# INTERMEDIATE PHASES IN SYNTHESIS OF AIPO$_4$-5 MOLECULAR SIEVE: A STUDY OF XRD, RAMAN SCATTERING AND TGA

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## SUMMARY

*In the world, aluminophosphate molecular sieves have been synthesized successfully; however, the intermediate phases and their evolution during crystallization process have not been studied systematically yet. In this work, the behaviors of the initial gel and the evolution of the intermediate phases during crystallization process of AlPO$_4$-5 molecular sieve using triethylamine as a template have been investigated. It has been shown that in the amorphous aluminophosphate gel phases, template triethylamine does exist in protonated form; and there appear a significant change, formation of 12-member rings of AlPO$_4$-5 structure, during the early stage of crystallization of AlPO$_4$-5. In addition, a proposition to explain the crystallization of AlPO$_4$-5 is also suggested.*

## I - INTRODUCTION

Microporous materials are a class of inorganic solids with regular pores and cavities in the size range of 0.5 - 2.0 nm, which are extensively used in industry as ion exchangers, sorbents and catalysts [1]. In addition to aluminosilicate zeolites, the aluminophosphate-based molecular sieves present the well-known family of such materials [2]. Some of them have the framework topologies similar to those of known zeolites and many have novel structures. AFI type aluminophosphates have attracted much attention due to their use in catalysis, separation technology and potential applications such as nonlinear optics and the nano technology [3 - 5]. The AFI structure is constructed from secondary building units of 4- or 6-member rings; and possesses wide one-dimensional 12-ring channel of 0.73 nm [6].

Although much data has been accumulated on the synthesis and a lot of effort has been directed toward understanding the crystallization, the mechanism of the formation of aluminophosphate-based molecular sieves has not been understood well [7]. These materials are normally prepared by hydrothermal synthesis using organic compounds as template agents and the process occurs through intermediate gel phases. However, structural properties of these gel phases have been poorly understood so far. The recent studies on the formation of aluminophosphate-based molecular sieves have shown that the amorphous AlPO species and a small amount of AlPO intermediate phases in crystal do form in the early stage of the crystallization [8 - 10]. However, to our knowledge, the role of templates and the formation of pore openings (defined as the number of T (or TO$_4$) units that shape the channel) in synthesis of AlPO$_4$-5 have been not mentioned yet. In this work, we have investigated intermediate phases in AlPO$_4$-5 synthesis using powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and

Raman spectroscopy measurements. On the basis of the characteristics obtained, the crystallization process including the role of template and the formation of pore openings is discussed, too.

## II - EXPERIMENT

In a typical synthesis, a slurry mixture of aluminum isopropoxide (16.34 g) in water (23.8 g) was stirred for 1h, orthophosphoric acid (9.22 g) diluted with water (5 g) was added dropwise to the stirred slurry and the stirring was continued for 12 h. TEA (4.05 g) was then added dropwise, and then the mixture was stirred for another 4h. The molar composition of the final gel was $1.0Al_2O_3.1.0P_2O_5.1.0TEA.40H_2O$. The gel sample was aged for 24 h at room temperature, and then a small portion of this aged gel was air-dried at room temperature. This sample is referred to initial AlPO gel (APO-1). To get intermediate phases and $AlPO_4$-5 molecular sieve, the rest of the gel was charged into three Teflon-lined autoclaves and all were transferred to an oven with a following heating program: from room temperature to 90ºC and keeping this temperature for 24 h (stage I), rising up to 170ºC and keeping this temperature for 3 h (stage II), and maintaining at 170ºC for further 21 h (stage III). After each stage, one autoclave was taken off from the oven. The samples collected from the stage I, II and III were denoted as APO-2, APO-3 and APO-4, respectively. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku (D/MAX-2000) diffractometer. Thermogravimetric analysis (TGA) was performed by DTA-50 and TGA-50H (Shimadzu). Raman scattering studies were carried out on T64000 spectrometer (Jobin-Yvon) with argon ion laser.

## III - RESULTS AND DISCUSSION

### 1. Powder X-ray diffraction

The phases obtained in the $AlPO_4$-5 synthesis were characterized by XRD and the results were presented in figure 1. The patterns indicate that mixing aluminum *iso*propoxide and orthophosphoric acid with TEA leads to an amorphous phase, APO-1 (figure 1a). Heating APO-1 at 90ºC for 24 h yields APO-2 to be still amorphous (figure 1b). The crystalline $AlPO_4$-5 starts to form after heating APO-2 at 170ºC for 3 h (figure 1c); and the crystallization was completed as heating the APO-2 at 170ºC for 24 h (figure 1d). It has been known that intermediate crystalline compounds do exist during the crystallization of several aluminophosphate-based molecular sieves [8-10, 11]. However, in this work, we have analyzed samples quenched at many stages but no intermediate crystalline compounds were observed during the crystallization.
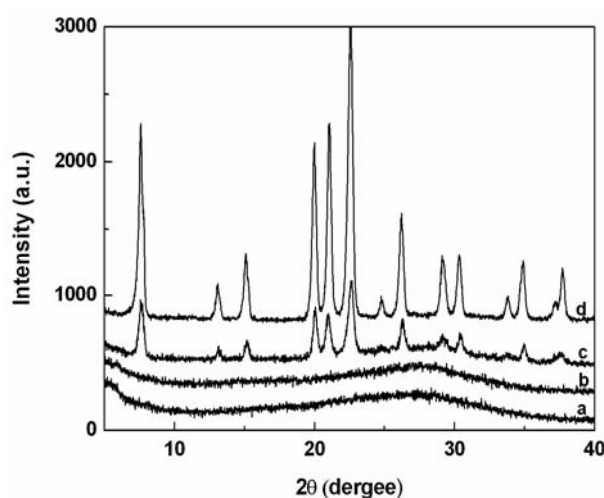


*Figure 1*: The XRD patterns of APO-1 (a), APO-2 (b), APO-3 (c) and APO-4 (d)

## 2. Thermogravimetric analysis

To investigate crystallization of AlPO$_4$-5, the phases were characterized by TGA and the results were shown in figure 2. The DTG curves indicated that each phase exhibits two steps of weight loss. The first one from room temperature to 150°C and the second one from 150°C to 400°C may be due to desorption of water and decomposition of TEA, respectively. Figure 2 shows a strong shift of the second peak from 235°C to 303°C as going from APO-1 to APO-2, while this one almost did not change from APO-2 to APO-3. The second peak significantly shifted to lower temperature by 132°C from APO-3 to APO-4.

For the initial gel, the strong intensity of the first DTG peak (Figure 2a) and the total mass loss of about 25% in this range suggest that numerous sites which can adsorb water do exist in the gel. The second peak possesses strong intensity and locates at high temperature of about 235°C, which may result from similar linkages of the TEA molecules with OH groups of H$_3$PO$_4$ in the gel. Indeed, if TEA molecules were protonated by water, they would be decomposed at a lower temperature, about 150°C [12]. From APO-1 to APO-2, the first DTG peak shifts to a higher temperature. This suggests that there have been changes occurring in the gel in which probably new bonds appear. In addition, it should be noted that the strong shift of the second peak to higher temperature indicates a dramatic change occurring in this stage. This result may be due to two following contributions: the TEA molecules are confined by new linkages yielded around them and they still link with H$^+$ of the amorphous AlPO.

The second peak does not change after heating further at 170°C for 3 h where AlPO$_4$-5 starts crystallizing, indicating a minor change of links between TEA and other components, but significant one of bonds between Al and P in this stage. The second peak significantly shifted to a lower temperature as the crystallization is completed by heating APO-2 at 170°C for 24 h (figure 2d). This result has been already explained by crystalline AlPO$_4$-5 having neutrally charged framework, thus TEA template molecules are protonated by water and decomposed at a lower temperature [12].
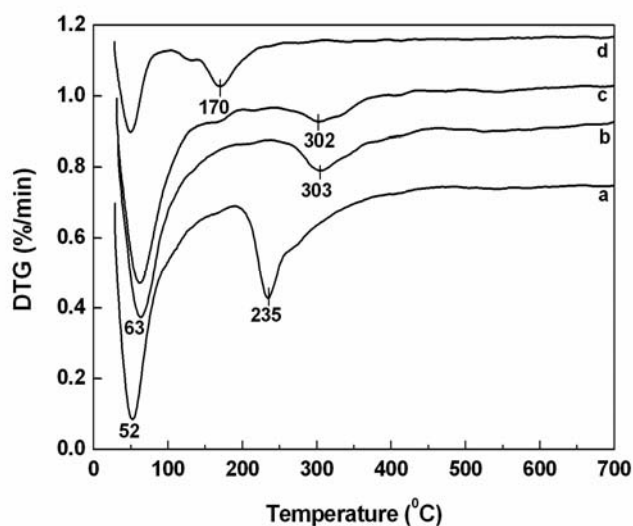


*Figure 2:* The DTG curves under flowing air of APO-1(a), APO-2 (b), APO-3 (c) and APO-4 (d)

## 3. Raman spectroscopy

To investigate evolution of the intermediate phases, they were also characterized by Raman spectroscopy and the spectra were displayed in figure 3. The Raman spectrum of triethylammonium chloride (TEAHCl) salt in aqueous solution with bands at 2890, 2950 and

2990 cm$^{-1}$ was also shown. These bands agree well with the previous report [13]. Fig. 3 reveals that the C-H stretching frequencies of the template in the initial AlPO gel were close to those of TEAHCl. This indicates that all TEA molecules in the initial gel do exist in protonated form that may be caused by linking with OH groups of phosphoric acid in the gel. Such acid sites are also explained in the synthesis of several aluminophosphate molecular sieves [8 - 10]. In a study on the synthesis of AlPO$_4$-11, Huang et al. [9] have shown that mixing aluminum hydroxide and phosphoric acid together with di-n-propylamine as a template agent at room temperature does yield a significant amount of amorphous AlPO species. Both tetrahedral and octahedral Al sites are present in this AlPO material, P(OH)$_x$[OAl(tet)]$_y$[OAl(oct)]$_{4-(x+y)}$ where x = 1 or 2, y $\leq$ 3. Apparently, the OH groups originated from H$_3$PO$_4$ can serve as acid sites.

It is worth to note that in the figure 3 the 258 cm$^{-1}$ peak appears in the spectrum of APO-2 and increases in intensity for the sample APO-3. This one became a stronger peak in the spectrum of APO-4. In an obvious study on the Raman spectra of a number of AlPO-based molecular sieves, Holmes et al. found that the breathing mode of the largest ring in the framework appears in the frequency range of 262 - 305 cm$^{-1}$ [14]. Thus, we consider that the 258 cm$^{-1}$ peak of Raman spectra in Figure 3 assigns to 12-member rings of the AlPO$_4$-5 framework and it is used as a signal to monitor the evolution of 12-member rings during crystallization of AlPO$_4$-5. This means that 12-member rings may appear in the gel sample heated for 24 h at 90ºC. It is well known that in synthesis of AlPO$_4$-5, species of Al and P oxides condense around TEA template molecules to form the framework. This result may show that the condensation to form 12-member rings occurs when the gel, heated for 24 h at 90ºC, is still amorphous. Probably, at this state, the TEA template molecules are confined as spacer in 12-member rings. This supports the significant change that leads to the strong shift of the second peak to higher temperature from APO-1 to APO-2 as mentioned above. The second DTG

peak remains constant (figure 2), while the 258 cm$^{-1}$ peak of Raman spectra (figure 3) increases in intensity as heating APO-2 further at 170ºC for 3 h. This may be explained by saying that in this stage the similar species containing 12-member rings form and these species act as nuclei. The major changes in the gel structure occurring during the early stages of reaction in which template molecules are confined in the rings were also shown in the formation of several microporous molecular sieves such as ZSM-5 [15], SAPO-44 [10].

From the literature [15 - 17] and the results obtained, we speculate that the formation of AlPO$_4$-5 may proceed through the following stages: mixing aluminum isopropoxide with phosphoric acid generates amorphous AlPO species as small oligomers having acid sites. These species assemble around TEA molecules through linking with acid sites and hydrogen bonds. This process takes advantage of further condensation between the AlPO species. Hydrothermal treatment at 90ºC for 24 h results in formation of 12-member rings containing TEA molecules. These 12-member rings have been not complete, still tightly link with TEA molecules and assemble along AFI channel intersections. This aggregation is responsible for nucleation. Further increase in heating temperature results in crystal growth through diffusion of the similar species to the surface of the growing crystallites to give a layer-by-layer growth mechanism that is regularly observed in growth of several microporous materials [15 - 17].

## IV - CONCLUSION

In the present work, we have investigated the evolution of the intermediate phases in AlPO$_4$-5 synthesis. The results indicate a significant change in the early stage of the crystallization, heating the initial gel at 90ºC for 24 h, during which the condensation occurs around TEA molecules to form 12-member rings of AlPO$_4$-5 structure. These rings aggregate along AFI channel intersections as nucleation for the crystal grow.

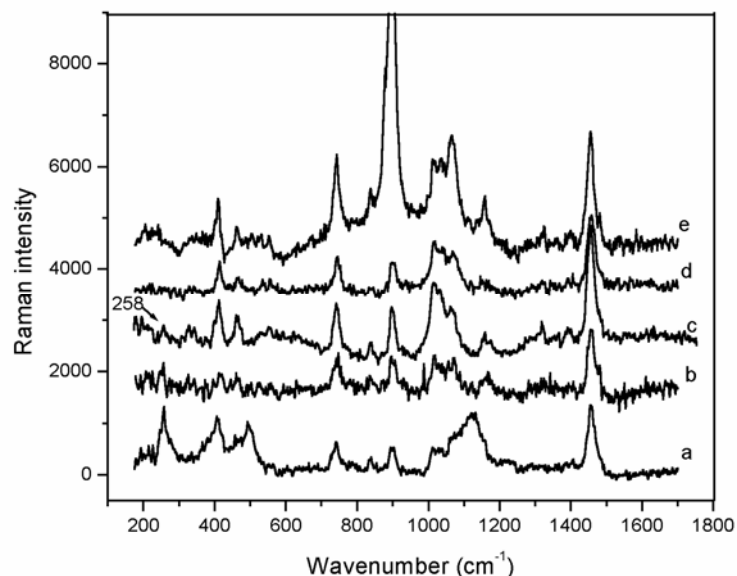*Figure 3:* The Raman spectra of APO-1 (d), APO-2 (c), APO-3 (b), APO-4 (a) and TEAHCl (e)

REFERENCES

1.  H. V. Bekkum, E. M. Flanigen, P. A. Jacobs, J. C. Jansen (Eds.). Introduction to Zeolite Science and Practice, 2$^{nd}$ ed., Elsevier, Amsterdam (2001).

2.  S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Canna, E. M. Flanigen. J. Am. Chem. Soc., 104, 1146 (1982).

3.  J. Caro, F. Marlow, K. Hoffmann, C. Striebel, J. Kornatowski, I. Girnus, M. Noack, P. Kolsch. Stud. Surf. Sci. Catal., 105, 2171 (1997).

4.  N. Wang, Z. K. Tang, G. D. Li, J. S. Chen. Nature, 408, 50 (2000).

5.  M. E. Davis. Nature, 417, 813 (2003).

6.  W. M. Meier, D. H. Olson. Atlas of Zeolite Structure Types, Butterworths, London, 18 (1987).

7.  C. S. Cundy, P. A. Cox. Microporous Mesoporous Mater., 82, 1 (2005).

8.  Y. Huang, B. A. Demko, C. W. Kirby. Chem. Mater., 15, 2437 (2003).

9.  Y. Huang, R. Richer, C. W. Kirby. J. Phys. Chem. B, 107, 1326 (2003).

10. Y. Huang, D. Machado, C. W. Kirby. J. Phys. Chem. B, 108, 1855 (2004).

11. O. B. Vistad, D. E. Akporiaye, K.P. Lillerud. J. Phys. Chem. B, 105, 12437 (2001).

12. K. H. Schnabel, G. Finger, J. Kornatowski, E. Loffler, C. Peuker, W. Pilz. Microporous Mater., 11, 293 (1997).

13. S. C. Popescu, S. Thomson, R. F. Howe. Phys. Chem. Chem. Phys., 3, 111 (2001).

14. A. J. Holmes, S. J. Kirkby, G.A. Ozin, D. J. Young. Phys. Chem., 98, 4677 (1994).

15. S. L. Burkett, M. E. Davis. J. Phys. Chem., 98, 4647 (1994).

16. S. L. Burkett, M. E. Davis. Chem. Mater., 7, 920 (1995).

17. S. L. Burkett, M. E. Davis. Chem. Mater., 7, 1453 (1995).