SYNTHESIS AND PROPERTIES OF SEVERAL ALUMINOPHOSPHATE MOLECULAR SIEVES

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ABSTRACT

The $AlPO_4$-5, $AlPO_4$-11, $AlPO_4$-20 and three new family members of aluminophosphate (named CNU-n, n=1,2, and 3, CNU: China, Nanjing University) have been synthesized hydrothermally in the presence of organic amines and quaternary ammonium templates. These samples are characterized by X-ray diffraction patterns and Infrared spectra. It is found that the framework topology of several samples have been changed after calcination. DTA shows no structural collapse below 950°C.

The adsorption properties of water and hydrocarbons on the samples were studied. The results show that the CNU-3 has the largest pore size, and can adsorb 1,3,5-trimethylbenzene but the CNU-1 adsorbs only water vapor. The CNU-2 may adsorb n-hexane but not benzene.

The intracrystalline pore volumes for water on all samples were obtained by TG or adsorption method. All results show that the water pore volumes are usually greater than the hydrocarbon pore volumes, reflecting the presence of additional pore volume accessible to H_2O but not to hydrocarbons.

INTRODUCTION

A novel class of aluminophosphate molecular sieves was discovered by Union Carbide Corporation in 1982.[1] It reperesents the first class of molecular sieves with framework oxide compositions free of silica. $AlPO_4$ molecular sieves can be synthesized hydrothermally in the presence of organic amines and quaternary ammonium templates. The organic template is crucial, and without it no sieves are formed. These $AlPO_4$ molecular sieves exhibit zeolite-like properties. Preliminary findings indicate that this class of molecular sieves will find use as adsorbents, catalyst, and catalyst supports.[1-5]

Up to now, more than 150 types of synthetic zeolites have been obtained, but only about 20 three-dimensional structures of $AlPO_4$ molecular sieves have been reported. One may predict that there will be more new structure types of $AlPO_4$ molecular sieves to appear.

In our work we have synthesized $AlPO_4$-n (n=5,11 and 20) and have found several new family members, named CNU-n (n=1,2 and 3) which were not reported previously. Their properties also have been studied.

SYNTHESIS OF ALUMINOPHOSPHATE MOLECULAR SIEVES

$AlPO_4$-5, -11 and -20 were synthesized by hydrothermal method.[1] The synthesis procedure involved combining equimolar portions of reactive hydrated alumina, phosphoric acid and water. This mixture formed an aluminophosphate gel to which was added an organic amine or quaternary ammonium salt. Generally, the reaction mixture was maintained at temperatures from 150 to 200°C for periods of one day to two weeks. Crystalline products were recovered by filtration, centrifugation and drying. The samples obtained were characterized by X-ray diffraction patterns and were found to be consistent with those of literature.[1]

CNU-1, -2 and -3 were obtained by the same hydrothermal method under the different conditions listed in Table 1. Their X-ray diffraction patterns are shown in Figures 1-3. It is found that they are new family members of aluminophosphate molecular sieves which have not been reported before.

Table 1

The conditions of synthesis

Samples	Compositions of the reaction mixture					Temperature for gel forming, °C	Crystallization		Templating agents
	HCl	R	Al_2O_3	P_2O_5	H_2O		temp. °C	time h	
$AlPO_4$-5	1	1	1		50	room temp.	200	24	TEAOH
$AlPO_4$-11	1	1	1		50	room temp.	200	24	$(i\text{-}C_3H_7)_2NH$
$AlPO_4$-20	1	1	1		50	room temp.	150	70	TMAOH
CNU-1	1	1	1		50	80	150	100	TMAOH
CNU-2	1	1	1		50	40	150	145	TBAOH
CNU-3	0.33	0.67	1		40	60	150	336	TEAOH

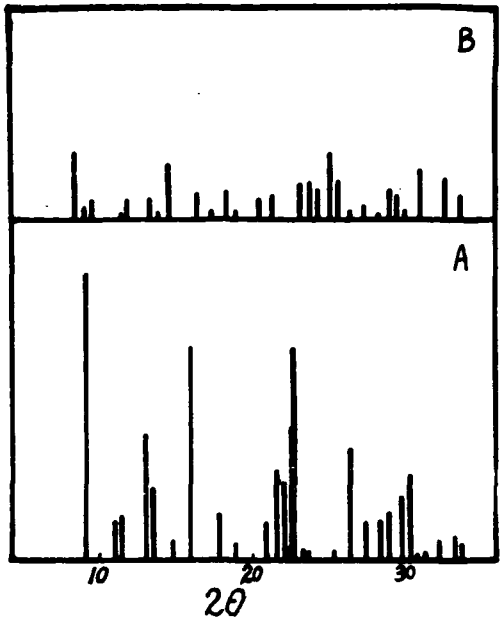


Fig. 1. The X-ray diffraction patterns of CNU-1
A - before calcination
B - after calcination

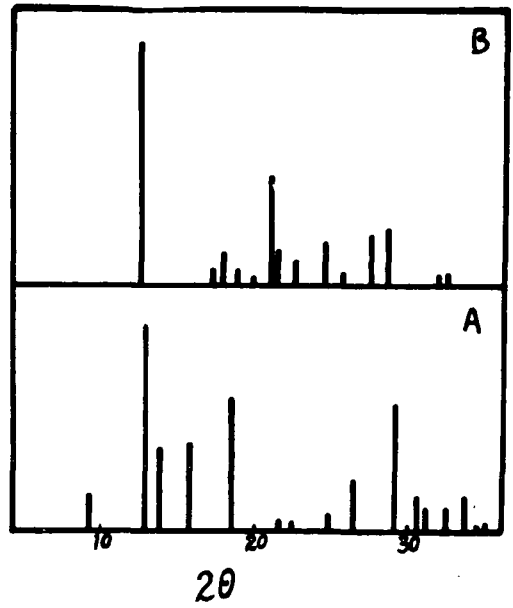


Fig. 2. The X-ray diffraction patterns of CNU-2
A - before calcination
B - after calcination

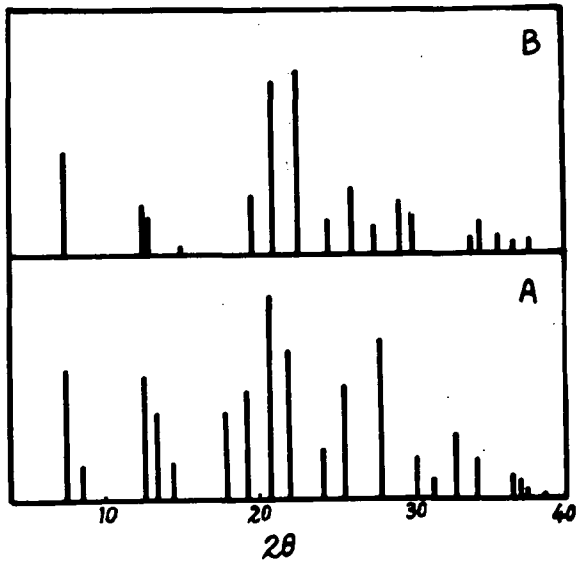


Fig. 3. The X-ray diffraction patterns of CNU-3
A - before calcination
B - after calcination

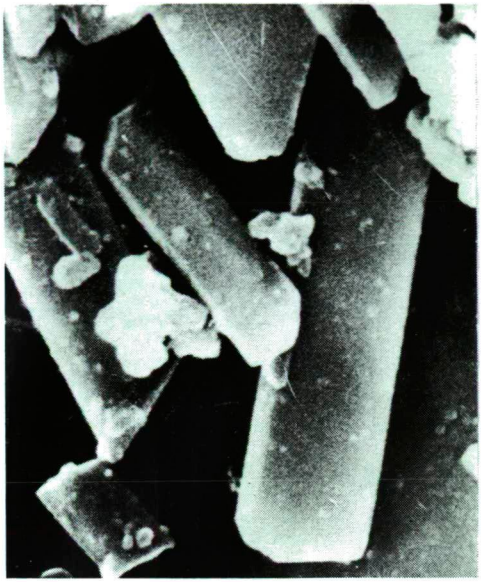
The results reveal that different family members require different templates, but more than one family members can be obtained using only one kind of templates. In our laboratory, by using the same template (TMAOH) $AlPO_4$-20 and CNU-1 were obtained at different conditions (see Table 1). The scanning electron micrographys of CNU-1, 2, 3 and $AlPO_4$-20 are shown in Figures 4, 5, 6 and 7 respectively.

We also obtained in the experiments that the organic template is crucial; without it no sieves but the dense $AlPO_4$ structures or known hydrates are formed. Therefore, a template is a species which seems to exert a unique structure-directing influence during crystallization of the molecular sieve. The action of a template appears to have both electronic and steric effects in generating pores and cages. In the case of the aluminophosphate molecular sieves all of which have the same composition with Al and P in equimolar proportion, each framework being thus neutral with nil exchanging cation. Therefore, the steric effects of templates seem to predominate.

PROPERTIES OF ALUMINOPHOSPHATE MOLECULAR SIEVES

Stability. The $AlPO_4$ molecular sieves obtained by us exhibit their excellent thermally stable properties, showing no structural collapse below 950°C by DTA method. From Figures 8-11 it can be illustrated that endotherm peaks with a maximum at about 250 to 280°C may be considered as the peaks of the desorption of template agent. Consequently the broad exotherm peaks at temperatures ranging from 300 to 600°C, in which generally there are two peaks may be attributed to the oxidation of nitrogen-containing compound and structure changes. The peak (or peaks) of endotherm below 160°C on the DTA curve is due to dehydration of the samples.

After calcinating the samples to remove the template at 600°C for 2 hours, and then rehydrating it with water, we found that the dehydration peaks generally appear at about 100°C. But the CNU-1 loses water in two steps with a maxima at 48°C and 106°C on the DTA curve. Sample CNU-3 has two dehydration peaks even before calcination. The results may be explained as follows: the water molecules in these samples occupy two different sites within the structure, having two kinds of volatilities. Both before and after calcination, the temperatures of dehydration of all the samples are between those of Faujasite and silicalite. Hence, they exhibit



1.0 um

Fig. 4. The SEM of CNU-1

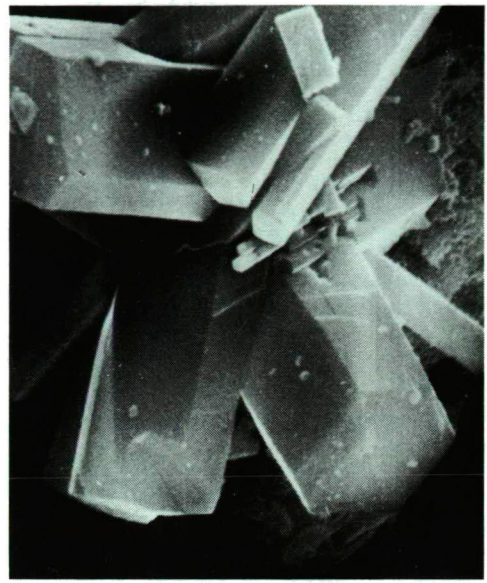


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Fig. 5. The SEM of CNU-2

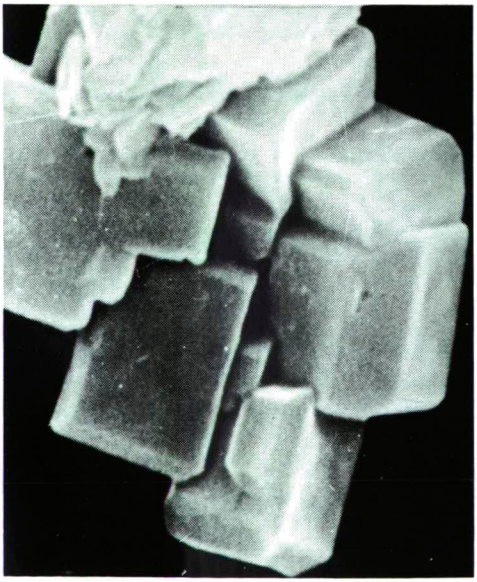

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Fig. 6. The SEM of CNU-3

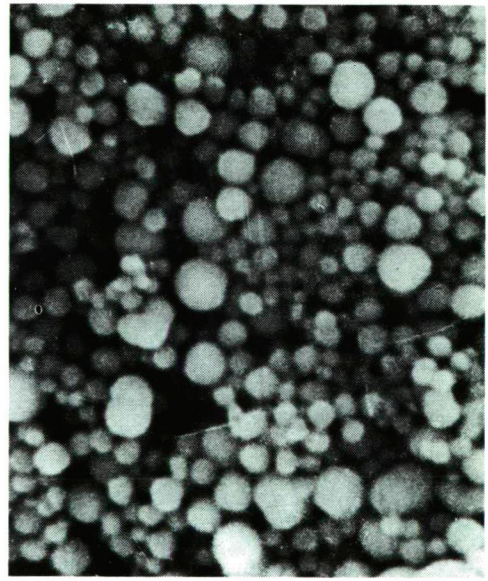

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Fig. 7. The SEM of $AlPO_4$-20

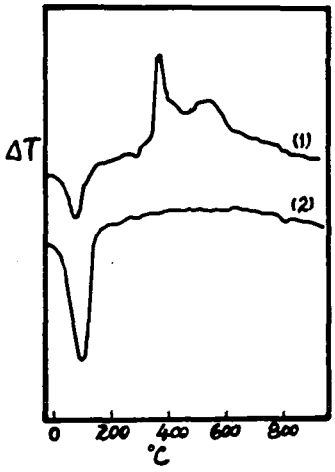

Fig. 8. The DTA curves of $AlPO_4$-5
(1) before calcination
(2) after calcination

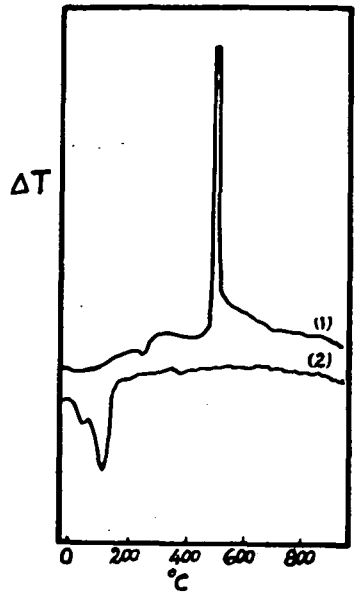

Fig. 9. The DTA curves of CNU-1
(1) before calcination
(2) after calcination

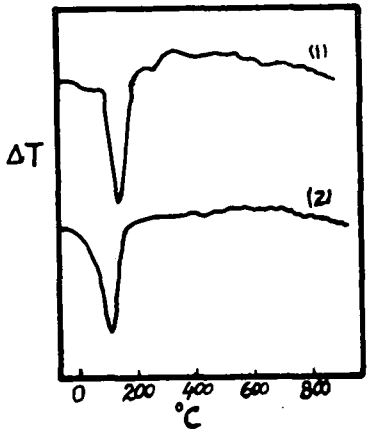

Fig. 10. The DTA curves of CNU-2
(1) before calcination
(2) after calcination

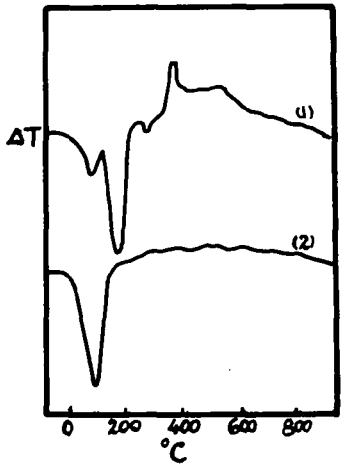

Fig. 11. The DTA curves of CNU-3
(1) before calcination
(2) after calcination

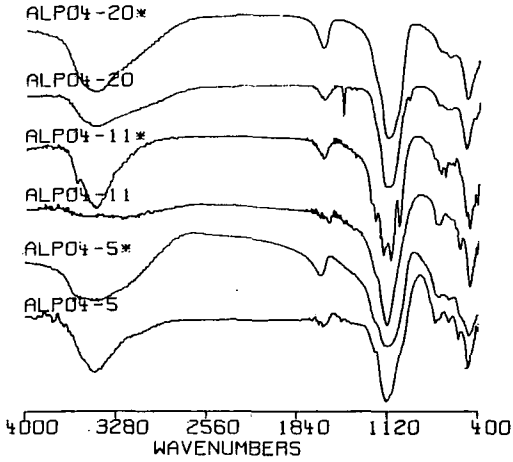

Fig. 12. IR spectra of $AlPO_4$-n
* after calcination

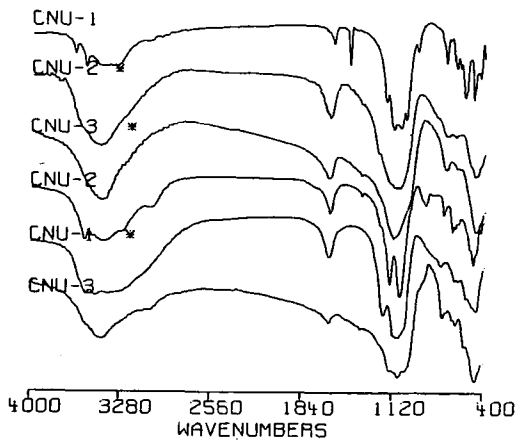

Fig. 13. IR spectra of CNU-n
* after calcination

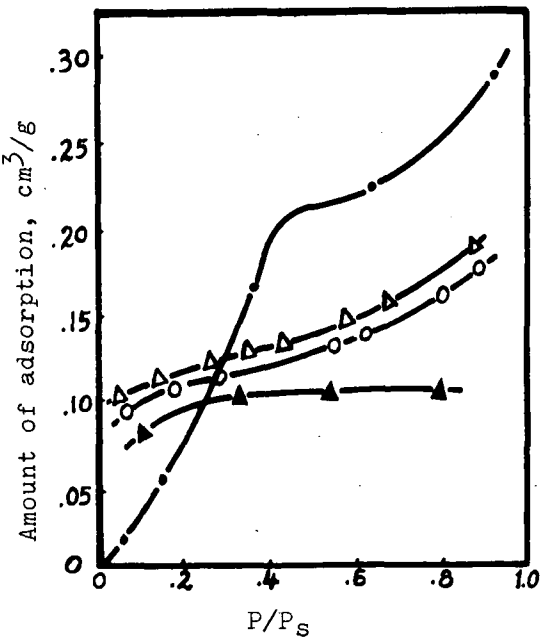

Fig. 14. The adsorption isotherms on $AlPO_4$-5
—●— H_2O, —△— benzene,
—○— cyclohexane
—▲— 1,3,5-trimethylbenzene

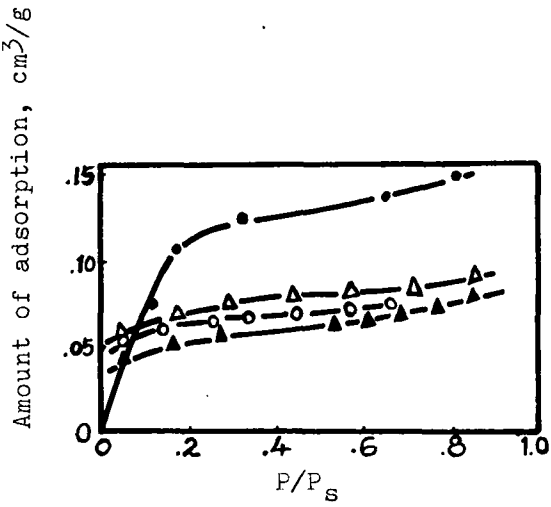

Fig. 15. The adsorption isotherms on $AlPO_4$-11
—●— H_2O
—△— n-benzene
—○— benzene
—▲— cyclohexane

less affinity for H_2O than the hydrophilic Faujasite, but more than the hydrophobic silicalite.

The structure change of the samples after calcination at 600°C for 2 hours and then rehydration of water was examined by the X-ray diffraction and Infrared spectroscopy (see Figures 12 and 13). The X-ray diffraction patterns and IR spectra of $AlPO_4$-5 and $AlPO_4$-20 changed very slightly, which implies that they did not undergo structural changes of framework. But the other samples changed obviously in their framework structures. For $AlPO_4$-11, after calcination, its X-ray pattern changed in accordance with that reported by Flanigen.[1] In our experiment the corresponding IR spectra was found to have changed too. It means that complete dehydration results in irreversible changes in the framework topolgy of $AlPO_4$-11. The behavior of CNU-n is anologous to that of $AlPO_4$-11.

Adsorption. The adsorption isotherms were measured on the samples with water and hydrocarbons by gravimetric method at room temperature. The results show that $AlPO_4$-20 and CNU-1 are small pore molecular sieves that admit only water. The water isotherms for $AlPO_4$-11 and CNU-1 are, roughly, similar to that of Type I, but the other samples are not so. Water sorption on $AlPO_4$-5 and CNU-3 at values of $P/P_s<0.2$ is unusually low, and there is a large increase between $P/P_s = 0.2$ and 0.4. The isotherm shapes of hydrocarbons for all samples are similar to those of Type I. Figures 14-17 show the isotherms of $AlPO_4$-5, $AlPO_4$-11, CNU-1 and CNU-3 respectively. The sample CNU-2 adsorbs water and n-hexane but not benzene. The adsorption properties of $AlPO_4$ molecular sieves are summarized in Table 2.

Table 2

Adsorption properties of $AlPO_4$ molecular sieves

Samples	Pore size (nm)	Intracrystalline pore volume for water cm^3/g	
		from adsorption at $P/P_s = 0.8$	from TG
$AlPO_4$-5	0.8	0.26	0.24
$AlPO_4$-11	0.61	0.15	0.17
$AlPO_4$-20	0.3	0.32	0.25
CNU-1	0.3	0.28	0.25
CNU-2	>0.41	0.19	0.18
CNU-3	0.8	0.21	0.22

From the results we can see that the intracrystalline pore volumes for water obtained by TG are similar to the data obtained by adsorption method. The volume of adsorption with hydrocarbons such as benzene on CNU-3 is about 50% of the volume of adsorption with water at P/P_S=0.5, while on $AlPO_4$-5 and $AlPO_4$-11 they are ~60% and ~80% respectively. In general, the water pore volumes are usually greater than the hydrocarbon pore volumes, reflecting the presence of additional pore volume accessible to water but not to hydrocarbons.

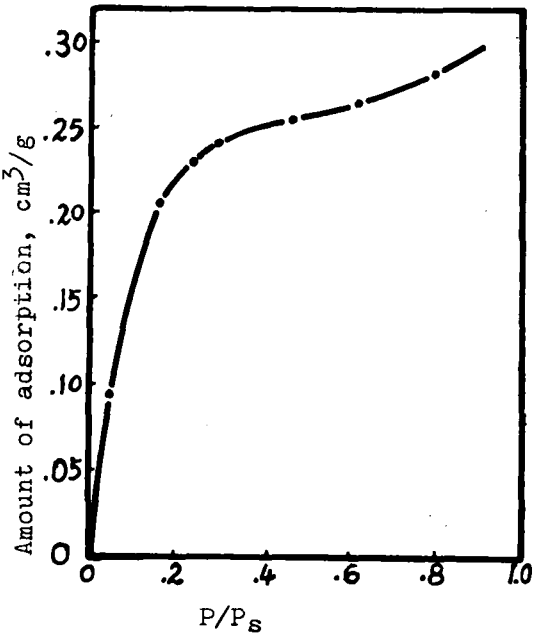

Fig. 16. The adsorption isotherms on CNU-1 with water

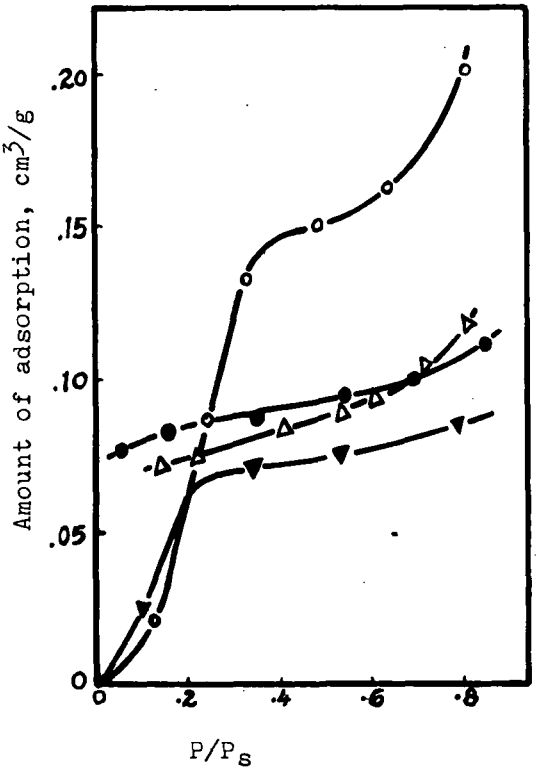

Fig. 17. The adsorption isotherms on CNU-3
—o— H_2O
—△— o-xylene
—●— cyclohexane
—▼— 1,3,5,-trimethylbenzene

Indeed, the samples of CNU-1, -2 and -3 are the new family members of aluminophosphate molecular sieves, as characterized by

the spectra of X-ray diffraction, DTA and IR. They possess the properties of sieves. The pore size of CNU-1 is similar to that of $AlPO_4$-20, CNU-2 can adsorb n-hexane but not benzene, and CNU-3 has large pore size in which 1,3,5-trimethylbenzene may enter.

REFERENCES

1. Wilson, S.T., Lok, B.M. and Flanigen, E.M., U.S.P. 4, 310, 440 (1982).
2. Haggin, J., Chem. Eng. News 60, No. 50, 9 (1982).
3. Haggin, J., Chem. Eng. News 61, No. 25, 36 (1983).
4. Wilson, S.T., Lok, B.M., Messina, C.A., Cannan, T.R. and Flanigen, E.M., J. Am. Chem. Soc. 104, 1146 (1982).
5. Stuck, G.D. and Dwyer, F.G., "Intrazeolite Chemistry", ACS Symposium Series 218, 79 (1983).