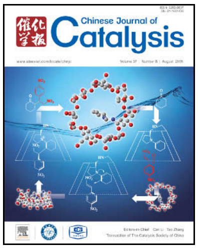
Chinese Journal of Catalysis 37 (2016) 1263–1274

available at www.sciencedirect.com

ScienceDirect

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



Article

Amine-functionalized boehmite nanoparticle-supported molybdenum and vanadium complexes: Efficient catalysts for epoxidation of alkenes

Mahdi Mirzaee *, Bahram Bahramian, Marieh Mirebrahimi

Department of Chemistry, Shahrood University of Technology, Shahrood, Iran

A R T I C L E I N F O

Article history:
Received 26 March 2016
Accepted 30 April 2016
Published 5 August 2016

Keywords:
Boehmite nanoparticles
Heterogeneous catalysts
Hexa-carbonyl molybdenum
Oxo-sulfate vanadium
Epoxidation

A B S T R A C T

Boehmite nanoparticles with a high surface area and a high degree of surface hydroxyl groups were covalently functionalized by 3-(trimethoxysilyl)-propylamine to support vanadium-oxo-sulfate and molybdenum hexacarbonyl complexes. These supported catalysts were then characterized by Fourier-transform infrared spectroscopy, powder X-ray diffraction, thermogravimetry and differential thermal analysis, X-ray-photoelectron spectroscopy, elemental analysis, inductively coupled plasma, and transmission electron microscopy techniques. The catalysts were subsequently used for the epoxidation of *cis*-cyclooctene, and the experimental procedures were optimized. The progress of the reactions was investigated by gas-liquid chromatography. Recycling experiments revealed that these nanocatalysts could be repeatedly used several times for a nearly complete epoxidation of *cis*-cyclooctene. The optimized experimental conditions were also used successfully for the epoxidation of some other substituted alkenes.

1. Introduction

Epoxides are well known as one of the most valuable intermediates for the production of commercially important chemicals such as polyglycols, polyamides, polyurethanes and many other polymers, pharmaceuticals, food additives, epoxy paints, dye-stuffs, flavour and fragrance compounds [1–8], and non-toxic PVC-plasticizers and stabilizers [8–10]. They are also valuable additives to lubricants and adhesives [8,11,12].

In addition to conventional Mo complexes, several other soluble complexes of V, W, Re, Mn, Ru, Co, Fe, and Ti have been employed as active homogenous catalysts for the epoxidation of alkenes [2,13–15]. However, these catalysts are toxic and expensive, and they must be completely separated from the products and waste. In this respect, the development of heterogeneous systems for improving the recovery of valuable catalysts is a very important aspect from an economic and ecological viewpoint. Furthermore, immobilization of the catalysts on supports with a high surface area in heterogeneous systems can efficiently improve the catalyst reactivity and enhance the turnover number (TON) of the catalytic procedure [2]. Anchoring catalysts on a solid surface disperses the active sites uniformly and protects them from dimerization by oxo-bridge formation [16]. Accordingly, various organic and inorganic materials have been used as insoluble supports in heterogeneous catalytic procedures. The organic insoluble supports include different types of polymers such as polybenzimidazole [13,17], polystyrene [13,18,19], polymethacrylate [13], polyaniline [20], and poly-divinylbenzene-allylamine [21]. In addition, ion exchange and epoxy resins [13,22], graphene oxide [23], multi-walled carbon nanotubes [16,24], ordered mesoporous carbon [25], silica [7,13,26], titanium silicate [13], MCM-41

---

* Corresponding author. Tel/Fax: +98-23-32395441; E-mail: mmirzaee@shahroodut.ac.ir

DOI: 10.1016/S1872-2067(16)62451-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 8, August 2016

[26–29], MCM-48 [29], SBA-15 [1,16,26,30,31], alumina [32], montmorillonite K-10 [13,33], coated magnetic particles [13,34], zeolites [16,35–37] and layered bimetal hydroxides [5] have been used as insoluble supports. Generally, inorganic supports have a higher chemical stability and surface area than organic ones. Additionally, the surface of some metal oxides and metal hydroxides is covered with hydroxyl groups. These groups create hydrophilic surfaces that provide valuable sites for grafting a wide range of functionalities. Subsequently, supporting various transition metals on these functionalities can produce active and stable catalysts for liquid-phase organic reactions.

Boehmite (γ-AlOOH) is an inorganic insoluble support that contains extra hydroxyl groups on its surface. It has been used as an absorbent, flame retardant [38], and an important precursor for preparing advanced catalysts, alumina, and alumina-derived ceramics [38,39]. We have used pure boehmite for the successful multi-component synthesis of highly substituted imidazoles [40]. Choudhary et al. [41] have also used pure boehmite for the catalytic epoxidation of styrene, although they reported that it was deactivated by the production and accumulation of water, and so it required continuous removal of water. Consequently, in this work, we used grafted boehmite nanoparticles (BNPs) with 3-(trimethoxysilyl)-propylamine (MSPA) to support two complexes of molybdenum and vanadium.

This strategy has been used for anchoring various metal complexes on different solid supports. However, almost all of them have changed the terminal amine group in MSPA to a Schiff base and then used it for the supporting metal complexes. We have also used this approach in our previous work [42]. In this work, grafted MSPA was used for the straight anchoring of metal complexes and then the supported catalysts were used in the epoxidation of various alkene substrates.

2. Experimental

2.1. Materials and methods

The required solvents and reagents were purchased from Merck or Fluka, and used without further purification. Fourier-transform infrared (FT-IR) spectra were recorded on a Bomem MB series FT-IR instrument at 4 cm^{-1} resolution using KBr pellets. ^{1}H NMR spectra were obtained in d6-DMSO using a Bruker AVANCE 300 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on a Phillips PW-1800 or STOE diffractometer with Cu K_α irradiation. Thermogravimetric (TG) analyses were performed in a Rheometric Scientific STA-1500 or BAHR Thermoanalyse GmbH with a heating rate of 10 °C min^{-1} in air. A 400-W Hg lamp was used for activation of the hexacarbonyl molybdenum complex. Elemental analyses were performed in a Hereans CHN-O-Rapid Analyzer. Transmission electron microscopy (TEM) was performed on a JEOL JSM-6360LV transmission electron microscope. Gas-liquid chromatography (GLC) was performed on a Shimadzu GC-16A instrument using a 2-m column packed with silicon DC-200. X-ray photoelectron spectroscopy (XPS) was performed on an ESCA 2000 system from VG Microtech using a monochromatized aluminum Kα anode.

2.2. Preparation of BNPs

Aluminium 2-butoxide was prepared by the reaction of aluminium with 2-butanol according to the general preparation procedure for aluminium alkoxides [43]. The prepared aluminium alkoxide was vacuum-distilled to obtain a high-quality aluminium alkoxide precursor. For a hydrothermal-assisted hydrolysis, according to our previous report [44], aluminium 2-butoxide was diluted in 2-butanol to 50%, and then loaded in a glass container. The glass container was placed in a 300-mL stainless steel autoclave. The gap between the autoclave chamber and the glass container was covered with 50 mL of distilled water, and then the autoclave was heated at 100 °C. Aluminium 2-butoxide was hydrolysed by diffusion of water vapour into the solution in the hydrothermal chamber. All manipulations of the aluminium alkoxides were performed on a Schlenk line. Their transfer into the autoclave was performed in a moisture-free atmosphere to prevent the hydrolysis of aluminium alkoxides prior to introducing it into the hydrothermal chamber. After 5 h, the autoclave was cooled down and the powder produced (BNPs) was filtered off and dried at 100 °C overnight.

2.3. Preparation of supported molybdenum and vanadium complexes on BNPs and amine-functionalized BNPs

For the preparation of amine-functionalized BNPs (AFBNPs), 1.00 g of BNPs was refluxed with MSPA (61 μL, 0.35 mmol) in dry toluene (50.0 mL) for 24 h (Scheme 1). The solid substance obtained was filtered off, washed three times with dry toluene, and dried at 100 °C overnight.

The $Mo(CO)_6$ and $VOSO_4 \cdot H_2O$ complexes were used to support on BNPs or AFBNPs (Scheme 1). For this purpose, $Mo(CO)_6$ (0.276 g, 1.05 mmol) was activated under ultraviolet light in tetrahydrofuran (THF, 20.0 mL) for 30 min. This activated molybdenum complex was then added to dry BNPs or AFBNPs, and the mixture was subsequently refluxed for 6 h. The mixture was then cooled down and filtered off, and the resulting precipitate was washed several times with THF and dried at 100 °C overnight. In a similar procedure, $VOSO_4 \cdot H_2O$ (0.200 g, 1.05 mmol) was refluxed with BNPs or AFBNPs in ethanol (20 mL) for 7 h. The resulting powder was washed several times with ethanol and dried at 100 °C overnight.

2.4. Catalytic epoxidation of alkenes

In a typical process, an appropriate round bottom flask equipped with a magnetic stirrer bar and a condenser was charged with an alkene, an oxidant, the catalyst (Mo-AFBNPs or V-AFBNPs), and solvent, and the mixture was then refluxed. All the reactions were performed at least two times, and the reaction progress was monitored by GLC. Because different alkenes have different reactivities toward oxidation, these reactions were continued until no further progress was observed. The