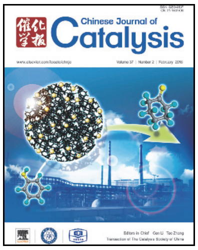
Chinese Journal of Catalysis 37 (2016) 273–280

available at www.sciencedirect.com

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



Article

The synthesis of Co-doped SAPO-5 molecular sieve and its performance in the oxidation of cyclohexane with molecular oxygen

Zhun Xiao, Wangcheng Zhan *, Yun Guo, Yanglong Guo, Xueqing Gong, Guanzhong Lu #

Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China

A R T I C L E I N F O

Article history:
Received 25 August 2015
Accepted 10 November 2015
Published 5 February 2016

Keywords:
SAPO-5 molecular sieve
Cobalt
Cyclohexane
Selective oxidation
Oxygen

A B S T R A C T

Silicoaluminophosphate (SAPO) molecular sieves doped with cobalt (Co-SAPO-5) were synthesized hydrothermally with different concentrations of Co. Each sample was characterized by X-ray diffraction, N_2 adsorption-desorption, scanning electron microscopy, ultraviolet-visible spectroscopy, temperature-programmed desorption of NH_3 (NH_3-TPD), and infrared spectrascopy of adsorbed pyridine (Py-IR). The results showed that Co was highly dispersed in the Co-SAPO-5 samples. In addition, a part of the Co content had been incorporated into the SAPO-5 framework, while the remainder existed on the surface as extra-framework Co. The surface areas of the Co-SAOP-5 samples were similar to the SAPO-5 sample. However, the pore volumes of the Co-SAOP-5 samples were lower than that of the SAOP-5 sample. As the concentration of Co increased, the pore volume gradually decreased because extra-framework cobalt oxide was present on the catalyst surface. NH_3-TPD and Py-IR results revealed that the amount of Brønsted acid and the total amount of acid for the Co-SAPO-5 samples were higher than that for the SAPO-5 sample. These values were also higher for samples with higher Co content. The catalytic activity of the Co-SAPO-5 samples was evaluated for the oxidation of cyclohexane with molecular oxygen. When Co was added to the SAPO-5 catalyst, the catalytic activity of the Co-SAPO-5 catalysts improved. In addition, the conversion of cyclohexane increased as the Co content in the Co-SAPO-5 catalysts increased. However, with a high conversion of cyclohexane (>6.30%), the total selectivity of cyclohexanone (K) and cyclohexanol (A) decreased sharply. The K/A ratio ranged from 1.15 to 2.47. The effects of reaction conditions (i.e., reaction temperature, reaction time, initial oxygen pressure, and the catalyst amount) on the performance of the Co-SAPO-5 catalysts have also been measured. Furthermore, the stability of the Co-SAPO-5 catalyst was explored and found to be good for the selective oxidation of cyclohexane by molecular oxygen.

1. Introduction

Cyclohexanone and cyclohexanol (KA) are important intermediates in the production of adipic acid and caprolactam, which are used in the manufacture of nylon-6 and nylon-66 polymers, respectively [1,2]. In addition, they are used as solvents for shellacs, lacquers and varnishes, stabilizers and homogenizers for soaps and synthetic detergent emulsions, and

---

* Corresponding author. Tel/Fax: +86-21-64252923; E-mail: zhanwc@ecust.edu.cn

Corresponding author. Fax: +86-21-64252827; E-mail: gzhlu@ecust.edu.cn

This work was supported by the National Basic Research Program of China (2010CB732300) and the National Natural Science Foundation of China (21103048).

DOI: 10.1016/S1872-2067(15)61014-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 2, February 2016

as the starting material in the synthesis of insecticides, herbicides, and pharmaceuticals [3]. The oxidation of cyclohexane is an important industrial process to produce cyclohexanone and cyclohexanol; however, the productivity of this process is very low by now [4]. Currently, the most important catalyst system in use for industrial cyclohexane oxidation employs homogeneous Co salts [5]. To prevent the over-oxidation of cyclohexane, conversion is generally kept below 5% and the total selectivity of cyclohexanone and cyclohexanol reaches 70%–80% [6].

The oxidation of cyclohexane with O_2 follows the radical chain mechanism [7]. Transition-metal ions, such as Co^{2+}, Cr^{3+}, Mn^{2+}, and Ce^{2+}, accelerate free radical chain reactions. Consequently, heterogeneous catalysts that contain these ions have been extensively used to catalyze cyclohexane oxidation [8]. On the other hand, molecular sieves based on aluminophosphates have been synthesized and exhibit a huge potential for catalytic applications because of their unique pore structure and low acidity [9,10]. However, doping heteroatoms into the aluminophosphate framework tends to break the charge balance and leads to an improvement in acidity [11–13]. Therefore, because of their mild acidity and shape selectivity, silicoaluminophosphate (SAPO) molecular sieves (such as SAPO-5) have been used as solid acid catalysts for some hydrocarbon reactions. Some of these reactions include the dehydration of ethanol [14], the hydroisomerization of 1-octene [15], the conversion of methanol to olefin [16], the dimerization of propene [17], and the epoxidation of styrene [18]. The enhanced selectivities and decreased deactivation rates were observed for both medium pore-sized SAPO and metalloaluminophosphate molecular sieves.

The main objective of this work was to heterogenize the conventional homogeneous Co salt catalysts by loading them onto a SAPO support. This work also evaluates how the activity for cyclohexane oxidation with O_2 was affected by the doping of SAPO-5 samples with Co. It is worth looking ahead to provide an efficient catalyst for the oxidation of cyclohexane with O_2.

2. Experimental

2.1. Synthesis of Co-SAPO-5 materials

The Co-doped SAPO-5 molecular sieves were synthesized by the hydrothermal method. The following chemicals were used: triethylamine (TEA) as the template, tetraethyl orthosilicate (TEOS) as the silica source, aluminum isopropoxide as the Al source, and H_3PO_4 as the phosphorus source. In a typical synthesis, a fixed amount of $Co(NO_3)_3·6H_2O$ solution was initially mixed with 5.76 g of phosphoric acid and 18 mL of deionized water. Next, 10.21 g of aluminum isopropoxide was added to the mixture and stirred at room temperature until completely dissolved. Then, 3.13 g of the TEOS was added dropwise to the solution and continuously stirring for 1 h. Finally, 3.5 mL of the TEA template was added and stirred for an additional 3 h. The initial gel formed was transferred to a Teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. After crystallization, the product was filtered, washed with deionized water, dried at 100 °C for 24 h, and calcined in air at 550 °C for 5 h to remove the template. The synthesized samples were recorded as Co-SAPO-5-*x*, where *x* represents the different Co/Si molar ratios in the initial gels.

The SAPO-5 molecular sieve was also prepared with the same procedure, except that no $Co(NO_3)_3·6H_2O$ was added.

2.2. Characterization of samples

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer using Cu K_α radiation (λ = 0.154056 nm) operating at 40 kV and 40 mA. The morphologies of the catalysts were analyzed with scanning electron microscopy (SEM) using a Hitachi S-3400N operated with a beam energy of 15 kV. The elemental compositions of the samples were analyzed with ICP (TJA IRIS ADVANTAGE 1000) and EDS (EDAX Falion). The Varian Cary 500 UV-Vis-NIR spectrophotometer was used to record the ultraviolet-visible (UV-vis) spectra in the range of 200–800 nm, with $BaSO_4$ as the reference. Infrared spectra of adsorbed pyridine (Py-IR) of the samples were analyzed using a Nicolet Nexus 670 FT-IR spectrometer.

NH_3-TPD was carried out in an in-house manufactured equipment. The sample was initially pretreated at 600 °C for 30 min and cooled to room temperature under N_2. It was then exposed to the 10% NH_3/N_2 mixture gas and allowed to adsorb NH_3 for 1 h. After this adsorption time, the sample was purged at room temperature for 1.5 h under N_2. Finally, the sample was heated at a rate of 10 °C/min to 600 °C.

2.3. Catalytic activity testing

The catalytic activities of the SAPO-5 and Co-SAPO-5 catalysts were investigated for the selective oxidation of cyclohexane with O_2 as the oxidant. No solvents were added during the process. In the typical reaction, 4 g of cyclohexane and 20 mg of catalyst were introduced into the reactor. After O_2 was charged to 0.5 MPa, the reactor was heated to 140 °C. The samples were stirred continuously and kept at 140 °C for 4 h. After the reaction was completed, the catalyst was separated by centrifugation. The reaction products were analyzed using a flame ionization detector and the Agilent 7890B gas chromatograph, which was equipped with an HP-5 capillary column. Methylbenzene was used as the internal standard.

Recycling tests were carried out on the regenerated Co-SAPO-5-0.2 catalyst. After the reaction was completed, the catalyst was separated from the reaction solution by filtration, washed three times with ethyl alcohol in a glass beaker (while stirring), dried at 100 °C for 6 h, and then calcined in air at 550 °C for 2 h. The regenerated catalyst was supplemented with fresh catalyst and its catalytic performance was tested and compared with the fresh catalyst.

3. Results and discussion

3.1. Characterization of catalysts

The powder XRD patterns of the synthesized Co-SAPO-5-*x*