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ARTICLE

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

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Abstract: Crystalline AlPO-5, SAPO-5, and metal substituted AlPO-5 (MeAlPOs) were prepared by the hydrothermal method and characterized by X-ray diffraction, N_2 adsorption-desorption, scanning electron microscopy, particle size distribution, inductively coupled plasma (ICP) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, NH_3 temperature-programmed desorption (TPD), H_2 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 AlPO-5. ICP, FT-IR spectra, and TG-DTG curves confirmed that Si or the metals were incorporated into the framework of the AlPO-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 AlPO-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

Microporous aluminophosphates (AlPO-*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, AlPO-5 (AFI) with one dimensional 12-ring channels (inner diameter 0.73 nm) has attracted the most attention. MeAlPOs 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

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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 SiO_2-Al_2O_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, AlPO-5, SAPO-5, and MeAlPOs (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%), $Co(CH_3COO)_2\cdot 4H_2O$ (99.5%), $Mn(CH_3COO)_2\cdot 4H_2O$ (99%) and $Cr(NO_3)_3\cdot 9H_2O$ (99%) were used as the sources of aluminum, phosphorus, cobalt, manganese, and chromium, respectively. MeAlPO-5 was synthesized from a gel with the following molar composition: 0.06Me:0.94Al:1.0 P:0.75 Et_3N:$20H_2O$. 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. AlPO-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 2θ = 4°–65°. 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 Matersizer 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 °C/min to 650 °C and held for 30 min under a flow of helium. After cooling to 100 °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 °C at a heating rate of 10 °C/min. For TPR, the samples were pretreated at a heating rate of 10 °C/min to 650 °C under a flow of helium. After cooling to 30 °C, the samples were heated from 30 to 650 °C at a rate of 10 °C/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 °C for 8 h. Thermogravimetric (TG) analysis was carried out on a TGA Q50 with a heating rate of 5 °C/min from 20 to 800 °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 $Ba(OH)_2$ 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 CH_3OH:H_2O 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 corre-