthesis gel was treated at 200°C in an autoclave for 1 h. The thus obtained mixture was filtered. The filtrate was added to one half of the remaining synthesis gel, the filter cake to the other half. The crystallization procedure was then carried out as usually. Whereas the crystals prepared by addition of the filter cake were of bad quality, and furthermore, contained impurities, the addition of the filtrate to the gel improved the quality of the resulting crystals, although they were only about 1200 μm in length (see SEM in Fig. 1, bottom right). These results were unexpected since, by seeding, the nucleation stage during the synthesis is by-passed [6], which means that during the crystal growth stage only a small

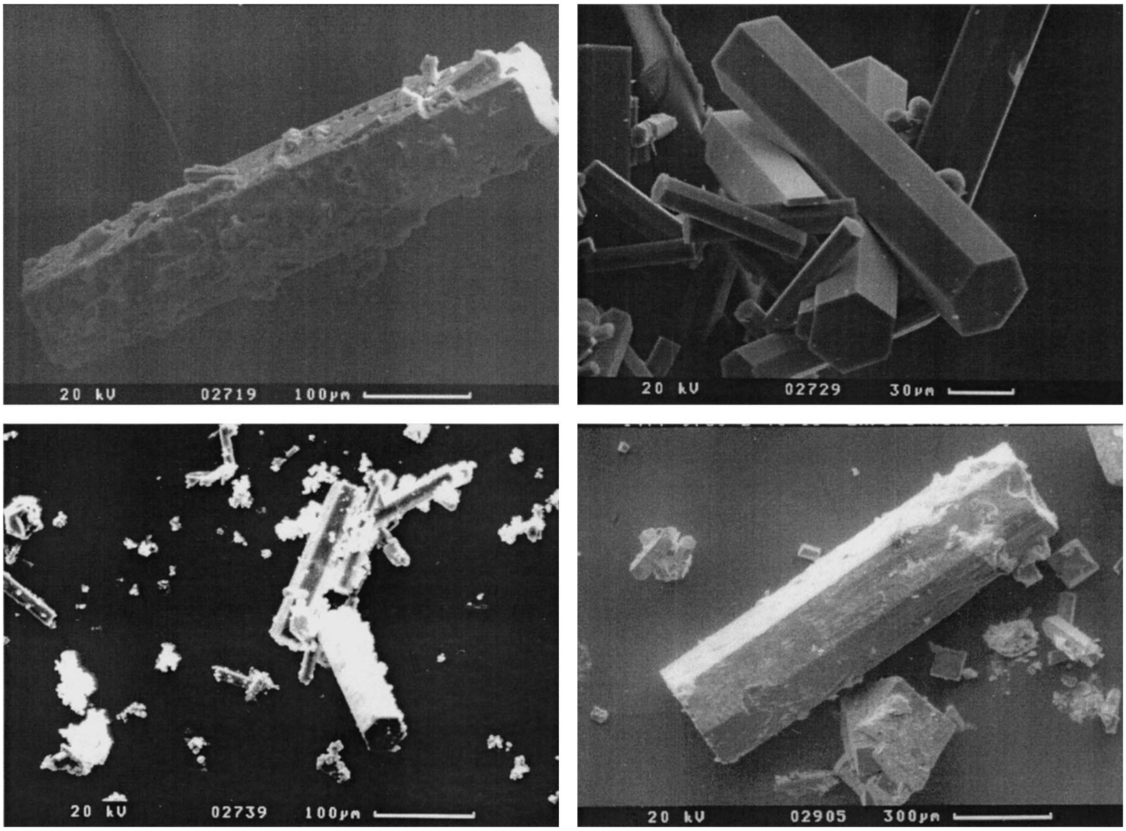

Fig. 2. Scanning electron micrographs of SAPO-5-a (top left), SAPO-5-b (top right), ZAPO-5-a (bottom left), and ZAPO-5-b (bottom right).

amount of nuclei is competing for nutrients in the gel which should actually result in larger crystals.

Since the quality of the SAPO-5 crystals synthesized according to the standard procedure was quite poor (see SEM in Fig. 2, top left), we investigated the effect of reducing the water content in the gel on the synthesis of SAPO-5. Crystals synthesized with one half of the usual amount of water were only about 200 μm in length but of excellent quality (see SEM in Fig. 2, top right). These results confirm the report by Müller et al. [7] stating that the amount of water in the synthesis mixture exerts a strong influence on the results of the synthesis.

ZAPO-5 was prepared with different Zn contents. The crystals grew larger with increasing Zn content up to a length of 1300 μm (see Table 1) but were always associated with amorphous by-products and/or ZAPO-34 (CHA-type phase), crystallizing with cubic morphology (see SEM in Fig. 2, bottom left and right).

Attempts to calcine the large crystals showed that rather high temperatures have to be applied in order to achieve complete removal of the template. In Fig. 3 the X-ray diffraction patterns of MgAPO-5-a before and after calcination at 800°C in air are depicted. The patterns are typical for the AFI topology and show that the structure is not affected by calcination. The X-ray diffraction patterns of ZAPO-5-a and ZAPO-5-b before calcination are shown in the lower half of Fig. 3. In comparison to the diffractograms of MgAPO-5 additional peaks are observed which can be attributed to ZAPO-34 as a second crystalline phase.

For further characterization of the quality of the AFI-type molecular sieves, MAS NMR spectroscopy was applied. ^{27}Al MAS NMR spectra (not shown) of

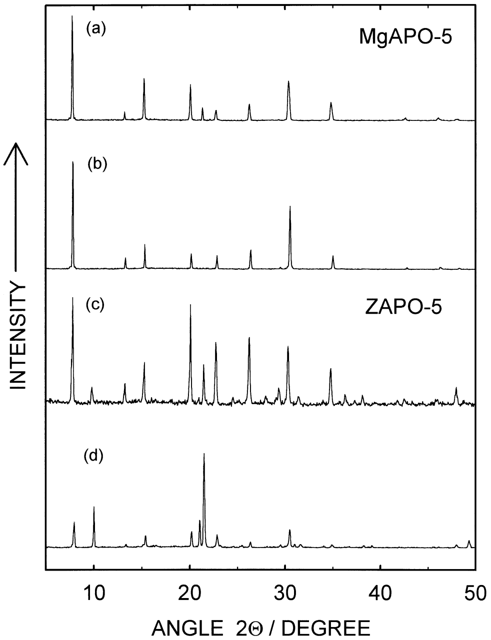

Fig. 3. X-ray diffraction patterns of MgAPO-5-a as-synthesized (a), MgAPO-5-a calcined (b), ZAPO-5-a as-synthesized (c), ZAPO-5-b as-synthesized (d).

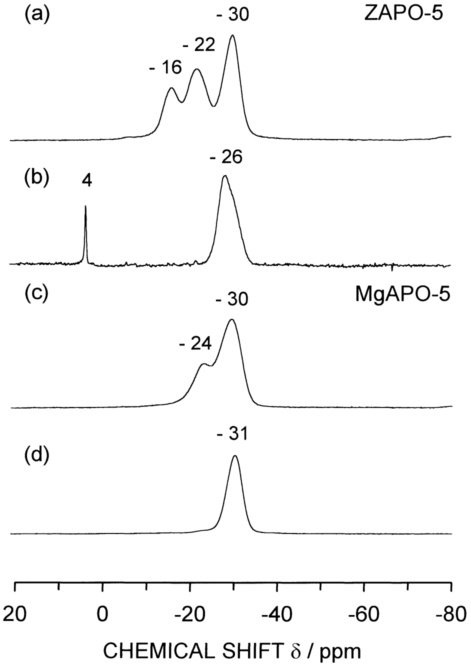

Fig. 4. ^{31}P MAS NMR spectra of as-synthesized ZAPO-5-a (a), calcined ZAPO-5-a (b), as-synthesized MgAPO-5-a (c), and calcined MgAPO-5-a (d).

the crystals were recorded before and after calcination. Apart from a single resonance around δ=38 ppm, which is expected for AlO_4 tetrahedra in aluminophosphate frameworks [8], the spectra do not show any peculiarities. The ^{31}P MAS NMR spectra of ZAPO-5-a and MgAPO-5-a are depicted in Fig. 4. In the as-synthesized sample of ZAPO-5-a three resonances at δ=−16, −22 and −30 ppm are detected, while after template removal at 800°C only the main resonance at δ=−26 ppm is observed. An additional very narrow line appears at δ=4 ppm which can be attributed to layered phosphates formed by the thermal collapse of ZAPO-34. In the as-synthesized sample of MgAPO-5-a, two lines are detected at δ=−30 and −24 ppm. The relative intensity of the latter line is considerably reduced after template removal. It is known that the ^{31}P MAS NMR spectrum of the parent $AlPO_4$-5 or SAPO-34 molecular sieve consists of only one narrow line at δ=−30 ppm [8]. This corresponds to a tetrahedral P(4Al) environment, in which the coordination shell surrounding phosphorus consists of four aluminum atoms. Additional lines are often taken as evidence for different $P(n\mathrm{Al}, m\mathrm{Mg})$ (n=4−m) environments around the PO_4 tetrahedron [9]. Our results indicate that such conclusions based just on as-synthesized samples have to be drawn with care. The additional lines might as well be provoked by interaction of phosphorus with template molecules [10] or by impurities of additional phases.

4. Conclusions

Large crystals of molecular sieves with the AFI-type topology ($AlPO_4$-5, SAPO-5, and MeAPO-5 with Me=Cr, Fe, Mg, Zn) could be synthesized using an optimized synthesis procedure. The largest crystals (up to ca. 1700 µm in length) were obtained for MgAPO-5. However, the surface of these large crystallites was not plain, but covered with holes. Upon addition of ethanol to the synthesis gel, smaller crystals of slightly improved quality were grown. The use of a nucleation gel resulted in rather long crystals of good quality. Through reduction of the water content in the gel, SAPO-5 crystals of excellent quality could be synthesized. ^{31}P MAS NMR spectra of different samples show up to three resonances between $\delta=-10$ and -40 ppm before calcination and only one resonance after the thermal treatment. Presumably, the TEtA molecules used as template interact in such a way with the *P* atoms of the framework that additional lines are provoked.

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