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Structure control of metal aluminum phosphate (MeAlPO-5) molecular sieves and applications in polyethylene glycol amination

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The structure and morphology of both pure AlPO-5s and nickel containing AlPO-5s were affected by the preparation conditions such as pH value, nickel incorporated method (hydrothermal method or traditional incipient wetness impregnation). The dense tridymite phase of AlPO-5 can be formed by two controlling factors. One is controlling the pH at lower value to the AlO_4 and PO_4 moleculars to form $AlPO_4$ with dense phase, and the other is used the excess nickel adding to increase the crystallinity of AlPO-5 to form dense tridymite phase. The reactivity of PEG-400 amination was also affected preparation methods and conditions. At higher nickel loading, the nickel supported on AlPO-5 prepared by traditional incipient wetness impregnation forms the surface nickel species, and both the surface nickel species and nickel incorporated species form by the hydrothermal method. The amination catalysis indicates that the reactivity of PEG-400 prepared by incipient wetness impregnation method was higher than that prepared by hydrothermal method. The formation of the dense tridymite phase of AlPO-5 can be further determined by the X-ray powder diffraction (XRD). The nickel containing AlPO-5s prepared with lower pH value possesses only the tridymite phase and exhibit higher catalytic reactivity. It appears that the trydimite structure can improve the catalytic activity for PEG-400 amination due to the grain size of the formed crystal of NiAlPO-5 is smaller than the catalyst without the formation of the trydimite phase.

KEY WORDS: nickel containing AlPO-5; dense tridymite phase; hydrothermal method; incipient wetness impregnation; PEG-400 amination.

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 carrier for pharmaceutics [1–4]. The starting materials, polyethyleneglycol (PEG) or polypropyleneglycol (PPG), are commercially available at large scales. In general, PEG and PPG can be aminated over a heterogeneous catalyst to do reductive amination or nucleophilic substitution amination to form specific polyamines [5]. The catalysts for the reductive amination are supported nickel catalyst or Ni–Cu–Cr metal mixture catalyst [1], and metal phosphate [5] for the nucleophilic substitution.

Aluminum phosphate (AlPO-*n*) molecular sieves have physical/chemical properties similar to the zeolites in some properties and more important applications have been used as adsorbents for separation and purification, catalyst supports and catalysts in the chemical process [6–9] due to their high specific surface area, thermal stability, and selectivity of reactant/product. This material has a hexagonal symmetry, and contains one-dimensional channel bounded by 12-membered rings with alternative composition of AlO_4 and PO_4 tetrahedron [6]. Generally speaking, the pure aluminum phosphate molecular sieves almost have no catalytic reactivity due to their electrically neutral skeleton, no Bronsted acid site and fewer Lewis acid site. However, the incorporation of a small amount of metal oxide such as Ga, Si, and Co oxide into aluminum phosphate can change their acidic properties and catalytic activities [10–12]. After changing the properties of AlPOs, they can catalyze various types of hydrocarbon transformation reactions such as cracking, alkylation, isomerization [13,14], and dehydration [15].

Previous studies on preparing pure AlPO-5 molecular sieves [16], it indicates that the structure and morphology of pure AlPO-5 synthesized by hydrothermal method depend on the gel mixture's composition, hydrothermal temperature, hydrothermal reaction time, and pH value. The structures of AlPO-5 molecular sieves can be further controlled by the addition of H_2O concentration, and the BET surface area of AlPO-5 changes as a function of H_2O concentration and pH value. The preparation of AlPO-5 at lower pH value enhances the formation rate of hexagonal pillar crystal to dense $AlPO_4$ phase, while the amorphous $AlPO_4$ forms at higher pH value and possesses lower BET surface area at lower pH value. Upon with/without pH control at various H_2O content, the composition of AlPO-5 molecular sieves still contains a $AlPO_4$ with AFI structure. Incorporating metals into the AlO_4 and PO_4 tetrahedron by hydrothermal method, the structure of MeAlPO-5 are mainly affected by the metal ion radius [17] and template type. For preparing pure AlPO-5s, the tridymite phase forms easily with pH control, however, it does not exist in the prepared conditions without pH

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control and lower H_2O content. It appears that the structure of AlPO-5 after incorporating Ni into the AlPO-5 frame work can be affected by the nickel incorporating method, nickel loading amount, H_2O content, and pH value. Thus, three types of nickel containing AlPO-5s were prepared in order to study the effect of previous factors on the NiAlPO-5 structure. Type 1 and type 3 were prepared by hydrothermal method noted as NiAlPO-5 (H_2O molar ratio = 35) and NiAlPO-5 (H_2O molar ratio = 100 and 450, pH = 3.5), respectively, in order to control the formation of tridymite phase by H_2O molar ratio and pH value, and study the morphology and structure of nickel containing AlPO-5s by various preparation conditions. The nickel precursor was directly added into the gel mixture to form nickel containing AlPO-5 via hydrothermal reaction. Type 2 noted as Ni/AlPO-5 (H_2O = 35) was prepared by traditional incipient wetness impregnation over the synthesized pure AlPO-5 (H_2O = 35) which was prepared by hydrothermal method with H_2O molar ratio equal to 35. Thus, the effect of preparation method on the morphology and structure of NiAlPO-5s can also be studied.

The results of PEG amination over supported nickel catalyst [18] show that the formation of amine (e.g. primary or secondary amine) products depends on the ammonia phase such as ammonium gas or ammonium hydroxide. When using ammonia as the amination source, the main products form primary amine, while using the ammonium the main products form secondary amine. The main objectives of the present work are: studying and controlling the nickel containing AlPO-5 morphology with various preparation parameters, then, using the structure of synthesized NiAlPO-5 molecular sieves to determine the catalytic performance and selectivity of amination reaction.

2. Experimental

2.1. Materials and preparation

Three types of nickel containing AlPO-5 molecular sieves were prepared by different methods and prepared conditions. Type 1 and type 3 were prepared by hydrothermal method [8,19] noted as NiAlPO-5 with Al_2O_3:P_2O_5:1.5Et_3N:35H_2O and NiAlPO-5 (H_2O molar ratio = 100 and 450, pH = 3.5), respectively. The nickel precursor, nickel nitride (Showa, 98 wt%), was added directly in the gel mixture after adding orthophosphoric acid, then adding Et_3N as a template. Type 2 noted as Ni/AlPO-5 (H_2O molar ratio = 35) was prepared by traditional incipient impregnation over synthetic pure AlPO-5 (H_2O = 35) by hydrothermal method.

Pseudoboehmite (CONDEA Chemie GmbH, 72.5 Al_2O_3 wt%) and orthophosphoric acid (Showa, 85 wt%) were used as aluminum and phosphorus source, respectively. For a typical preparation of NiAlPO-5 with Al_2O_3:P_2O_5:1.5 Et_3N:100H_2O and pH = 3.5 by hydrothermal method, a 7.11 g of pseudoboehmite was combined with a 30 g of distilled water into a slurry by 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. Upon 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, a specific amount of nickel precursor was added into the gel mixture and stirred for 2 h. At last, a 7.65 g triethylamine (Et_3N, Showa) used as a template agent was added to the gel mixture and stirred for additional 2 h. Before transferring the gel mixture to the teflon-lined autoclave to perform hydrothermal reaction, the pH value of the mixture needs to be controlled at 3.5 by adding H_2SO_4. Finally, the finishing gel was transferred into a teflon-lined autoclave without stirring and placed into a preheated forced convection oven to form crystal at 200 °C for 16 h. The upper layer liquid was removed out 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. The prepared conditions and characterizations of synthetic NiAlPO-5 molecular sieves are listed in table 1.

2.2. BET surface area measurement

The BET surface area of pure AlPO-5 molecular sieves are about 206–274 m^2/g and affected by preparation method [16]. The catalytic performance is depended on the active metal type and dispersity of metal over the support or in the pore structure. The refection of dispersity on the BET surface area can be used to determine a relation between catalytic performance of PEG-400 amination and dispersity of metal in the structure.

A high-performance volumetric physisoption apparatus (Micromeritics ASAP 2010) are used to determine the BET surface area of the different type of NiAlPO-5 molecular sieves. A 0.1–0.4 g of sample was first degassed with flowing 30 cc/min He gas to remove the impurities and water on the sample. Then, the nitrogen gas was introduced into the sample quartz tube to perform the adsorption of nitrogen under the liquid nitrogen temperature and calculate the surface area from the amount on 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 (such as AFI or AEL structure etc.) of the formed crystal and also used to study the nickel effect on the structure or morphology of AlPO-5 after incorporating nickel. The analysis was carried out by using the X-ray powder diffraction instrument (MAC Science,

Table 1
Physical properties and PEG-400 amination catalysis of the NiAlPO-5 catalysts

Type 1 (H_2O = 35)	Grain size (nm)	BET (m_2/g)	Structure (XRD)	Composition (FTIR)	Amine yield (%)	Selectivity (%)	
						1° amine	2° amine
AlPO-5	19	206–274	AFI	$AlPO_4$	0.0	–	–
5% NiAlPO-5	19	184	AFI	$AlPO_4$	9.7	99	1
20% NiAlPO-5	87	147	AFI	$AlPO_4$	10.5	73	7
25 % NiAlPO-5	44	53	AFI + Tridymite	$AlPO_4$	22.4	0	100
35% NiAlPO-5	74	3	Tridymite	$AlPO_4$	18.3	6	94
Type 2 (Impregnation)							
10% Ni/AlPO-5	–	–	AFI	$AlPO_4$	28.5	64	36
20% Ni/AlPO-5	33	169	AFI	$AlPO_4$	45.6	48	52
30% Ni/AlPO-5	33	138	AFI	$AlPO_4$	43.2	44	56
Type 3							
20% NiAlPO-5 (H_2O = 100, pH = 3.5)	31	14	Tridymite	$AlPO_4$	27.8	0	100
20% NiAlPO-5 (H_2O = 450, pH = 3.5)	29	13	Tridymite	$AlPO_4$	57.8	0	100

Note: The grain size was calculated by Scherrer's formular.

MO3XHF) with CuK_α radiation source ($\lambda = 1.54056$ nm) and the scanning rate was 5 deg/min with 2θ from 5° to 60° under the controlling of 40 kV and 30 mA. The peak position was contrast with the JCPDS-International Center for Diffraction Data to determine the composition and crystalline morphology.

2.4. FT-IR spectroscopy measurement

FT-IR spectroscopy was used to monitor and analyzed the function groups of the NiAlPO-5 molecular sieves and determine the composition of NiAlPO-5 molecular sieves to make sure the synthesized NiAlPO-5 molecular sieves possessing the composition of $AlPO_4$ in the AlPO-5 molecular sieves after the addition of nickel. Take 0.01 g of dried synthesized NiAlPO-5 molecular sieve mixed with 0.2 g of dried KBr powder and pressed into a 13 mm disc. The FT-IR spectra of the AlPO-5 molecular sieves were recorded on a FT-IR spectrometer (Perkin-Elmer Paragon 500) with a resolution 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 FT-IR spectra can provide the information of the composition of the formed NiAlPO-5 crystals.

2.5. Scanning electron microscopy (SEM)

It found that the composition of the formed NiAlPO-5 crystals prepared by various preparation methods was similar by using both the FT-IR and XRD analysis, but the structure of AlPO-5 crystal phase was very different. Thus, SEM technology was further used to distinguish the difference phases of the NiAlPO-5 molecular sieves prepared by various methods. SEM was carried out using a TOPCON ABT-150S to study the effect on the crystalline structure with the control of the H_2O molar ratio and pH value. Take a little of dried synthesized NiAlPO-5 molecular sieve to disperse on the sample stage with carbon-adhesive tap and analyze with 10–15 kV.

2.6. Amination of polyethylene glycol-400 (PEG-400) over nickel containing AlPO-5s

A known amount of PEG-400 with ~30 wt% of ammonia solution was loaded into a 600 cm^3 autoclave (Parr, model 4563). About 5 g of three types of Ni containing AlPO-5 molecular sieve was also added into the reactor. It was ensured that all valves and screws on the reactor were closed and tightened. The reactor was then pressurized by nitrogen gas to ~2 bar and released to atmospheric pressure. The last step was repeated for three times in order to purge out the air in the reactor. After the purging steps, hydrogen gas was introduced into the reactor till the reactor pressure has reached ~9 bar. Finally, the total pressure of the reactor was increased to ~34 bar by introducing nitrogen gas. The amination reaction was performed at 250 °C with stirring rate of 200 rpm for about 6 h. The titration method was used to calculate the total amine yield of collected samples. In addition, it can be used to distinguish from primary and secondary amine and calculate the selectivity of primary and secondary amine.

2.7. Analysis of amination products

The amount of amine product noted as M_{amine} has been monitored by the titration method to calculate the amination yield. To determine the amination selectivity, the amine products were also analyzed by titration method with of primary and secondary amine, the amine product was also be analyze by titration method with adding acetic anhydride and salicylaldehyde to determine the amount of 3° amine and 2° + 3° amine, respectively. The detail procedure was described in the following.

About 0.2 g of amine product was mixed in the 50 mL beaker with appropriate amount of acetic anhydride and heating to about 40–50 °C, and let the acetic anhydride completely react with the amine product to determine the amount of 3° amine. The bromophenol blue was added as the indicator and the titration was performed with 0.1 N HCl. To determine the amount 2° + 3° amine, the salicylaldehyde was added instead of the acetic anhydride to react with the amine product. According to the above titration results, the amount of 1° and 2° amine noted as $M_1°$ and $M_2°$ and amine selectivity can be calculated by the following equations:

$$\mathrm{M}_{1^\circ} = \mathrm{M}_\mathrm{T} - \mathrm{M}_{2^\circ+3^\circ}$$

$$\mathrm{M}_{2^\circ} = \mathrm{M}_{2^\circ+3^\circ} - \mathrm{M}_{3^\circ}$$

$$S_{1^\circ} = \frac{\mathrm{M}_{1^\circ}}{\mathrm{M}_\mathrm{T}} \times 100\%$$

$$S_{2^\circ} = \frac{\mathrm{M}_{2^\circ}}{\mathrm{M}_\mathrm{T}} \times 100\%$$

where M_T is the total amine amount including 1°, 2°, and 3° amine; $\mathrm{M}_{2^\circ+3^\circ}$ is the amount of 2° and 3° amine; M_{3° is the amount of 3° amine; S_{1° is the selectivity of 1° amine; S_{2° is the selectivity of 1° amine.

2.8. Amination mechanisms of PEG-400 over NiAlPO-5s

For reduction amination, the reaction mechanisms involve two steps: one is that the PEG is dehydrogenated by the catalyst to form the ketone; the other is that the ketone is amination by ammonium hydroxide and hydrogenation to form the polyetheramine. The FT-IR analysis has proved that the mechanisms of amination over NiAlPO-5s are related to the reduction amination. To prove that the ketone was formed in the first step, the amination was performed without the presence of hydrogen and ammonium hydroxide in order to avoid the hydrogenation process, and the product was also analyzed by FT-IR. If the ketone was formed, the peak of ketone appears around 1720 cm^{-1}. The intermediate product was further reacted with the hydrogen and ammonium hydroxide to form the polyetheramine which the peak appearing in the region of 1250–1020 cm^{-1} is contributed to the C–N vibration of the amine.

To study the mechanism of PEG-400 amination, the change of average molecular weight before and after amination is an important index to understand the formation of amine by either addition or condensation pathway. If the amine was formed by addition pathway to form primary amine, the average molecular weight was increased with integral times. On the contrary, if the amine was formed by condensation pathway to form secondary amine, the average molecular weight was increased slightly. Thus, it can be analyzed by gel-permeation chromatography (GPC) method to study the change of average molecular weight and determine the amination mechanism.

3. Results and discussion

3.1. BET surface area

BET measurements of NiAlPO-5 molecular sieves prepared by various methods and conditions are listed in table 1. To compare the BET results of Type 1 with Type 2, the surface area of Type 1 decreases dramatically from 274 to 3 m^2/g with increasing Ni loading due to the location of Ni metal into the frame structure of the AlO_4 and PO_4 tetrahedrons while the Ni metal of Type 2 are well-dispersed on the surface of AlPO-5 structure and the surface area decreases from 274 to 138 m^2/g. It appears that the traditional incipient wetness impregnation can well disperse the Ni metal on the AlPO-5 surface. The surface area of Type 3 is about 13–14 m^2/g much smaller than the other two types at the same nickel loading. This is due to the collapse of the AlO_4 and PO_4 tetrahedrons and the formation of the tridymite phase.

3.2. XRD analysis

The X-ray powder diffraction patterns of the Ni containing AlPO-5 molecular sieves are shown in figures 1–4 and the corresponding grain size of NiAlPO-5 are also shown in table 1. For Type 1 (in figure 1) with Ni loading below 25%, the characteristic peaks at $2\theta = 7.6°$, 12.9°, 14.9°, 19.8°, 21.2°, 22.5°, 26.0°, 29.2°, 30.1°, 34.7° and 37.9°, indicates that the synthesized NiAlPO-5 molecular sieves with $\mathrm{H_2O}$ molar ratio = 35 form a crystal of AlPO_4 with a AFI structure [20]. The AFI structure of AlPO_4 and tridymite phase coexist in the 25% NiAlPO-5 ($\mathrm{H_2O} = 35$). However, only the tridymite phase exist in the structure with the additional peaks at $2\theta = 20.5°$ and 21.6° with the nickel loading reach to 35%. These peaks contribute to the dense AlPO_4 phase of tridymite type [21] and the AFI structure does not exist due to the higher nickel concentration in the gel mixture that makes the frame structure of the AlO_4 and PO_4 tetrahedrons collapsed. For Type 2, the Ni/AlPO-5 ($\mathrm{H_2O} = 35$) molecular sieves still possess AFI structure even the nickel loading reach to 30%. The results are shown in figure 2 by using XRD analysis. Only the Ni/AlPO-5 ($\mathrm{H_2O} = 35$) with higher nickel loading prepared by impregnation method, possesses the additional peaks at $2\theta = 37.4°$ and 43.5° which are contributed to the nickel oxide crystallites and the surface well-dispersed nickel particle can agglomerate at higher Ni loading. This result is consistent with the BET surface area measurement and demonstrates that the traditional incipient wetness impregnation

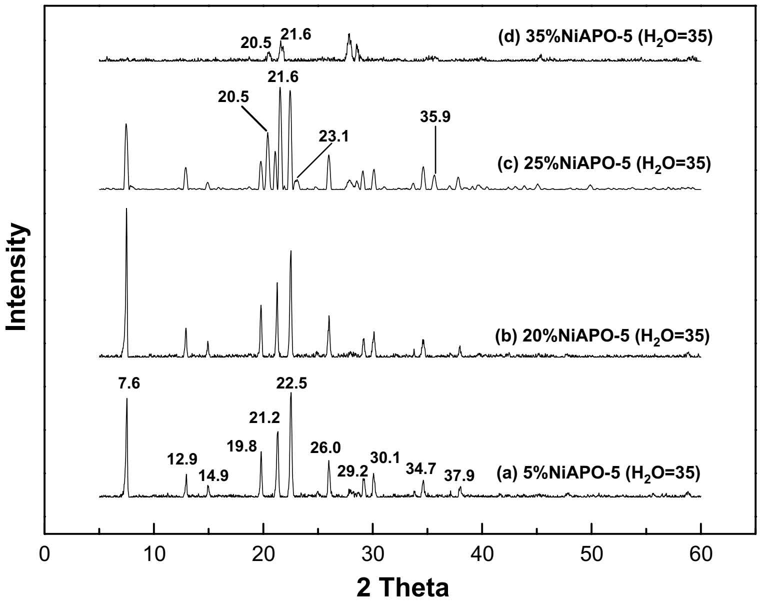


Figure 1. XRD patterns of NiAlPO-5 as a function of Ni loading.

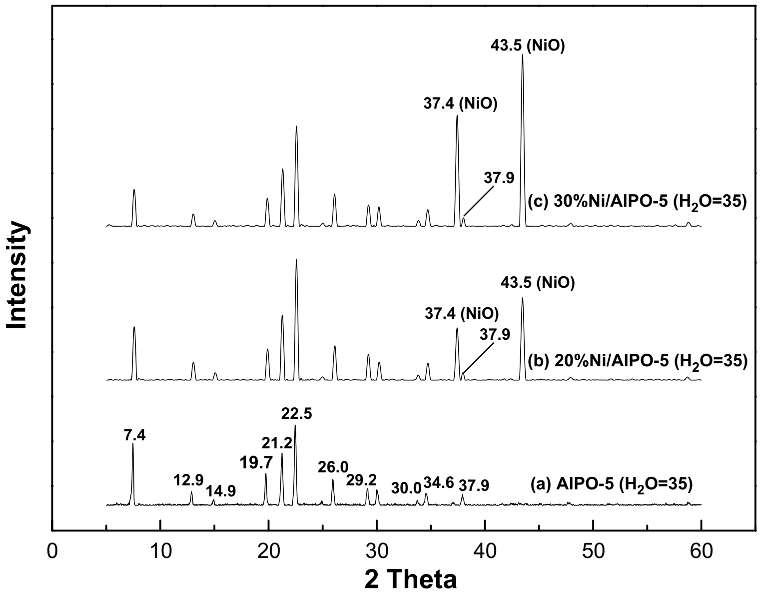


Figure 2. XRD patterns of NiAlPO-5 as a function of Ni loading.

method can make the nickel particle well-dispersed on the framework of AlPO-5. For Type 3 (in figure 4), the prepared NiAlPO-5 molecular sieves only possesses the tridymite phase with the XRD peaks at $2\theta = 20.5°$, 21.6°, 23.1°, 27.2° and 35.9°. The Type 3 is easily formed tridymite phase with pH control than Type 1. In order to know that weather nickel incorporating or pH control is the major factor to form the tridymite phase. The lower nickel loading sample such as 5% and 10% NiAlPO-5 ($H_2O = 100$, $pH = 3.5$) were prepared and their XRD analysis results were shown in figure 3. It appears that the tridymite phase was also formed even though the nickel loading was only 5% under lower pH value. Thus, the pH value is the primary factor to control the formation of tridymite phase, and without pH control the tridymite phase can also be obtained by increasing nickel loading. The results point out that the preparation methods and conditions affect the synthesized NiAlPO-5 molecular sieves, and can be use to control the catalytic performance. The XRD analysis is also a powerful technology to determine the grain size of the formed crystal by Scherrer's formula [22] and to understand the relation between grain size and catalytic performance.

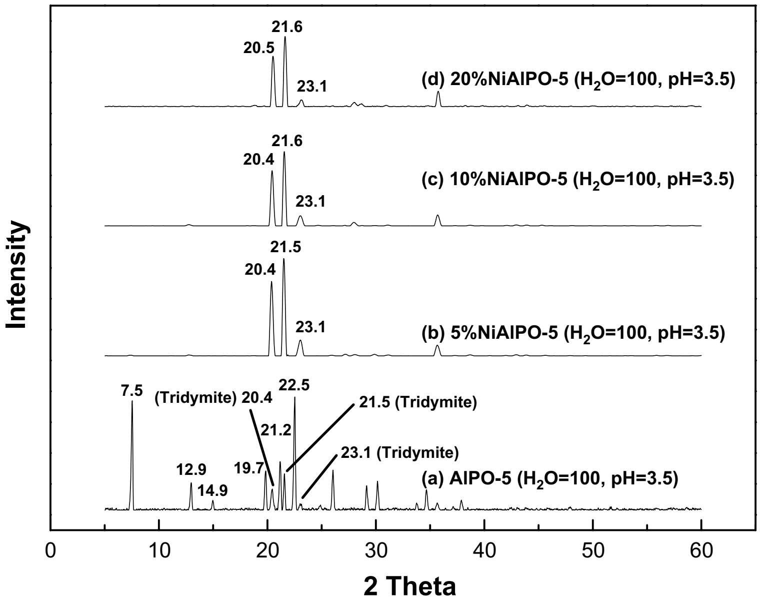


Figure 3. XRD patterns of tridymite phase forms with pH = 3.5 and various Ni loading.

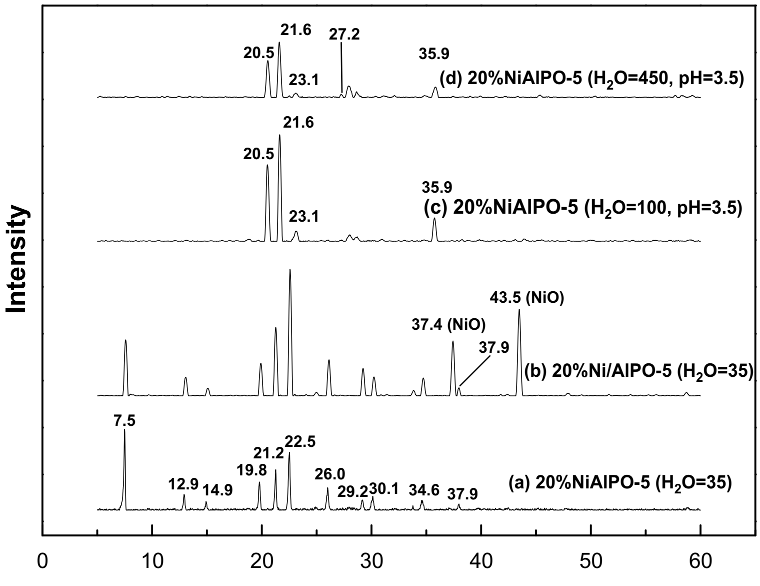


Figure 4. XRD patterns of 20% NiAlPO-5 prepared by various methods.

3.3. FT-IR spectroscopy

FT-IR studies on nickel containing AlPO-5 molecular sieves prepared by various methods are shown in figures 5 and 6. It appears that all vibrational modes are contributed to the $AlPO_4$ compound even using with various preparation methods. The characteristic peaks appearing 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 [23], respectively. Thus, the preparation method can affect on the structure of the formed NiAlPO-5, but has no effect on the composition of nickel containing AlPO-5 molecular sieves.

3.4. SEM

The SEM images in figure 7 show that the structural morphologies of the pure AlPO-5 and nickel containing AlPO-5 prepared by various methods. Figure 7(a), (f), and (h) are the SEM images of pure AlPO-5s prepared with various conditions. Without pH control and with H_2O content equal to 35 (in figure 7 (a)), the morphology of AlPO-5 is not well defined; while with pH control

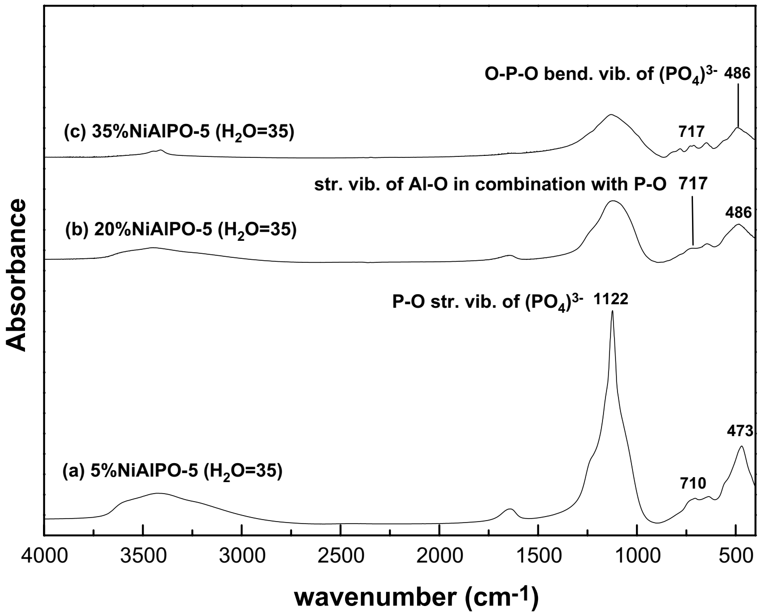


Figure 5. FTIR spectra of NiAlPO-5 as a function of Ni loading.

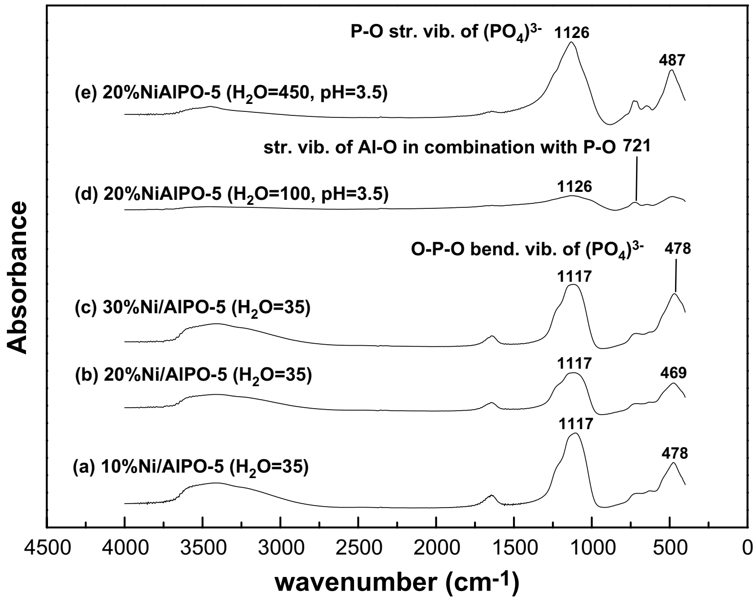
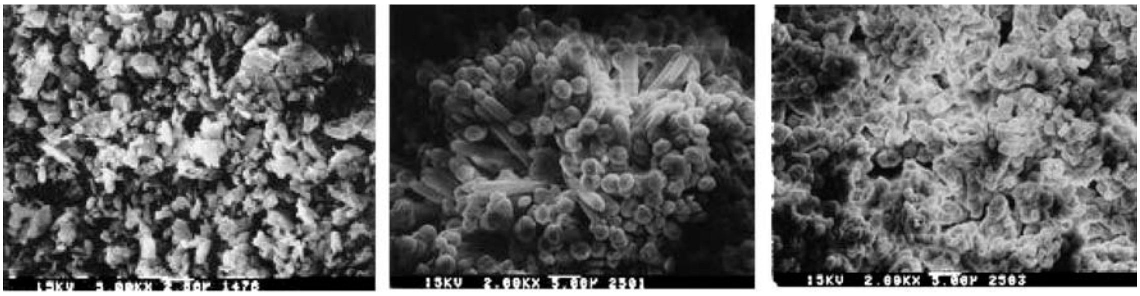


Figure 6. FTIR spectra of NiAlPO-5 prepared by various methods.

at 3.5 and higher H_2O content (in figure 7(f) and (h)), the AlPO-5 possesses the hexagonal pillar crystal, especially with higher H_2O content equal to 450, the hexagonal pillar crystal forms easily with radiation form. Figure 7(b), (c), (d), (e), (g), and (i) are the morphologies of NiAlPO-5s after nickel incorporated into AlPO-5. The Type 2 (in figure 7(d) and (e)) prepared by traditional incipient impregnation, do not possess the hexagonal pillar crystal while the Type 1 and Type 3 possessing with the pillar crystal or hexagonal pillar crystal covered by the nickel particle, and the grain size of these two types is larger than that of the Type 2. These results are consistent with the results of XRD analysis. To compare the results in figure 7(h) and (i), it points out that higher nickel loading will make the original structure of pure AlPO-5 collapse. Thus, the hexagonal pillar crystal with radiation form is not observed.

3.5. Amination of polyethylene glycol-400 (PEG-400) over nickel containing AlPO-5s

The catalytic studies on PEG-400 amination over nickel containing AlPO-5s are shown in table 1. The



(a) AlPO-5 (H_2O=35) (b) 25% NiAlPO-5 (H_2O=35) (c) 35% NiAlPO-5 (H_2O=35)

(d) 20% Ni/AlPO-5 (H_2O=35) (e) 20% Ni/AlPO-5 (H_2O=35) (f) AlPO-5 (H_2O=100, pH=3.5)

(g) 20% NiAlPO-5 (H_2O=100, pH=3.5) (h) AlPO-5 (H_2O=450, pH=3.5) (i) 20% NiAlPO-5 (H_2O=450, pH=3.5)

Figure 7. SEM images of pure AlPO-5 and NiAlPO-5 prepared by various methods.

results indicate that the pure AlPO-5 molecular sieves possess no catalytic activity. For Type 1, the amine yield increases with increasing the nickel loading from 9.7% to 22.4% and the selectivity of amine is primary amine at lower amine yield while the main product switches to secondary amine at higher amine yield. For 25% NiAlPO-5 ($H_2O = 35$) and 35% NiAlPO-5 ($H_2O = 35$), both of these two catalysts possessing with the tridymite phase, but the 25% NiAlPO-5 exhibits higher amine yield due to the smaller grain size. The total amine yield of the Type 2 catalyst is higher than that of the Type 1 catalyst due to the higher nickel dispersity and the selectivity of amine is about 50% of primary amine. The nickel containing AlPO-5s with only tridymite phase in Type 3 possess the highest amine yield and the main product is totally secondary amine. It appears that the trydimite structure can improve the catalytic activity for PEG-400 amination due to the grain size of the formed crystal of NiAlPO-5 is smaller than the sample without the formation of trydimite phase. The mechanism of PEG-400 amination is different for using metal phosphate as the catalyst to perform the nucleophilic substitution amination [5]. The amination mechanisms are the same in the previous studies on the Ni/Al_2O_3 catalysts for reduction amination [18]. The OH functional group in the PEG starts the dehydrogenation and forms the ketone intermediate by the catalytic of NiAlPO-5 catalyst. The ketone intermediate further reacts with ammonia to form an imine intermediate. The imine intermediate finally reacts with the ketone intermediate to form the observed secondary amine. Upon the presence of excess water in the reactor, the imine intermediate becomes more basic than ammonia and is favor to react with the ketone intermediate to form the secondary amine. Thus, the higher amine yield makes more secondary amine forms.

3.6. Mechanism of PEG-400 amination

The results of FT-IR analysis for mechanism study of PEG-400 amination was shown in figure 7. It indicates that the IR peak belongs to the ketone appearing at

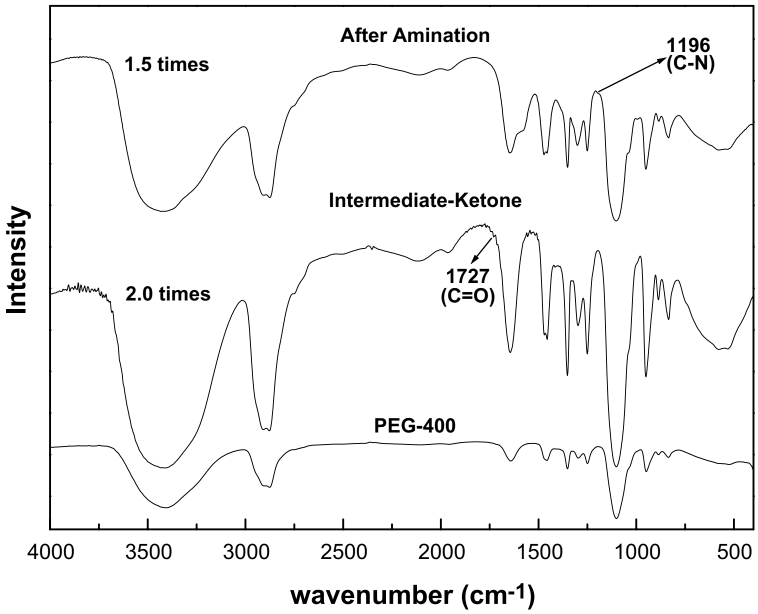
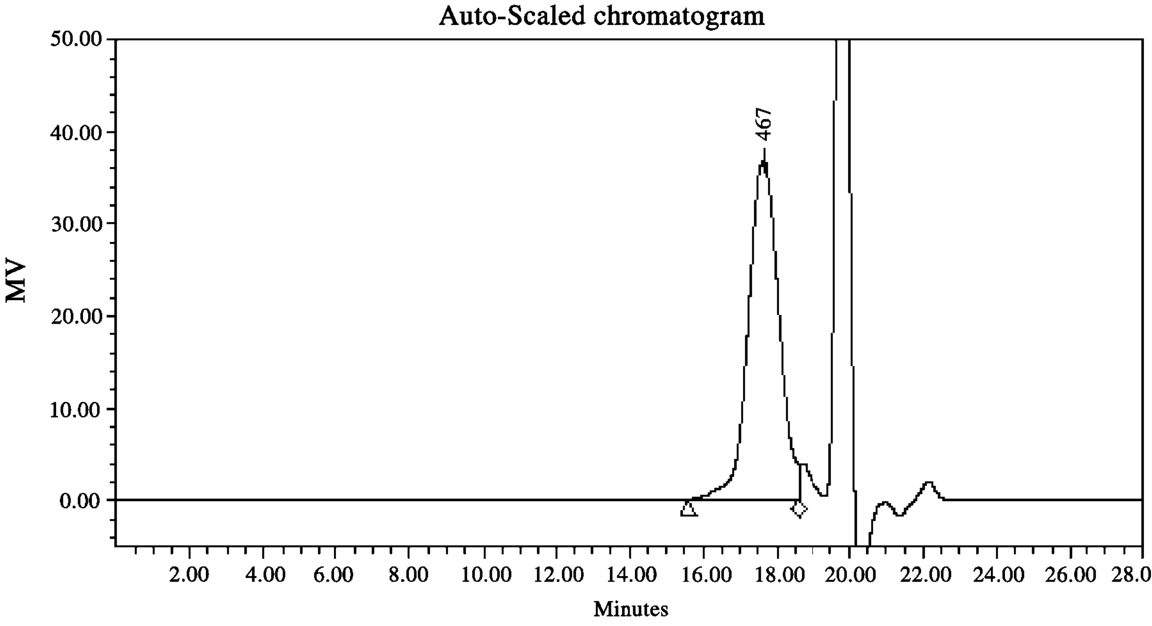


Figure 8. FTIR spectra of PEG-400 amination over NiAlPO-5s.

1727 cm^{-1} which contributes to the C=O vibration and forms without the addition of hydrogen and ammonium hydroxide. After the amination of ketone with the presence of ammonium hydroxide, the IR peak belongs to the amine of C–N vibration appearing at 1196 cm^{-1}.

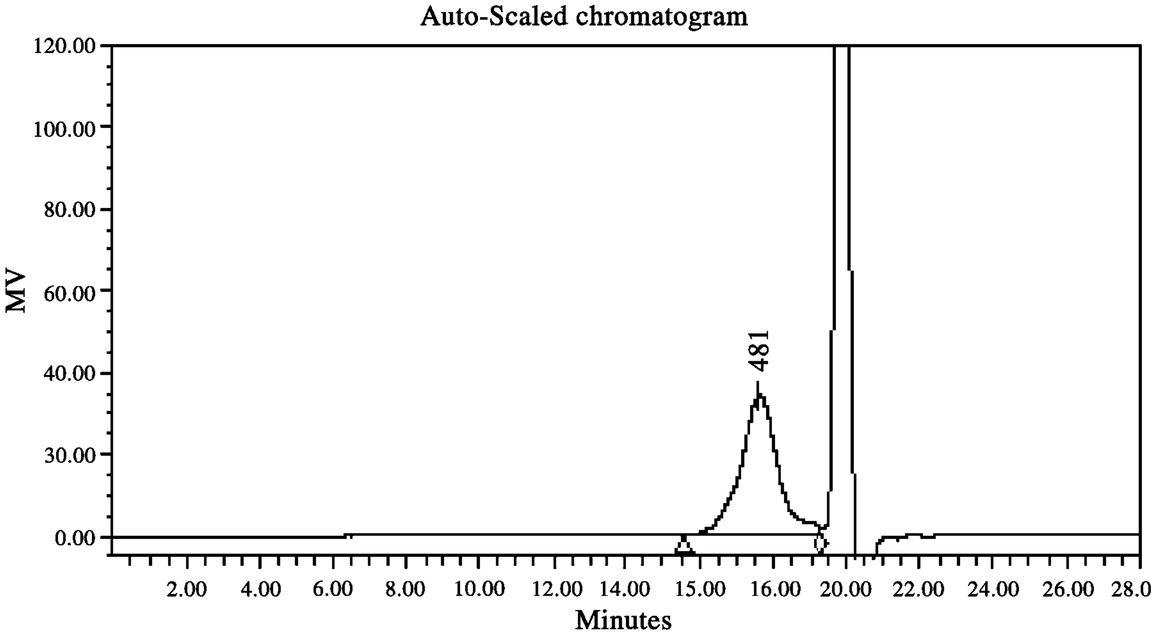
The GPC results in the figures 7 and 8 before and after amination pointed out that the average molecular was changed from 467 to 481 and the polydispersity was also slightly increased from 1.232 to 1.526. This indicates that the molecular weight and dispersity after



Results

	Name	RT	Area	% Area	MP (Dallons)	Mn (Dallons)	Mw (Dallons)	Mz (Dallons)	Polydispersity
1	*4*	17633	2105775	100.00	*467*	*412*	*508*	*637*	*1.231733*

Figure 9. GPC analysis data of PEG-400.



Results

	Name	RT	Area	% Area	MP (Dallon)	Mn (Dallon)	Mw (Dallon)	Mz (Dallon)	Polydispersity
1	*4*	17.607	2355207	100.00	*481*	*358*	*547*	*735*	*1.525633*

Figure 10. GPC analysis data of PEG-400 after amination over NiAlPO-5s.

amination was obviously increased due to the formation of secondary amine from smaller molecular by condensation method.

The results from FT-IR and GPC studies show that the amination mechanisms on the NiAlPO-5 catalysts are similar to those on the Ni/Al_2O_3 catalysts for reduction amination [18]. The OH functional group in the PEG-400 starts the dehydrogenation and forms the ketone intermediate by the catalytic reaction of the NiAlPO-5 catalyst. The ketone intermediate further reacts with ammonia to form an imine intermediate. The imine intermediate finally reacts with the ketone intermediate to form the observed secondary amine. Upon the presence of excess water in the reactor, the imine intermediate becomes more basic than ammonia and is favor to react with the ketone intermediate to form the secondary amine. Thus, the higher amine yield makes more secondary amine product (figures 9 and 10).

4. Conclusions

The structure and morphology of nickel containing AlPO-5 molecular sieves are different from pure AlPO-5 molecular sieves due to the incorporation nickel into the framework of AlPO-5. The structure and morphology also be affected by the various preparation methods and conditions. The pH value is the primary factor to control the formation of tridymite phase, and without pH control the tridymite phase can also be obtained by increasing nickel loading. For Type 2 prepared by traditional incipient wetness impregnation method, the amine yield is higher than the Type 1 prepared by hydrothermal method due to the surface nickel particle was formed on the surface of pure AlPO-5s and not into the framework of AlPO-5s. For the Type 2 prepared by hydrothermal method with pH control at 3.5, the NiAlPO-5 only possesses the tridymite phase without the AFI structure. The dense tridymite phase makes the smaller grain size of the formed crystal of AlPO-5 reduce and enhance the catalytic reactivity of PEG-400 amination. By controlling the nickel loading method, the structure and morphology of nickel containing AlPO-5 molecular sieves change from the large hexagonal pillar crystal of pure AlPO-5 to dense tridymite phase and smaller grain size, and make the catalytic performance better.

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