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Effect of synthesis pH and H_2O molar ratio on the structure and morphology of aluminum phosphate (AlPO-5) molecular sieves

Chia-Ming Chen and Jih-Mirn Jehng*

Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan, ROC

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AlPO-5 molecular sieves were prepared by the hydrothermal reaction of a gel mixture with the following compositions: $Al_2O_3:P_2O_5:Et_3N:H_2O = 1:1:1.5:x$, where x is between 100 and 750 H_2O molar ratio. The structure and morphology of the AlPO-5 molecular sieves depend on the gel mixture's composition, hydrothermal temperature, hydrothermal reaction time, and pH. Without pH control, the AlPO-5 structure changed from a spherical shape at $H_2O = 100$ to a hexagonal pillar shape at $H_2O = 450$. With pH control in the range of about 2.5–3.5, the hexagonal pillar crystals began to form at $H_2O = 100$ and an island of hexagonal pillars with radiation form appeared at $H_2O = 300$–450 due to the formation of a tridymite type of dense $AlPO_4$ phase. It appears that the formation rate of hexagonal pillar crystals to form a dense $AlPO_4$ phase is favorable under acidic conditions, and an amorphous AlPO-5 structure forms under basic conditions. Thus, the H_2O concentration and pH value have a dramatic effect on the AlPO-5 structure.

KEY WORDS: AlPO-5 molecular sieve; H_2O concentration; pH control; hexagonal pillar crystal; tridymite structure.

1. Introduction

Derivatives obtained from polyetherpolyamine have many applications in chemical industries including curing agents for epoxy resins, plasticizers, cross-linking agents for textiles, defoamers, and drug carriers for pharmaceutics [1–4]. The starting materials, polyethyleneglycol (PEG) or polypropyleneglycol (PPG), are commercially available on a large scale. In general, PEG and PPG can be aminated over a heterogeneous catalyst to achieve reductive amination or nucleophilic substitution amination to form specific polyamines [5]. The catalysts for reductive amination are supported nickel catalysts or Ni–Cu–Cr metal mixture catalysts [1], and metal phosphate or metal aluminum phosphate molecular sieves [5] for nucleophilic substitution.

Aluminum phosphate (AlPO-*n*) molecular sieves have physical/chemical properties similar to the zeolites, and their more important applications have included use as adsorbents for separation and purification, catalyst supports, and catalysts in chemical processes [6–9]. This material has a hexagonal symmetry, and contains one-dimensional channels bounded by 12-membered rings with alternate composition of AlO_4 and PO_4 tetrahedrons [6]. AlPOs are found to be electrically neutral with a P/Al ratio near one, possessing both Lewis and Brønsted acidities. Incorporation of a small amount of metal oxide such as Ga, Si, and Co oxide into aluminum phosphates can change their acidic properties and catalytic activities [10–12].

In previous studies of PEG amination over supported nickel catalysts [13], it was shown that the formation of amine (e.g. primary or secondary amine) products depends on the ammonia phase such as ammonia gas or ammonium hydroxide. When using ammonia as the amination source, the main products form primary amines, while using ammonium hydroxide the main products form secondary amines. The preliminary test of PEG amination over NiAlPO-5 appears that the most products form primary amines. With regard to industrial safety, the use of ammonia is more dangerous than ammonium hydroxide; thus, we want to increase the selectivity of primary amine using NiAlPO-5 as the amination catalyst. The main objectives of the present work are studying and controlling the AlPO-5 morphology with various preparation parameters. The addition of Ni metal into the AlPO-5 framework structure is then studied as a potential catalyst for the amination reaction.

2. Experimental

2.1. Materials and preparation

The AlPO-5 molecular sieve was prepared by the hydrothermal reaction according to previous studies [8,14] with different compositions. The gel mixture consisted of the following composition $Al_2O_3:P_2O_5:1.5\,Et_3N:xH_2O$, where x is the molar ratio of H_2O, which varied from 100 to 750.

Pseudoboehmite (CONDEA Chemie GmbH, 72.5 wt% Al_2O_3) and orthophosphoric acid (Showa,

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* To whom correspondence should be addressed.
E-mail: jmjehng@dragon.nchu.edu.tw

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85 wt%) were used as aluminum and phosphorus source, respectively. For a typical preparation of AlPO-5 with composition $Al_2O_3:P_2O_5:1.5Et_3N:100H_2O$, 7.11 g pseudoboehmite was combined with 30 g distilled water, and the slurry was mechanically stirred for 12 h. Then, a solution of 11.53 g orthophosphoric acid mixed with 60 g distilled water was slowly added into the slurry. With the addition of the orthophosphoric acid, the slurry turned into a viscous gel. After stirring for 2 h, the gel became a fluid-like solution. Subsequently, 7.65 g triethylamine (Et_3N, Showa) used as a template agent was added to the gel mixture and stirred for 2 h. Before transferring the gel mixture to a teflon-lined autoclave to perform the hydrothermal reaction, the pH value of the gel mixture needs to be controlled in order to compare the crystal structure difference of AlPO-5 with the uncontrolled pH value in the gel mixture [8]. In this study, the pH value of gel mixture was adjusted by H_2SO_4 or NH_4OH to be 2.5 ± 0.2, 3.5 ± 0.2, and 6.5 ± 0.2, respectively. Finally, the finished gel was transferred into a teflon-lined autoclave without stirring and placed into a preheated forced convection oven to form crystals at 200 °C for 16 h. The upper liquid layer was removed and the bottom crystal was washed, filtered with distilled water several times, and dried at 110 °C for 12 h. The template was removed by calcining in air at 550 °C for 12 h.

2.2. *BET surface area measurement*

A high-performance volumetric physisorption apparatus (Micromeritics ASAP 2010) was used to determine the pore size distribution and BET surface area of the supported nickel catalysts. An amount of 0.1–0.4 g of sample was first degassed with flowing He gas ($30\,cm^3/min$) to remove the impurities and water on the sample. Then, nitrogen gas was introduced into the sample quartz tube to effect the adsorption of nitrogen at liquid nitrogen temperature and calculate the surface area from the amount of nitrogen molecules adsorbed.

2.3. *X-ray powder diffraction (XRD) analysis*

X-ray powder diffraction technology was used to analyze the composition and crystalline morphology (AFI, AEL, etc.) of the crystals formed. X-ray measurements were carried out using an X-ray powder diffraction instrument (MAC Science, MO_3XHF) with a $CuK\alpha$ radiation source ($\lambda = 1.54056$ nm). The scanning rate was 5°/min with 2θ from 5 to 60°, at 40 kV and 30 mA.

2.4. *FTIR spectroscopy measurement*

FTIR spectroscopy was used to monitor and analyze the functional groups to determine the composition of the AlPO-5 molecular sieves. Dried synthetic AlPO-5 molecular sieve (0.01 g) was mixed with 0.2 g of dried KBr powder and pressed into a 13 mm disk. FTIR spectra of the AlPO-5 molecular sieves were recorded using a FTIR spectrometer (Perkin-Elmer Paragon 500) with a resolution of $2\,cm^{-1}$ by scanning 50 times from 300 to $4000\,cm^{-1}$ at room temperature. Combining the results of X-ray powder diffraction patterns and FTIR spectra can provide information on the composition of the AlPO-5 crystals formed.

2.5. *Scanning electron microscopy (SEM)*

It was found that the composition of the crystals formed was the same with various H_2O molar ratios using FTIR and XRD analysis, but the structure of the AlPO-5 crystal phase was very different. SEM was used to distinguish the different phases of the AlPO-5 with various H_2O molar ratios. SEM was carried out using a TOPCON ABT-150S to study the effect on the crystalline structure of H_2O molar ratio change and pH control.

2.6. *Differential scanning calorimetry (DSC)*

If the AlPO-5 molecular sieves have both crystal and amorphous phases in their structure, it is not easy to distinguish them using only SEM or XRD. If the AlPO-5 molecular sieves have a crystal phase, sharp endothermic peaks (melting point of crystals) will appear in the DSC plots. If there is a broad peak, this indicates the AlPO-5 molecular sieves are amorphous. The DSC analysis was performed under nitrogen flow ($52\,cm^3/min$) with a heating rate of 10 °C/min from 40 to 350 °C. The sample weight was about 3 mg. A TA Instruments V2.6D thermal analyzer was used.

3. Results and discussion

3.1. *BET surface area*

BET measurements of the AlPO-5 molecular sieves, with various H_2O molar ratios and with/without pH control (see figure 1), have shown that the AlPO-5 surface area decreases with increasing H_2O molar ratio, and there is no change with/without pH control. However, a high or low pH value results in lower surface area. It appears that increasing the H_2O content decreases the surface area, and the surface area can be controlled by the appropriate pH value.

3.2. *XRD analysis*

The X-ray powder diffraction patterns of the AlPO-5 molecular sieve are shown in figure 2. The characteristic peaks shown in figures 2(a)–(c), at $2\theta = 7.4$, 12.9, 14.9, 19.7, 21.2, 22.5, 25.9, 29.1, 30.0, 34.5, and 37.9° indicate that the synthetic AlPO-5 molecular sieves with various

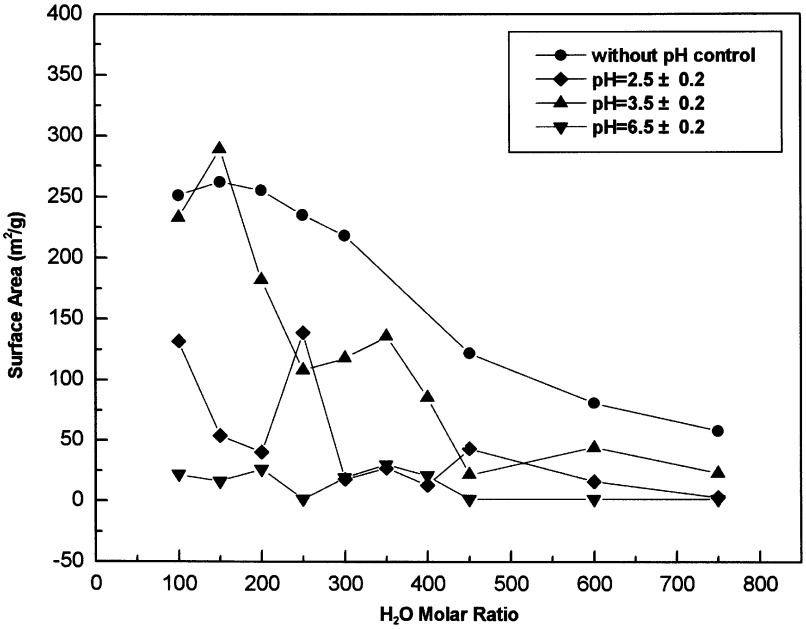


Figure 1. Effect of H_2O content and pH value on BET surface area.

H_2O content form crystals of $AlPO_4$ with an AFI structure [15], except for the sample with pH control at 6.5 ± 0.2. The XRD patterns of AlPO-5 with pH of 2.5 and 3.5 (figures 2(b) and (c)) have some additional peaks at $2\theta = 20.5$, 21.6, 21.7, 23.1, and 35.9°. These peaks indicate the dense $AlPO_4$ phase of tridymite type [16], but the crystals still possess the AFI structure. On the basis of the types of metal-centered polyhedra in the framework, the AlPO-*n* families are divided into three groups [17]: (1) those frameworks consisting only of alternating corner-linked tetrahedra; (2) dense phases such as berlinite or tridymite containing only octahedra and tetrahedra; and (3) frameworks composed of some combination of 4-, 5-, and 6-coordinated aluminum. These results are consistent with the SEM images: the crystalline structures are in the form of hexagonal pillars with radiation due to the dense $AlPO_4$ phase of tridymite type. The XRD patterns for pH = 6.5 are

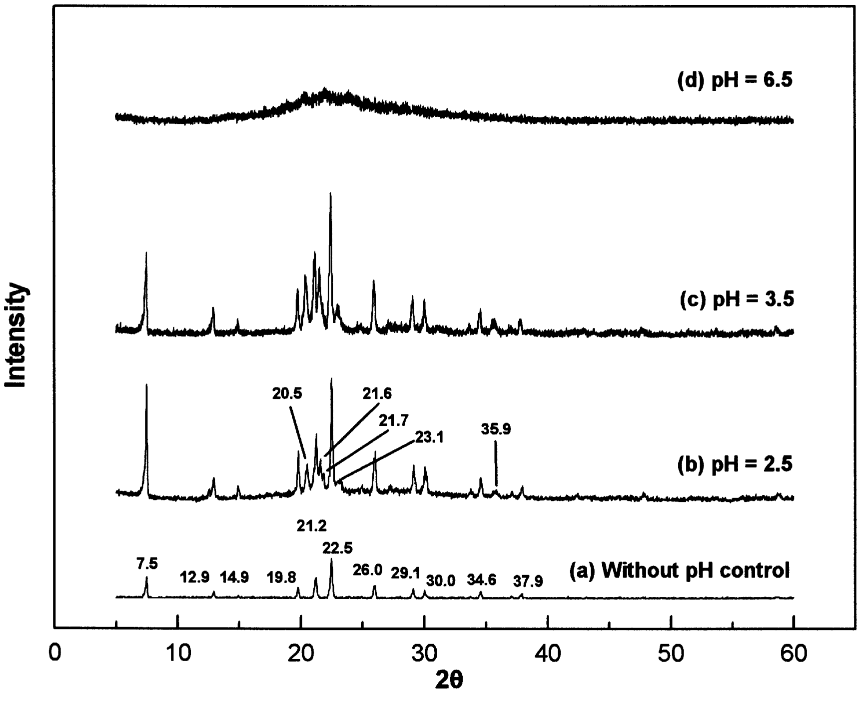


Figure 2. XRD patterns of AlPO-5 with different pH values.

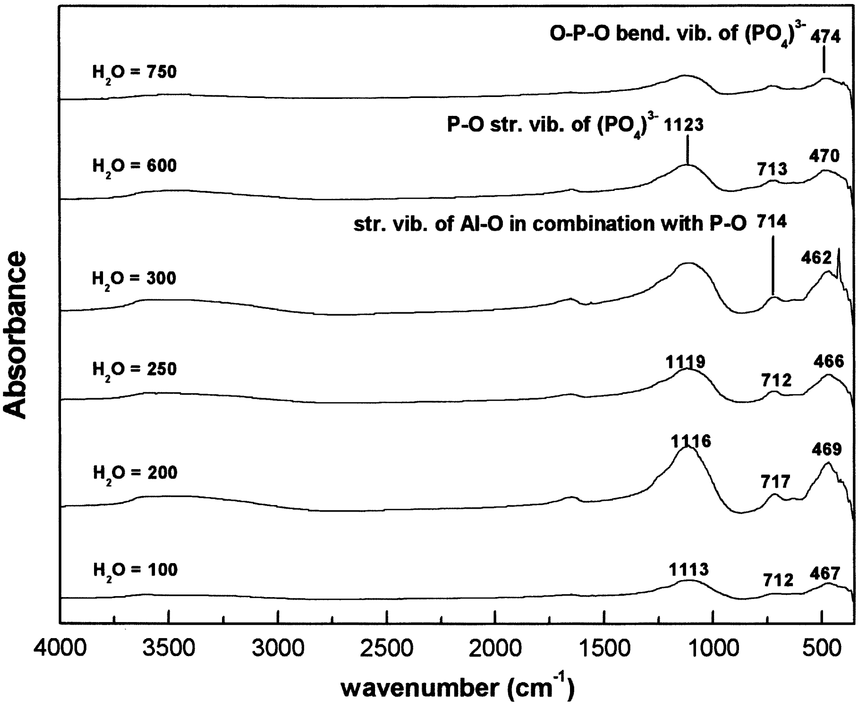


Figure 3. FTIR spectra of AlPO-5 with various H_2O contents.

different from those for pH = 2.5 and 3.5 due to the fact that the crystal and amorphous phases may coexist in the synthetic AlPO-5 molecular sieves (see figure 2(d)). Thus, the crystalline phase of AlPO-5 molecular sieve can be controlled by the pH value of the gel mixture. The crystal phase is predominant under acid conditions, and the amorphous phase forms under neutral or basic conditions.

3.3. *FTIR spectroscopy*

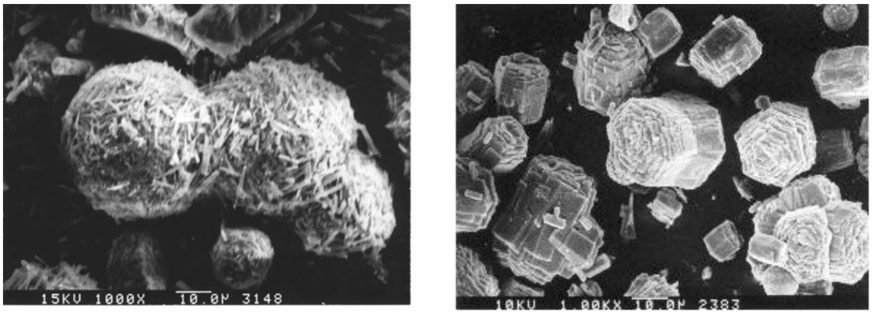
From the results of FTIR spectroscopy studies on AlPO-5 with various H_2O contents shown in figure 3, it appears that all peaks are contributed by the $AlPO_4$ compound. The characteristic peaks at about 474, 714, and 1120 cm^{-1} are assigned to the O–P–O bending vibration, P–O stretching vibration of $(PO_4)^{3-}$, and stretching vibration of Al–O in combination with P–O [18], respectively. With pH control at about 2.5, 3.5, and 6.5 or without pH control, the FTIR studies indicate that the composition of AlPO-5 is a $AlPO_4$ compound, even the amorphous phase with pH control at 6.5. It appears that the pH value can affect the structure of AlPO-5, but has no effect on the composition of AlPO-5 molecular sieves.

3.4. *SEM*

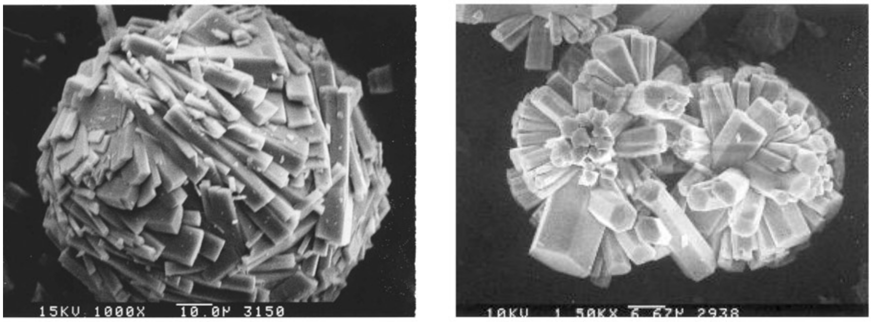
SEM is a very effective technique to distinguish the various structural morphologies of the AlPO-5 and the effect of H_2O content on the crystal structure. The SEM images in figure 4 show the morphologies of the different AlPO-5s changing with the H_2O content and pH value. Without pH control, the morphology of AlPO-5 changes from spherical with $H_2O = 100$ molar ratio to hexagonal pillar with $H_2O = 450$ molar ratio; while with pH control at 3.5 ± 0.2, the morphology of AlPO-5 changes from spherical with $H_2O = 100$ molar ratio to hexagonal pillar with $H_2O = 200$ molar ratio. It shows that with pH control at 3.5 ± 0.2, the hexagonal pillar crystal forms rapidly both with lower H_2O molar ratio and with increasing H_2O content. Furthermore, the crystals formed with pH control at 3.5 and 2.5 were denser than those without pH control. However, with higher pH at 6.5 ± 0.2, the hexagonal pillar does not form at any H_2O content.

3.5. *DSC*

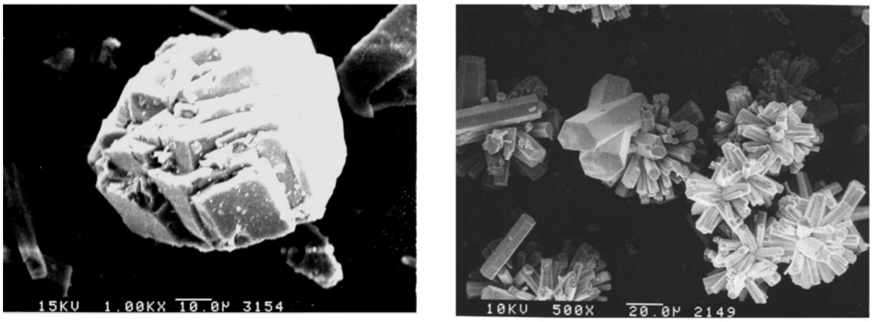
The DSC results in figures 5 and 6 show that with various H_2O molar ratios and pH control at 2.5 and 3.5 ± 0.2, some distinct endothermic peaks are present at about 100–200 °C. This means that the AlPO-5 molecular sieves have more than one crystal melting point at different temperatures. The results also show that with pH control at lower pH value, the AlPO-5 molecular sieves possess a crystal phase when the H_2O molar ratio is changed from 100 to 750. With pH control at 6.5 ± 0.2 (figure 7), a broad peak appears at about 150–250 °C with H_2O molar ratio of 150 and 450. This



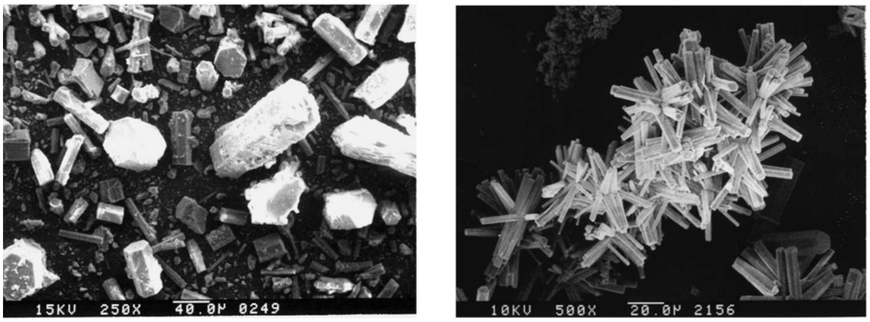
A1. H_2O=100, T=200 °C, Time=16 hr **A2. H_2O=100, T=200 °C, Time=16 hr, pH=3.5**



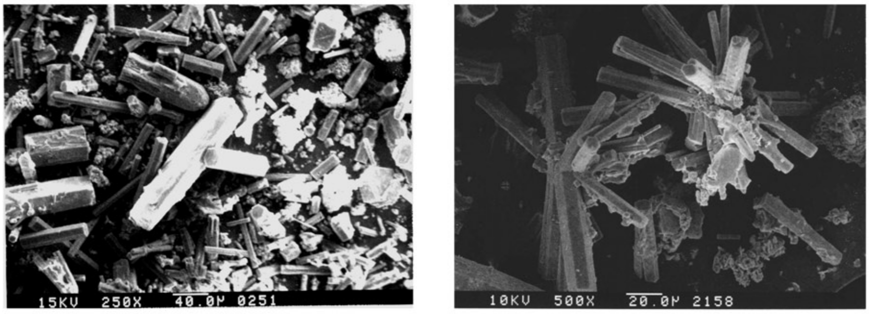
B1. H_2O=200, T=200 °C, Time=32 hr **B2. H_2O=200, T=200 °C, Time=32 hr, pH=3.5**



C1. H_2O=300, T=200 °C, Time=48 hr **C2. H_2O=300, T=200 °C, Time=48 hr, pH=3.5**

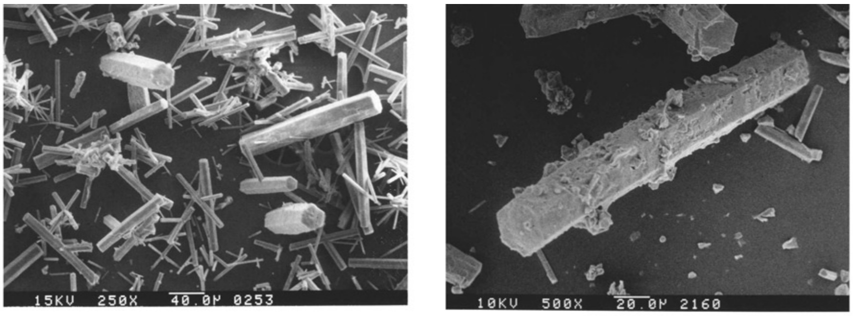


D1. H_2O=450, T=200 °C, Time=72 hr **D2. H_2O=450, T=200 °C, Time=72 hr, pH=3.4**

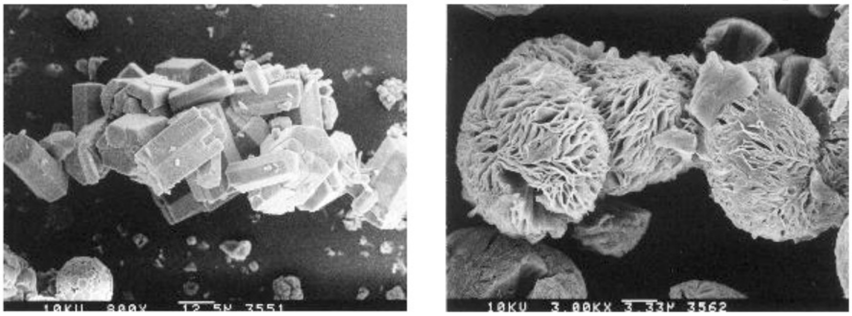


E1. H_2O=600, T=200 °C, Time=96 hr **E2. H_2O=600, T=200 °C, Time=96 hr, pH=3.5**

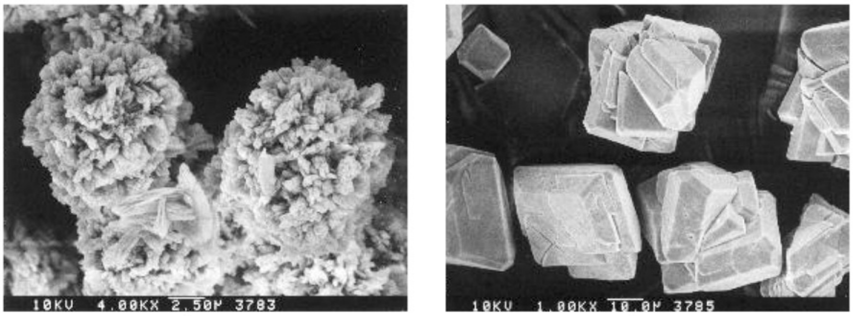
Figure 4. SEM images of AlPO-5 with various H_2O contents and pH values.



F1. H_2O=750, T=200 °C, Time=120 hr **F2. H_2O=750, T=200 °C, Time=120 hr, pH=3.3**



G1. H_2O=100, T=200 °C, Time=16 hr, pH=2.5 **G1. H_2O=100, T=200 °C, Time=16 hr, pH=6.5**



H1. H_2O=750, T=200 °C, Time=120 hr, pH=2.5 **H2. H_2O=750, T=200 °C, Time=120 hr, pH=6.5**

Figure 4. Continued.

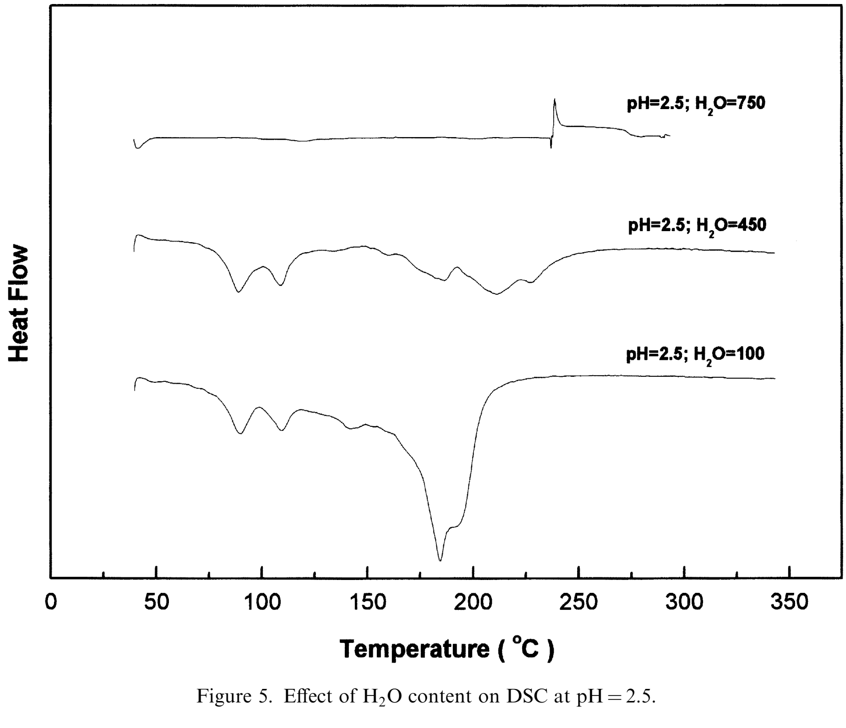


Figure 5. Effect of H_2O content on DSC at pH = 2.5.

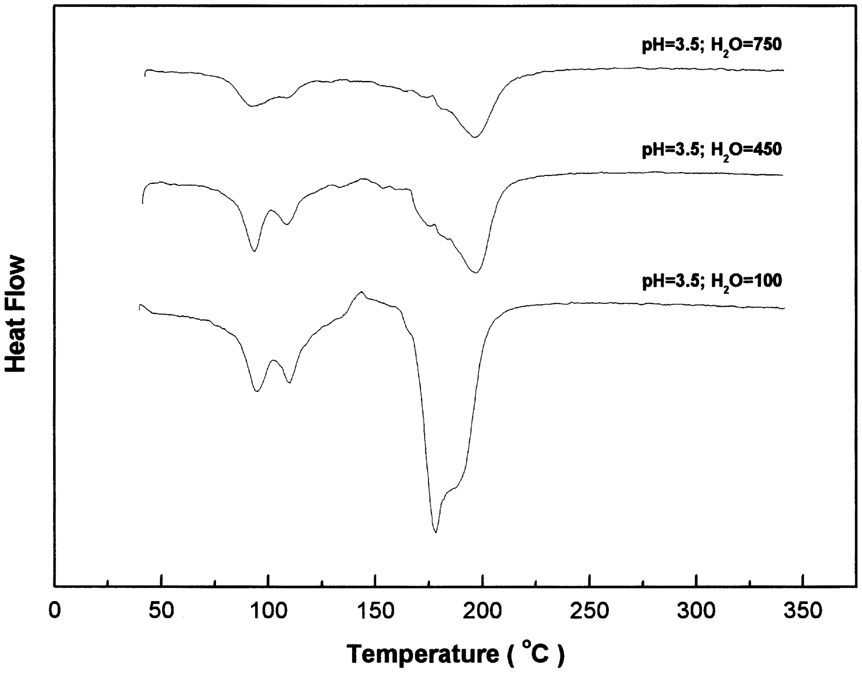


Figure 6. Effect of H_2O content on DSC at pH = 3.5.

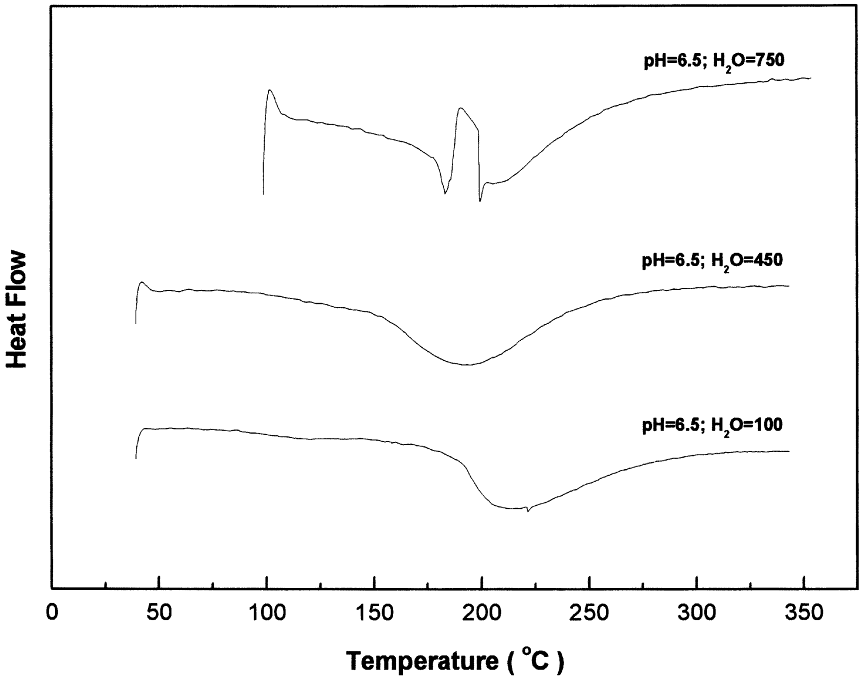


Figure 7. Effect of H_2O content on DSC at pH = 6.5.

shows that the AlPO-5 has different melting points of the crystalline phase, and it is amorphous. The results are consistent with the results of SEM and TEM. When the H_2O molar ratio is changed to 750 (figure 7), the results are significantly changed. The shape of the DSC trace is similar for AlPO-5 with $H_2O = 150$ and 450, but it has two additional endothermic peaks around 175 and 200 °C. This shows that the crystal and amorphous phases coexist at higher pH value and H_2O molar ratio.

4. Conclusions

The structures of AlPO-5 molecular sieves depend on the composition of the gel mixture and other factors such as hydrothermal temperature, hydrothermal reaction time, and pH value of the gel mixture. The different preparation conditions change the properties of AlPO-5 molecular sieves such as BET surface area, surface acidity, structure, and morphology. The structures of AlPO-5 molecular sieves are controlled by H_2O concentration, and BET surface area of the AlPO-5s changes with different H_2O concentration and with/without pH control. Preparation of AlPO-5 at a lower pH of about 2.5–3.5 enhances the formation rate of hexagonal pillar crystal to dense $AlPO_4$ phase, while at a higher pH of about 6.5 the amorphous $AlPO_4$ forms and the BET surface area is lower than for pH values of 2.5 and 3.5. With various H_2O contents for pH control at 2.5 and 3.5 or without pH control, the composition of AlPO-5 molecular sieves is still a $AlPO_4$ compound with an AFI structure. The BET surface area decreases with increasing H_2O content. The results of this study indicate that a hexagonal pillar crystal forms under acid conditions, and the hexagonal pillar crystal structure collapses into an amorphous phase under neutral and basic conditions.

Acknowledgments

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