Catalysis Letters 7 (1990) 367–376

ORGANIC-FREE VPI-5: SYNTHESIS AND CHARACTERIZATION OF $AlPO_4$-H1

B. DUNCAN, R. SZOSTAK *

Zeolite Research Program, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

K. SORBY

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo 3, Norway

and J.G. ULAN

National Center for Electron Microscopy, Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, U. of California, Berkeley, California 94720, U.S.A.

Received 30 August 1990; accepted 9 October 1990

VPI-5, aluminophosphate synthesis, H1, H1(GTRI)

The aluminophosphate H1 first reported by D'Yvoire in 1961 has been prepared in highly crystalline pure form from a reactive gel system without aging in the absence of an organic additive. Potential seeding in this system was avoided by using new crystallization vessels. Its physical and thermal properties are identical to that of VPI-5. These results indicate that VPI-5 does not represent a new microporous phase but rather H1 prepared in the presence of organic additives.

1. Introduction

In 1982 researchers at the Union Carbide Corporation reported the successful synthesis of a large number of new microporous molecular sieves based on an aluminophosphate framework [1]. Though crystalline aluminophosphate phases had been previously reported, the application of known zeolite synthesis methods, such as the use of organic amines to help promote crystallization, extended the number of structures in the $AlPO_4$ family of materials. In 1988 an 18 member ring $AlPO_4$, identified as VPI-5 [2] was crystallized in the presence of an amine with an X-ray diffraction pattern similar to that of a material called H1, prepared

---

* Individual to whom correspondence should be addressed.

in an organic-free system by D'Yvoire [3] in 1961. The similarity between the diffraction patterns of these two materials raises the question of the role of the organic additive in producing the unique 18 member ring aluminophosphate. The task was undertaken to optimize the H1 phase in the absence of organics in order to determine if H1 and VPI-5 represent the same microporous structure. The preparation of the same molecular sieve framework with and without organic additives is not new as it is well documented in the zeolite literature [4–8].

2. Experimental procedure

H1 was prepared from a reactive aluminophosphate gel system using a modification of the synthesis procedure described by D'Yvoire [3,9]. The optimum batch composition which produces highly crystalline H1 (referred to as H1 (GTRI)) is:

$Al_2O_3 : 0.8\ P_2O_5 : 1\ HCl : 50\ H_2O$.

No aging of the mixture prior to crystallization was necessary. Because of the low pH (ca. 1) of this system, and the high solubility of the aluminum hydroxide used, crystallization of H1 occasionally occurred from clear solutions depending on the Al/P/HCl ratio. New autoclaves were used to limit the possibility of seeding the system with VPI-5 crystals. Crystallization occurred readily from the new autoclaves after 4 hours at temperatures between 120 and 150 ° C. Aluminum hydroxide (Pfalz and Bauer) was used as a source of aluminum, and phosphoric acid (85% Fisher) as the source of phosphorous. By using optical microscopy it was observed that small needle and fan shaped crystals of H1 were produced. Similar morphology is found for VPI-5. Some batches also contained other phases identified as H2 and H3. After synthesis, the crystals were recovered through filtration and dried at room temperature overnight. A portion of the crystalline material was heated to 100 ° C for two hours in dry flowing air, resulting in conversion to a different crystalline material. This new crystal was identified as $AlPO_4$-8 by comparison with the X-ray powder diffraction pattern for $AlPO_4$-8 prepared from similar thermal treatment of a sample of VPI-5 synthesized in the presence of di-n-propylamine [11]. The X-ray powder diffraction data was collected on a Rigaku X-ray powder diffractometer with CuK_α radiation. All spectra were recorded at 60–70% humidity. The infrared spectra were recorded as thin KBr wafers containing approximately 10 wt% sieve using a Perkin-Elmer Infrared Spectrometer Model 698, computer assisted. Adsorption capacities were determined for water and n-hexane using a McBain-Bakr adsorption unit. TGA/DTA were recorded on a Perkin-Elmer TGA/DTA using a heating rate of 10 ° C/min in air.

3. VPI-5 vs. H1: Claims of uniqueness

VPI-5 is prepared from reactive aluminophosphate gels in the presence of organic amines. Di-n-propyl amine cations, tetrabutylammonium cations as well as other amine cations are all shown to encourage crystallization of this material in pure form. In contrast, H1 was prepared from an organic-free reactive aluminophosphate gel as a minor component of a mixture with H2 [3]. A comparison of the X-ray diffraction lines for H1, H2 and VPI-5 are shown in table 1. Claims that VPI-5 is unique from H1 are based on (1) crystallization in the presence of an organic amine and (2) the lack of thermal stability observed for a mixture of H1 and H2 where H1 was reported to convert to tridymite upon

Table 1
Comparison of the X-ray powder diffraction data of $AlPO_4$-H1 [3], VPI-5 [2] and $AlPO_4$-H2 [3] with a sample of high purity H1 (H1 (GTRI)).

H1		H2		H1 (GTRI)		VPI-5	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
16.53	FFF	–	–	16.54	100	16.43	100
–	–	–	–	9.52	2	9.49	2
		8.48	FFF				
8.23	f			8.23	23	8.23	14
6.16	f			6.20	5	6.21	6
		5.87	m				
–	–			5.49	3	5.48	2
		4.96	mf				
–	–	4.74	f	4.75	11	4.75	6
		4.55	fff				
		4.25	f				
–	–	4.09	m	4.12	18	4.08	20
		4.06	FF	4.06	9	4.05	22
–	–	4.04	ff				
3.97	f			3.96	9	3.97	14
3.93	m			3.87	9	3.94	15
–	–	3.75	F	3.77	17	3.77	10
		3.66	F				
–	–	3.64	f	3.60	6	3.64	4
–	–			3.42	1	3.41	2
3.28	m	3.24	m	3.28	18	3.28	16
–	–	3.14	f	3.16	7	3.17	5
–	–	3.08	F	3.08	6	3.08	7
–	–	3.01	f			3.03	4
2.95	f	2.933	ff	2.95	13	2.95	8
–	–	2.875	f	2.90	5	2.90	5
		2.819	mf				
2.74	f			2.74	12	2.74	7
		2.697	mf				

mild heating [3,10,12] and VPI-5 converted to $AlPO_4$-8 [11]. It has been noted by Davis and co-workers that another phase identified by D'Yvoire as H3 in his organic-free crystallization of the aluminophosphates is also a common impurity phase in their VPI-5 synthesis further suggesting that similarities between the D'Yvoire and Davis systems might exist.

D'Yvoire's synthesis of H1 never resulted in a pure single phase which would allow extensive characterization of the material to be undertaken. H2 was found to co-crystallize under conditions employed giving rise to diffraction lines which overlapped with those of H1 making identification of all the lines due to pure H1 impossible from such a mixture (see table 1). Comparing the diffraction pattern for H1 with VPI-5, only the unique H1 lines appear to be reported by D'Yvoire. H2 contains may lines common to both materials which can be seen by comparison of the diffraction lines for a mixture of H1 and H2 with the diffraction pattern reported for VPI-5 (see table 1). In order to further substantiate the claim that VPI-5 and H1 are related, the H1 phase must be optimized from systems producing mixtures of H1, H2 and H3.

4. Comparison of VPI-5 and H1 (GTRI)

D'Yvoire's H3, H4 and H5 in addition to VPI-5 can be crystallized from reactive aluminophosphate gels containing dipropylamine. To prove the similarity between H1 and VPI-5, we prepared H1 in high purity without the presence of an organic through optimization of D'Yvoire's synthesis [3,9]. HCl, an impurity present in many of the early preparations of $Al(OH)_3$, was deliberately added in order to examine the effect such an impurity would have on influencing the course of crystallization. The interrelationship between D'Yvoire's H1, H2, H3 and H4 when the three parameters, Al_2O_3, P_2O_5 and HCl, were varied are shown in table 2. Optimization of the H1 phase was achieved in alumina rich gels with

Table 2
Parameter study in the synthesis of D'Yvoire's aluminophosphates *

Al_2O_3	P_2O_5	HCl	H_2O	Time (hr)	Temp. (°C)	Product
1	0.6	0.1	50	4	145	H2/H3
1	0.6	0.5	50	4	145	H1/H3
1	0.8	0.1	50	4	140	(H1)/H2/H3
1	0.8	0.3	50	4	140	H1/H2/(H3)
1	0.8	0.8	50	4	140	H1/(H2)/(H3)
1	0.8	1.0	50	4	140	H1
1	0.8	1.0	50	18	140	H4
1	1.2	0.1	50	4	145	H3/(H4)

* products listed in parentheses indicate the presence of that phase as a minor impurity.

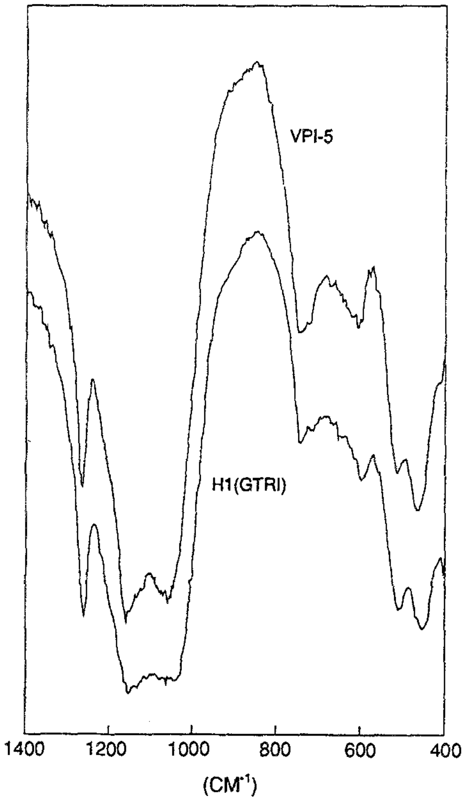

Fig. 1. Mid-infrared spectra of H1 (GTRI) (bottom) and VPI-5 (top) showing the similarity between the two materials.

higher concentrations of HCl. No phases, other than those reported by D'Yvoire were observed to form in this system.

As shown in table 1, the X-ray powder diffraction data for (H1 (GTRI)) is consistent with that of VPI-5 also shown in the table. The infrared framework vibrations between 1400 and 400 cm^{-1} which are unique to VPI-5 are identical to those of H1 (GTRI). The infrared spectrum of H1 (GTRI) and VPI-5 are shown in fig. 1. The TGA/DTA for H1 (GTRI), shown in fig. 2, is also characteristic of VPI-5. The adsorption properties of H1 were examined. The water adsorption capacity is comparable to that of VPI-5 (ca. 25 wt% H_2O adsorbed), and the adsorption of n-hexane was less than 3 wt%. The low adsorption capacity stems from pore closure in the material due to partial conversion to $AlPO_4$-8 during the activation stage of the adsorption analysis. This was confirmed by X-ray diffraction showing the presence of 10% $AlPO_4$-8 which was generated from H1 (GTRI) in the adsorption unit. This type of pore closure behavior because of $AlPO_4$-8 intergrowths in the crystal is also commonly observed in samples of VPI-5 prepared in the presence of di-n-propylamine [11]. DPA prepared VPI-5 also has absorption capacities for H_2O and n-hexane of 25 and 3 wt% respectfully.

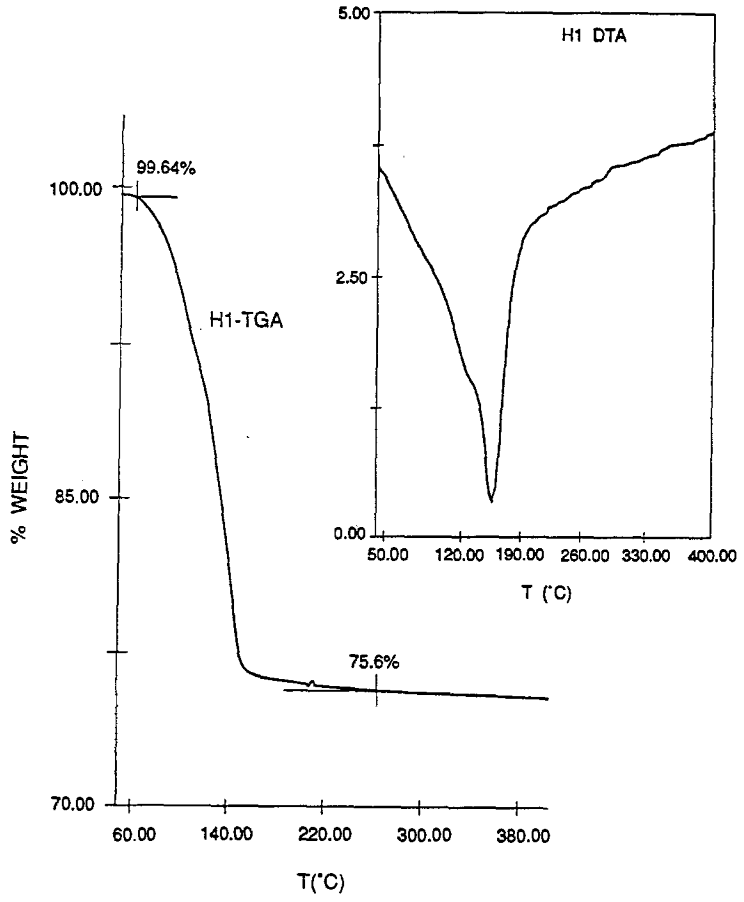

Fig. 2. TGA/DTA trace between room temperature and 400 °C for H1 (GTRI) taken in air with a heating rate of 10 °C/min. Similar water loss behavior is also observed for VPI-5 in this range.

The thermal behavior of this material has also been examined. High purity samples of H1 (GTRI) do not convert to tridymite upon thermal treatment but instead convert to $AlPO_4$-8, a property previously shown to be unique to VPI-5 [11]. The X-ray powder diffraction patterns for H1 (GTRI) and thermally treated H1 (GTRI) [a.k.a. $AlPO_4$-8] is shown in fig. 3a and 3b. In samples containing a mixture of H1 with H2 with $H1 \cong H2$ (fig. 3c), thermal treatment produces only weak $AlPO_4$-8 lines along with strong reflections coincident with tridymite (fig. 3d). For samples were $H1 \ll H2$, only the tridymite lines would readily be observed. Thus the low concentration of H1 in D'Yvoire's mixtures may explain the possible earlier misassignment of the H1 thermal product.

Based on (1) the extensive information available in the literature on the role of the organic in crystallizing zeolite molecular sieves, (2) the preparation of a pure sample of H1 prepared without the use of an organic additive with physical properties shown to be characteristic of VPI-5, and (3) the similarity between the

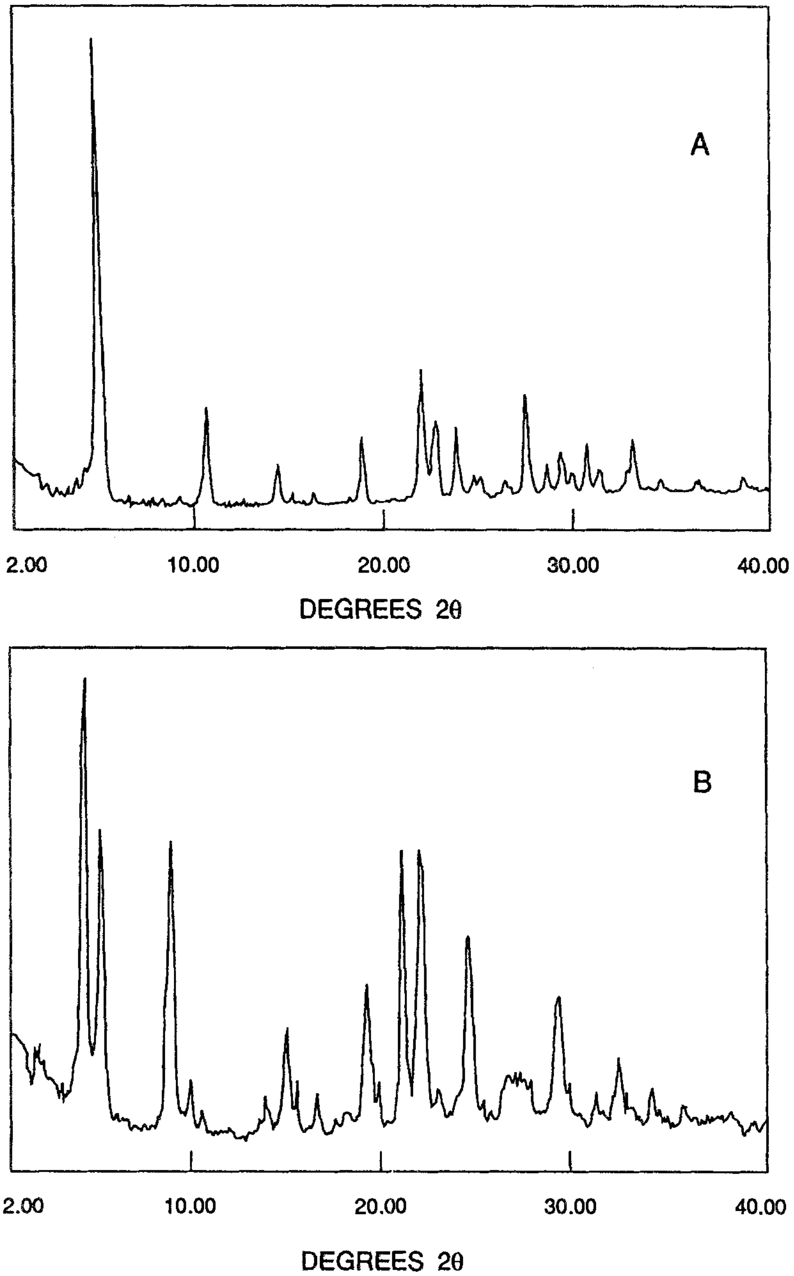

Fig. 3. X-ray powder diffraction patterns of (A) high crystallinity, high purity, H1 (GTRI), (B) thermally treated (A) (100 ° C, 2 hours) with pattern characteristic of $AlPO_4$-8, (C) mixture of H1 and H2, (D) thermally treated (C) (100 ° C, 2 hours). Note the intensity of the three peaks in the center of the diffraction pattern in (D); these are coincident with tridymite. The AlPO-8 lines are broad and barely discernable in this mixture of thermally treated H1 and H2 (arrows indicate major $AlPO_4$-8 peaks).

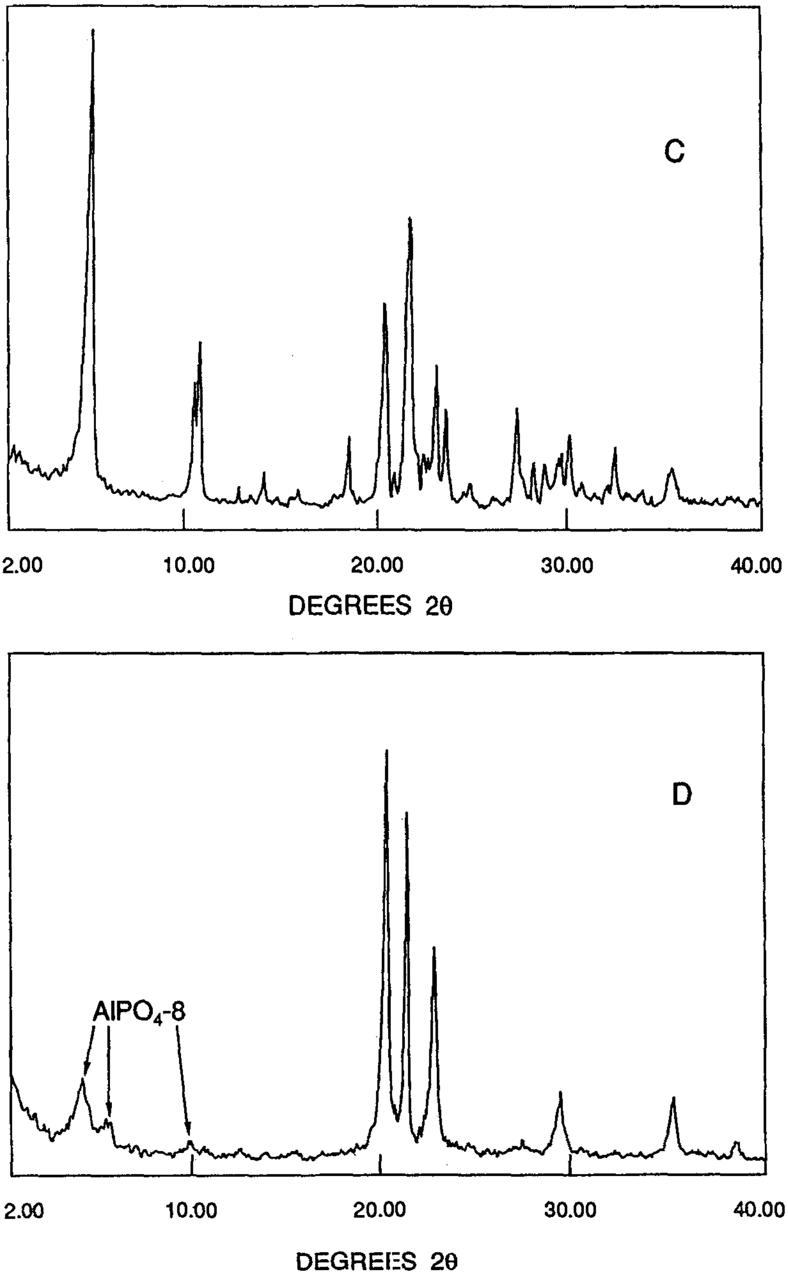

Fig. 3 (continued).

thermally unstable VPI-5 phase which readily converts to $AlPO_4$-8 upon heating to 100 °C [11] and organic-free H1, it must be concluded that VPI-5 and H1 do not differ. VPI-5 and H1 represent the same crystalline phase.

References

[1] S. Wilson, B. Lok and E.M. Flanigen, US 4, 310, 440 (1982).

[2] M.E. Davis, C. Saldarriaga, C. Montes, J. Garces and C. Crowder, Zeolites 8 (1988) 362;
M.E. Davis, C. Montes, P.E. Hathaway, J.P. Arhancet, D.L. Hasha and J.M. Garces, J. Am. Chem. Soc. 111 (1989) 3919.

[3] F. D'Yvoire, Bull. Soc. Chem., Fr., (1961) 1762.

[4] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification* (Van Nostrand-Reinhold, New York, 1989).

[5] G.T. Kerr, Inorg. Chem. 5 (1966) 1537.

[6] P.A. Jacobs and J.A. Martens, *Synthesis of high silica aluminosilicate zeolites*, Studies in Surface-Science and catalysis, Vol. 33 (Elsevier, NY, 1987).

[7] V.P. Shiralkar and A. Clearfield, Zeolites 9 (1989) 363.

[8] J.M. Berak and R. Mostowicz, in: *Zeolites: Synthesis, Structure, Technology, Application*, Studies in Surface Science and Catalysis, Vol. 24, eds. B. Drzaj et al. (Elsevier, NY, 1985) 47.

[9] R. Szostak, B. Duncan, K. Sorby and J.G. Ulan, *MRS Proceedings, Symposium S*, Fall 1990.

[10] M.E. Davis, C. Montes, P.E. Hathaway, J.M. Garces, in: *Zeolites: Facts, Figures, Future*, Studies in Surface Science and Catalysis 49A (1989) 199;
Paper presented at the 8 th International Zeolite Conference, Amsterdam, The Netherlands, July 10-14, 1989;
M.E. Davis, C. Montes, J.M. Garces, *Zeolite Synthesis*, ACS Symposium Series 398, ACS, Washington, D.C., 1989, 291.

[11] K. Sorby, R. Szostak, J.G. Ulan and R. Gronsky, Catal. Lett. 6 (1990) 209.

[12] M.E. Davis and D. Young, in: *Int. Sym. on Chem. of Microporous Crystals*, Tokyo (in press) (1990).