Vapor-phase transport synthesis of ZnAPO-34 molecular sieve

Lixiong Zhang and George R. Gavalas*

Chemical Engineering 210-41, California Institute of Technology, Pasadena, CA 91125, USA.
E-mail: gavalas@cheme.caltech.edu

Received (in Bloomington, IN, USA) 3rd September, 1998, Revised manuscript received 19th November 1998, Accepted 20th November 1998

ZnAPO-34 molecular sieve can be synthesized by the vapor-phase transport technique using triethylamine as a structure-directing agent.

Aluminium phosphate molecular sieves (AlPO-n) are crystalline framework structures formed from alternating AlO_4 and PO_4 tetrahedra.[1,2] Their pore sizes and adsorption properties are similar to those of zeolites but their framework is electrically neutral. By substitution of divalent ions of metals like Co or Zn for part of the aluminium ions, the framework acquires negative charges balanced by acidic protons possessing acidic catalytic activity.[3]

Since the first report on AlPO preparation,[1] interest in these materials has increased because of their potential as adsorbents, catalysts or catalyst supports[4,5] and, more recently, as membranes for gas separations.[6] The attractive properties of AlPOs that distinguish them from zeolites are their generally higher thermal stability and easier incorporation of metals in the framework.[1,4]

Zeolites and AlPOs are conventionally prepared by hydrothermal synthesis,[7] but zeolites can be prepared by other techniques as well, such as solvothermal synthesis[8] and vapor-phase transport (VPT).[9–11] The VPT technique involves crystallization of dry gel in a vapor phase containing organic template and water, and has certain advantages over other methods including minimum use of expensive organic template, elimination of the need to separate products from mother liquid, and production of molecular sieve coatings on various substrates.

Since 1990 when Xu *et al.*[9] first synthesized ZSM-5 by exposure of dry amorphous aluminosilicate gels in a vapor of ethylenediamine, triethylamine (Et_3N) and water, zeolites, such as ANA, FER, MOR and CHA, have been synthesized by several groups by VPT.[10,11] However, the VPT technique has not been applied so far to aluminophosphate molecular sieves. The purpose of this communication is to report synthesis of ZnAPO-34 molecular sieve by the vapor-phase transport technique.

Hydrothermal synthesis of ZnAPO-34 is normally carried out using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent (SDA).[12] However, because TEAOH is non-volatile, we carried out the VPT synthesis using Et_3N as the SDA. Before attempting VPT synthesis we verified that normal hydrothermal synthesis of ZnAPO-34 using Et_3N is feasible. The hydrogel for the hydrothermal synthesis was the same as reported in literature[12] except that Et_3N was used instead of TEAOH. The product was characterized by XRD and SEM and, as shown in Fig. 1(a), it has the same cubic morphology as that prepared using TEAOH.[12] Analysis of the powder XRD pattern shown in Fig. 2(a) verified the that the product was ZnAPO-34 and the unit cell constants calculated were a = 13.746, b = 13.746, c = 14.730 Å (trigonal system, hexagonal axes) in agreement with those reported previously.[13]

VPT synthesis of ZnAPO-34 using Et_3N as organic template was carried out next. Dry gels for this synthesis were prepared by adding the specified quantities of zinc acetate, aluminium isopropoxide, and phosphoric acid into water successively. The system was stirred vigorously at room temperature to a homogeneous mixture each time prior to the addition of the next component. The resulting mixture was dried either at room temperature or at 90 °C overnight. VPT syntheses of ZnAPO-34 were conducted in a 23ml Teflon-lined stainless steel autoclave.

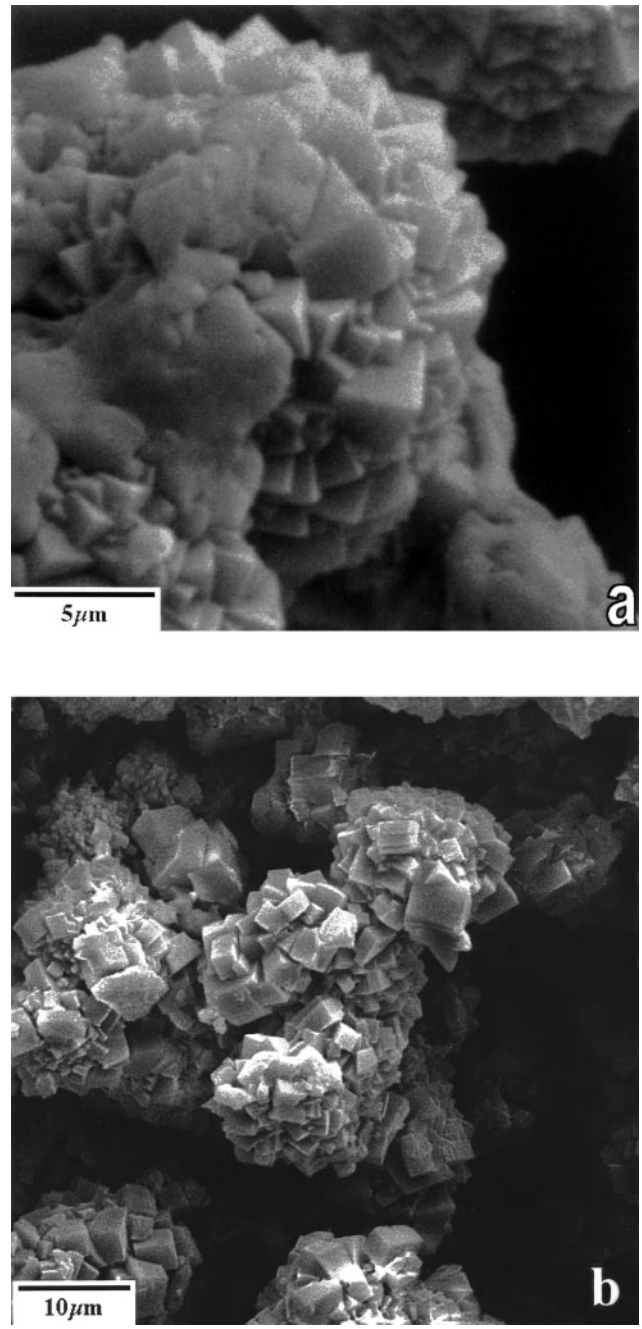

Fig. 1 Scanning electron micrograms of (a) product prepared by hydrothermal synthesis using Et_3N as a structure-directing agent; (b) product prepared by the VPT technique.

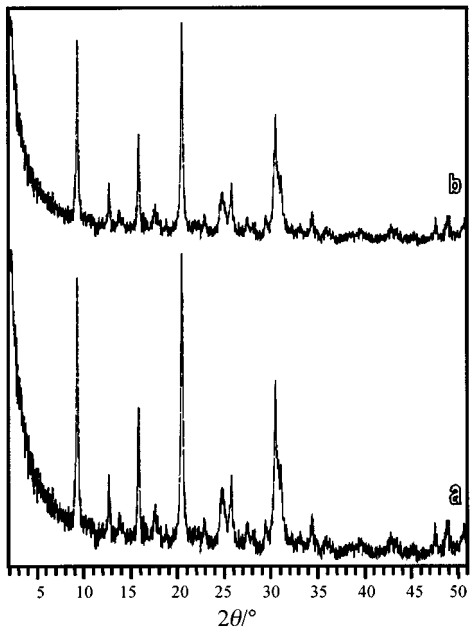

Fig. 2 XRD patterns of (a) product prepared by hydrothermal synthesis using Et_3N as a structure-directing agent; (b) product prepared by the VPT technique.

About 6 ml of a mixture of Et_3N and water was poured into the bottom of the autoclave. The dry gel was placed on a Teflon plate, which was installed in the autoclave above the liquid level. The autoclave was placed into a convection oven preheated to 170 °C and maintained at that temperature for 24 h. The autoclave was subsequently quenched in tap water and the products were washed, dried and characterized by SEM and XRD.

Table 1 lists the synthesis composition and resulting products. In the first set of experiments, the dry gel was prepared using the composition $0.4ZnO:0.8Al_2O_3:1P_2O_5:75H_2O$. Fig. 1(b) shows that the morphology of the resulting product is the same as that of Fig. 1(a). The XRD pattern of the product shown in Fig. 2(b) is also identical to that of Fig. 2(a).

Table 1 Experimental conditions and results.

Entry	Composition for synthesis of amorphous gel	Liquid phase	Result by XRD
1	$0.4ZnO:0.8Al_2O_3:1P_2O_5:75H_2O$[a]	$2Et_3N:150H_2O$	ZnAPO-34
2	$0.4ZnO:0.8Al_2O_3:1P_2O_5:150H_2O$[a]	$2Et_3N:150H_2O$	ZnAPO-34
3	$0.4ZnO:0.8Al_2O_3:1P_2O_5:150H_2O$[b]	$2Et_3N:150H_2O$	ZnAPO-34
4	$0.4ZnO:0.8Al_2O_3:1P_2O_5:150H_2O$[b]	$99Et_3N:1H_2O$	ZnAPO-34
5	$0.4ZnO:0.8Al_2O_3:1P_2O_5:150H_2O$[b]	$2Et_3N$:150EtOH	Amorphous
6	$0.4ZnO:0.8Al_2O_3:1P_2O_5:300H_2O$[b]	$2Et_3N:150H_2O$	ZnAPO-34
7	$0.4ZnO:0.8Al_2O_3:1P_2O_5$:150EtOH[b]	$2Et_3N:150H_2O$	Amorphous
8	$0.4SiO_2:0.8Al_2O_3:1P_2O_5:150H_2O$[b]	$2Et_3N:150H_2O$	SAPO-34

[a] Gel was dried at ambient temperature. [b] Gel was dried at 90 °C.

The other preparations listed in Table 1 involved the following variations. Some gels were prepared with different amounts of water or were dried at 90 °C. In one preparation the liquid phase contained 99% Et_3N. In another it contained Et_3N and ethanol instead of water. Finally in one experiment the gel was prepared with ethanol instead of water. As shown in Table 1, the VPT synthesis product was always ZnAPO-34 as long as the gel was initially prepared using water and the liquid placed at the bottom of the autoclave contained water. Even 1% water contained in sample 4 was evidently sufficient. However, if the gel was prepared using ethanol or if the liquid introduced into the autoclave was an ethanol–Et_3N mixture, the product was amorphous. Entry 8 in Table 1 shows that SAPO-34 can also be prepared using VPT method with Et_3N as the structure-directing agent.

Funding of this work by Elf Atochem, North America, Inc. is greatly appreciated. We thank Ms Lin Luo for analyzing the XRD patterns.

Notes and references

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem . Soc.*, 1982, **104**, 1146.
2 R. Szostak, *Molecular Sieves*, van Nostrand Reinhold, New York, pp. 254–281.
3 Z. Zhao and R. Zhao, *Zeolites*, 1993, **13**, 634.
4 J. Das, S. P. Lohokare and D. K. Chakrabarty, *Indian J. Chem., Sect. A*, 1992, **31**, 742.
5 S. T. Wilson, B. M. Lok, C. A. Messina and E. M. Flanigen, in *Proc. 6th Int. Zeol. Conf.*, ed. D. Olson and A. Bisio, Butterworth, London, 1984, pp. 97–109.
6 J. C. Poshusta, T. A. Vu, J. L. Falconer and R. D. Noble, *Proc. Int. Workshop on Zeolitic Membranes and Films*, Gifu, Japan, June 28–30, 1998, pp. 9–12.
7 M. E. Davis and R. L. Lobo, *Chem. Mater*., 1992, **4**, 756.
8 D. M. Bibby and M. P. Dole, *Nature*, 1985, 317.
9 W. Xu, J. Dong, J. Li and F. Wu, *J. Chem. Soc., Chem. Commun*., 1990, 755.
10 M. H. Kim, H.X. Li and M. E. Davis, *Microporous Mater*., 1993, **1**, 191.
11 M. Matsukata, N. Nishiyama and K. Ueyama, *Microporous Mater*., 1993, **1**, 219.
12 N. N. Tusar, V. Kaucic, S. Geremia and G. Vlaic, *Zeolites*, 1995, **15**, 708.
13 A. Tuel, I. Arcon, N. N. Tusar, A. Meden and V. Kausic, *Microporous Mater*., 1996, **7**, 271.

Communication 8/09399G