金属取代型 AIPO-5 分子筛催化剂上环己烷亚硝化一步法合成己内酰胺

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摘要: 采用水热法制备了一系列结晶态的 AIPO-5 (磷酸铝分子筛), SAPO-5 (硅磷酸铝分子筛) 和 MeAlPOs (金属取代型磷酸铝分子筛) 催化剂, 利用 X 射线衍射、N₂ 吸附脱附法、扫描电镜、粒度分布、电感耦合等离子光谱、红外光谱、NH₃ 程序升温脱附、H₂ 程序升温还原和热重-微分热重分析对催化剂进行了表征, 并考察了其催化环己烷亚硝化一步法制备己内酰胺的反应活性。结果表明, 随着 Si 或金属原子引入 AIPO-5 结构中, 催化剂的 Lewis 弱酸中心增加, 同时出现了 Brønsted 强酸中心。相对于 AIPO-5, 具有较大比表面积和较多酸中心的 SAPO-5 和 CrAPO-5 表现出较好的环己烷亚硝化反应活性, 后者环己烷转化率为 8.16%, 己内酰胺选择性达 68.17%。

关键词: 金属取代型磷酸铝分子筛; 己内酰胺; 环己烷; 一步法; 亚硝化

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One-Step Cyclohexane Nitrosation to ϵ -Caprolactam over Metal Substituted AIPO-5

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Abstract: Crystalline AIPO-5, SAPO-5, and metal substituted AIPO-5 (MeAlPOs) were prepared by the hydrothermal method and characterized by X-ray diffraction, N₂ adsorption-desorption, scanning electron microscopy, particle size distribution, inductively coupled plasma (ICP) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, NH₃ temperature-programmed desorption (TPD), H₂ temperature-programmed reduction, and thermogravimetric-differential thermogravimetric (TG-DTG) analysis. All the samples crystallized with the AFI structure. TPD profiles showed that stronger Brønsted acid sites appeared and the number of Lewis acid sites increased when Si or a metal was introduced into the framework of AIPO-5. ICP, FT-IR spectra, and TG-DTG curves confirmed that Si or the metals were incorporated into the framework of the AIPO-5. The catalytic properties of the samples in cyclohexane nitrosation to ϵ -caprolactam were studied. SAPO-5 with a larger BET surface area, more Lewis acid sites, and stronger Brønsted acid sites gave better activity and selectivity than AIPO-5. Among the MeAlPOs, CrAPO-5 with the larger BET surface area, more Lewis acid sites, and stronger Brønsted acid sites gave the better result with a conversion of 8.16% and ϵ -caprolactam selectivity of 68.17%.

Key words: metal substituted aluminophosphate molecular sieve; ϵ -caprolactam; cyclohexane; one-step method; nitrosation

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Microporous aluminophosphates (AIPO-*n*) have received considerable attention since the 1980s, and researchers have tried to develop new applications. After the aluminophosphate molecular sieve was firstly synthesized by Wilson et al. [1], numerous aluminophosphate type molecular sieves were developed. Aluminophosphate molecular sieves are made from corner-sharing AlO_4 and PO_4 tetrahedra. These tetrahedra form a three dimensional network containing channels and pores, which make them particularly attractive for adsorption and catalytic reaction. Among these aluminophosphate type molecular sieves, AIPO-5 (AFI) with one dimensional 12-ring channels (inner diameter 0.73 nm) has attracted the most attention. MeAIPOs and SAPO family materials are produced when framework Al^{3+} and P^{5+} ions of the aluminophosphates molecular sieves are substituted by metal cations (Co, Mn, Cr, Mg, V, Ga, Fe, Zn, etc.) or silicon [2,3]. Metal substituted aluminophosphates molecular sieves have attracted great interest in recent years for their acid and redox properties [4–8], which have given remarkable catalytic performance in many reactions. FeAPO-5, CoAPO-5, and MnAPO-5 molecular sieves have exhibited good activity in many reactions, especially in cyclohexane oxidation to form cyclohexanone and cyclohexanol [9,10]. Raja and co-workers [11] found that these materials catalyzed the ammoximation of cyclohexanone to ϵ -caprolactam with ammonia and H_2O_2 .

ϵ -Caprolactam is an important intermediate in the polymer industry used for the production of nylon-6 and plastics. All current commercial processes for ϵ -caprolactam production are based on benzene or toluene [12], in which caprolactam is manufactured by Beckmann rearrangement of cyclohexanone oxime with oleum as a reaction medium, and cyclohexanone oxime is synthesized from cyclohexanone and hydroxylamine sulfate in the presence of ammonia. Recently, researchers have studied Beckmann rearrangements in the vapor phase using solid acid catalysts and molecular sieves [13,14]. Liquid phase Beckmann rearrangement using phosphotungstic acid has been carried out [15]. The most common route to ϵ -caprolactam is a multi-step process, which has low atom efficiency and produces large volumes of salt waste [16–18]. It is very attractive to simplify the traditional ϵ -caprolactam synthesis processes. Our previous work reported the synthesis of ϵ -caprolactam from cyclohexane and nitrosyl sulfuric acid in the presence of fuming sulfuric acid catalyzed by a series of transition metal supported on AlVPO composite or $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts [19–23]. This provides a novel strategy for the one-step synthesis of ϵ -caprolactam from cyclohexane.

There is no report on the single-step production of ϵ -caprolactam catalyzed by metal substituted aluminophosphate molecular sieves. In this paper, AIPO-5, SAPO-5, and MeAIPOs (CoAPO-5, MnAPO-5, and CrAPO-5) were synthesized by the hydrothermal method. The catalytic properties of these materials in cyclohexane nitrosation for the production of ϵ -caprolactam were studied.

1 Experimental

1.1 Catalyst preparation

Pseudoboehmite (75% Al_2O_3), H_3PO_4 (85%), $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (99.5%), $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (99%) and $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (99%) were used as the sources of aluminum, phosphorus, cobalt, manganese, and chromium, respectively. MeAIPO-5 was synthesized from a gel with the following molar composition: 0.06Me:0.94Al:1.0P:0.75 Et_3N :20 H_2O . Triethylamine (99%) was used as the template.

A typical synthesis procedure is as follows. A solution of metal salts was prepared by dissolving the metal sources in deionized water. The calculated amount of pseudoboehmite was hydrolyzed for 30 min in a polypropylene beaker under stirring. Then the solution of metal salts was added into the alumina slurry at room temperature. After stirring for 1 h, diluted orthophosphoric acid was added dropwise into the gel solution and stirring was continued for another 2 h. Then, triethylamine was added into the mixed gel solution and stirred for 2 h. Finally, the mixture gel was sealed in a Teflon-lined stainless steel autoclave and heated to 180 °C under autogeneous pressure for 48 h. Afterwards, the gel was separated by filtration, washed with deionized water, dried at 120 °C overnight, and then calcined at 550 °C for 24 h in flowing air. AIPO-5 was synthesized according to the above method, SAPO-5 molecular sieves was synthesized using silica sol (30%) as the silicon source.

1.2 Catalyst characterization

The AFI structure and crystallinity of the samples were confirmed by X-ray diffraction (XRD) on a Japan Rigaku D/Max 2550 VB⁺ 18 kW X-ray diffractometer used under the conditions: 40 kV, 30 mA, Cu K_α radiation, with a scanning rate of 1°/min in the range of $2\theta = 4^\circ\text{--}65^\circ$. The morphology and dimensions of the samples were examined using scanning electron microscopy (SEM) with a JSM-6610LV spectrometer. The particle size distributions of the samples were determined by a Mastersizer 2000 using

the scattering of a He-Ne laser beam by the solid material suspended in deionized water. Separation of the solid powders was by an ultrasonic bath with incorporated stirrer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrometer. The spectra of the samples were acquired in the wave number range of 400–4000 cm^{-1} .

Temperature-programmed desorption (TPD) of NH_3 and temperature-programmed reduction (TPR) were carried out on a CHEMBET-3000 instrument. For TPD, the samples were pretreated at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ to 650 $^{\circ}\text{C}$ and held for 30 min under a flow of helium. After cooling to 100 $^{\circ}\text{C}$, a mixture of 10% NH_3 -90% He was introduced until the acid sites of the catalyst were saturated with NH_3 . Finally, desorption was carried out from 10 to 650 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. For TPR, the samples were pretreated at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ to 650 $^{\circ}\text{C}$ under a flow of helium. After cooling to 30 $^{\circ}\text{C}$, the samples were heated from 30 to 650 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ under a flow of 10% H_2 -90% Ar (v/v).

The specific surface areas of the samples were determined by N_2 adsorption-desorption on a ASAP 2020 M+C automated gas sorption system. The samples were first pretreated under vacuum at 120 $^{\circ}\text{C}$ for 8 h. Thermogravimetric (TG) analysis was carried out on a TGA Q50 with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ from 20 to 800 $^{\circ}\text{C}$ under 40 ml/min nitrogen.

1.3 Catalytic studies

Catalytic reactions were performed in a 100 ml glass reactor. Typically, 10 g cyclohexane, 0.5 g catalyst, 8 g nitrosyl sulfuric acid, and 24 g 50 wt% fuming sulfuric acid were added into the reactor. After it was sealed, the reactor was heated to the reaction temperature under magnetic stirring. Upon reaching the reaction temperature, the cyclohexane was continuously refluxed. When the reaction was stopped, unreacted cyclohexane was removed by a rotary evaporator. The remaining liquid was dissolved in deionized water in an ice-water bath and treated with $\text{Ba}(\text{OH})_2$ to neutralize H_2SO_4 . After adjusting the pH to neutral, the product was filtered for subsequent analysis. The reaction product was analyzed on a LC-20AT and SPD-20A liquid chromatographs with 20:80 of $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ as eluant and detected at the wavelength of 210 nm.

2 Results and discussion

2.1 Characterization results

Figure 1 shows the XRD patterns of SAPO-5, CoAPO-5, MnAPO-5, CrAPO-5, and AlPO-5. The XRD patterns corresponded well to the patterns of the AFI structure. A very

Fig. 1. XRD patterns of different samples. (1) SAPO-5; (2) CoAPO-5; (3) MnAPO-5; (4) CrAPO-5; (5) AlPO-5.

small concentration of the CHA structure appeared in SAPO-5. It has been observed that AFI can be converted into CHA because it has less thermodynamic stability than CHA [24,25]. Except for the peaks due to AlPO-5, no other phase appeared in CoAPO-5, MnAPO-5, and CrAPO-5, which indicated that these samples were highly crystallized in the AFI structure. The crystallinity of SAPO-5 was 88.48% and the crystallinity of AlPO-5, CoAPO-5, MnAPO-5, and CrAPO-5 were all above 90%.

The lattice constant and crystallinity of the samples are listed in Table 1. The values of d_{100} for CoAPO-5, MnAPO-5, and CrAPO-5 were 1.207, 1.209, and 1.218 nm, respectively. These values are larger than that of AlPO-5 (1.193 nm). The lattice constant a increased with the metal substitution of Al atom in the aluminophosphate network. The reason may be that the metals are larger than the Al^{3+} or P^{5+} atoms. In contrast, the values of d_{100} and the lattice constant a of SAPO-5 were smaller than AlPO-5, which can be explained by that the Al–O bond (0.053 nm) is longer than the Si–O bond (0.042 nm). The d_{100} values gave the sequence of ionic radii as $\text{P}^{5+} < \text{Si}^{4+} < \text{Al}^{3+} < \text{Co}^{2+} < \text{Mn}^{2+} < \text{Cr}^{2+}$ and $\text{P}^{5+} < \text{Si}^{4+} < \text{Al}^{3+} < \text{Co}^{3+} < \text{Mn}^{3+} < \text{Cr}^{3+}$, which is in agreement with the ionic radii data shown in Table 2 [26]. The corresponding XRD peaks of the MeAlPOs are shifted to the left with respect to AlPO-5, which may be because the lattice constants increased with metal substitution of Al atoms in the aluminophosphate network. These data indi-

Table 1 Physical properties of AlPO-5 and MeAlPOs

Sample	BET surface area (m^2/g)	Crystallinity (%)	Lattice constant		
			d_{100}/nm	$a = b$ (nm)	c/nm
AlPO-5	276.6	94.45	1.193	1.374	0.840
SAPO-5	291.8	88.48	1.185	1.366	0.846
CoAPO-5	257.0	92.32	1.207	1.388	0.824
CrAPO-5	285.9	93.39	1.218	1.397	0.820
MnAPO-5	287.6	93.82	1.209	1.391	0.822

Table 2 Ionic radii of the metal ions

Metal ion	Ionic radius (nm)
Al ³⁺	0.053
P ⁵⁺	0.034
Si ⁴⁺	0.042
Co ²⁺	0.072
Co ³⁺	0.063
Mn ²⁺	0.080
Mn ³⁺	0.066
Cr ²⁺	0.087
Cr ³⁺	0.069

cated that the metals were incorporated into the framework of the AIPO-5.

The BET surface areas of AIPO-5, SAPO-5, and the MeAIPOs catalysts are summarized in Table 1. The BET surface area of AIPO-5 was 276.6 m²/g, which is in agreement with the literature [27]. The BET surface areas of SAPO-5, MnAPO-5, and CrAPO-5 were larger than that of AIPO-5, while that of CoAPO-5 was smaller than the AIPO-5. This would affect its activity in cyclohexane nitrosation.

The SEM images of the synthesized SAPO-5 and MeAIPOs are shown in Fig. 2. Like the typical morphology of MeAIPO-5, the structures of SAPO-5, CoAPO-5, MnAPO-5, and CrAPO-5 are mainly a hexagonal pillar

Fig. 2. SEM images of SAPO-5 (a), CoAPO-5 (b), MnAPO-5 (c), and CrAPO-5 (d).

Table 3 Composition of the samples measured by ICP

Sample	Composition in gel					Composition measured by ICP					
	Me (mol)	Al (mol)	P (mol)	Me/Al	Me/P	Me (mol)	Al (mol)	P (mol)	(Me+Al)/P	(P-Al)/P (%)	Me/(wt%)
AIPO-5	—	1.00	1.00	—	—	—	1.00	1.00	—	—	—
CoAPO-5	0.06	0.94	1.00	0.064	0.06	0.032	0.942	1.00	0.97	5.84	1.28
MnAPO-5	0.06	0.94	1.00	0.064	0.06	0.033	0.935	1.00	0.97	6.52	1.38
CrAPO-5	0.06	0.94	1.00	0.064	0.06	0.027	0.938	1.00	0.97	6.22	1.06

Sample	Composition in gel					Composition measured by ICP					
	Si (mol)	Al (mol)	P (mol)	Si/Al	Si/P	Si (mol)	Al (mol)	P (mol)	(Si+P)/Al	(Al-P)/Al (%)	Si/(wt%)
SAPO-5	0.60	1.00	1.00	0.60	0.60	0.465	1.00	0.692	1.16	30.80	8.46

Fig. 3. Particle size distributions of SAPO-5 (1), CoAPO-5 (2), MnAPO-5 (3), CrAPO-5 (4), and AIPO-5 (5).

structure with a middle collapse. For CrAPO-5, there was the superimposition of the middle collapsed hexagonal pillars, which led to its bigger morphology structure than the other MeAIPOs. Particle size distributions are shown in Fig. 3. The particles of the MeAIPOs were centered at 17.36 μm, and were a little larger than AIPO-5.

The elemental composition ratio analyzed by ICP is shown in Table 3. The Me/P molar ratios ranged from 0.027 to 0.033 in CoAPO-5, MnAPO-5, and CrAPO-5 measured by ICP, which were less than that in the gel composition. This indicated that not all the metal ions in the gel were incorporated into the framework and the metal atom content did not depend directly on the gel composition. The (Me+Al)/P ratios were close to 1, which indicated that there were metals incorporated into the framework of the AIPO-5. The (P-Al)/P ratios indicated that the replacement percentage of Al atoms were 5.84%, 6.52%, and 6.22% in the MeAIPOs. Also, the molar contents of Si and P were smaller than the gel composition. The (Si+P)/Al and (Al-P)/Al ratios were 1.16 and 30.80, which showed that part of the P atoms in SAPO-5 were replaced by Si atoms and the replacement percentage was 31%.

The FT-IR spectra of AIPO-5, SAPO-5, and the MeAIPOs are presented in Fig. 4. The vibrations at 3478 and

1653 cm^{-1} were attributed to the bond stretching and bending vibrations of water molecules [28]. The peaks appearing at 1103 and 467 cm^{-1} were characteristic of aluminophosphates, and were attributed to the asymmetric stretching vibration of the P–O–Al unit and the P–O or Al–O bending vibrations in the AlPOs material [29]. With the introduction of Si and metals, there was a slight change in the spectra of SAPO-5 and MeAlPOs. The splitting of the peak at 467 cm^{-1} may be due to the presence of the metals. Moreover, the vibration bands of SAPO-5, CoAPO-5, MnAPO-5, and CrAPO-5 in the region of 1071, 1020, 1074, and 1055 cm^{-1} were shifted to lower wavenumbers with respect to AlPO-5. The reason may be that the Co–O, Mn–O, and Cr–O bonds are longer than the Al–O bond and the Si–O bond is longer than the P–O bond. These data also confirmed that Si and the metals were incorporated into the framework of the AlPO-5.

Fig. 4. FT-IR spectra of SAPO-5 (1), CoAPO-5 (2), MnAPO-5 (3), CrAPO-5 (4), and AlPO-5 (5).

The NH_3 -TPD profiles of the different samples are shown in Fig. 5. The peak at 140 °C for AlPO-5 and the peaks at 200 °C for SAPO-5, CoAPO-5, MnAPO-5, and CrAPO-5 were due to weakly bonded ammonia adsorbed on weak Lewis acid sites. The number of Lewis acid sites increased as Si or metal was introduced into the framework of AlPO-5. The transition metal substituted AlPOs (MeAlPOs) show a marked tendency for Lewis acidity. Peaks between 300 and 600 °C were detected with SAPO-5 and MeAlPOs, which were attributed to ammonia desorption from Brønsted acid sites. This suggested that stronger acid sites appeared when Si or metal was introduced into the framework of AlPO-5. When P^{5+} is replaced by Si^{4+} , or Al^{3+} is isomorphously replaced by a lower valence state metal atom such as Co^{2+} , Mn^{2+} , or Cr^{2+} , the framework is negatively charged and Brønsted acid sites are generated [30]. Among the MeAlPOs, CrAPO-5 exhibited the most Lewis acid sites and strongest Brønsted acid sites.

Fig. 5. NH_3 -TPD profiles of SAPO-5 (1), CoAPO-5 (2), MnAPO-5 (3), CrAPO-5 (4), and AlPO-5 (5).

The H_2 -TPR profiles of the catalysts are shown in Fig. 6. The reduction peaks of bulk Co_3O_4 can be assigned to a two-step reduction of Co_3O_4 to CoO and then to Co^0 [31,32]. It can be seen from Fig. 6(1) that the TPR profile is more complex for CoAPO-5 than the bulk Co_3O_4 . The temperature peak at 118 °C may be attributed to the reduction of Co_3O_4 to Co metal and possibly partial reduction of highly dispersed Co_3O_4 to CoO [33]. The appearance of the peak at this temperature in CoAPO-5 may be caused by the weak interaction between the highly dispersed Co_3O_4 and the zeolite framework. The pretreatment of the sample has some effect on the reduction temperature. The peak located at 394 °C with a weak shoulder at 380 °C has been assigned to the reduction of incorporated Co_3O_4 to Co species via CoO [31]. In Fig. 6(2), the main peak at 369 °C with two shoulders at 335 and 444 °C was attributed to the reduction of Mn_2O_3 to MnO . The weak interaction between the metal oxides and the zeolite framework led to the low temperature shift of the peak. For CrAPO-5, the major peaks were detected at 261 and 350 °C with a broad shoulder at 460 °C.

Fig. 6. H_2 -TPR profiles of CoAPO-5 (1), MnAPO-5 (2), and CrAPO-5 (3).

The peak detected at 261 °C was assigned to the reduction of Cr^{4+} on the surface of catalyst, while the peak at 350 °C was attributed to the reduction of Cr^{3+} to Cr^{2+} , using the report of Ilieva et al. [34].

Figure 7 illustrates the TG-DTG curves of the catalysts. The mass loss detected between 20 and 140 °C of the TG curve of AIPO-5 was attributed to water desorption (5.97%) and the loss from 140 to 350 °C was due to template desorption (6.19%). DTG peaks near 83 and 197 °C were observed during these two mass losses. The loss of water from the SAPO-5 catalyst occurred at 86 °C (5.45%) and the removal of the template (7.58%) occurred at 460 °C, which were much higher than the template removal temperature of AIPO-5. The mass losses of CoAPO-5, MnAPO-5, and CrAPO-5 due to water desorption were similar to those of AIPO-5 and SAPO-5. As for CoAPO-5, the template was removed at 147 to 300 °C (3.45%) and 477 °C (3.91%). The mass loss of MnAPO-5 was similar to CoAPO-5, with the template removed at 145 to 300 °C (3.77%) and 477 °C (4.08%). As for CrAPO-5, the template was removed at 150 to 360 °C (4.88%) and 440 °C (2.99%). It can be seen from the above results that the template of AIPO-5 was completely removed at a lower temperature of around 300 °C while the template removal of SAPO-5 and the MeAPOs were at a much higher temperature. The higher template removal temperature indicated that there were stronger interactions between the framework and the template, which

may be due to the introduction of Si or metal.

2.2 Catalytic tests

Representative results for the nitrosation of cyclohexane over the AIPO-5, SAPO-5, and the MeAPOs catalysts are shown in Table 4. In the absence of a catalyst, the conversion of cyclohexane was very limited and it was mainly converted to benzene sulfonic acid with very low selectivity for ϵ -caprolactam. In contrast, ϵ -caprolactam was efficiently obtained from cyclohexane and nitrosyl sulfuric acid over the catalysts, which indicated that the catalysts played an important role in promoting the conversion of cyclohexane and the formation of ϵ -caprolactam. From the results we can see that the catalytic activity increased with the increase of the BET surface area. SAPO-5 with the largest BET surface area gave the largest conversion of 9.85%. CoAPO-5 with the smallest BET surface area gave the smallest conversion of 6.67%. These results indicated that the adsorption capacity of the catalysts depended on the BET surface area and the catalyst with the larger BET surface area more efficiently promoted nitrosyl sulfuric acid decomposition and gave better cyclohexane conversion. The NH_3 -TPD spectra suggested that more weak acid sites and stronger acid sites appeared as Si or metal was introduced into the framework of AIPO-5. It has been found that more Lewis acid sites and Brønsted acid sites are helpful in cyclohexane nitrosation to give better selectivity for ϵ -caprolactam [22,23], which was attributed to the efficient rearrangement of the nitroso cyclohexane intermediate on the stronger Brønsted acid sites. Compared with AIPO-5, SAPO-5 gave better activity and selectivity for ϵ -caprolactam, which may be due to its larger BET surface area, more Lewis acid sites, and stronger Brønsted acid sites. Among the MeAPOs, CrAPO-5 with largest BET surface area, most Lewis acid sites, and strongest Brønsted acid sites gave the best result with a conversion of 8.16% and ϵ -caprolactam selectivity of 68.17%. It can be seen that the BET surface area, acid sites and their strength play important roles in cyclohexane nitrosation to ϵ -caprolactam.

Fig. 7. TG-DTG curves (solid and dotted, respectively) for SAPO-5 (1), CoAPO-5 (2), MnAPO-5 (3), CrAPO-5 (4), and AIPO-5 (5).

Table 4 Activity of different catalysts for nitrosation of cyclohexane

Catalyst	Conversion of cyclohexane (%)	Product distribution (%)		
		ϵ -Caprolactam	Benzene sulfonic acid	Others
None	1.95	4.29	95.13	0.58
AIPO-5	7.80	46.00	51.18	2.82
SAPO-5	9.85	49.00	49.72	1.28
CoAPO-5	6.67	61.12	37.53	1.35
CrAPO-5	8.16	68.17	30.68	1.15
MnAPO-5	8.64	52.91	45.85	1.24

Reaction conditions: nitrosyl sulfuric acid:oleum = 1:3 (mass ratio), cyclohexane 10 g, catalyst 0.5 g, 81 °C, 24 h.

3 Conclusions

Crystalline AlPO-5, SAPO-5, and MeAlPOs were prepared by the hydrothermal method. The MeAlPOs had stronger Brønsted acid sites due to Si or metal introduced into the framework of AlPO-5 and the number of Lewis acid sites also increased. The catalytic properties of these materials were studied with cyclohexane nitrosation for the production of ϵ -caprolactam. The catalysts played an important role in promoting the conversion of cyclohexane and formation of ϵ -caprolactam. The catalytic activity increased with the BET surface area and Brønsted acid sites help give better selectivity for ϵ -caprolactam. Among the MeAlPOs, CrAPO-5 with the larger BET surface area, more Lewis acid sites, and stronger Brønsted acid sites gave the better result with a conversion of 8.16% and ϵ -caprolactam selectivity of 68.17%. The BET surface area, acid sites, and their strength played important roles in cyclohexane nitrosation to ϵ -caprolactam.

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