JOURNAL OF
Materials
CHEMISTRY

Systematic studies on the effect of water content on the synthesis, crystallisation, conversion and morphology of $AlPO_4$-5 molecular sieve

Ya Wan, Craig D. Williams,* Catherine V. A. Duke and Jeff J. Cox

School of Applied Sciences, University of Wolverhampton, Wolverhampton, UK WV1 1SB.
E-mail: C.Williams@wlv.ac.uk

Received 28th July 2000, Accepted 14th September 2000
First published as an Advance Article on the web 10th November 2000

The $AlPO_4$-5 molecular sieve is successfully synthesized using the gel composition $(C_2H_5)_3N:Al_2O_3:P_2O_5:xH_2O$. It is shown that the water content in the starting molar gel composition plays a dominant role in the synthsis of $AlPO_4$-5. When the water content is low, the conversion of reagents to $AlPO_4$-5 is nearly complete and the synthesized products have better crystallisation, higher crystallinity and the ideal Al/P ratio. SEM also reveals that there is a preference for the formation of thin hexagonal platelets in $AlPO_4$-5 samples synthesized from starting molar gel compositions with 10 or 20 H_2O. Reducing the water content in the molar gel composition also results in a longer shelf life for $AlPO_4$-5. Similar structures and thermal behaviour of all of the synthesized samples are also observed in their XRD, FTIR and TGA analysis.

1. Introduction

$AlPO_4$-5 is an important member of the large family of aluminophosphate molecular sieves with large pores, uncharged framework and excellent thermal stability.[1] Extensive investigation of the synthesis and characterization of $AlPO_4$-5 has been undertaken because of its potential applications in industry either as an absorbent or as an excellent shape-selective supporting carrier for catalysts.[2–4] $AlPO_4$-5 molecular sieve has been synthesized both in aqueous and non-aqueous media using hydrothermal methods. The synthesis of $AlPO_4$-5, in aqueous media, usually employs a molar gel composition $R:Al_2O_3:P_2O_5:40H_2O$, where R is an organic templating agent.[2] In previous work, we have reported the effect of the water content in the gel composition on the conversion of reagents.[5] In this study, the effects of the water content in the starting gel composition on the synthesis, crystallization and morphology of $AlPO_4$-5 are investigated systematically. The techniques used for the characterisation of newly synthesised $AlPO_4$-5 are XRD, SEM, XRF, TGA and FTIR. ICP analysis is used to determine the content of Al and P in the mother liquors.

2. Experimental

2.1. Hydrothermal synthesis of $AlPO_4$-5

In the hydrothermal synthesis of $AlPO_4$-5, the new gel compositions are $R:Al_2O_3:P_2O_5:xH_2O$, where $x = 10$, 20 and 30, and R represents an organic templating agent. The previously preferred patented gel composition, $R:Al_2O_3:P_2O_5:40H_2O$, was also used. The organic templating agent used was triethylamine (99.9%, BDH, GPR). Other reagents used for the synthesis were pseudoboehmite (73% Al_2O_3, VERSAL 900), H_3PO_4 (85% wt% solution in water, Aldrich Chemical Company Inc.) and distilled water. In a typical synthesis, using the starting molar gel composition $R:Al_2O_3:P_2O_5:30H_2O$, the reaction mixture was prepared according to the following procedures. 9.90 g H_3PO_4 and 18.12 g water were added to a polypropylene beaker, and a clear solution was obtained by shaking. 6.00 g Al_2O_3 powder was added to the clear solution and stirred with a plastic rod until a white uniform paste was obtained. Finally, 4.34 g triethylamine was added to the paste, which was stirred to a uniform reaction mixture. The loss of triethylamine from volatilisation has to be taken into consideration. Consequently, the final reaction mixture should be 38.36 g. The initial pH of the reaction mixture was then measured using a hand-held Whatman PHA 300T pH meter. Then the reaction mixture was ready for crystallization.

11.50 g aliquots were transferred into pre-weighed Teflon liners (18 ml in volume), and the liners were placed in stainless steel autoclaves and sealed. The well-sealed autoclaves were put into an oven set at 200 °C under static conditions. The autoclaves were removed from the oven at different times and quenched immediately to room temperature. Before the solid products were separated, the final pH of the reacted mixture was measured. The solid products were roughly separated using centrifugation, which was carried out at 4 000 rpm for 20 min. The roughly separated solid products were washed a further 8 times using distilled water and after each washing the solid products were centrifuged again. Following the final separation, the solid products were dried in an air oven at 40 °C for about 20 h and then ground to fine powders, which were used for analysis by XRD, XRF, SEM, FTIR and TGA. The solution from washing the solid products, *i.e.* the mother liquors, were combined and made up to 500.0 ml or 1000.0 ml in volumetric flasks for ICP analysis.

2.2. ICP measurement of mother liquors

A Thermo TJA Ash plasma 300 inductively coupled plasma (ICP) instrument was used to measure the conversion of reagents to $AlPO_4$-5 product from analysis of the mother liquors remaining after the $AlPO_4$-5 solid products were filtered off. For samples 1 to 14, 18 to 21, 25 to 28, C and D, the mother liquors are clear solutions, which had to be diluted before measurement. The mother liquors for samples 15 to 17 and 22 to 24, however, were milky liquids to which a bit of ultrapure NaOH had to be added to produce clear dilute solutions.

DOI: 10.1039/b006127l

2.3. Methods for the calculation of Al/P ratios in $AlPO_4$-5 solid products

Two independent methods are used to calculate the Al/P ratios in the synthesized $AlPO_4$-5 solid products. One is to use XRF results from the measurement of solid products and the other is to use ICP results from the measurement of the corresponding mother liquors. When the ICP results are used to calculate the Al/P ratios, it is assumed that all of the reagents except those left in the mother liquors have been transferred to the $AlPO_4$-5 solid products.

The formula for the calculation of P/Al ratios by XRF analysis of the solid products is:

$$\mathrm{P/Al}=\frac{W_{\mathrm{s}}C_{\mathrm{P_2O_5}}}{M_{\mathrm{P_2O_5}}}\frac{M_{\mathrm{Al_2O_3}}}{W_{\mathrm{s}}C_{\mathrm{Al_2O_3}}}=\frac{C_{\mathrm{P_2O_5}}M_{\mathrm{Al_2O_3}}}{M_{\mathrm{P_2O_5}}C_{\mathrm{Al_2O_3}}} \quad (1)$$

where W_{s} is the weight of the solid products; C_{P2O5} and C_{Al2O3} are the normalised weight percentages of P_2O_5 and Al_2O_3 respectively in the $AlPO_4$-5 solid products, which are obtained from XRF results; M_{P2O5} is the molecular weight of P_2O_5 and M_{Al2O3} is the molecular weight of Al_2O_3.

The formula for the calculation of P/Al ratios in the relevant $AlPO_4$-5 solid products from XRF analysis of mother liquors is:

$$\mathrm{P/Al}=\frac{W_{\mathrm{a}}C_{\mathrm{P}}T_{\mathrm{P}}M_{\mathrm{Al}}}{W_{\mathrm{a}}C_{\mathrm{Al}}T_{\mathrm{Al}}M_{\mathrm{P}}}=\frac{C_{\mathrm{P}}T_{\mathrm{P}}M_{\mathrm{Al}}}{C_{\mathrm{Al}}T_{\mathrm{Al}}M_{\mathrm{P}}} \quad (2)$$

where W_{a} is the weight of original reaction mixture; C_{P} and C_{Al} are the percentages of phosphorus and Al respectively in the initial reaction mixture; M_{P} is the atomic weight of P and M_{Al} represents the atomic weight of Al. The remaining two quantities in eqn. (2), T_{P} and T_{Al}, are the conversions of P and Al to $AlPO_4$-5 in weight percentage. They are given as:

$$T_{\mathrm{P}}=(1-\frac{W_{\mathrm{P}}}{W_{\mathrm{a}}C_{\mathrm{P}}})\times 100 \quad (3)$$

$$T_{\mathrm{Al}}=(1-\frac{W_{\mathrm{Al}}}{W_{\mathrm{a}}C_{\mathrm{Al}}})\times 100 \quad (4)$$

where W_{P} is the total weight of P in its mother liquor and W_{Al} is the total weight of Al in its mother liquor. Both W_{P} and W_{Al} are obtained from the ICP results.

2.4. Method for the calculation of the chemical compositions of $AlPO_4$-5 solid products from XRF and TGA

The chemical compositions of $AlPO_4$-5 solid products can be calculated from a combination of XRF and TGA analyses using the following equation:

$$\begin{aligned}&\mathrm{Al_2O_3:P_2O_5:(C_2H_5)_3N:H_2O}\\&=\frac{C_{\mathrm{Al_2O_3}}}{M_{\mathrm{Al_2O_3}}}:\frac{C_{\mathrm{P_2O_5}}}{M_{\mathrm{P_2O_5}}}:\frac{C_{\mathrm{R}}}{M_{\mathrm{R}}}:\frac{C_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}\end{aligned} \quad (5)$$

where C_{Al2O3} = normalised concentration of Al_2O_3 (wt%) in the $AlPO_4$-5 solid products obtained from XRF measurement; $\mathrm{M_{Al2O3}}$ = molecular weight of Al_2O_3; C_{P2O5} = normalised concentration of P_2O_5 (wt%) in the $AlPO_4$-5 solid products obtained from XRF measurement; M_{P2O5} = molecular weight of P_2O_5; C_{R} = normalised concentration of $(C_2H_5)_3N$ (wt%) in the $AlPO_4$-5 solid products determined from TGA analysis; M_{R} = molecular weight of $(C_2H_5)_3N$; C_{H2O} = normalised concentration of H_2O (wt%) in the solid products determined from TGA analysis; M_{H2O} = molecular weight of H_2O.

There are also two additional supplementary relations for eqn. (5):

$$C_{\mathrm{R}}+C_{\mathrm{H_2O}}=\mathrm{LOI\ (wt.\%)} \quad (6)$$

and

$$C_{\mathrm{Al_2O_3}}+C_{\mathrm{P_2O_5}}=100-\mathrm{LOI} \quad (7)$$

where LOI is the percentage weight loss on ignition.

2.5. Characterization techniques

X-Ray diffraction (XRD) is used to determine the structures, crystallinity and unit parameters of $AlPO_4$-5. The crystallinity is determined from XRD data using the following equation:[6]

$$\mathrm{Crystallinity}=\frac{\sum I}{\sum I_{\mathrm{S}}}\times 100 \quad (8)$$

where I is the line intensity in the XRD spectrum for the synthesized samples while I_{s} is that for the standard sample. The standard used is usually the sample with the highest crystallinity which contains no amorphous or unreacted materials as identified by XRD analysis and supported by scanning electron microscopy. The intensities of the XRD lines at d = 11.8, 4.5, 4.24, 3.97, 5.93, 3.43 are chosen for the calculation of crystallinity.

XRD analysis was performed on a Philips 1710 X-ray diffractometer interfaced to a DEC MicroVAX minicomputer with Philips APD software that includes a search/match and search/refine facility for the determination of unit cell parameters using the ICDD database. CuKα radiation was used with a scanning speed of 0.020° s^{-1}. The 2θ peak angle between 3.0 and 50.0 was scanned.

The synthesized samples were also characterised using scanning electron microscopy (SEM), X-ray fluorescence (XRF), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The equipment used for SEM was a Camscan SV2 scanning electron microscope and the coating equipment used was an Emscope SC500 Sputter Coater. Fisons ARL 8410 sequential X-ray spectrometer was employed for XRF analysis using a semi-quantitative analysis (ASQ) program. For TGA analysis, a Perkin-Elmer series 7 instrument was used, which has flowing nitrogen gas and a PE7500 computer with TAS 7 software. In TGA studies the weight of the samples was between 12 and 30 mg and the temperature range was from 35 to 800 °C with a heating rate of 10 °C min^{-1}. FTIR analysis was performed on a Nicolet Impact 404 spectrophotometer interfaced with a 486DX microprocessor and FTIR software OMNIC, version 2. The sample discs for FTIR analysis were made from the synthesized samples mixed with dry KBr (ratio 1 : 200). Spectra were scanned over the range 400 to 4000 cm^{-1} with a resolution of 16. 20 scans were co-added.

3. Results and discussion

3.1. Structure and crystallisation from XRD

The XRD results for samples A to D and 1 to 28 are summarised in Table 1. The XRD analysis shows that samples A to C and 1 to 28, synthesized using triethylamine as template, are $AlPO_4$-5 without impurities.[7,8] As a typical example, Fig. 1 shows the XRD pattern for sample 5 synthesised in 24 h from the starting gel composition with $10H_2O$. For sample D synthesised in 48 h from the starting gel composition with $40H_2O$, the XRD result indicates that it is $AlPO_4$-5 mixed with minor impurities. It can also be seen from Table 1 that the crystallization time strongly depends on the water content in the gel compositions. When $x = 10$, pure $AlPO_4$-5 can be synthesized in 3 to 66 h. When $x = 20$, however, pure $AlPO_4$-5 can be synthesized in a longer period from 3 to 95 h. When $x = 30$, pure $AlPO_4$-5 can be synthesized in 3 to 48 h. Further increasing the water content to $x = 40$ leads to a narrower ranger of crystallization time from 3 to 24 h. The optimum gel composition for the synthesis of $AlPO_4$-5 with the widest range of cystallization time is $(C_2H_5)_3N : Al_2O_3 : P_2O_5 : 20H_2O$.

The values of crystallinity in Table 1 were obtained from the XRD patterns of the relevant samples. Fig. 2 shows the dependence of the crystallinity on the crystallisation time and water content of the starting gel compositions at 200 °C. The

Table 1 Synthesis conditions, XRD results and chemical formulation (from XRF andTGA) for samples 1 to 28 and A to D

No.	T^a/°C	t^b/h	X^c	XRD^d	c^e (%)	Chemical formulae^f $Al_2O_3:P_2O_5:Et_3N:H_2O$	LOI (%)^g
1	200	3	10	5	100	1.00 : 0.97 : 0.24 : 0.59	13.2
2		4		5	100	1.00 : 0.95 : 0.26 : 0.56	13.2
3		5		5	98.9	1.00 : 0.96 : 0.25 : 0.56	12.9
4		20		5	100	1.00 : 0.95 : 0.24 : 0.66	13.4
5		24		5	96.9	1.00 : 0.95 : 0.24 : 0.71	13.6
6		44		5	98.6	1.00 : 0.97 : 0.24 : 0.50	12.6
7		48		5	100	1.00 : 0.96 : 0.23 : 0.39	11.8
A		66		5	96.5	—	—
8	200	3	20	5	92.7	1.00 : 0.97 : 0.23 : 0.95	14.3
9		4		5	99.2	1.00 : 0.93 : 0.24 : 0.74	13.7
10		5		5	100	1.00 : 0.90 : 0.23 : 0.65	13.0
11		20		5	100	1.00 : 0.98 : 0.25 : 0.76	13.5
12		24		5	100	1.00 : 0.95 : 0.25 : 0.66	13.4
13		44		5	100	1.00 : 0.96 : 0.25 : 0.43	12.0
14		48		5	100	1.0 : 0.97 : 0.25 : 0.37	11.4
B		95		5	100	—	—
15	200	3	30	5	67.2	1.00 : 0.84 : 0.21 : 1.46	17.1
16		4		5	77.8	1.00 : 0.90 : 0.21 : 1.27	15.9
17		5		5	83.2	1.00 : 0.89 : 0.22 : 0.99	14.4
18		16.1		5	86.8	1.00 : 0.91 : 0.22 : 0.37	11.0
19		20		5	91.7	1.00 : 0.92 : 0.22 : 0.46	11.5
20		22		5	86.9	1.00 : 0.94 : 0.22 : 0.31	10.6
21		24		5	86.4	1.00 : 0.97 : 0.22 : 0.40	10.8
C		48		5	97.8	1.00 : 0.95 : 0.21 : 0.42	10.6
22	200	3	40	5	61.5	1.00 : 0.88 : 0.22 : 1.19	16.0
23		4		5	74.8	1.00 : 0.90 : 0.21 : 1.16	15.6
24		5		5	71	1.00 : 0.92 : 0.22 : 0.92	14.1
25		16.1		5	84.8	1.00 : 0.88 : 0.20 : 0.39	10.8
26		20		5	86.4	1.00 : 0.86 : 0.20 : 0.34	10.8
27		22		5	84.2	1.00 : 0.90 : 0.21 : 0.45	11.2
28		24		5	81	1.00 : 0.93 : 0.21 : 0.42	10.6
D		48		5^h	80.5	1.00 : 0.95 : 0.21 : 0.41	10.4

[a] Crystallization temperature. [b] Crystallization time. [c] Water content in molar gel composition, $R:Al_2O_3:P_2O_5:XH_2O$. [d] 5 = $AlPO_4$-5. [e] Crystallinity (%). [f] Determined from XRF and TGA. [g] Obtained from TGA analysis. [h] $AlPO_4$-5 mixed with impurities.

water content obviously had a dramatic effect on the crystallinity of $AlPO_4$-5. When $x=40$, the synthesised $AlPO_4$-5 had a crystallinity ranging from 61 to 86% and its highest crystallinity could only be achieved when the crystallisation time reached 20 h. A further increase in the crystallisation time tended to decrease the crystallinity slightly. When $x=30$, within 20 h of crystallization time the synthesised samples achieved crystallinity ranging from 67 to 91% and the crystallinity increased with crystallisation time. Above 24 h, the crystallinity decreased slightly with crystallization time, and a further increase in crystallization time to 48 h resulted in the highest crystallinity of 98% at this water content. 100% crystallinity was observed when the water content was lowered to either $x=20$ or $x=10$.

In the preparation of the initial reaction mixture, the pH values were recorded. It was found that the pH values of the initial reaction mixtures increased from 2.0 to 4.0 when the water content decreased from 40 to 10 in the starting molar gel compositions. In addition, the calculated molar concentrations of templating reagents in the starting molar gel composition were 1/43, 1/33, 1/23 and 1/13 when the water content was 40, 30, 20 and 10 respectively. According to Newalkar *et al.*,[3] both a higher initial pH value and a higher concentration of template in the starting reaction mixture will lead to faster crystallisation of $AlPO_4$-5 molecular sieves. This agrees with our results and explains why shorter crystallisation times and much higher crystallinity can be achieved when the starting gel composition has a lower water content.

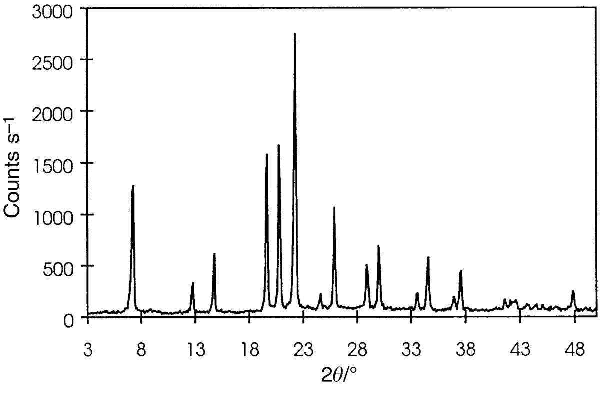

Fig. 1 XRD pattern for sample 5.

3.2. Conversion of reagents and ratio of Al : P in solid products from ICP analysis of mother liquors

Table 2 shows the summarised results for conversion of the reagents and Al : P molar ratio in the synthesized solid, which are obtained from ICP analysis of the respective mother liquors. It can be seen from Table 2 that the gel composition $(C_2H_5)_3N:Al_2O_3:P_2O_5:10H_2O$ produces both the highest conversion and the highest Al : P ratio in the corresponding solid products within 5 h crystallization. At this optimum gel composition, $AlPO_4$-5 molecular sieves can be synthesised nearly stoichiometrically and at the same time the conversion and the Al : P ratio in the solid products are dependent on the crystallisation time. About 4% of the reagents remain in the mother liquor as synthesis waste when the crystallization time reaches 5 h. After 24 h of crystallization, almost all of the Al and P in the reagents have been transferred to $AlPO_4$-5. A further increase in the crystallization time, however, tends to reduce the conversion and the Al : P ratio in the solid products. As a comparison, when gel compositions contain $40H_2O$,

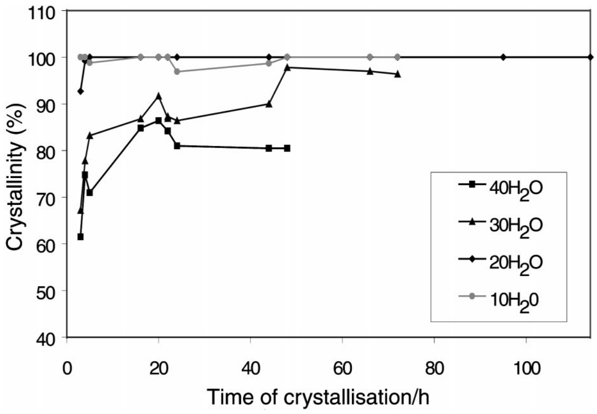

Fig. 2 Crystallisation of $AlPO_4$-5 at 200 °C.

which is conventionally used, 20% of the reagents remain in the mother liquor as synthesis waste after 5 h of crystallization. If the crystallisation time is increased to 24 h, 7% of reagents are still left in the mother liquor as synthesis waste.

As explained earlier, the lower water content results in the higher initial pH value of the reaction mixture and leads to the higher and fewer defects from the crystal growth, which consquently enhance the conversion of reagent.

3.3. Measurement of chemical composition using XRF and TGA

The chemical formulae for the synthesized samples are given in Table 1, which are obtained from the combination of XRF and TGA analysis. For samples 1 to 14, the Al : P ratios in their chemical compositions are almost identical to the ideal which is Al : P = 1 : 1. For samples 15 to 28 (except sample 21), the Al : P ratios are slightly lower than those synthesised from the starting gel compositions with 20 or 10 H_2O. Compared with the established gel composition using $40H_2O$, the synthesis waste can be greatly reduced using the new gel compositions with either 10 or $20H_2O$.

Table 2 Conversion of reagents and Al : P ratio in solid products from using ICP analysis

Sample	Crystallisation time/h	Conversion (wt.%) Al	P	Al/P (molar ratio)	*X*(water content)
1	3	94.4	88.7	1.00 : 0.94	10
2	4	91.5	85.3	1.00 : 0.94	
3	5	98.1	94.2	1.00 : 0.96	
4	20	99.3	94.6	1.00 : 0.96	
5	24	99.6	96.8	1.00 : 0.97	
6	44	98.3	93.0	1.00 : 0.95	
7	48	97.1	92.3	1.00 : 0.95	
8	3	91.7	85.9	1.00 : 0.94	20
9	4	92.4	84.6	1.00 : 0.92	
10	5	95.5	89.7	1.00 : 0.94	
11	20	97.9	92.8	1.00 : 0.95	
12	24	96.5	91.7	1.00 : 0.95	
13	44	99.6	94.6	1.00 : 0.95	
14	48	99.3	94.6	1.00 : 0.96	
15	3	75.2	60.9	1.00 : 0.81	30
16	4	81.2	70.9	1.00 : 0.87	
17	5	88.9	79.0	1.00 : 0.90	
18	16.1	93.8	86.8	1.00 : 0.92	
19	20	96.2	89.8	1.00 : 0.93	
20	22	96.5	90.4	1.00 : 0.94	
21	24	99.1	92.5	1.00 : 0.93	
C	48	98.5	91.5	1.00 : 0.93	
22	3	73.5	61.6	1.00 : 0.85	40
23	4	83.5	72.3	1.00 : 0.87	
24	5	84.5	75.2	1.00 : 0.89	
25	16.1	96.7	88.7	1.00 : 0.92	
26	20	95.5	89.4	1.00 : 0.94	
27	22	96.4	90.1	1.00 : 0.93	
28	24	99.4	90.1	1.00 : 0.91	
D	48	98.9	91.6	1.00 : 0.93	

It can also be seen from Table 1 that the average molar fraction of template is 0.24 in samples 1 to 7 which have $10H_2O$ in their starting gel composition. For samples 8 to 14 with $20H_2O$ in their starting molar gel composition, the average molar fraction of template is 0.25. This suggests that samples 1 to 14 have a similar synthesis mechanism at the initial growth of nuclei in their crystal structures. The molar fractions of template, for samples 15 to 28, C and D, however, are between 0.20 and 0.22 which are smaller than those in samples 1 to 14. This is probably due to the lower concentration of template in their starting reaction mixture.

The Al/P ratios were also determined using ICP and the results are given in Table 2. The comparison of the Al/P molar ratios in Table 2 with those in Table 1 shows very good agreement.

3.4. Investigation of crystal morphology using SEM

Fig. 3 shows SEM images for sample 24 synthesized from a gel composition with $40H_2O$ using triethylamine as template. In Fig. 3a the crystal morphology is spherical, where the spheres are comprised of agglomerations of platelets whose details are shown in Fig. 3b. Further study shows that most of the crystals have single spheres and the spheres are built up from hexagonal platelets. It is also observed that when crystallization time is 16 h, a few fine crystals of $AlPO_4$-5 are formed with long hexagonal rods.

Fig. 4 shows the SEM images for sample 15 synthesized from the gel composition with $30H_2O$. In Fig. 4a, a large crystal is formed by the adhesion of two spheres, and on the surface of the large crystal there are several small hexagonal platelets. Fig. 4b shows the morphology of a fine crystal, which is a thin hexagonal platelet. Fig. 4c is the morphology of a large crystal comprised of two spheres. Its surface is incomplete or damaged and some small hexagonal crystals have already grown in the damaged areas. Overall half of the crystals in sample 15 are large spheres and half of them are fine crystals with thin hexagonal platelets. As with sample 24, when the crystallization time is 16 h, a few fine crystals with long hexagonal rods are also formed.

Fig. 5 shows SEM images for samples 1, 6 and 9, which are synthesized with $10H_2O$, $10H_2O$ and $20H_2O$ respectively in their gel compositions using triethylamine as template. All of the crystals in Fig. 5 are thin hexagonal platelets. Further studies have revealed that most of the crystals under these conditions are hexagonal platelets. Spheres are only observed occasionally. In these hexagonal platelets, the bottom and top surfaces are very large, while the prism is very short, making them look like discs. No long hexagonal rods are found even for samples crystallised for up to 48 h.

The micrographs in Figs. 3, 4 and 5 clearly show that $AlPO_4$-5 has a preference for hexagonal mophology when there are either 10 or $20H_2O$ in the starting reaction mixture, and a preference for spherical morphology when 30 or $40H_2O$ is used in the starting reaction mixture. Combining the results in this part with the template factors from chemical formulae in section 3.3, we may conclude that samples with more template trapped within their channels tend to form hexagonal crystals. Otherwise spherical morphology samples are formed.

3.5. Thermal stability and FTIR spectroscopy

Fig. 6 shows the first derivative TGA curves for samples 5, 12, 16, 23 and 27 synthesized from the gel compositions with 10, 20, 30, 40 and $40H_2O$ respectively. All of the TGA curves for

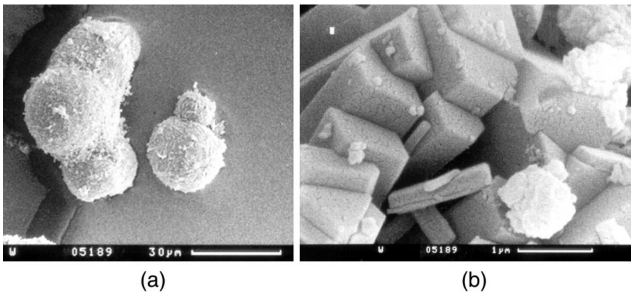

Fig. 3 SEM image for sample 24 with $40H_2O$ in the gel composition.

samples 1 to 28, C and D have three distinct regions (peaks) of weight loss between 35 and 800 °C. The temperature range for the first peak is from 67 to 103 °C, which is attributed to the loss of water from channels in the sample structure since its peak is under 100 °C. The temperature of the first peak also increases with decreasing water content in the gel composition. The temperature of the second peak for all samples is consistently around 200 °C. This peak results from the loss of the triethylamine template, which occupied the channel in the initial growth of nuclei, during the crystallization. As shown in Fig. 6, the curve for sample 23 (synthesized with $40H_2O$) has a wide shoulder around 240 °C after the second peak. The first derivative TGA curves for samples 22 and 24 also have the same wide shoulder around 240 °C. This is probably caused by the lower crystallinity of these samples. The wide shoulder is not observed for samples 25 to 28 and B although they are also synthesized with $40H_2O$. For samples 1 to 14 synthesized with 10 or $20H_2O$ in their gel compositions, a shoulder at about 150 °C before the second peak, like those in Fig. 6 for samples 5 and 12, can always be observed. The temperature range of the third peak for all of the samples is from 420 to 480 °C. Compared with the other two peaks, the third peak has a quite small weight loss and can be attributed to the loss of protonated triethylamine template.[9–11]

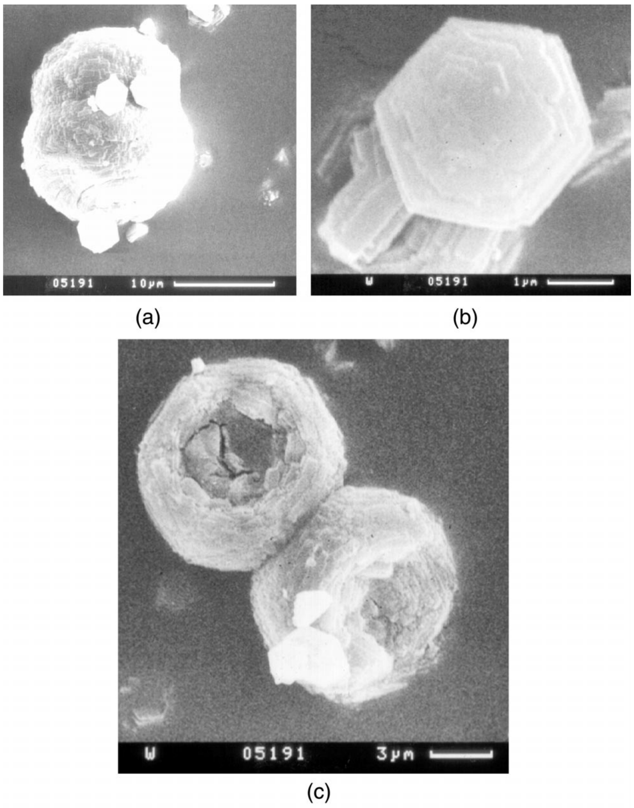

Fig. 4 SEM images for sample 15 with $30H_2O$ in the gel composition.

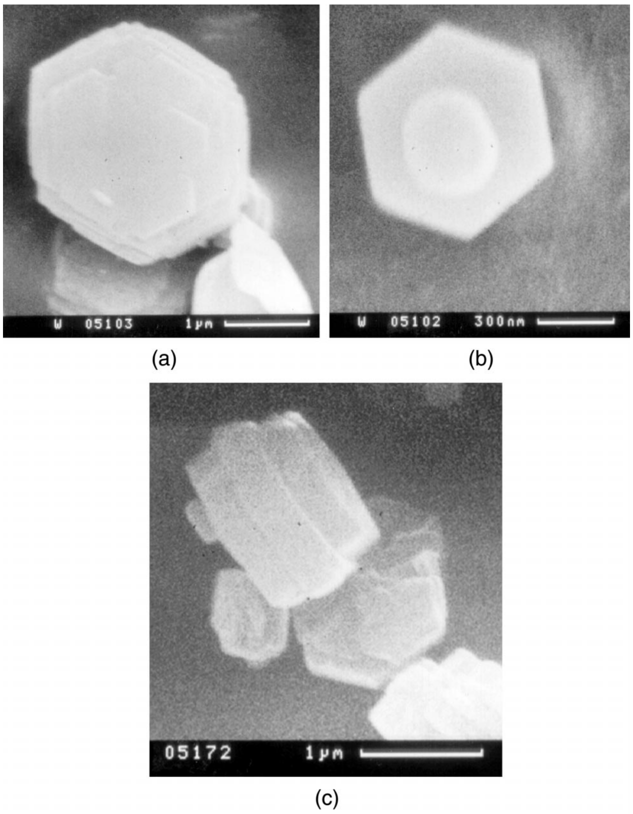

Fig. 5 SEM images for samples 1 (a), 6 (b) and 9 (c) with $10H_2O$, $10H_2O$ and $20H_2O$ respectively in their gel compositions.

The TGA analysis also indicates that the amount of the water in $AlPO_4$-5 solid products synthesised from the same gel composition decreases with the crystallisation time, while the template content remains stable in respect of crystallization time. Therefore, the total amount of water and template entrapped in the channel systems of $AlPO_4$-5 must decrease with the crystallization time. This is reflected in their total LOI (loss on ignition, %) in Table 1. The TGA results in Table 1 also show that the total LOI values do not decrease significantly with the crystallization time for samples synthesized from gel compositions with 10 or $20H_2O$. However, the total LOI values decrease more rapidly with the crystallisation time for samples synthesised from gel compositions with 30 or $40H_2O$. This is an indication that when there is higher water

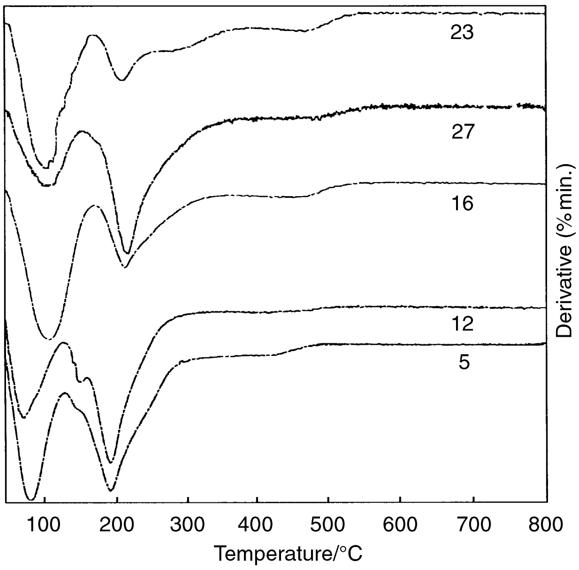

Fig. 6 Derivative curves from TGA for $AlPO_4$-5 samples.

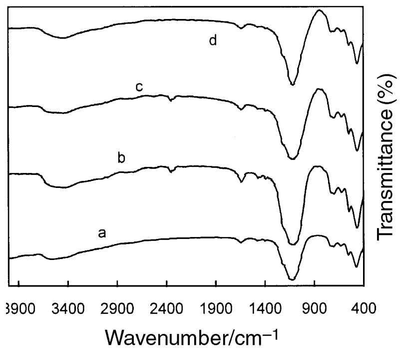

Fig. 7 FTIR spectra for samples 5 (a), 13 (b), 17 (c) and 24 (d).

content in the starting gel composition, more water will be entrapped in the solid products. It is known that excess water in contact with aluminophosphate frameworks tends to hydrolyze the framework, leading to framework breakdown.[12]

Fig. 7 shows representative FTIR spectra of the framework of samples 5, 13, 17 and 24, which are synthesized with 10, 20, 30 and 40H_2O respectively in their gel compositions. In all of the four spectra, there is an asymmetric TO_4 vibration band at 1130 cm^{-1}accompanied by a shoulder at around 1215 cm^{-1}. There is also a symmetric stretching band at around 720 cm^{-1}. In addition, two bands around 640 and 486 cm^{-1} are observed which can be attributed to double ring and T–O bending. In brief, the FTIR data for all of the synthesized samples exhibit typical characteristics of $AlPO_4$-5.[7]

4. Conclusions

$AlPO_4$-5 molecular sieve is synthesised at 200 °C using the new gel composition $(C_2H_5)_3N : Al_2O_3 : P_2O_5 : xH_2O$, where $x = 10$, 20 and 30. The conversion of reagents to the $AlPO_4$-5 solid product is almost complete using the new gel composition, as compared to the conventional one. Better crystallization, higher crystallinity and a nearly ideal ratio for Al/P are also achieved. A longer shelf life of the newly synthesized $AlPO_4$-5 is expected because of the lower water content entrapped in the solid products, as indicated in TGA analysis.

When $AlPO_4$-5 samples are synthesized from the starting molar gel compositions with 10 or 20 H_2O, there is a preference for the formation of thin hexagonal platelets. Spheres are the preferred morphology when the samples are synthesised from the gel compositions with 30 and 40 H_2O.

Acknowledgements

The authors thank Mr I. S. Young in La Roche Chemicals for the supply of Versal 900 alumina.

References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *US Patent* 4 310 440, 1982.
2 S. T. Wilson, B. M. Lok, C. A. Messina and E. M. Flanigen, *Proceedings of the Sixth International Zeolite Conference*, ed. D. Olson and A. Bisio, Butterworths, 1984, pp. 97–109.
3 B. L. Newalkar, B. V. Kamath, R. V. Jasra and S. G. T. Bhat, *Zeolites*, 1997, **18**, 286.
4 D. S. Sholl and K. A. Fichthorn, *J. Chem. Phys.*, 1997, **107**, 4384.
5 Y. Wan, C. D. Williams, J. J. Cox and C. V. A. Duke, *Green Chem.*, 1999, **1**(3), 169.
6 R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, 1989, p. 290.
7 R. Szostak, *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, 1992, p. 8.
8 Alphabetical Indexes Powder Diffraction File Sets 1-46, International Centre For Diffraction Data, ICDD, USA, 1996, p. 877.
9 N. J. Tapp, N. B. Milestone and L. James Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1801.
10 L. M. Parker, D. M. Bibby and J. E. Patterson, *Zeolites*, 1984, **4**, 168.
11 Chr. Minchev, V. Vatchev and S. Mintova, *Thermochim. Acta*, 1995, **264**, 59.
12 B. Hampson, H. F. Leach, B. M. Lowe and C. D. Williams, *Zeolites*, 1989, **9**, 521.