



Full paper/Mémoire

# Heterogenization of a molybdenum Schiff base complex as a magnetic nanocatalyst: An eco-friendly, efficient, selective and recyclable nanocatalyst for the oxidation of alkenes

Saeed Rayati\*, Payam Abdolalian

Department of Chemistry, K.N. Toosi University of Technology, PO Box 16315-1618, Tehran 15418, Iran

## ARTICLE INFO

## Article history:

Received 3 January 2013

Accepted after revision 18 March 2013

Available online 13 May 2013

## Keywords:

Green oxidation

Magnetic nanoparticles

Olefins

Heterogeneous nanocatalyst

Molybdenum Schiff base complex

## ABSTRACT

A Schiff base ligand derived from 5-bromo-2-hydroxybenzaldehyde and 2,2'-dimethylpropylenediamine ( $H_2L$ ) and its corresponding dioxomolybdenum(VI) complex ( $Mo(O)_2L$ ) has been synthesized and characterized by spectroscopic methods. The adsorption of  $Mo(O)_2L$  on the surface of silica-coated magnetite nanoparticles via hydrogen bonding led to the formation of  $(\alpha-Fe_2O_3)-MCM-41-Mo(O)_2L$  as a heterogeneous catalyst. FT-IR and atomic absorption spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize and investigate the new nanocatalyst. A practical catalytic method for the efficient and highly selective oxidation of a wide range of olefins with hydrogen peroxide and *tert*-butyl hydroperoxide in ethanol over the prepared molybdenum nanocatalyst was investigated. Under reflux conditions, the oxidation of cyclooctene with *tert*-butyl hydroperoxide or hydrogen peroxide led to the formation of epoxide as the sole product. The catalyst was reused at least six times without a significant decrease in catalytic activity or selectivity, and without detectable leaching of the catalyst.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## 1. Introduction

Since heterogeneous catalysts are easily separated and reused, many efforts have been dedicated to the development of heterogeneous catalysts [1–5]. MCM-41 (Mobil Composition of Matter No. 41) is one of the materials most commonly used as supports for the heterogenization of homogeneous catalysts [1,6–10]. Heterogenization can be achieved by the entrapment or grafting of the active catalysts on the surfaces or inside the pores of a solid support, such as silica, alumina, or ceria. Grafting can be achieved by covalent binding [11–18], electrostatic interactions [19,20] or by hydrogen bonding with the support [11,12,21–23]. Since magnetic field provides a convenient

and low-cost method for the separation of solid particles of a suspension, using modified MCM-41s with  $Fe_3O_4$  as ideal appropriate supporting materials, it has attracted much attention [5,7,24–27]. Magnetically recoverable materials have been used in a wide range of catalytic reactions, including oxidations, hydrogenations, photocatalysis, and C–C bond formation, as well as in novel applications in asymmetric synthesis, hydration, Knoevenagel condensations, and  $CO_2$  cyclo-addition reactions [28–30]. On the other hand, dioxidomolybdenum(VI) complexes are of interest as models for molybdoenzymes [31–33] and used as catalysts for the epoxidation of olefins [34–40].

The objective of this work is to immobilize a molybdenum Schiff base complex onto magnetite nanoparticles with the hydrogen bonding method to obtain a heterogeneous molybdenum magnetic nanocatalyst for the epoxidation of olefins. The advantages of this system are the facile and fast recovery of the solid catalyst at the

\* Corresponding author.

E-mail addresses: rayati@kntu.ac.ir, srayati@yahoo.com (S. Rayati).

end of reaction as well as its good activity and selectivity for epoxide formation.

## 2. Experimental

### 2.1. Instruments and reagents

Infrared spectra were recorded on KBr pellets using a Unicam Matson 1000 FT-IR. A Bruker FT-NMR 500 (500 MHz) spectrometer was utilized to obtain the NMR spectra. A Varian AA240 atomic absorption spectrometer was used for molybdenum determination. The high-power ultrasonic cleaning unit Bandelin Super Sonorex RK-100H with ultrasonic peak output 320 W and HF power 80 W<sub>eff</sub> has been used. The melting points were measured on an Electro thermal 9100 apparatus. X-ray powder diffraction (XRD) was carried out on a Philips X'Pert diffractometer using the Cu K $\alpha$  radiation. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-1460 field emission scanning electron microscope using an ACC voltage of 15 kV. Transmission electron microscopy (TEM) image were obtained with a Zeiss EM-900 transmission electron microscopy device using an ACC voltage of 80 kV. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column (phenyl methyl siloxane 30 m  $\times$  320 mm  $\times$  0.25 mm) and a flame ionization detector.

2,2'-Dimethylpropylenediamine, 5-bromo-2-hydroxybenzaldehyde, molybdenyl acetylacetonate and hydrogen peroxide (solution 27% in water) were used as received from commercial suppliers. The solvents were dried and distilled by standard methods before use. Other chemicals were purchased from Merck or Fluka chemical companies.

### 2.2. Preparation of the Schiff base ligand (H<sub>2</sub>L)

The Schiff base ligand was prepared by the reported methods [41,42].

### 2.3. Preparation of molybdenum(VI) complex

The molybdenum complex (Fig. 1) was prepared as follows: the Schiff base ligand, H<sub>2</sub>L (0.468 g, 1 mmol) was dissolved in 20 mL of ethanol. An ethanolic solution of molybdenyl acetylacetonate (0.326 g, 1 mmol) was added and the reaction mixture was refluxed for 1 h. The light orange solution was concentrated to yield orange powders. The products were washed with warm ethanol. Mo(O)<sub>2</sub>L: Yield: 83%, 0.493 g, D.p.: > 295, Selected FT-IR data,  $\nu$  (cm<sup>-1</sup>): 2922 (C–H), 1614 (C=N), 1520 (C=C), 826 and 913 (Mo–O). <sup>1</sup>H NMR ( $\delta$ ): 0.75, 1.17 (s, 6H, NCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>N), 1.18 (s, 2H, N=CH), 3.38–4.63 (4H, NCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>N), 6.54–7.60 (m, 6H, ArH), 8.04–8.12 (s, 2H, N=CH).

### 2.4. Preparation of the ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-MCM-41-Mo(O)<sub>2</sub>L

Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were prepared by the chemical co-precipitation method reported in the literature [10,43]. Briefly, a solution with molar composition of 3.2 FeCl<sub>3</sub>:1.6 FeCl<sub>2</sub>:1 CTABr:39 NH<sub>4</sub>OH:2300 H<sub>2</sub>O was used for the preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles at room

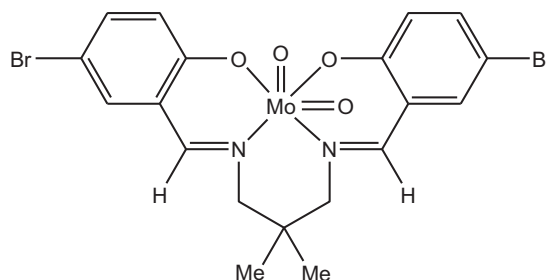


Fig. 1. General structure of the used dioxomolybdenum complex.

temperature under N<sub>2</sub> atmosphere. The magnetic MCM-41 was prepared by adding 20 mL of the Fe<sub>3</sub>O<sub>4</sub> colloid after sonication to a 1 L solution with molar composition 292 NH<sub>4</sub>OH:1 CTABr:2773 H<sub>2</sub>O under vigorous mixing and sonication. Then, sodium silicate (16 mL) was added, and the mixture was allowed to react at room temperature for 24 h under consecutive mixed conditions. The magnetic MCM-41 was filtered and washed. The surfactant template was then removed from the synthesized material by calcination at 450 °C for 4 h and so (Fe<sub>3</sub>O<sub>4</sub>)-MCM-41 was converted to ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-MCM-41 [10]. ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-MCM-41 (3 g) was suspended in 60 mL of chloroform with sonication. To this mixture, an excess amount of Mo(O)<sub>2</sub>L was added, and the resulting mixture was stirred for 12 h with a mild magnetic agitator at room temperature, then filtered to obtain a brick-red precipitate, which was washed with chloroform as a Mo(O)<sub>2</sub>L solvent, and finally dried in air. The preparation of ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-MCM-41-Mo(O)<sub>2</sub>L is shown in Fig. 2.

### 2.5. General heterogeneous green oxidation procedure

Catalytic experiments were carried out in a 10-mL glass flask fitted with a water condenser. In a typical procedure, 0.5 mmol cyclooctene, 0.015 g of ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-MCM-41-Mo(O)<sub>2</sub>L and 2 mL (20 mmol) of H<sub>2</sub>O<sub>2</sub> were added in 3 mL of ethanol. The reaction mixture was refluxed for 8 h. The reaction products were monitored at periodic time intervals using gas chromatography (GC). The oxidation products were identified by comparison with authentic samples (retention times in GC).

## 3. Results and discussion

### 3.1. Characterization of the ligand and of the dioxomolybdenum(VI) complex

#### 3.1.1. IR spectral studies

A practical list of IR spectral data is presented in Table 1. The comparison of the spectra of the complex with the ligand provides evidence for the coordination mode of the ligand in the dioxomolybdenum(VI) complex. A sharp band appearing at 1626 cm<sup>-1</sup>, due to  $\nu$ (C=N) (azomethine), shifts towards the lower wave numbers by 12 cm<sup>-1</sup> and appears at 1614 cm<sup>-1</sup>. This observation indicates the involvement of the azomethine nitrogen in coordination with the molybdenum center [44]. The IR spectra of the Mo complex showed two characteristic

Download English Version:

<https://daneshyari.com/en/article/170607>

Download Persian Version:

<https://daneshyari.com/article/170607>

[Daneshyari.com](https://daneshyari.com)