A Rapid Synthesis of the Molecular Sieve $AlPO_4$-5 with Aluminium Triisopropoxide

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A rapid method is reported for the hydrothermal synthesis of $AlPO_4$-5 by which the 100% pure crystalline phase is obtained in 90 min at 150 °C using aluminium triisopropoxide, phosphoric acid and tripropylamine in the system free of F^- ions.

The hydrothermal synthesis of $AlPO_4$-5, using pseudoboehmite and aluminium isopropoxide under different conditions of temperature (150–200 °C) and pH (3–4) has been reported[1–3] (Table 1) to take from 8 to 24 h to reach completion. In the presence of F^-, $AlPO_4$-5 synthesis takes 2–9 h.[4] In view of the commercial potential[5] of $AlPO_4$-5 as an adsorbent and catalyst support, a faster low-temperature synthesis is desirable for time and energy efficiency. We now report that by using aluminium isopropoxide in a weakly acidic (pH 6.5–7.0) medium but in the absence of F^-, the hydrothermal synthesis of $AlPO_4$-5 can be achieved at 150 °C in 90 min with a gel composition of $1.5Pr_3N$–Al_2O_3–P_2O_5–$40H_2O$. Aluminium triisopropoxide (BDH) and 85% (*m/m*) orthophosphoric acid (Reidel-dehaen, Germany) were used, with tripropylamine (Merck, Germany) as the templating agent. The products were characterized by X-ray diffraction (Rigaku, Dmax 3), scanning electron microscopy (Jeol JSM-35C) and water adsorption (McBain spring balance).

In a typical synthesis, a slurry of aluminium triisopropoxide in water at 28 ± 1 °C was stirred mechanically for 3 h. Orthophosphoric acid was added to the stirred slurry; stirring

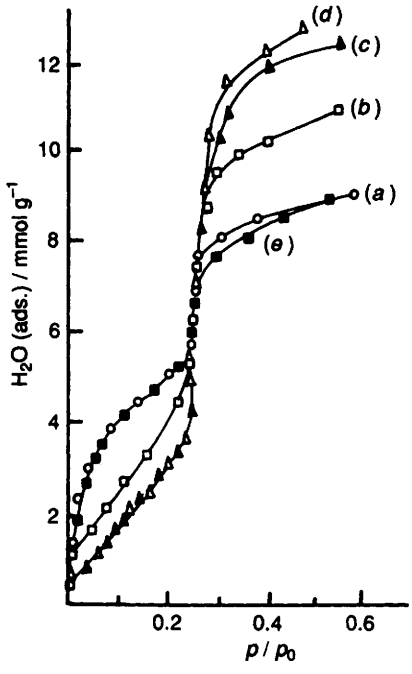

Fig. 1 Water adsorption isotherms at 298 K for $AlPO_4$-5 samples after preparation times of (*a*) 30; (*b*) 60; (*c*) 75; (*d*) 90; and (*e*) 150 min

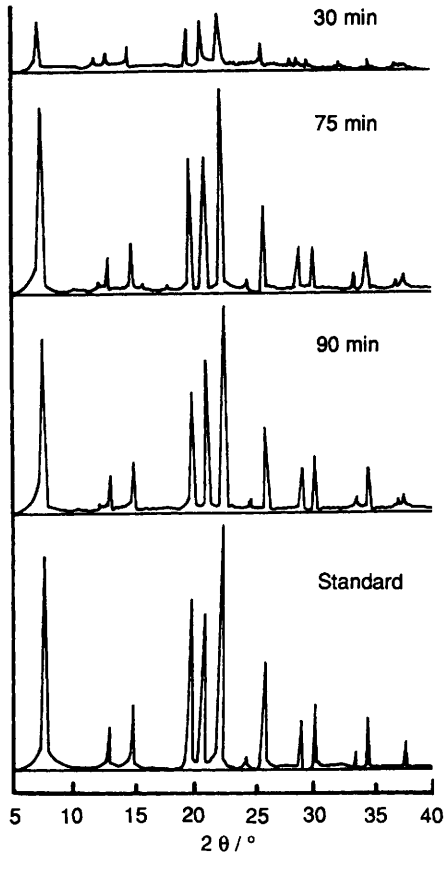

Fig. 2 X-Ray powder diffraction for $AlPO_4$-5 samples after different preparation times

Table 1 Hydrothermal synthesis of $AlPO_4$-5

Al Source	*T*/°C	*t*/h	pH	H_2O/Al_2O_3	Ref.
Pseudoboehmite	150	24	3.0–4.0	40	1(*d*)
Boehmite	200	24	—	—	1(*e*)
Al_2O_3	150	24	3.5	40	1(*f*)
Pseudoboehmite	160	72	3.5	40	1(*g*)
Pseudoboehmite	150	8	4.2	40	2
Al_2O_3, hydrate	150	24	3.4	—	3(*a*)
Al_2O_3, hydrate	190	24	3.5	300–1000	3(*b*)
Pseudoboehmite	200	24	—	—	3(*c*)
Aluminium isopropoxide	170	240	—	318	3(*d*)[a]
Aluminium hydroxide	190	2–9	5.5–7.0	40–100	4[a]

[a] Synthesis in the presence of F^- ions.

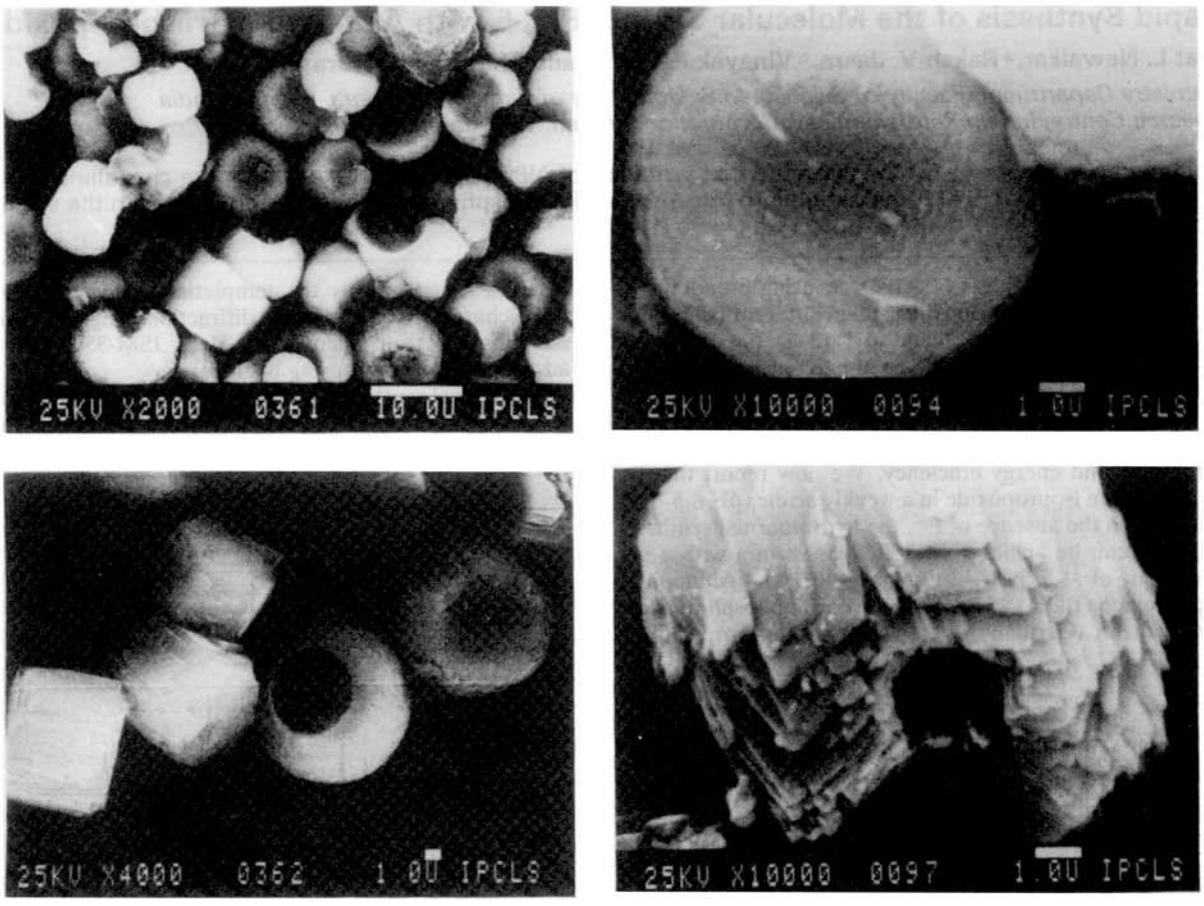

Fig. 3 SEM photographs of $AlPO_4$-5 samples; 90 min preparation time. White bars indicate scales in indicated numbers of microns.

Table 2 X-Ray crystallinity and water adsorption capacity W_{ad} of samples of $AlPO_4$-5 after different crystallization times

t/min	Crystallinity (%)	H_2O (ads.)/ mmol g^{-1} ($p/p_0 = 0.4$)
30	30.4	8.5
60	81.1	10.1
75	98.6	11.9
90	99.6	12.2
150	45.9	8.2
Standard sample	100.0	12.2

was then continued for 2 h. Tripropylamine was added and the mixture was stirred until a homogeneous gel was obtained with a pH of *ca.* 6.7. The gel was heated in a stainless steel autoclave (75 ml) at 1.5 °C min^{-1} to 150 °C. The temperature was then maintained to ±1 °C for the required time. The autoclave was cooled, and the product filtered off, washed with warm distilled water, dried at 110 °C and finally calcined at 540 °C in air for 10–12 h.

To study the progress of crystallization, samples were taken after 30, 60, 75, 90 and 150 min at 150 °C. The XRD patterns and water adsorption isotherms (Figs 1 and 2) show that an $AlPO_4$-5 phase of high purity is obtained after 75 min, the highest purity being obtained after 90 min (see Table 2). The $AlPO_4$-5 sample used as the reference was synthesized under standard conditions[2] from pseudoboehmite. The purity of the standard was established by comparing its XRD data with literature data.[6,7] Water adsorption capacity also is the highest for the 90 min sample, showing that the optimum reaction time for this synthesis is about 90 min. SEM (Fig. 3) of the 90 min sample shows polycrystalline as well as approximately 13 μm aggregates of plate-like morphology, agreeing with observations in the literature.[6]

B. L. N. thanks UGC, New Delhi, for financial assistance.

Received, 20th September 1993; Com. 3/05669D

References

1 (*a*) S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146; (*b*) S. T. Wilson, B. M. Lok and E. M. Flanigen, *US Pat.*, 4310440, 1982; (*c*) E. Jahn, D. Müllar, W. Wieker and J. Richter-Mendau, *Zeolites*, 1989, **9**, 177; (*d*) V. R. Choudhary and D. B. Akolekar, *J. Catal.*, 1987, **103**, 115; (*e*) M. R. Gelsthorpe and C. R. Theocharis, *Catalysis Today*, 1988, **2**, 613; (*f*) B. Hampson, H. F. Leach, B. M. Lowe and C. D. Williams, *Zeolites*, 1989, **9**, 521; (*g*) A. S. T. Chiang, C. K. Lee and Z. H. Chang, *Zeolites*, 1991, **11**, 380.

2 S. T. Wilson, *Stud. Surf. Sci. Catal.*, 1991, **58**, 137.

3 (*a*) X. Ren, S. Komarneni and D. M. Roy, *Zeolites*, 1991, **11**, 142; (*b*) G. Finger, J. Richter-Mendau, M. Bülow and J. Kornatowski, *Zeolites*, 1991, **11**, 443; (*c*) N. J. Tapp, N. B. Milestone and D. M. Bibby, *Zeolites*, 1988, **8**, 183; (*d*) S. Qiu, W. Pang, H. Kessler and J. L. Guth, *Zeolites*, 1989, **9**, 440.

4 Y. Xu, P. J. Maddox and J. M. Thomas, *Polyhedron*, 1989, **8**, 819.

5 D. Barthomeuf and A. deMallmann, *Ind. Eng. Chem. Res.*, 1990, **29**, 1435. D. Barthomeuf, *US Pat.*, 4482776, 1984; 4593150, 1986.

6 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *ACS. Sym. Ser.*, 1983, **218**, 7a.

7 R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, 1989, pp. 289, 303.