Journal of Molecular Catalysis A: Chemical 351 (2011) 210–216

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Preparation of mesoporous SiO_2–Al_2O_3 supported Co or Mn catalysts and their catalytic properties in cyclohexane nitrosation to ε-caprolactam

Fang Hao[a], Jun Zhong[a], Ping-Le Liu[a,*], Kui-Yi You[a], Chao Wei[b], Hua-Jie Liu[c], He-An Luo[a,*]

[a] College of Chemical Engineering, Xiangtan University, Xiangtan 411105, China
[b] College of Chemical and Biological Engineering, Changsha University of Science & Technology, Changsha 410004, China
[c] College of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

ARTICLE INFO

Article history:
Received 9 June 2011
Received in revised form 9 October 2011
Accepted 11 October 2011
Available online 17 October 2011

Keywords:
Mesoporous crystalline SiO_2–Al_2O_3
Supported transition metal catalysts
ε-Caprolactam
Cyclohexane
Nitrosation

ABSTRACT

Mesoporous crystalline SiO_2–Al_2O_3 was prepared by hydrothermal synthesis method and its supported Co or Mn catalysts were prepared by impregnation method. These prepared materials were characterized by XRD, XPS, NH_3–TPD, BET, FT-IR and TG–DSC. It reveals that the metals are substituted into the framework as the form of $MnCo_2O_4$, Mn_3O_4, MnO, Co_3O_4 and stronger acid sites appear. Furthermore, Pyridine FT-IR spectra and NH_3–TPD results indicate that both Brønsted and Lewis acid sites exist on these SiO_2–Al_2O_3 supported transition metal catalysts and Mn/SiO_2–Al_2O_3 exhibits higher Brønsted acid content. BET results show that SiO_2–Al_2O_3 with middle Si/Al molar ratio has larger surface area and pore volume. The surface area and pore volume of SiO_2–Al_2O_3 decrease after the introduction of the transition metals. The catalytic properties in the cyclohexane nitrosation to ε-caprolactam were performed and Mn/SiO_2–Al_2O_3 exhibits better activity and selectivity to the ε-caprolactam.

1. Introduction

ε-Caprolactam is an important precursor for the manufacture of nylon-6 and plastics. The ever-increasing industrial demand for nylon-6 necessitates the development of environmentally benign method for the production of ε-caprolactam [1].

The commercial production of ε-caprolactam is still based on classical technologies. Cyclohexanone oxime is synthesized from cyclohexanone and hydroxylamine sulfate in the presence of ammonia. Then the Beckmann rearrangement in fuming sulfuric acid is carried out, and neutralization is followed to liberate the lactam [2,3]. The shortcomings of this classical process are its complex routes and a large amount of ammonium sulfate formed as by-product [2–4].

One of the improvements for the production of ε-caprolactam was direct ammoximation of cyclohexanone with ammonia and hydrogen peroxide catalyzed by TS-1 [5–7]. Researchers have studied Beckmann rearrangements in vapor phase using solid catalysts such as metal oxides and zeolites [8–13]. Liquid-phase Beckmann rearrangements using solid acid catalysts and zeolites have been carried out [14,15]. A few examples of solvent-free organo-catalyzed Beckmann rearrangements have been reported [16], as well as in supercritical water [17]. The research group of Cambridge University developed a process for the production of ε-caprolactam from cyclohexanone by using bifunctional heterogeneous nanoporous aluminophosphates catalysts containing isolate acidic and redox sites [18,19].

It can be seen that it is very attractive to replace those former mentioned complex routes with a new simple process. Naylor and Anderson developed a process for the synthesis of cyclohexanone oxime by cyclohexane photoreaction with nitrosyl chloride [20]. Compared with the classical routes, this photochemical process is simpler and the overall selectivity to ε-caprolactam is higher. However, it is of high energy consumption and the formation of NOCl is very problematic and environmentally unfriendly. Up to now, only Japan Toray Ltd. has this PNC (Photonitrosation of cyclohexane) commercial process [21]. Therefore, the development of a new catalytic system for replacing the photochemical process is highly desirable. ε-Caprolactam can be prepared in a single-step 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 amorphous SiO_2–Al_2O_3 prepared by sol–gel method [22–25]. It provides a novel strategy for one-step synthesis of ε-caprolactam from cyclohexane.

The metal-containing mesoporous zeolites have attracted great interests as catalysts due to their acidity, redox, shape-selectivity and recyclable properties [26,27]. In this paper, we aim to search for suitable catalysts and studied their catalytic properties in the cyclohexane nitrosation to ε-caprolactam. Several types of mesoporous crystalline SiO_2–Al_2O_3 supported transition metal catalysts were

---

* Corresponding authors. Tel.: +86 73158293545; fax: +86 73158298267.
E-mail addresses: liupingle@xtu.edu.cn (P.-L. Liu), heanluo@126.com (H.-A. Luo).

1381-1169/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2011.10.010

prepared and characterized in this work. We found that these catalysts could efficiently catalyze the reaction of cyclohexane with nitrosyl sulfuric acid to afford ε-caprolactam via one-step in the presence of fuming sulfuric acid.

2. Experimental

2.1. Catalyst preparation

SiO_2–Al_2O_3 were prepared from $Al(OH)_3$ and tetraethyl orthosilicate by hydrothermal synthesis method, and triethylamine was used as template. The $Al(OH)_3$ was added into the water and then the tetraethyl orthosilicate was added after stirring 2 h. Afterwards, the template was introduced dropwise under vigorous stirring. The gel was stirred for 2 h before being sealed in a Teflon-lined stainless steel autoclave, then it was heated to 120 °C under autogeneous pressure for 12 h. Finally, the gel was separated by filtration, washed with deionized water, and dried at 110 °C for 12 h. The obtained SiO_2–Al_2O_3 was used as catalyst support.

The SiO_2–Al_2O_3 supported transition metal catalysts were prepared by impregnation method. The metal precursor of cobalt acetate or manganese acetate was firstly dissolved in the deionized water to obtain a solution of 0.4 mol/l, then the previous obtained SiO_2–Al_2O_3 was impregnated in cobalt acetate or manganese acetate solution under stirring. After 2 h, the mixture was filtrated and dried at 110 °C for 12 h. Finally, the obtained solid was calcinated at 600 °C for 6 h in air at a heating rate of 2 °C min^{-1}.

2.2. Catalyst characterizations

X-ray diffraction (XRD) data were collected on a Japan Rigaku D/Max 2550 VB^+ 18 kW X-ray diffractometer under the following conditions: 40 kV, 30 mA, Cu Kα radiation, with a scanning rate of 1° min^{-1} in the range of $2\theta = 3$–70°.

The surface composition and surface electronic state were analyzed by X-ray Photoelectron Spectroscopy (XPS) using Kratos Axis Ultra DLD instrument at 160 eV pass energy. Al Kα radiation was used to excited photoelectrons.

$$\text{Conversion}\,(\%) = \frac{[\text{the amount (mol) of starting cyclohexane} - \text{the amount (mol) of cyclohexane recovered}]}{\text{the amount (mol) of nitrosyl sulfuric acid}} \times 100\% \qquad (1)$$

$$\text{Selectivity}\ (\%) = \frac{\text{the amount (mol) of caprolactam}}{[\text{the amount (mol) of starting cyclohexane} - \text{the amount (mol) of cyclohexane recovered}]} \times 100\% \qquad (2)$$

Temperature programmed desorption (TPD) of NH_3 was carried out on a CHEMBET-3000 instrument. The samples were pretreated at a heating rate of 10 °C min^{-1} to 650 °C and was held for 30 min under a flow of helium. After cooling to 100 °C, a mixture of 10% NH_3 to 90% He was introduced until the acid sites of the catalyst were saturated with NH_3. Finally, desorption was carried out from 10 °C to 650 °C at a heating rate of 10 °C min^{-1}.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrometer. The spectra of the samples were acquired in the wavenumber range of 400–4500 cm^{-1}. Pyridine FT-IR was used to distinguish the nature of the acid sites.

Specific surface area, pore volume and pore size distribution of the samples were determined by N_2 adsorption–desorption on a NOVA-2200e automated gas sorption system.

Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analysis were recorded on Mettler Toledo TGA/DSC 1 with a heating rate of 5 °C min^{-1} from 20 °C to 800 °C under 40 ml min^{-1} nitrogen.

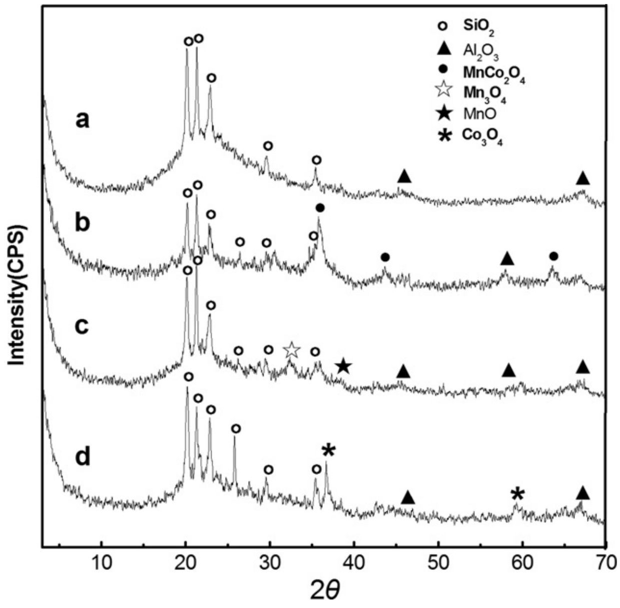

Fig. 1. XRD patterns. (a) SiO_2–Al_2O_3, (b) Co–Mn/SiO_2–Al_2O_3, (c) Mn/SiO_2–Al_2O_3, (d) Co/SiO_2–Al_2O_3.

2.3. Catalytic reaction

Cyclohexane nitrosation was carried out 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. Then it was heated to 81 °C under stirring and reacted under this temperature for 24 h. After reaction the unreacted cyclohexane was removed by rotary evaporator. The remained liquid was dissolved by deionized water in ice-water bath and treated with $Ba(OH)_2$ to neutralize H_2SO_4. The reaction products were analyzed on a LC-20AT and SPD-20A liquid chromatograph with 20:80 of CH_3OH:H_2O as eluant and detected at wavelength of 210 nm.

The conversion and the selectivity were calculated using the following formulas (Eqs (1) and (2)).

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the X-ray diffraction patterns of the SiO_2–Al_2O_3 and the SiO_2–Al_2O_3 supported transition metal catalysts. The XRD patterns of all the samples have the tridymite crystal structures, which is different from amorphous SiO_2–Al_2O_3 prepared by sol–gel method in the work of Liu et al. [25]. The XRD patterns of SiO_2 are in the region of 20.4–35.5° and the XRD peaks detected around $2\theta = 45.8°$ and 66.9° are attributed to γ-Al_2O_3. Besides the XRD peaks corresponding to the SiO_2–Al_2O_3, the XRD patterns of Co–Mn/SiO_2–Al_2O_3, Mn/SiO_2–Al_2O_3 and Co/SiO_2–Al_2O_3 catalysts exhibit the presence of additional XRD features. The peaks of 35.9°, 43.6° and 63.6° in curve b are attributed to $MnCo_2O_4$, which is formed when Co and Mn are introduced into the SiO_2–Al_2O_3 synchronously. The peaks of 32.3° and 38.3° in curve Mn/SiO_2–Al_2O_3 belong to Mn_3O_4 and MnO, respectively [28]. And the peaks of 36.6° and 59.3° in curve d are attributed to Co_3O_4, which are in good agreement with that reported by Yu et al. [29].