

Synthesis and Characterization of a Novel Crystalline AlPO_4 Molecular Sieve, CFAP-7

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(Received: 19 August 1986; in final form: 5 January 1987)

Abstract. The novel crystalline aluminophosphate CFAP-7, having a characteristic X-ray powder diffraction pattern, has been synthesized hydrothermally in a system consisting of di-*n*-butylamine– $(\text{NH}_4)_2\text{O}$ – P_2O_5 – Al_2O_3 – H_2O at 120 to 140°C, the P_2O_5 and Al_2O_3 sources of which were provided by $(\text{NH}_4)_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3$ in aqueous solution, respectively. Investigations by DTA, TG, DTG, XRD, and IR indicate transformation of the original product (form A) into more stable crystal forms B and C on heating at about 180°C and 240°C, respectively, while liberating water and amine. Isotherms for the adsorption of water and methanol at 23°C show that both form B and form C are molecular sieves with a window dimension of 4.3–4.9 Å, and a methanol volume adsorption greater than that of water.

Key words: Aluminophosphate, molecular sieves, CFAP-7.

1. Introduction

Aluminophosphate molecular sieves represent a new class of microporous inorganic crystalline material. In 1982, Wilson *et al.* [1] first published a patent on the synthesis of about 20 AlPO_4 molecular sieves. Since then a series of aluminophosphates containing Si^{4+} , Fe^{3+} , and M^{2+} (M represents Mg, Co, Zn and Mn) have been prepared and named SAPO [2, 3, 4], FAPO [5] and MePO [6], respectively. Al_2O_3 sources were pseudoboehmite, $\text{Al}(\text{OH})_3$, or aluminum isopropoxide, and the P_2O_5 source was orthophosphoric acid H_3PO_4 . In an investigation on hydrothermal crystallization of the P_2O_5 – Al_2O_3 – H_2O system, the author [7] discovered that aluminophosphate molecular sieves could be crystallized in a reaction mixture prepared from $(\text{NH}_4)_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3$ aqueous solution with certain amounts of amine. Now we report a novel crystalline aluminophosphate, which has a characteristic X-ray powder diffraction pattern, has been synthesized in such a mixture with di-*n*-butylamine, and has been named CFAP-7.

2. Synthesis of CFAP-7

CFAP-7 was hydrothermally synthesized in the DBA (di-*n*-butylamine)– $(\text{NH}_4)_2\text{O}$ – Al_2O_3 – P_2O_5 – H_2O system. The sources of P_2O_5 and Al_2O_3 were $(\text{NH}_4)_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ as a crystalline powder and $\text{Al}_2(\text{SO}_4)_3$ solution (Al_2O_3 –7.035%), respectively. All chemicals used were reagent grade.

According to the composition of the reaction mixture, a definite amount of $\text{Al}_2(\text{SO}_4)_3$ solution was mixed with $(\text{NH}_4)_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ with stirring to produce a mixture. Then a fixed amount of DBA was added to the mixture with vigorous stirring until a homogeneous gel was formed. The gel was then poured into a small autoclave with a volume of 20 or 40 cm^3 and

Table I. Synthesis examples (DBA-(NH₄)₂O-Al₂O₃-P₂O₅-H₂O system)

Example	Molar composition of reactant mixture					Conditions		Material ^a of liner	Initiation of crystallization	Phase of product
	DBA	(NH ₄) ₂ O	P ₂ O ₅	Al ₂ O ₃	H ₂ O	Temp. (°C)	Period (h)			
1	1	3	1	1	67	120	64	G	Spontaneously	CFAP-7
2	1	3	1	1	67	140	60	G	Spontaneously	CFAP-7
3	1	3	1	1	67	160	44	G	Spontaneously	CFAP-7 + CFAP-18 ^b
4	1	3	1	1	67	180	24	G	Spontaneously	CFAP-18 + CFAP-6 ^c + CFAP-7
5	1	3	1	1	67	200	24	G	Spontaneously	CFAP-6
6	1	3	1	1	67	200	24	S	Spontaneously	CFAP-18
7	1	3	1	0.7	49	140	24	G	Seeds of CFAP-7	CFAP-18
8	1	3	1	1	67	140	24	G	Seeds of CFAP-7	CFAP-7
9	1	3	1	1.2	80	140	24	G	Seeds of CFAP-7	CFAP-7 + CFAP-18
10	1	3	1	1.4	92	140	72	G	Seeds of CFAP-7	CFAP-7 + unknown phase 1 ^d
11	1	2.1	0.7	1	66	140	48	G	Seeds of CFAP-7	CFAP-7 + unknown phase 2 ^e
12	1	3.9	1.3	1	69	140	24	G	Seeds of CFAP-7	CFAP-18
13	1	4.5	1.5	1	70	140	24	G	Seeds of CFAP-7	CFAP-18
14	0.7	3	1	1	67	140	24	G	Seeds of CFAP-7	CFAP-7
15	1.2	3	1	1	67	140	24	G	Seeds of CFAP-7	CFAP-18 + CFAP-7
16	1.4	3	1	1	67	140	24	G	Seeds of CFAP-7	CFAP-18

^a G-GG17 hard glass, S-stainless steel.

^b CFAP-18, a novel unstable AlPO₄ phase with the following major X-ray diffraction data (Å): 7.56(M), 6.73(V-VS), 5.96(VS), 4.66(M), 4.57(M), 4.19(W-M), 4.13(M), 3.75(W-M), 3.03(W), 2.80(M).

^c CFAP-6, a novel AlPO₄ molecular sieve with the following major X-ray diffraction data (Å): 9.24(S-VS), 8.57(VS), 5.06(M), 4.14(M), 3.63(M), 3.33(M).

^d Unknown phase 1 with the following major X-ray diffraction data (Å): 5.02, 3.50, 3.02, 2.99.

^e Unknown phase 2 with the following main X-ray diffraction data (Å): 10.27, 5.21, 5.01, 4.72, 4.60, 4.33, 3.50, 3.02, 3.00.



Fig. 1. Scanning electron micrograph of CFAP-7.

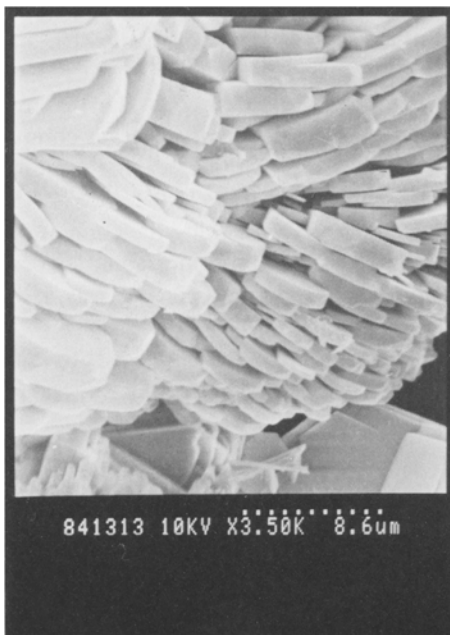


Fig. 2. Scanning electron micrograph of CFAP-6.

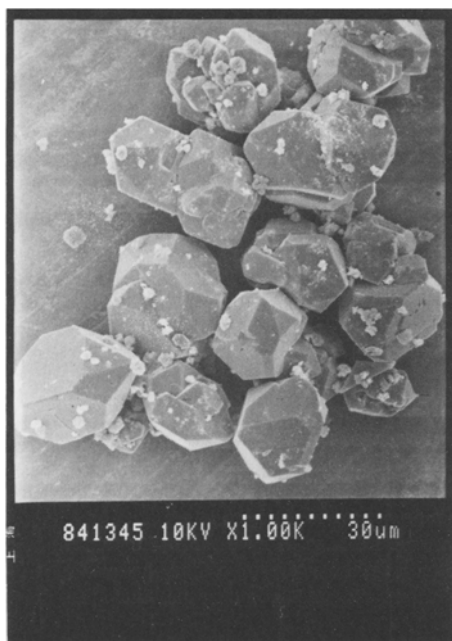


Fig. 3. Scanning electron micrograph of CFAP-18.

lined with GG 17 glass or stainless steel. The autoclave was heated in an oven and a hydrothermal reaction under static conditions was carried out at constant temperature with an accuracy of $\pm 2^\circ\text{C}$. The reaction product was filtered, washed, and dried by IR lamp, and then identified by X-ray powder diffraction.

Examples of syntheses are shown in Table I. It was apparent that the major factors influencing the formation of CFAP-7 were reaction temperature and reactant composition. A good yield of CFAP-7 was obtained in the range of 120 to 140°C for the same reaction composition. Other crystalline aluminophosphates, such as CFAP-6 [8] and CFAP-18, were formed at higher temperature as shown for samples 1 to 5. By varying the content of Al_2O_3 (samples 7 to 10), P_2O_5 (11 to 13) and DBA (14 to 16), some impurities could be produced. Molar composition of the reaction mixture suitable for preparing CFAP-7 was as follows: $\text{DBA} : (\text{NH}_4)_2\text{O} : \text{P}_2\text{O}_5 : \text{Al}_2\text{O}_3 : \text{H}_2\text{O} = (0.7-1.0) : 3 : 1 : 1 : 67$.

The use of GG 17 glass as the autoclave liner and addition of CFAP-7 seeds to initiate the crystallization led to a more pure CFAP-7, with better reproducibility and a decrease in the time of reaction.

3. Characterization of CFAP-7

3.1. MORPHOLOGY

Scanning electron microscopy shows block aggregates of CFAP-7 up to 10–15 μm consisting of small plates with a thickness of less than 1 μm (see Figure 1). In comparison with CFAP-7 there are entirely different habits for CFAP-6 [8] and CFAP-18, as shown in Figures 2 and 3.

X-RAY PATTERNS

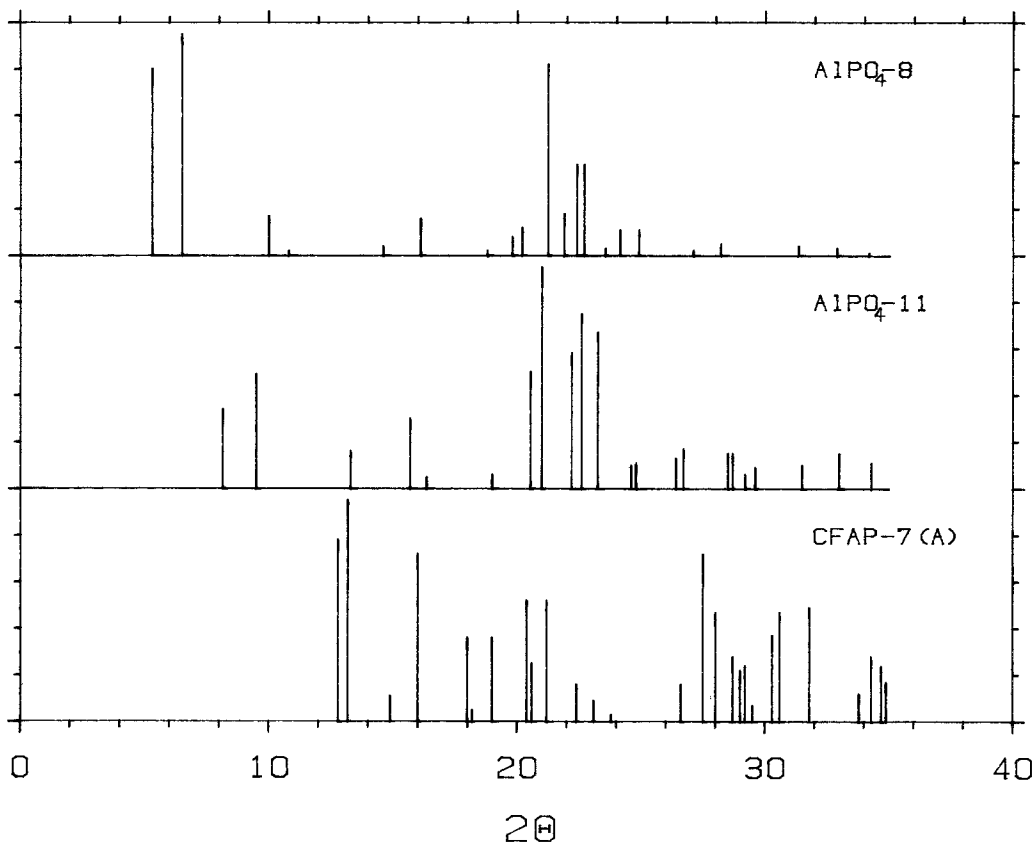


Fig. 4. X-ray powder diffraction patterns.

3.2. CHEMICAL COMPOSITION

Analysis of the original CFAP-7 product by chemical methods gave the following results: $\text{Al}_2\text{O}_3 = 32.60\%$, $\text{P}_2\text{O}_5 = 43.25\%$, $\text{N} = 2.69\%$, $\text{DBA} = 22.87\%$, $\text{H}_2\text{O} = 1.29\%$. From this, the CFAP-7 framework possesses the molar composition $\text{P}_2\text{O}_5 : \text{Al}_2\text{O}_3 = 0.95 : 1$.

3.3. X-RAY POWDER DIFFRACTION AND THERMAL ANALYSIS

The X-ray powder diffraction pattern of the original CFAP-7 product is entirely different from that of $\text{AlPO}_4\text{-8}$ and $\text{AlPO}_4\text{-11}$ prepared in the di-*n*-butylamine- $\text{P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ system by Wilson *et al.* [1] (see Figure 4). It is also different from the pattern of all other AlPO_4 [1] and SAPO [2,3,4] molecular sieves reported.

DTA, TG, and DTG curves for CFAP-7 at $10^\circ\text{C min}^{-1}$ in N_2 (shown as Figure 5) indicate three endotherms at 178, 193, and 273°C with an accompanying 22.2% weight loss. X-ray powder diffraction patterns of samples calcined at 170 and 240°C for 3 h, respectively, are evidently different from that of the original CFAP-7 product. These facts verified that the more

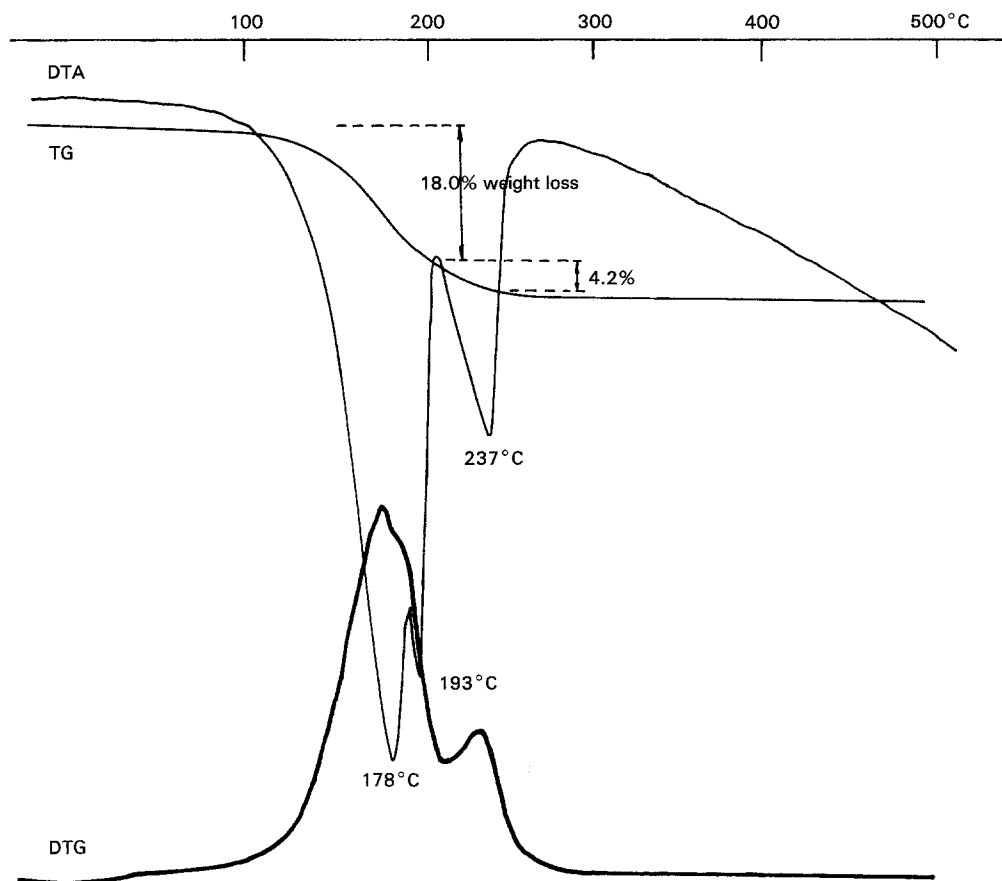


Fig. 5. Thermograms of the original product of CFAP-7.

stable crystal forms were transformed from the original product on heating at 170 and 240 °C while liberating water and amine. The original product is referred to as CFAP-7(A) or form A, the form produced by heating at 170 °C is CFAP-7(B) or form B, and the form produced by heating at 240 °C is CFAP-7(C) or form C. The X-ray powder diffraction data of these forms are listed in Table II. Experiments proved that form C was stable in the range 240 to 500 °C.

3.4. ADSORPTION ON CFAP-7

Sorption behavior have been investigated using a Sartorius 4433 ultramicrobalance. Adsorption isotherms for water and methanol, shown in Figure 6, for CFAP-7(B) and CFAP-7(C) at 23 °C show characteristics similar to sorption on molecular sieves. The volume of methanol (4.3 Å in molecular size) adsorbed is about 14 cm³/100 g, which is greater than that of water (2.7 Å in molecular size). This may be caused by a stronger affinity for adsorption of methanol with weaker polarization. The fact that the weight of hexane (4.9 Å in molecular size) adsorbed on CFAP-7(B) and (C) is less than 1%, allows one to conclude that the free window dimension of both forms is in range of 4.3 to 4.9 Å produced by the 8-ring structure.

In comparison with CFAP-7(B) and (C), AlPO₄-8 possesses a 6 to 10 Å window size and

Table II. X-ray powder diffraction data^a for CFAP-7

CFAP-7(A)			CFAP-7(B)			CFAP-7(C)		
2 θ (deg)	d (Å)	Relative intensity	2 θ (deg)	d (Å)	Relative intensity	2 θ (deg)	d (Å)	Relative intensity
12.8	6.91	78	11.7	7.56	12	13.1	6.75	19
13.2	6.70	100	13.2	6.70	100	14.1	6.28	100
14.9	5.94	11	14.0	6.32	61	16.9	5.24	78
16.0	5.53	72	15.9	5.57	6	18.5	4.79	17
18.0	4.92	36	16.8	5.27	33	20.7	4.29	94
18.2	4.87	5	17.6	5.03	3	21.4	4.15	94
19.0	4.67	36	19.0	4.67	21	21.6	4.11	72
20.4	4.35	52	20.7	4.29	55	23.4	3.80	94
20.6	4.31	25	21.4	4.15	52	25.2	3.53	83
21.2	4.19	52	23.4	3.80	45	28.6	3.12	21
22.4	3.97	16	25.2	3.53	38	29.9	2.99	17
23.1	3.85	9	26.7	3.34	9	30.1	2.97	17
23.8	3.74	3	28.5	3.13	12	31.4	2.85	61
26.6	3.35	16	30.0	2.98	45	33.7	2.66	29
27.5	3.24	72	31.4	2.85	36			
28.0	3.18	47	32.2	2.78	11			
28.7	3.11	28	33.8	2.65	39			
29.0	3.08	22						
29.2	3.06	24						
29.5	3.03	7						
30.3	2.95	37						
30.6	2.92	47						
31.8	2.81	49						
33.8	2.65	12						
34.3	2.61	28						
34.7	2.58	24						
34.9	2.57	17						

^a Rigaku diffractometer, CuK α radiation.

AlPO₄-11 possesses a window size of about 6 Å. On the other hand, although the pore size is close to that of AlPO₄-14 [1] synthesized from isopropylamine, the H₂O adsorption capacity of CFAP-7(B) and (C) is considerably lower.

3.5. INFRARED ABSORPTION SPECTROSCOPY

The IR spectra of CFAP-7 shown in Figure 7 were obtained with a Perkin-Elmer 983 G IR spectrometer with a scanning range of 180 to 4000 cm⁻¹. Discs of KBr and CFAP-7 powder were used. Two vibrations at 3507 cm⁻¹ and 3344 cm⁻¹ of CFAP-7(A) are assigned to the N-H stretch and a vibration at 1421 cm⁻¹ to an N-H deformation in DBA. The vibration at 1624 cm⁻¹ for CFAP-7(A) may be caused by water. As the temperature is raised to 240 or 350°C and CFAP-7(C) is formed, these vibrations disappear. Otherwise, in the range 300 to 1300 cm⁻¹, where bands are considered to be associated with the framework structure, the differences in the IR spectra of CFAP-7(A) and CFAP-7(B) with regard to wave number and intensity are obvious. Two vibrations at 969 and 598 cm⁻¹ vanish and a set of weak IR

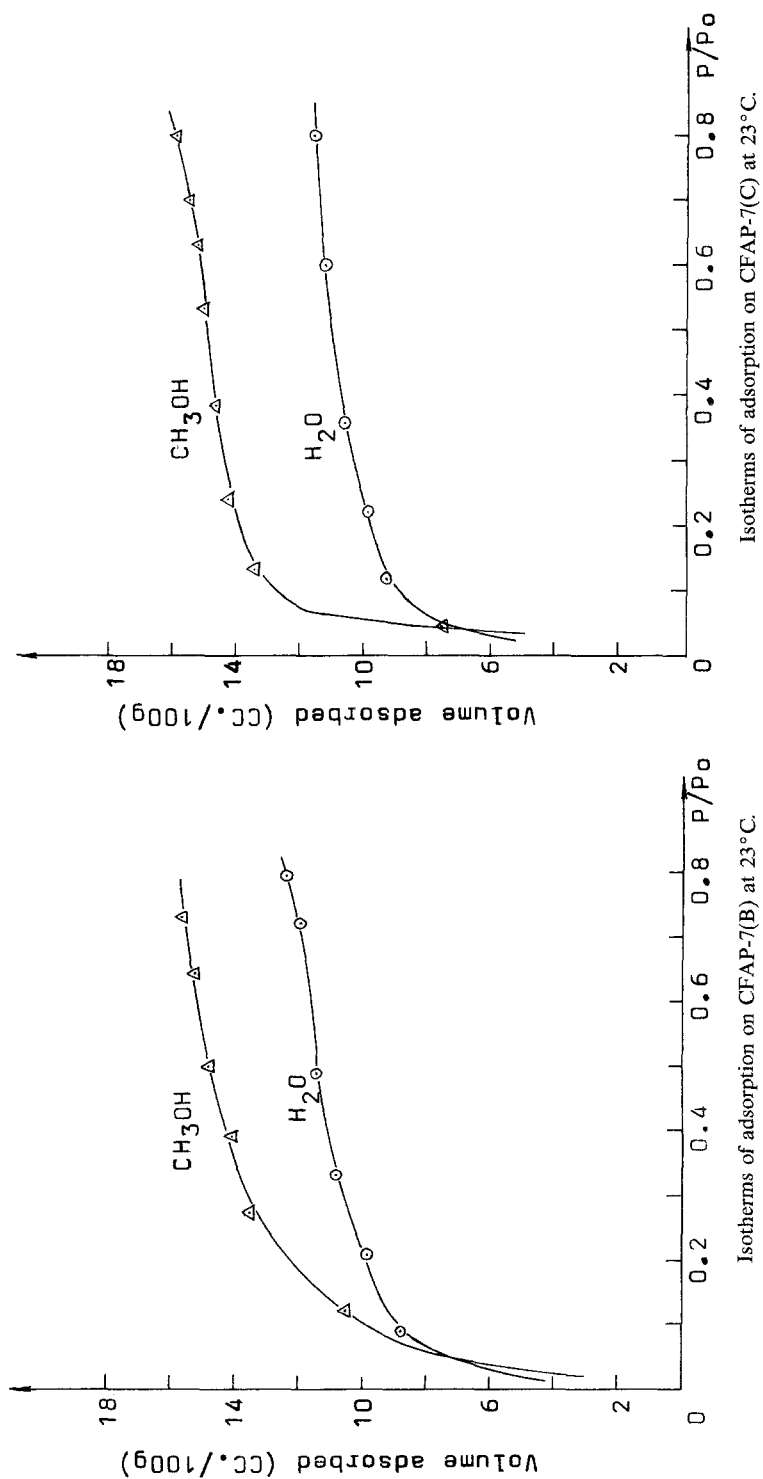


Fig. 6. Isotherms of adsorption on CFAP-7(B) and CFAP-7(C).

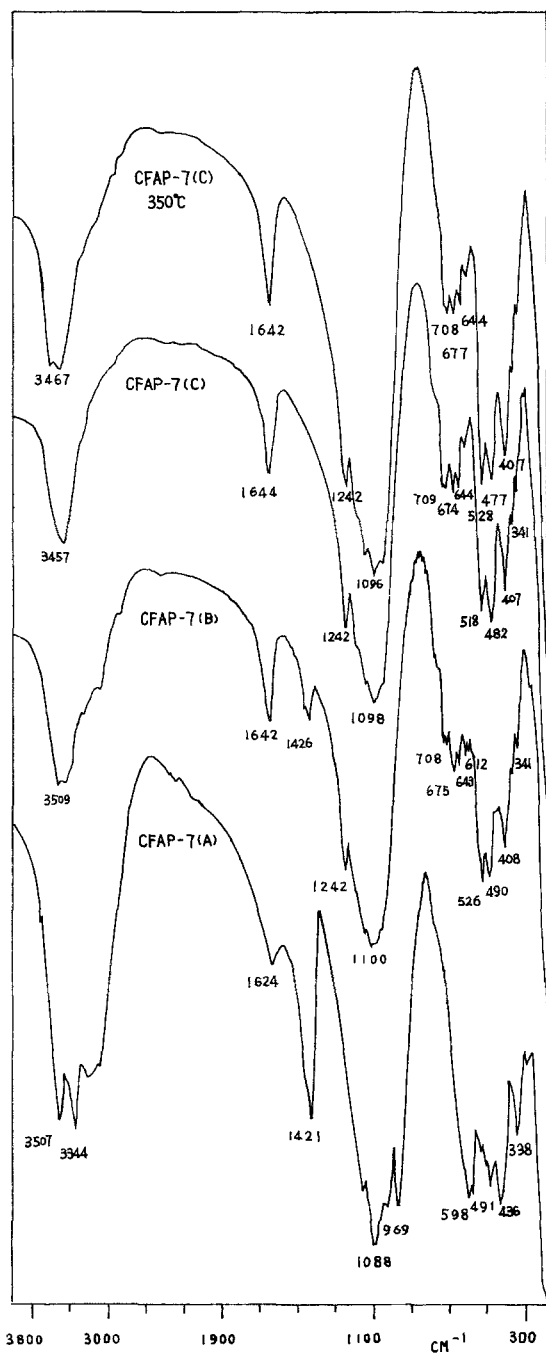


Fig. 7. IR spectra of CFAP-7.

absorption bands in the range 610 to 710 cm^{-1} appear. Unlike the IR spectra of zeolites [9] and of the aluminophosphate molecular sieves $\text{AlPO}_4\text{-21}$ or CFAP-2 [10], absorption bands are found at about 1100 cm^{-1} and 380 cm^{-1} . These are assigned to internal tetrahedron vibrations, and are composed of more than three vibrations. In region of 610 to 710 cm^{-1} the vibrations change both in number and in relative intensity in going from CFAP-7(B) to CFAP-7(C). CFAP-7(C) shows the same IR pattern before and after being calcined at 350 °C for 3 h. This indicates the thermal stability of CFAP-7(C) at temperatures above 240 °C. Since the CFAP-7 crystal structure is unknown, it is difficult to discuss an exact assignment for each vibration.

Acknowledgement

This work was supported by the Science Fund of the Chinese Academy of Sciences.

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