

Synthesis of the Molecular Sieve $\text{AlPO}_4\text{-5}$ with an Unequal Molar Ratio of Al_2O_3 to P_2O_5

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The aluminophosphate molecular sieve $\text{AlPO}_4\text{-5}$ in which the molar ratio of Al_2O_3 to P_2O_5 is in the range from 1.43 : 1 to 2.21 : 1 has been synthesized and characterized by X-ray powder diffraction and ^{31}P and ^{27}Al solid-state magic angle spinning NMR spectroscopy.

The aluminophosphate molecular sieve $\text{AlPO}_4\text{-5}$ is a member of the $\text{AlPO}_4\text{-}n$ family,¹ and can be prepared by hydrothermal and non-aqueous methods² in the presence of an amine. It is also obtained from a synthesis medium containing F^- anions.³ It is a porous material with the framework oxide composition being free of silicon. After thermal decomposition of the template, the three-dimensional molecular sieve has the general composition $\text{Al}_2\text{O}_3 \cdot 1.0 \pm 0.2\text{P}_2\text{O}_5$.⁴ It is a type of absorbent or catalyst carrier which has potential practical utility. We now report that the molecular sieve $\text{AlPO}_4\text{-5}$ with molar ratios of Al_2O_3 to P_2O_5 in the range 1.43 : 1 to 2.21 : 1 may be prepared from the system $\text{HF-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Et}_3\text{N-Pr}^n\text{N}$.

In our experiments, stoichiometric amounts of active Al_2O_3 , H_2O , 42% aqueous HF and 85% aqueous H_3PO_4 were mixed and stirred to homogeneity. Et_3N and Pr^nN were then added, and the mixture was stirred for about 10 min. The mixture was heated in an autoclave lined with Teflon at 453 ± 2 K for 38 h. After crystallization, the samples were washed with distilled water, dried at 378 ± 2 K, and characterized by X-ray powder diffraction (Rigaku 2034), ^{31}P MAS NMR (Bruker 400), ^{27}Al MAS NMR (Varian XL-200), probe reaction of *o*-xylene isomerization and chemical analysis. The samples used to determine the chemical composition were

dipped in acetylacetone (38% solution in ethanol) for about 5 h for dealumination of the extra-framework aluminium.⁵

Fig. 1(a) shows the XRD pattern of the sample in Run 2. The locations and intensities of the peaks in the pattern are similar to those previously reported for $\text{AlPO}_4\text{-5}$,¹ except for the relative intensities of the peaks at $2\theta = 20.91$ and 26.09° .

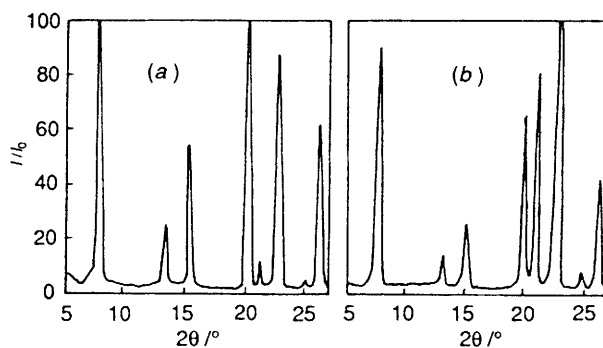


Fig. 1 X-Ray powder diffraction (XRD) patterns of $\text{AlPO}_4\text{-5}$ samples: $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 =$ (a) 1.96; (b) 0.98

Table 1 Preparation of AlPO₄-5 samples

Run	Molar proportions of reactants						Phase	F ⁻ : Al ₂ O ₃ : P ₂ O ₅
	HF	Al ₂ O ₃	P ₂ O ₅	Et ₃ N	Pr ⁿ ₃ N	H ₂ O		
1	3.0	2.3	1	2.4	0.32	50	AlPO ₄ -5	0.91 : 2.21 : 1.0
2	2.3	2.1	1	2.3	0.27	50	AlPO ₄ -5	0.67 : 1.96 : 1.0
3	2.0	1.9	1	2.2	0.27	50	AlPO ₄ -5	0.38 : 1.80 : 1.0
4	1.0	1.5	1	1.5	0.20	50	AlPO ₄ -5	0.30 : 1.43 : 1.0
5	—	1.9	1	2.2	0.27	50	AlPO ₄ -5 +MCM-2 +A ^a	

^a A = amorphous.

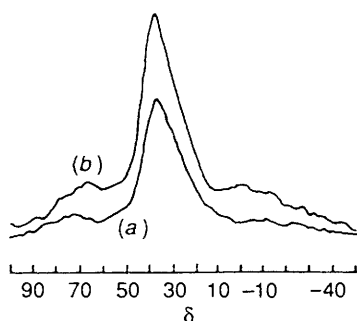


Fig. 2 ²⁷Al MAS NMR spectrum of AlPO₄-5 samples: Al₂O₃/P₂O₅ = (a) 1.96; (b) 0.98 [δ values in ppm from external Al(H₂O)₆³⁺ in aqueous Al(NO₃)₃]

Table 1 shows molar ratios of Al₂O₃ to P₂O₅ in the products in the range 1.43–2.21 : 1; the ratios of F⁻ to (Al₂O₃ - 1) are not regular. If HF is not used in the synthesis, the product is a mixture of MCM-2, AlPO₄-5 and amorphous material (see Run 5). Therefore, a molecular sieve AlPO₄-5 with unequal molar ratios of Al₂O₃ to P₂O₅ can be synthesized. The presence of HF is necessary for a uniform phase to be obtained.

The sample with Al₂O₃/P₂O₅ = 1.96 was characterized by ²⁷Al and ³¹P MAS NMR spectroscopy and isomerization of *o*-xylene. Fig. 2(a) shows the ²⁷Al MAS NMR spectrum, which includes a peak at δ 36.3, but no peak at δ 0. This shows the absence of octahedral aluminium. The sample of AlPO₄-5 with Al₂O₃/P₂O₅ = 0.98 gives a similar spectrum [Fig. 2(b)]. The ³¹P MAS NMR spectrum (Fig. 3) shows two peaks, at δ -28.5 and -17.2. According to ref. 6, AlPO₄-5 shows a

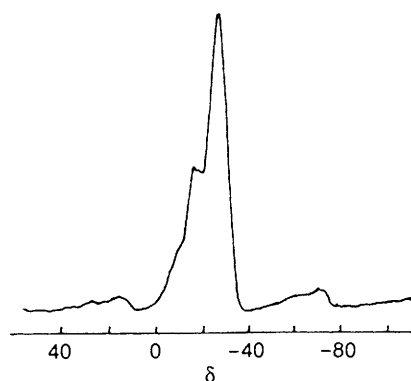


Fig. 3 ³¹P MAS NMR spectrum of AlPO₄-5 sample with Al₂O₃/P₂O₅ = 1.96 (δ values in ppm from external 85% aqueous H₃PO₄)

peak at δ (³¹P) -28.6, consistent with tetrahedral phosphorus, and similar to our results. However, the reported spectrum⁶ does not show the peak at δ -17.2 which we observe for the sample with Al₂O₃/P₂O₅ = 11.96, providing evidence for the presence in our sample of two types of phosphorus atoms in different chemical environments. The ³¹P and ²⁷Al MAS NMR and chemical analysis results are therefore consistent with the presence of the extra aluminium in the framework.

The sample with Al₂O₃/P₂O₅ = 1.96 and 0.98 were calcined at 773 K for 5 h; at 673 K the isomerization of *o*-xylene took place to the extent of 4.6% on the former, but did not take place on the latter, showing the presence of a limited number of Brønsted acid sites in the sample with Al₂O₃/P₂O₅ = 1.96.

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