Preparation by microwave irradiation of nanometre-sized $AlPO_4$-5 molecular sieve

Hongbin Du, Min Fang,† Wenguo Xu, Xianping Meng and Wenqin Pang

Department of Chemistry, Jilin University, Changchun 130023, P. R. China

The influence of the synthesis conditions on the crystallization and crystal size of $AlPO_4$-5 molecular sieve is investigated in a $(TEA)_2O$–Al_2O_3–P_2O_5–H_2O system. The initial mixture composition and the crystallization method affect the crystallization and the crystal size of the product. Microwave heating of the synthesis mixture results in the formation of $AlPO_4$-5 with nanometre-sized particles.

Aluminophosphate molecular sieves are important materials that are commonly used as catalysts, catalyst supports and adsorbents. Among them is the well known $AlPO_4$-5, which was first discovered in 1982 by Flanigen and co-workers.[1,2] A large number of papers on the synthesis of $AlPO_4$-5 have now been published,[1–5] because of both its zeolite properties and its potential applications as advanced materials.[6–9]

In the utilization of zeolites as catalysts, catalyst supports and adsorbents, the crystal size affects the performance (activity, selectivity, rates of adsorption) simply by altering the diffusion path-length through the crystallites.[10,11] Previous studies have shown that the smallest crystals are most effective as catalysts as long as the catalytic reaction proceeds in the internal void.[12,13] Currently, there is increasing interest in ultrafine particles of molecular sieves based on their potential catalytic applications and their possible use as precursors for thin-film formation.[14] However, only a few kinds of zeolites with nanometre-sized particles have been synthesized, *i.e.* sodalite, A, Y, ZSM-5 and L.[15–18] To our knowledge, there is very little information on the preparation of aluminophosphate molecular sieves with ultrafine particles in the literature.

Recently, microwave heating has been applied successfully to the preparation of zeolites such as A,[19] Y[20] and ZSM-5,[20] as well as the recently reported large $AlPO_4$-5 crystals.[21] Compared to the conventional hydrothermal crystallization, microwave heating of zeolite synthesis mixtures can drastically reduce the crystallization time, often accompanied by the formation of small crystals.[19,20] This prompted us to explore its use as a method for the synthesis of nanometre-sized crystals of $AlPO_4$-5.

The present paper focuses on the preparation of $AlPO_4$-5 with nanometre-sized particles. The influence of the synthesis conditions on the crystallization and crystal size of $AlPO_4$-5 is discussed in a $(TEA)_2O$–Al_2O_3–P_2O_5–H_2O system.

Experimental

$AlPO_4$-5 molecular sieve was synthesized using orthophosphoric acid (H_3PO_4, 85%), aluminium hydroxide [$Al(OH)_3$, 99%], tetraethylammonium hydroxide (TEAOH, 25%) and distilled water as reactants. The chemical composition of the initial gel was $1.0Al_2O_3:xP_2O_5:y(TEA)_2O:zH_2O$, where x, y and z are changed systematically with $x=1.1$, $y=0.7$ and $z=50$ as the basis to study the influence of the gel composition on the crystallization and crystal sizes.

A typical synthesis procedure is described as follows. An appropriate amount of aluminium hydroxide was added to the hot orthophosphoric acid which was diluted by *ca.* 1/3 of the total water. After stirring for *ca.* 1 h, TEAOH was added dropwise to the above solution, followed by addition of the remaining water. The mixture was stirred for 6 h, and statically aged for 12 h under ambient conditions to form a nearly transparent homogeneous gel. For the conventional hydrothermal synthesis of $AlPO_4$-5, the gel was transferred into a 20 ml PTFE-lined stainless steel autoclave and heated at 333 K in an oven for a specified time, typically 7 h. The product was recovered by centrifugation (at 15 000 rpm for 5–15 min), washed repeatedly with distilled water (centrifuged and redispersed in water) and dried at ambient temperature. For the preparation under agitation, the autoclave was rotated at *ca.* 45 rpm in the oven. In the case of the microwave heating preparation of $AlPO_4$-5, the gel was charged into a 20 ml PTFE autoclave. The crystallization was carried out in a modified domestic microwave oven operating at 2450 MHz. The reaction mixture was heated quickly at a heating rate of *ca.* 2 K s^{-1} from room temperature to the crystallization temperature of 323–333 K and then held at the final temperature for 7–25 min.

The products were identified by means of XRD on a Rigaku D/MAX-IIIA diffractometer with Cu-Kα radiation. Scanning electron images (SEM) and transmission electron images (TEM) were taken on Hitachi X-650 and JEM-100CXII microscopes, respectively.

Results and Discussion

Effect of the P_2O_5 content

The effect of the P_2O_5 content on the crystallization and crystal size of $AlPO_4$-5 is summarized in Table 1. It can be seen that the P_2O_5 content in the gel plays an important role in the crystallization of $AlPO_4$-5 molecular sieve: an excess of P_2O_5 usually results in the formation of an unknown phase, while with insufficient P_2O_5 in the gel aluminium hydroxide contaminates the $AlPO_4$-5 crystals. Suitable P_2O_5/Al_2O_3 molar ratios for the formation of pure $AlPO_4$-5 range from 1.0 to 1.2.

It can also be seen that the P_2O_5/Al_2O_3 ratio influences crystal size. As shown in Fig. 1, a high P_2O_5/Al_2O_3 molar ratio favours the formation of $AlPO_4$-5 composed of large aggregates. At P_2O_5/Al_2O_3 ratios from 1.0 to 1.1, uniform plate-like crystallites are obtained.

Effect of the template content and pH value in the gel

The influence of the template content on the synthesis of $AlPO_4$-5 is shown in Fig. 2. It seems that tetraethylammonium hydroxide as a template favours the formation of small crystallites of $AlPO_4$-5, in contrast to triethylamine as the template, which usually favours the formation of large $AlPO_4$-5 crystals.[5] In the $(TEA)_2O/Al_2O_3$ ratio range from 0.6 to 1.0, pure $AlPO_4$-5 with small crystallites is obtained. Scanning electron images show that the $(TEA)_2O$ content also affects the crystal

† *Current address*: Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada E3B 6E2.

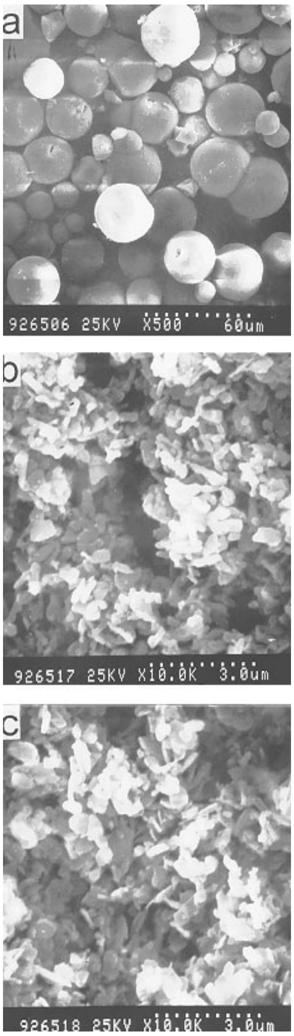

Fig. 1 SEM images of $AlPO_4$-5 synthesized with a P_2O_5/Al_2O_3 ratio of (a) 1.2, (b) 1.1 and (c) 1.0

Fig. 2 SEM images of $AlPO_4$-5 synthesized with a $(TEA)_2O/Al_2O_3$ ratio of (a) 0.6, (b) 0.8 and (c) 1.0

Table 1 Influence of the P_2O_5/Al_2O_3 ratio on the crystallization

	gel composition					
no.	$(TEA)_2O$	Al_2O_3	P_2O_5	H_2O	product	crystal habit
F1600	0.7	1.0	1.4	50	unidentified	—
F1601	0.7	1.0	1.2	50	$AlPO_4$-5	irregular, sphere, 10–30 μm
F1602	0.7	1.0	1.1	50	$AlPO_4$-5	uniform, 0.3 μm
F1603	0.7	1.0	1.0	50	$AlPO_4$-5	uniform, 0.8 μm
F1604	0.7	1.0	0.8	50	$AlPO_4$-5 + $Al(OH)_3$	—

morphology (Fig. 2). When the $(TEA)_2O/Al_2O_3$ ratio decreases from 0.6 to 1.0, the average crystal size of $AlPO_4$-5 decreases and the crystal-size distribution becomes narrower. These facts indicate that at the highest $(TEA)_2O$ content more nuclei that are responsible for nucleation and subsequent crystallization are formed, and the nucleation rate to crystal growth rate ratio increases. Similar observations have been reported by Finger *et al.*[5]

Since an increase in the $(TEA)_2O$ content enhances the alkalinity, the effect of pH is investigated in a separate experiment by adding hydrochloric acid (pH 5.4 and 5.8). The standard gel has a pH value of 6.4 [$(TEA)_2O/Al_2O_3 = 0.7$]. As can be seen from Fig. 3, the growth of $AlPO_4$-5 is rather sensitive to changes in the pH value. At the lowest pH in the gel, large aggregates form. As the gel pH is increased from 5.4 to 5.8 to 6.4 smaller crystals result (see Fig. 3). This suggests increased nucleation, at the expense of growth, as the pH is increased within this limited region. These phenomena are similar to those caused by the $(TEA)_2O$ content, *i.e.* a high $(TEA)_2O$ content results in an increase in the pH value in the gel, thus accelerating the nucleation rate and leading to the formation of small crystallites with a narrow crystal-size distribution.

Effect of water content

Variation of the water content results in changes to both the nucleation rate and the crystal growth rate, as indicated in Fig. 4. Dilution of the reaction gel decreases the nucleation rate. The products obtained from diluted gels contain large spherical agglomerates and tiny needle-shaped crystallites. On the other hand, concentration of the gel enhances the nucleation rate, resulting in the formation of uniform small $AlPO_4$-5 crystals. However, a further decrease in the water content leads to the formation of crystallites with various sizes

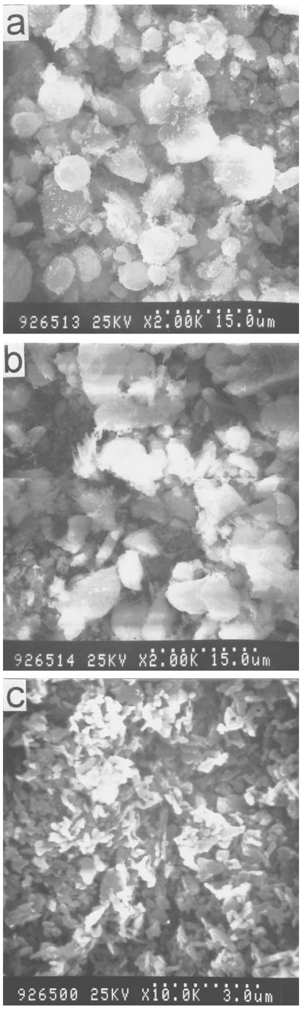

Fig. 3 SEM images of $AlPO_4$-5 synthesized with a pH value in the gel of (a) 5.4, (b) 5.8 and (c) 6.4

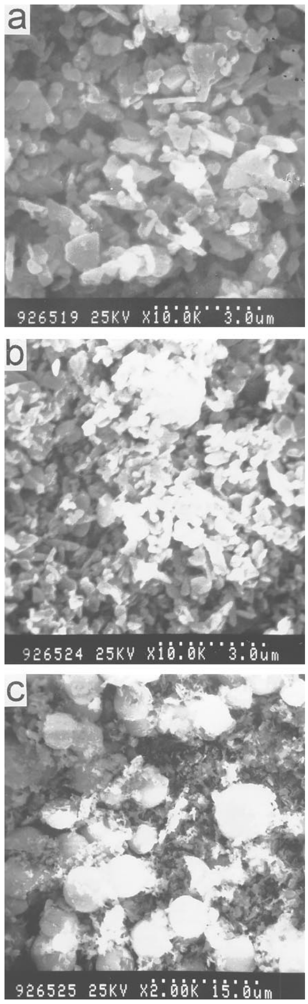

Fig. 4 SEM images of $AlPO_4$-5 synthesized with an H_2O/Al_2O_3 ratio of (a) 40, (b) 50 and (c) 72

[Fig. 4(a)], probably due to the inhomogeneity of the condensed gel.

Effect of crystallization conditions

The relationship between the crystallization temperature and the crystal size of the products was investigated by fixing the crystallization time. Good crystalline products are obtained at 413–453 K, and the crystal size is not distinctly dependent on the temperature.

The crystallization method has an influence on the crystal size of $AlPO_4$-5. Results from Fig. 5 show that stirring of the gel during the crystallization period is an important factor in determining the crystal size of $AlPO_4$-5. Stirring leads to the formation of smaller crystallites than those obtained under static conditions, probably because more nucleation centres are created by agitation of the gel.

Moreover, it is of interest to note that microwave heating of the aluminophosphate gel produces $AlPO_4$-5 crystallites with much smaller crystals in comparison with those obtained by the conventional heating (Fig. 6). Similar results have been observed in the syntheses of zeolites A, Y and ZSM-5,[19,20] which are attributed to simultaneous and abundant nucleation under microwave radiation.

Under microwave heating conditions, the influence of the synthesis conditions on the crystal size was investigated. The synthesis conditions and the crystallization products are summarized in Tables 2 and 3. Compared with the conventional hydrothermal synthesis ($P/Al = 1.0$–1.2 in the gel in this work), preparation of $AlPO_4$-5 by microwave heating is possible in a

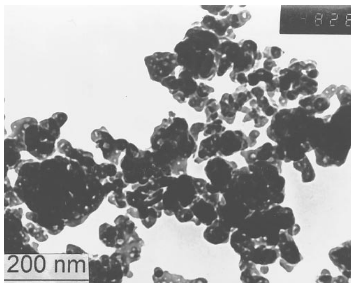

Fig. 5 TEM image of $AlPO_4$-5 synthesized under stirring

broader reaction mixture composition range. Moreover, the $AlPO_4$-5 crystals thus obtained usually have smaller sizes. From Table 2, one can see that the P_2O_5/Al_2O_3 ratio in the reaction mixture is crucial in determining the products and the crystal size. $AlPO_4$-5 is formed in the P_2O_5/Al_2O_3 ratio range from 1.1 to 1.8, outside this range either $Al(OH)_3$ coexists with $AlPO_4$-5 or an unknown phase instead of $AlPO_4$-5 is crystallized. At $P_2O_5/Al_2O_3 = 1.1$, nanocrystals of $AlPO_4$-5 can be obtained when $(TEA)_2O/Al_2O_3$ is fixed at 0.7 [Fig. 6(a)]. With the increase in the P_2O_5/Al_2O_3 ratio, the yields of the products decrease and large crystallites are easily obtained. It seems that a relatively low P_2O_5/Al_2O_3 ratio favours the formation of $AlPO_4$-5 with small crystals. Similar results have been reported by Girnus *et al.*[21]

The $(TEA)_2O/Al_2O_3$ ratio also plays an important role in the crystallization, as shown in Table 3. A low $(TEA)_2O$ content usually results in the formation of $AlPO_4$–C, and with an

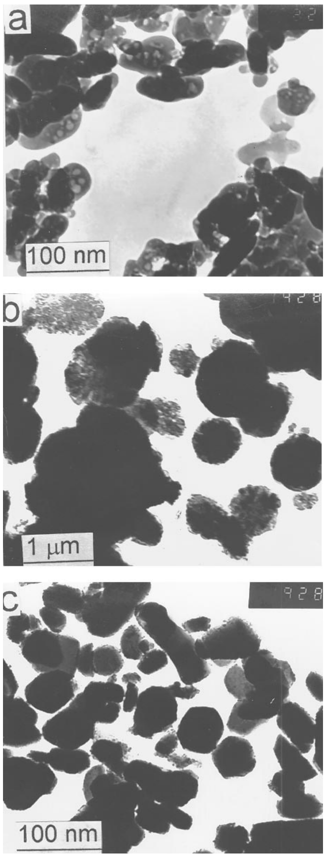

Fig. 6 TEM images of $AlPO_4$-5 synthesized by microwave heating: (a) sample W126, (b) sample W131 and (c) sample W133

excess of $(TEA)_2O$ in the gel amorphous phases are obtained. Pure $AlPO_4$-5 is crystallized in the $(TEA)_2O/Al_2O_3$ ratio range from 0.7 to 1.1. The synthesized $AlPO_4$-5 samples usually consist of nanometre-sized crystals or loose agglomerates, as shown in Fig. 6.

The XRD pattern of sample W126 (see also Tables 2 and 3) is shown in Fig. 7(a). The peak positions are similar to those for $AlPO_4$-5 prepared by conventional hydrothermal synthesis [Fig. 7(b)], but the intensities are different. The X-ray diffraction line-broadening of this sample is most probably due to the size effect of the small particles. Similar observation has been reported in the case of zeolite L.[18] Transmission electron

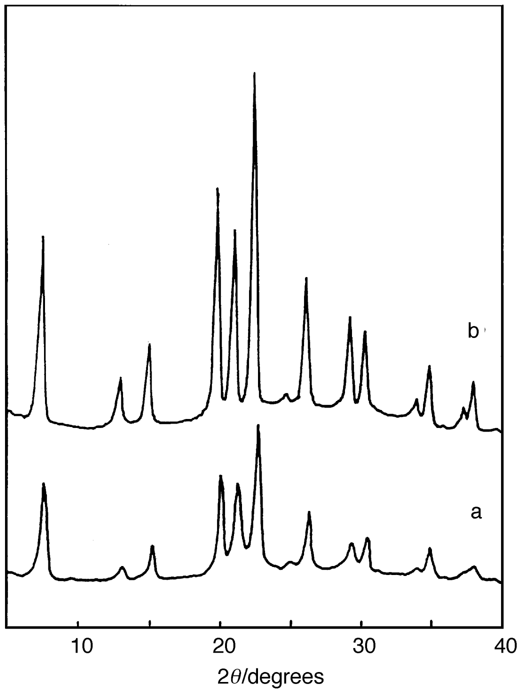

Fig. 7 XRD patterns of $AlPO_4$-5 samples synthesized by using (a) microwave heating (sample W126) and (b) conventional hydrothermal methods (sample F1602)

microscopy shows that the specimen consists of fine particles with sizes as small as *ca.* 50 nm [Fig. 6(a)].

Conclusions

Aluminophosphate $AlPO_4$-5 crystals with small sizes were synthesized using TEAOH as a template. Various synthesis parameters such as P_2O_5/Al_2O_3, $(TEA)_2O/Al_2O_3$, H_2O/Al_2O_3 ratios and the crystallization method influence the crystallization and the crystal size of $AlPO_4$-5. The synthesis of $AlPO_4$-5 with uniform small crystals requires appropriate reaction mixture compositions. By microwave heating, $AlPO_4$-5 is synthesized successfully, and the product usually consists of smaller particles than those synthesized by the conventional hydrothermal method. At $(TEA)_2O/Al_2O_3=0.7–1.1$ and $P_2O_5/Al_2O_3=1.1$, $AlPO_4$-5 with nanometre-sized is crystallized.

Table 2 Influence of the P_2O_5/Al_2O_3 ratio on the crystallization of $AlPO_4$-5 under microwave heating

	gel composition						
no.	$(TEA)_2O$	Al_2O_3	P_2O_5	H_2O	P_2O_5/Al_2O_3	product	av. size/nm
W142	0.7	1.4	1.1	50	0.8	$AlPO_4$-5 + $Al(OH)_3$	—
W126	0.7	1.0	1.1	50	1.1	$AlPO_4$-5	50
W138	0.7	0.8	1.1	50	1.4	$AlPO_4$-5	200
W137	0.7	0.6	1.1	50	1.8	$AlPO_4$-5	300
W136	0.7	0.5	1.1	50	2.2	unidentified	—

Table 3 Influence of the $(TEA)_2O/Al_2O_3$ ratio on the crystallization of $AlPO_4$-5 under microwave heating

	gel composition						
no.	$(TEA)_2O$	Al_2O_3	P_2O_5	H_2O	$(TEA)_2O/Al_2O_3$	product	av. size/nm
W125	0.5	1.0	1.1	50	0.5	$AlPO_4$-C	—
W126	0.7	1.0	1.1	50	0.7	$AlPO_4$-5	50
W131	0.9	1.0	1.1	50	0.9	$AlPO_4$-5	<50
W133	1.1	1.0	1.1	50	1.1	$AlPO_4$-5	60
W142	1.3	1.0	1.1	50	1.3	am[a]	—

[a]Am = amorphous.

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