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Synthesis of Molecular Sieve $AlPO_4$-12

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Abstract. A member of the novel family of crystalline microporous aluminophosphates, $AlPO_4$-12, was synthesized by hydrothermal crystallization using different aluminum-containing compounds. Three new crystalline phases were obtained by varying the composition of the reaction mixture. The effect of the synthesis conditions on the hydrothermal process and the kinetics of crystallization are discussed. The apparent activation energies obtained for $AlPO_4$-12 are 20.9 and 14.6 kcal/mol for nucleation and crystallization, respectively. The adsorption isotherms of one $AlPO_4$-12 product were measured.

Key words: Aluminophosphate, molecular sieves, crystallization, kinetics

1. Introduction

In 1982, E. M. Flanigen and her co-workers developed a new family of aluminophosphate molecular sieves which broadens the type of shape-selective catalysts and adsorbents available to chemical engineers [1]. The structure of $AlPO_4$-12, a member of the new family, was determinated by J. B. Parise [2]. It was pointed out that the channels of $AlPO_4$-12 contain ethylenediamine which is hydrogen bonded to a hydroxy group on the sheet and arranged along the channels in the structure suggesting its influence as a structure-directing agent during crystal growth. The purpose of this study was to synthesize $AlPO_4$-12 molecular sieve using different synthetic conditions and different reaction materials, to analyze factors which affect the crystallization of $AlPO_4$-12, and to measure its adsorption properties.

2. Experimental

Synthesis runs were carried out in a 500 ml stainless steel pressure vessel with automatic temperature-controller. After each run the vessel was cleaned with concentrated sodium hydroxide solution at 180 °C to eliminate the remaining crystals.

All the reactant materials involved in this study were chemical reagent grade (C. P. or L. R.) and distilled water was used.

In a typical run, a stoichiometric amount of sodium aluminate solution was added to the appropriate amount of phosphoric acid with the required amount of water. Then, the proper amount of ethylenediamine was added to the above mixture and an aluminophosphate gel was formed. The composition of the final reaction mixture was: (0.5–3.0) $C_2H_8N_2 : Al_2O_3 : P_2O_5 : (40\text{–}70)\ H_2O$. It was sealed in the vessel which was placed in an oil bath, and the contents were allowed to crystallize statically. The synthesized samples were washed, filtered, and dried at 110 °C. A Rigaku 2034 X-ray diffractometer using Ni-filtered Cu$K\alpha$ radiation (3 kW) was employed to make the qualitative and quantitative phase identification of the crystallized samples. The adsorption isotherms were measured with a quartz balance in a vacuum system at 10^{-4} mmHg.

3. Results and Discussion

Under the conditions mentioned above, in the $NaAlO_2/H_3PO_4/H_2O/NH_2{-}C_2H_4{-}NH_2$ system, crystallization of $AlPO_4$-12 was carried out within the temperature range 160–180 °C for 60–100 h. The crystalline phase was identified as $AlPO_4$-12, using X-ray powder diffraction analysis. The diffraction patterns (peak locations and intensities) of the crystalline products were found to be very similar to that previously reported for $AlPO_4$-12 [1]. The *d*-spacing and intensities of a typical sample are shown in Table I.

Table I. The *d*-spacings and intensities of $AlPO_4$-12 crystals of this study

d	$100 \times I/I_0$
14.37	25
6.66	60
4.25	100
3.99	43
3.74	53
2.90	41

The detailed studies of the crystallization and properties of $AlPO_4$-12 are delineated as follows:

3.1. THE EFFECT OF THE ALUMINIUM-CONTAINING COMPOUND

Using other aluminium-containing compounds such as $Al(OH)_3$, $AlCl_3$, $Al(NO_3)_3$, and $Al_2(SO_4)_3$, the same crystalline phase as that shown in Table I could also be obtained, as can be seen from Table II. However, in the runs using $AlCl_3$, $Al(NO_3)_3$ and $Al_2(SO_4)_3$, the original mixture was more viscous and the period required for crystallization was longer. Shorter periods of crystallization and a finer crystalline product result when $NaAlO_2$ is the source of aluminium.

Table II. Crystallization data

Sample	Al containing compounds	Time (h)	Temp. (°C)	Product phase
T-1	$Al(OH)_3$	56	180	$AlPO_4$-12
T-2	$NaAlO_2$	85	180	$AlPO_4$-12
T-3	$AlCl_3$	181	180	$AlPO_4$-12
T-4	$Al(NO_3)_3$	175	180	$AlPO_4$-12
T-5	$Al_2(SO_4)_3$	168	180	$AlPO_4$-12

3.2. THE EFFECT OF THE ORGANIC AMINE

There is a certain concentration range of ethylenediamine needed in the reaction mixture. The ethylenediamine/Al_2O_3 mole ratio should be within the range 0.5–3.0, and usually larger than 1.5. It was observed that the precipitate was amorphous if there were no organic amine cations in the system. When using another organic amine, triethanolamine, to replace ethylenediamine, other crystalline phases were found to coexist with $AlPO_4$-12. The product was amorphous when using an alcohol as the 'template'. All the results implied that ethylenediamine appears to have a strong 'template' or 'structural directing' effect for the formation of the $AlPO_4$-12 crystals.

The larger the amount of organic amine, the longer the nucleation time required, as has been noted previously [4]. The relationship is shown in Figure 1.

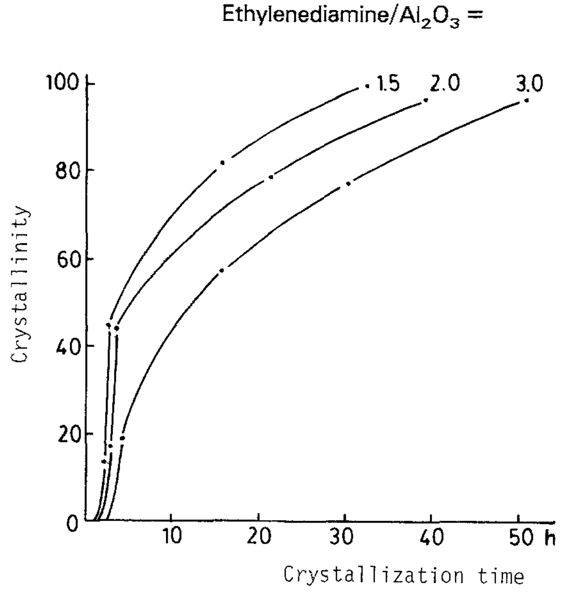

Fig. 1. Effect of the amount of organic amine (ethylenediamine) on crystallization time.

3.3. THE THREE NEW CRYSTALLINE PHASES

Two new aluminophosphates, referred to as $AlPO_4$-x_1 and $AlPO_4$-x_2, are characterized by their X-ray powder diffraction patterns in Figures 2 and 3, respectively. They were obtained when there was no sodium in the reaction system. Replacement of ethylenediamine by *n*-butyric amine led to another crystalline product, $AlPO_4$-x_3. Its X-ray powder diffraction pattern is shown in Figure 4.

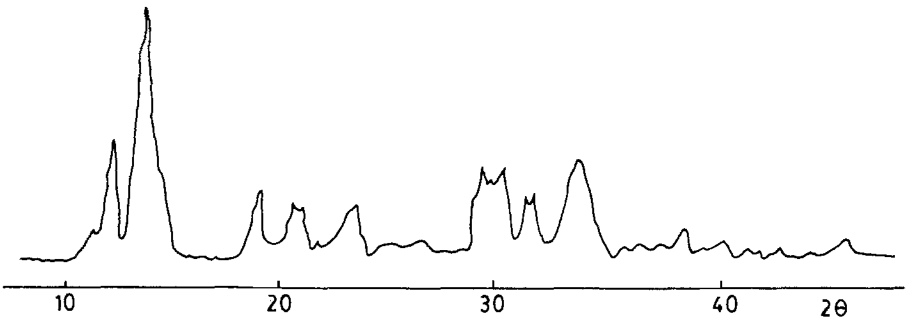

Fig. 2. X-ray powder diffraction pattern of $AlPO_4$-x_1.

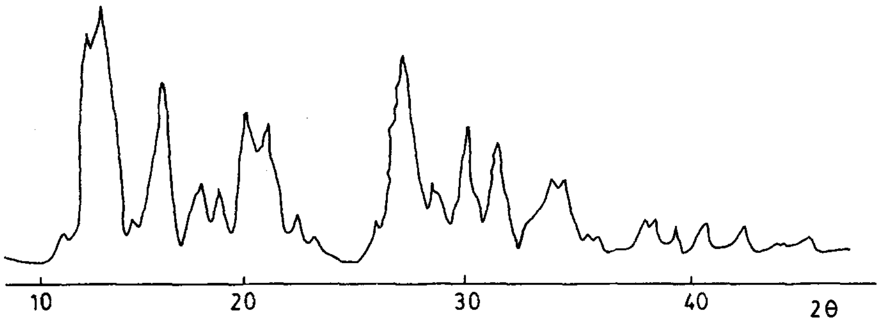

Fig. 3. X-ray powder diffraction pattern of $AlPO_4$-x_2.

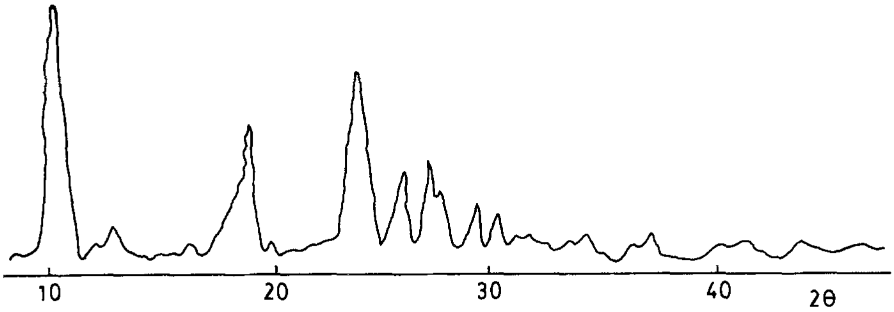

Fig. 4. X-ray powder diffraction pattern of $AlPO_4$-x_3.

3.4. THE EFFECT OF ALKALITY

The alkality (i.e. the alkali content in the reaction mixture) is an important factor for the crystallization of $AlPO_4$-12. Fine $AlPO_4$-12 crystals were obtained when the pH of the system before crystallization began $(pH)_{pre}$, was in the range of 4–6. When the range was 5–6, the crystallization time was shorter. Usually, the value of the pH after the fine crystals formed, $(pH)_{post}$, was 7–8. Thus, the difference between $(pH)_{pre}$ and $(pH)_{post}$, was 2–3 pH units, with the accomplishment of crystallization.

3.5. KINETIC STUDY OF CRYSTALLIZATION

As expected, temperature affected the crystallization rate considerably. The higher the crystallization temperature, the shorter the induction period, which can be seen from Figure 5.

We have performed a kinetic study of the crystallization of $AlPO_4$-12 in order to determine the kinetic parameters, E_n and E_c, the apparent activation energies for nucleation and crystallization, respectively. Following the literature [3], a reaction mixture composition of 1.5 ethylenediamine/Al_2O_3/P_2O_5/$73H_2O$ was selected to synthesize the $AlPO_4$-12 crystals and to draw a standard-line for the dependence of the peak intensities on the product crystallinity. In the same system, the sum of the intensities of the peaks at 2θ values of 20.9, 22.3, 23.85, 25.05, 26.50, and 31.15° during different times in the crystallization are used to express the extent of crystallization, i.e., the crystallinity. Assuming nucleation and crystal growth to be the rate-limiting steps during the induction period and crystallization period, respectively, the dependence of the rates on temperature for three synthesis temperatures of 160, 170, and 180°C, is expressed by the Arrhenius equation $d \ln \gamma / d(1/T) = E/R$.

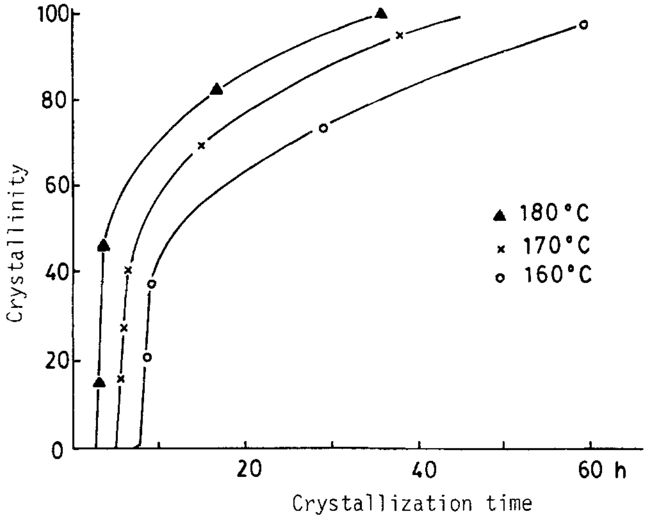

Fig. 5. Dependence of crystallization of AlPO$_4$-12 on temperature.

Figure 6 illustrates the dependence of the rate of crystallization and induction period on temperature. The calculated values of the activation energies were 20.9 and 14.6 (kcal/mol), for E_n and E_c, respectively.

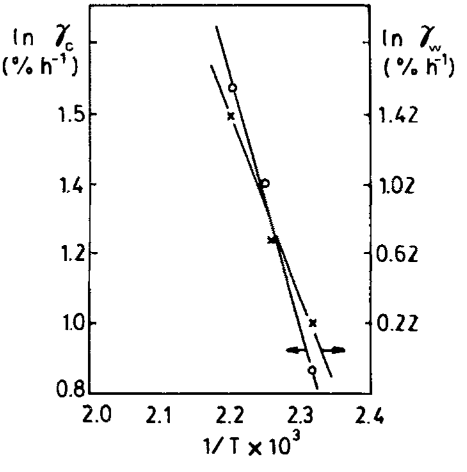

Fig. 6. Dependence of the rate of crystallization and induction period on temperature for AlPO$_4$-12.

3.6. THERMAL STABILITY

The thermal stability of AlPO$_4$-12 is not as good as other members of the aluminophosphate family and zeolites. Calcining at a temperature of 350°C in air changes the crystal structure, although the structure remained unchanged after being calcined at 320°C for 2 h, as shown in Figure 7.

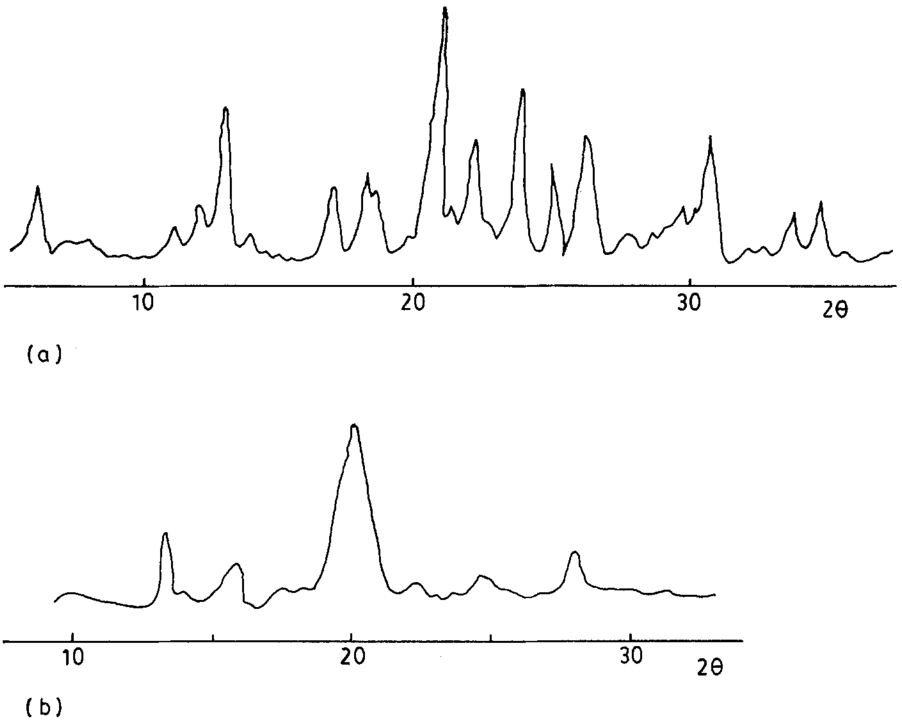

Fig. 7. The X-ray diffraction patterns of $AlPO_4$-12 after being calcined at (a) 350°C and (b) 320°C.

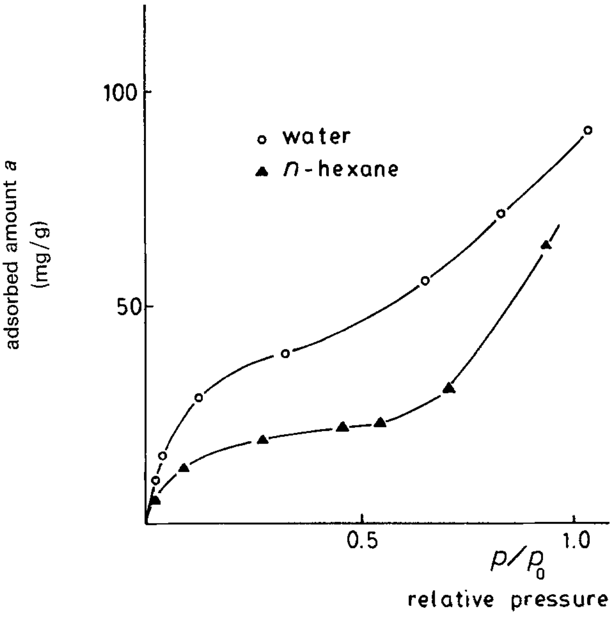

Fig. 8. Adsorption isotherms of water and *n*-hexane on $AlPO_4$-12 (No. T-2, see Table II) at 20°C.

3.7. ADSORPTION PROPERTIES

The adsorption properties of the synthesized $AlPO_4$-12 sample were measured. The adsorption isotherms of water and *n*-hexane on $AlPO_4$-12 molecular sieve are shown in Figure 8, which indicates that molecular sieve $AlPO_4$-12 is hydrophilic, and its pores are wide enough to adsorb molecules like *n*-hexane.

4. Summary

$AlPO_4$-*n* molecular sieve crystallization is a complex chemical problem similar to zeolite crystallization. Thus, the synthesis of $AlPO_4$-12 is strongly influenced by many aspects of the basic chemistry, such as aluminophosphate gel composition, pH-value, classes of template, and amount of organic amine.

As $AlPO_4$-12 is a two-dimensional layer type material, its structure is unstable. Although its pores may adsorb molecules like *n*-hexane, its adsorption capacity is less.

The three new crystalline phases, $AlPO_4$-x_1, $AlPO_4$-x_2, and $AlPO_4$-x_3, are worthy of further study.

References

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