

Synthesis and Characterization of the Novel Molecular Sieve CFSAPO-1

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Abstract. A novel type of molecular sieve named CFSAPO-1 was synthesised hydrothermally in a system of MA(methylamine)– Al_2O_3 – P_2O_5 – SiO_2 – H_2O at 150°C . The molar composition of reactants was: MA : Al_2O_3 : P_2O_5 : SiO_2 : H_2O = (0.8–1.2) : 1 : (0.8–1.2) : (0.4–3) : 40. XRD, IR, thermoanalysis, and adsorption studies show that the original product CFSAPO-1 is transformed into a form with molecular sieve properties after calcination. The free dimension of the adsorption window of the form is 5.8–6.2 Å. There were no distinctly thermal effects on the DTA curve at 600°C and 800°C related to two transformations detected by X-ray diffraction.

Key words: Molecular sieves, silicophosphoaluminate, CFSAPO-1.

1. Introduction

At the beginning of this decade, a new class of molecular sieves which were different from aluminosilicate zeolites were prepared. The Union Carbide Corporation first reported the AlPO_4 molecular sieves in 1982 [1] and the silicophosphoaluminate molecular sieves (SAPO) in 1984 [2, 3]. SAPO show interesting framework structures like AlPO_4 molecular sieves and ion-exchange properties. Recently, a series of aluminophosphate molecular sieves with Fe, Mg, Zn, Co, and Mn were reported [4, 5]. The synthesis, chemistry and catalysis of these nonaluminosilicate molecular sieves are being studied because of their special structures and properties [6, 7].

A novel type of silicophosphoaluminate named CFSAPO-1 was synthesised hydrothermally in a system of Al_2O_3 – P_2O_5 – SiO_2 – H_2O with the simplest amine–methylamine (MA) added as a template. CFSAPO-1 possesses a characteristic X-ray powder diffraction pattern. The original CFSAPO-1 was transformed into a form with molecular sieve properties upon heating to a certain temperature.

2. Synthesis of CFSAPO-1

2.1. RAW MATERIALS

Alumina source: pseudoboehmite, produced by Changling Petroleum Process Plant ($\text{Al}_2\text{O}_3 = 59.2\%$). Phosphorous source: orthophosphoric acid ($\text{H}_3\text{PO}_4 = 85.3\%$). Silica source: silicasol ($\text{SiO}_2 = 24.52\%$, $\text{Na}_2\text{O} = 0.644\%$). MA: MA aqueous solution of reagent grade ($\text{MA} = 38.2\%$).

2.2. SYNTHESIS

A reactant mixture was prepared by combining pseudoboehmite with water, orthophosphoric acid, silicasol, and MA in that order. After the addition of each chemical, the reactant was stirred until formation of a homogeneous mixture was achieved. Finally, the mixture was poured into a stainless steel autoclave with 30 cm³ volume and heated at an assigned constant temperature with a precision of $\pm 2^\circ\text{C}$ in an oven. The solid product was washed with water, filtered, and then dried by IR lamp.

2.3. CRYSTALLIZATION OF CFSAPO-1

Table I shows data related to crystallization experiments.

Unwanted products are formed at higher temperatures (200°C) or lower temperatures (120°C). The best reaction temperature is about 150°C with a reaction period of 23 h. When

Table I. Synthesis examples

No.	Molar composition of reactants					Reaction conditions		Phases of product
	Al ₂ O ₃	P ₂ O ₅	SiO ₂	MA	H ₂ O	Temperature (°C)	Period (h)	
1	1	1	0.4	1	40	120	144	CFSAPO-1 + unknown impurity
2	1	1	0.4	1	40	150	23	CFSAPO-1
3	1	1	0.4	1	40	200	23	CFSAPO-1 + unknown impurity
4	1	1	1	1	40	150	23	CFSAPO-1 + unknown impurity
5	1	1.2	1	1	40	150	23	CFSAPO-1
6	1	1.2	1	1.2	40	150	29	CFSAPO-1
7	1	0.8	1	1	40	150	23	CFSAPO-1
8	1	1	1	1.2	40	150	23	CFSAPO-1
9	1	1	1	0.8	40	150	23	CFSAPO-1
10	1	1	1	0.8	40	150	72	CFSAPO-1 + Tridymite ^a
11	1	1	2	1	40	150	23	CFSAPO-1
12	1	1	2	1	40	150	72	CFSAPO-1
13	1	1	3	1	40	150	72	CFSAPO-1

^a Tridymite is a silicophosphoaluminate with the structure of AlPO₄ tridymite.

the molar composition of SiO₂ was higher than 1, the product purity was influenced by the concentration of MA but not by that of P₂O₅ and SiO₂. The molar composition of the reaction mixture for CFSAPO-1 crystallization is as follows: MA:Al₂O₃:P₂O₅:SiO₂:H₂O = (0.8–1.2):1:(0.8–1.2):(0.4–3):40.

3. Properties of CFSAPO-1

3.1. MORPHOLOGY AND OPTICAL PROPERTIES

The microphoto of CFSAPO-1 (see Figure 1) was taken with a Shimadzu S-520 scanning electron microscope. It shows that spherical crystals of CFSAPO-1 up to a size of 150–200 μm are aggregates of small rectangular plates. Upon investigation by an optical microscope with crossed Nicols and a gypsum plate inserted, a weak birefringence of CFSAPO-1 was found.



Fig. 1. Scanning electron micrograph of CFSAPO-1.

3.2. CHEMICAL COMPOSITION

The results of chemical analysis of CFSAPO-1 are as follows: $\text{Al}_2\text{O}_3 = 31.99\%$, $\text{P}_2\text{O}_5 = 44.03\%$, $\text{SiO}_2 = 6.07\%$, $\text{MA} = 10.74\%$, $\text{H}_2\text{O} = 7.17\%$. The molar composition of CFSAPO-1 is: $1.10 \text{ MA} \cdot 1.00 \text{ Al}_2\text{O}_3 \cdot 0.99 \text{ P}_2\text{O}_5 \cdot 0.32 \text{ SiO}_2 \cdot 1.27 \text{ H}_2\text{O}$.

3.3. THERMOANALYSIS

Thermograms of the original CFSAPO-1 in air (see Figure 2) were performed with a Rigaku PTC-10A thermoanalysis instrument at $10^\circ\text{C}/\text{min}$ from room temperature to 1000°C .

Differential thermal analysis of CFSAPO-1 shows two endotherms at 78°C and 258°C accompanied by a weight loss. The endotherms at 78°C and 258°C may be associated with dehydration and deamination, respectively. In the range 258°C to 1000°C , the DTA curve does not show distinct thermal effects, but X-ray diffraction patterns indicate that there are two phase changes in this temperature range.

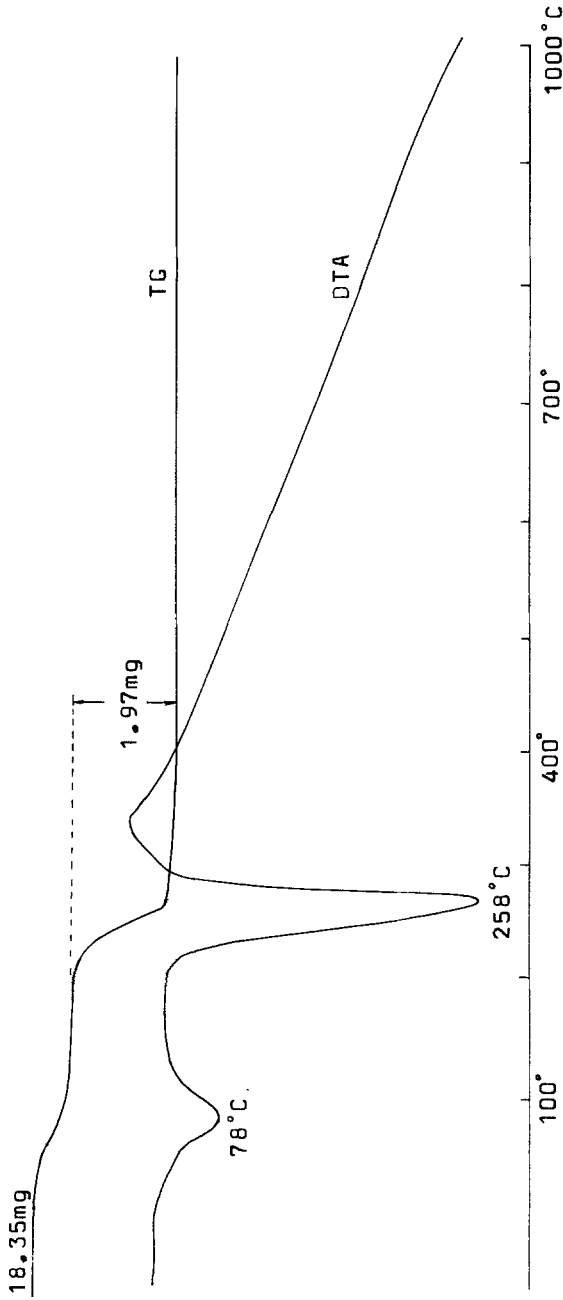


Fig. 2. Thermograms of the original product of CFSAPO-1.

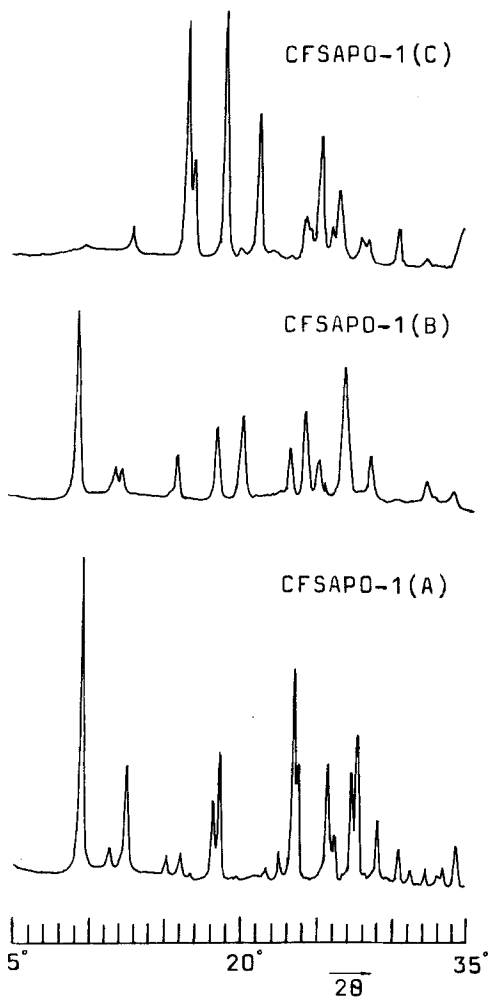


Fig. 3. XRD patterns of CFSAPO-1.

3.4. X-RAY POWDER DIFFRACTION

X-ray powder diffraction patterns (Figure 3) were obtained with a Rigaku D/MAX-IIA diffractometer. Experimental conditions: $\text{CuK}\alpha$ 40 kV 20 mA, scan speed $4^\circ/\text{min}$, scan range $5^\circ\text{--}35^\circ$ (2θ).

There is no change in the framework of CFSAPO-1 calcined at 140°C , but two transformations into more stable forms occur in the range $300^\circ\text{C}\text{--}800^\circ\text{C}$, and a structure of AlPO_4 tridymite is formed on heating above 800°C . The original product and the sample calcined at 140°C are called CFSAPO-1(A). Forms calcined in the range of $300^\circ\text{C}\text{--}600^\circ\text{C}$ and $600^\circ\text{C}\text{--}800^\circ\text{C}$ are called CFSAPO-1(B) and CFSAPO-1(C), respectively. The characteristic X-ray powder diffraction data of CFSAPO-1(A), (B), and (C) are given in Table II. The transformations at 600°C and 800°C detected by diffraction do not show distinctly thermal effects on the DTA curve.

Table II. X-ray powder diffraction data of CFSAPO-1

CFSAPO-1(A)			FSAPO-1(B)			CFSAPO-1(C)		
2θ (deg)	d (Å)	Relative intensity	2θ (deg)	d (Å)	Relative intensity	2θ (deg)	d (Å)	Relative intensity
10.20	8.67	100	9.88	8.95	100	9.83	9.00	2
10.40	8.51	60	12.18	7.27	25	13.07	6.77	10
11.87	7.46	7	12.61	7.02	18	16.70	5.31	89
13.00	6.81	31	15.62	5.67	6	17.18	5.16	37
15.42	5.75	7	16.05	5.52	34	19.27	4.61	100
15.54	5.70	9	18.56	4.78	56	20.38	4.36	4
16.49	5.38	8	20.11	4.42	68	21.54	4.13	41
17.12	5.18	2	20.93	4.24	5	23.73	3.75	2
18.63	4.76	25	22.38	3.97	4	24.56	3.62	17
19.06	4.66	37	22.94	3.88	8	25.65	3.47	45
21.43	4.15	1	23.63	3.77	40	26.37	3.38	10
22.10	4.02	3	24.58	3.62	66	26.82	3.32	25
23.02	3.86	8	25.41	3.51	26	28.28	3.16	10
23.93	3.72	62	25.95	3.43	10	28.82	3.10	8
24.22	3.67	36	27.06	3.30	64	30.73	2.91	12
24.48	3.64	19	27.37	3.26	92	32.60	2.75	3
25.72	3.46	13	28.39	3.14	7			
26.16	3.41	35	28.88	3.09	26			
26.62	3.35	13	30.80	2.90	3			
27.73	3.22	32	32.30	2.77	17			
28.11	3.17	39	32.92	2.72	8			
29.07	3.07	3	34.07	2.63	11			
29.43	3.03	18						
30.02	2.98	3						
30.87	2.90	10						
31.62	2.83	4						
32.63	2.74	6						
33.39	2.68	4						
33.79	2.65	6						
34.69	2.59	11						

^a Rigaku diffractometer, CuK α radiation.

3.5. INFRARED SPECTRA

IR spectra were recorded with a Perkin-Elmer 983G IR spectrometer (Figure 4) in the range 4000–200 cm^{-1} . Discs were made by mixture with KBr. The IR spectrum of CFSAPO-1(A) is complicated, particularly in the region 1200–200 cm^{-1} . It may mean that CFSAPO-1(A) possesses an imperfect tetrahedral framework. The vibration at 3240 cm^{-1} is assigned to an N–H stretch, and absorptions at 1511 cm^{-1} and 1469 cm^{-1} are assigned to N–H bend vibrations. After calcination, these three vibrations disappear in the IR spectrum of CFSAPO-1(B) since the methylamine is no longer present.

After calcination at 500 °C for 8 h, the number of IR vibrations in CFSAPO-1(B) is reduced, and they show a characteristic pattern of a tetrahedral framework structure. The strongest vibration at 1112 cm^{-1} can be assigned to an asymmetric stretch of the aluminophosphate tetrahedron, and a strong absorption at 478 cm^{-1} to a bending vibration of T–O bonds [8, 9]. The IR Spectrum of CFSAPO-1(C) formed after calcination at 700 °C for 8 h also shows

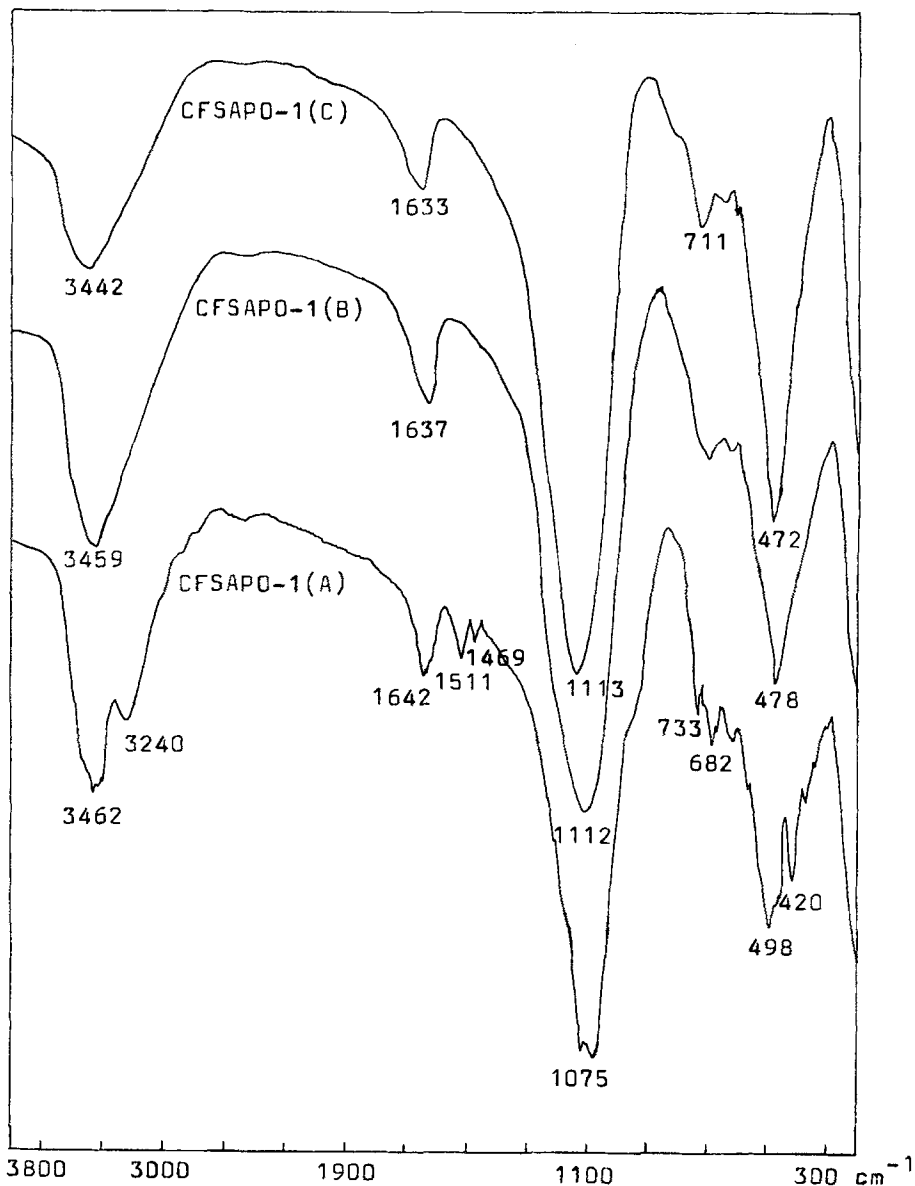


Fig. 4. IR spectra of CFSAPO-1.

characteristics of a tetrahedral structure just like CFSAPO-1(B). Adsorption experiments indicated that CFSAPO-1(C) was a dense form without a porous structure, adsorbing water only at a very low level. The vibrations of O-H bonds at 1633 cm^{-1} and 3442 cm^{-1} are probably caused by water adsorbed on the outer surface.

3.6. ADSORPTION PROPERTIES

Adsorption isotherms of CFSAPO-1(B) shown in Figure 5 were obtained with a Sartorius 4433 ultra-microbalance. It shows that CFSAPO-1(B) possesses a structure with

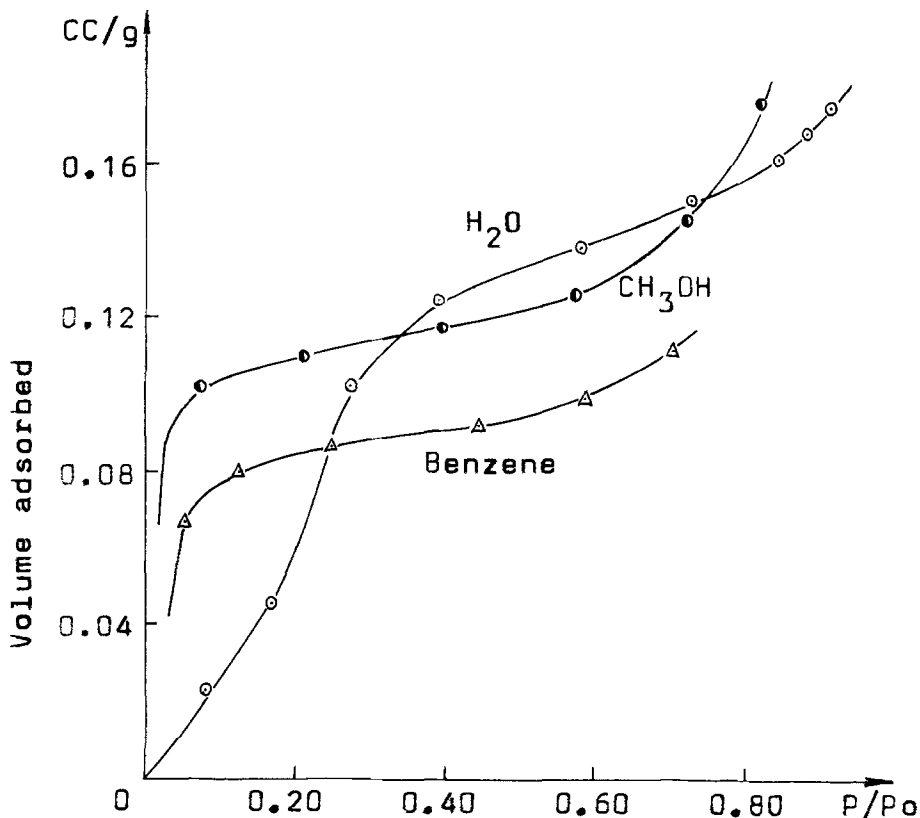


Fig. 5. Adsorption isotherms of CFSAPO-1(B).

the characteristics of a molecular sieve. Since the adsorption capacity of cyclohexane is about 0.5%, the free dimension of the adsorption window of CFSAPO-1(B) is between 5.8–6.2 Å. According to the adsorption capacities of water, methanol, and benzene, the major adsorption cavities of CFSAPO-1(B) may be constructed by 10 or 12 rings.

4. Conclusions

CFSAPO-1(B) possesses molecular sieve properties with a pore window size of 5.8 to 6.2 Å. There were several SAPO molecular sieves reported [2,3], such as SAPO-11 (Pr₂NH as template, 6 Å in window size), SAPO-31 (Pr₂NH, > 6.2 Å), SAPO-37 (TMAOH and TPAOH, > 6.2 Å), and SAPO-41 (TBAOH, 6.2 Å). However, CFSAPO-1 was prepared in a system with methylamine. This has not been reported in references on the synthesis of silicophosphoaluminate molecular sieves [2,3]. Since the X-ray powder pattern of CFSAPO-1 is entirely different from that of all other AlPO₄ and SAPO molecular sieves [1,2,3], including SAPO-11, 31, 37, and 41, it demonstrates the existence of a novel framework structure. This indicates that SAPO molecular sieves with larger pore sizes could be synthesised by using a smaller organic base as a template.

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References

1. S. T. Wilson, B. M. Lok, and E. M. Flanigen: *European Patent* **43**, 562 (1982).
2. B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan, and E. M. Flanigen: *U.S. Patent* **4**, 440, 871 (1984).
3. S. W. Kaiser: *European Patent* **105**, 512 (1984).
4. C. A. Messina, B. M. Lok, and E. M. Flanigen: *European Patent* **131**, 946 (1985).
5. S. T. Wilson and E. M. Flanigen: *European Patent* **132**, 708 (1985).
6. S. T. Wilson, B. M. Lok, E. M. Flanigen, C. A. Messina and R. T. Cannan: *ACS Symposium Series*, No. 218 (Intrazeolite Chemistry) (1983), pp. 79–106.
7. E. G. Derouane and R. Ballmoos: *European Patent* **147**, 991 (1985).
8. D. W. Breck: *Zeolite Molecular Sieves*, Wiley, New York (1972), pp. 415–424.
9. Y. Long, L. Dong, and Z. Gao: *Chem. J. Chinese Univ.* **7**, 100 (1986).