



Immobilized molybdenum–thiosemicarbazide Schiff base complex on the surface of magnetite nanoparticles as a new nanocatalyst for the epoxidation of olefins

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ABSTRACT

In this work, a new magnetically recoverable nanocatalyst was developed by immobilization of thiosemicarbazide ligand on the surface of silica coated magnetite nanoparticles (SCMNPs) through Schiff base condensation and followed complexation with $\text{MoO}_2(\text{acac})_2$. Characterization of the prepared nanocatalyst was performed with different physicochemical methods such as Fourier transform infrared (FT-IR) and atomic absorption spectroscopies, X-ray diffraction (XRD), vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA), field-emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The prepared catalyst catalyzed the epoxidation of olefins and allyl alcohols with tert-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP) quantitatively with excellent selectivity toward the corresponding epoxides under mild reaction conditions.

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1. Introduction

Design and construction of hybrid nanomaterials with tunable physical properties have attracted extensive interest in material chemistry [1–6]. This field of research bridges different types of chemistry (organic, inorganic, and coordination) to materials science and also opens many possibilities for physical properties. These materials embody the desirable features of both inorganic and organic materials. The ability to integrate the chemical functionality and diversity of soft matter onto a mechanically robust inorganic scaffold has long been of interest in numerous applications especially catalysis [7–9].

Soluble transition metal complexes (i.e. homogeneous catalysts) catalyze numerous interesting chemical reactions including C–C bond formation, oxidation reactions, etc. [10–12]. However, recovering these catalysts from solution poses a considerable challenge. Catalyst separation and recycling are essential steps in catalytic processes and affect the overall process economy. Attaching these homogeneous catalysts to solid supports that are easy to recover and retain the activity of the homogeneous catalysts would have numerous benefits in terms of process design and environmental factors. Facile recovery and reuse while maintaining high catalytic activity of the supported homogeneous catalysts offer a particularly efficient catalyst for a wide variety of reactions.

Thus, design of new hybrid nanomaterials which have appropriate interactions between the support and active components is of great importance for catalytic purposes [7–9,13].

On the other hand, it was known that molybdenum (VI) based catalysts, especially the cis-dioxomolybdenum species, have high catalytic activities for the selective epoxidation of olefins. Although great efforts have been made to immobilize homogeneous molybdenum catalysts on the surface of various supports such as functionalized polymers [14–17], zeolites [18–21], mesoporous molecular sieves [22–30], and multi-walled carbon nanotubes (MWCNTs) surfaces [31–33] there are a little reports in the literature regarding covalent attachment of molybdenum complexes on the silica coated magnetite nanoparticles [34–36].

Surface modified magnetite nanoparticles can be used as support to prepare heterogenized catalysts that are more accessible to the reagents as compared to classic heterogeneous systems [34–44]. Magnetite nanoparticles which can be easily produced by the co-precipitation of Fe(II) and Fe(III) salts in basic conditions have superparamagnetic properties that give it exceptional behaviors suitable both for catalytic reactions in solution and for magnetic recovery. These nanoparticles are easily dispersible and have no tendency to aggregate in solution, but are readily magnetized by an external magnetic field which favors their easy separation from the reaction mixture. In addition, internal diffusion limitations of porous supports can be avoided, because all of the available surface area of the nonporous magnetite nanoparticles is external. The surface of magnetite nanoparticles can be functionalized to protect the magnetite core from chemical

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reactions and also provide functional groups for immobilization of desired catalytic species.

Our current interest in the immobilization of molybdenum complexes on different supports [25–29,33–35] led us to investigate the preparation and characterization of a new covalently attached molybdenum hybrid nanomaterial on the surface of silica coated magnetite nanoparticles. The preparation of this hybrid nanomaterial is based on successive Schiff base condensation of amine modified silica coated magnetite nanoparticles with terephthaldehyde and thiosemicarbazide to give a supporting ligand to which molybdenum was coordinated in final step. The main advantage of the system is relatively strong interaction of molybdenum complex attached on the surface of magnetite nanoparticles which prevent from leaching to reaction mixture during catalytic reactions. The presence of thiosemicarbazide as good donor ligand enhances the catalytic activity of the prepared nanomaterial in the epoxidation of olefins. On the other hand, due to the presence of magnetite core, the prepared hybrid nanomaterial has superparamagnetic properties which make its easy recovery and reuse in catalytic reactions.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from Merck chemical company and used without further purification. $\text{MoO}_2(\text{acac})_2$ was prepared according to literature [45] and its structure was confirmed by spectroscopic methods.

Fourier transform infrared (FT-IR) spectra were recorded on Rayleigh WQF-510 spectrophotometer using pellets of the materials diluted with KBr. Chemical analyses of the samples were carried out with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer. The crystalline phase of the prepared nanomaterial was identified by means of X-ray diffraction measurements using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) on a SIEFERT XRD 3003 PTS diffractometer in the 2θ range of $10\text{--}80^\circ$. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) in the magnetic field range of -8000 Oe to 8000 Oe at room temperature. Thermogravimetric measurements were made on a Perkin Elmer Diamond Thermogravimeter. The temperature was increased to 700°C using a rate of $10^\circ\text{C}/\text{min}$ in static air. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a Philips EM 208 S instrument with an accelerating voltage of 100 kV . Samples were prepared for TEM by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera.

2.1.1. Preparation of silica coated magnetite nanoparticles (SCMNPs) and aminopropyl modified SCMNP (AmpSCMNPs)

Magnetite nanoparticles (MNPs) were prepared according to reported method [42]. For preparation of SCMNP, the magnetite nanoparticles (1 g) were dispersed in deionized water in a 250 ml round-bottom flask with sonication and then an aqueous solution of TEOS (10% (v/v), 80 ml) was added, followed by glycerol (50 ml). The pH of the suspension was adjusted to 4.5 using glacial acetic acid, and the mixture was then stirred and heated at 90°C for 2 h under a nitrogen atmosphere. After cooling to room temperature, the silica coated magnetite nanoparticles was separated from the reaction mixture using a permanent magnet and washed several times with distilled water and methanol. The obtained SCMNP (2 g) were suspended in ethanol (100 ml) and then aminopropyltrimethoxysilane (2 ml) was added under dry nitrogen

atmosphere. The mixture was refluxed for 12 h and the resultant solid was magnetically separated, washed with methanol to remove the unreacted residue of silylating reagent and then vacuum dried at 80°C .

2.1.2. Immobilization of thiosemicarbazide on the surface of silica coated magnetite nanoparticles

The prepared AmpSCMNPs (2 g) suspended in 100 ml of ethanol with sonication were mixed with excess of terephthaldehyde (4 mmol) and the resultant mixture was refluxed for 24 h . The resultant solid (named as tereph-SCMNPs) was separated magnetically and washed with ethanol several times to remove the unreacted residue of the terephthaldehyde. Afterwards, the obtained tereph-SCMNPs (2 g) were suspended in ethanol (100 ml) and thiosemicarbazide (4 mmol) was added under dry nitrogen atmosphere. The mixture was refluxed for 24 h and the resultant solid, named as thio-SCMNPs, was magnetically separated, washed with methanol to remove the unreacted reagents and then vacuum dried at 80°C .

2.1.3. Immobilization of molybdenum complex on the surface of magnetite nanoparticles

Excess of $\text{MoO}_2(\text{acac})_2$ (4 mmol) was dissolved in ethanol (50 ml). The prepared thio-SCMNPs (2 g , dried in vacuum oven at 80°C) was then added to this solution with sonication and the mixture was refluxed for 12 h . After separation with an external magnet, the product was washed with methanol to remove unreacted $\text{MoO}_2(\text{acac})_2$. The resultant MoO_2 -thio-SCMNPs material was then dried under vacuum at 80°C .

2.2. Catalytic epoxidation of olefins in the presence of MoO_2 -thio-SCMNPs

Epoxidation of olefins was carried out in a 25 ml round bottomed flask equipped with a condenser and a magnetic stirrer. Tert-butylhydroperoxide (80% in di-tertiary butyl peroxide) or cumene hydroperoxide (80% in cumene) were used as oxidants. In a typical procedure, to a mixture of catalyst (100 mg) and olefin (8 mmol) in chloroform (10 ml) oxidant was added (14.4 mmol) under nitrogen atmosphere and the mixture was refluxed for appropriate time. Samples were withdrawn periodically and after dilution with chloroform and cooling were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a FID detector. Products were quantified using isooctane (1 g , 8.75 mmol) as internal standard. GC-MS of products were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25). In order to perform the recovery test, the epoxidation of cyclooctene was allowed to proceed 2 h . The catalyst was then recovered magnetically at the reaction temperature and the solution was decanted into a clean 25 ml flask and refluxed for 24 h . The conversions and selectivities were determined after 2 and 24 h .

The molybdenum content of recycled catalyst was measured with above mentioned atomic absorption spectrometer after digestion of the filtered catalyst in hydrochloric acid solution.

3. Results and discussion

3.1. Preparation of MoO_2 -thio-SCMNPs nanomaterial

The sequence of reactions in the functionalization of magnetite nanoparticles (MNPs) with molybdenum thiosemicarbazide derived Schiff base complex has been shown in Fig. 1. First, the external surface of MNPs was coated with a silica shell to obtain silica coated magnetite nanoparticles (SCMNPs). Then, treatment of

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