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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 MoO₂(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 tertbutyl 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 molvbdenum 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. $MoO_2(acac)_2$ 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 Cu Ka radiation $(\lambda = 1.54 \text{ Å})$ on a SIEFERT XRD 3003 PTS diffractometer in the 2θ range of 10-80°. 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 °C/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 aminoropropyl modified SCMNPs (AmpSCMNPs)

Magnetite nanoparticles (MNPs) were prepared according to reported method [42]. For preparation of SCMNPs, 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 SCMNPs (2 g) were suspended in ethanol (100 ml) and then aminoropropyltrimethoxysilane (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 $^\circ$ 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 $MoO_2(acac)_2$ (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 $MoO_2(acac)_2$. 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 $\text{MoO}_2\text{-thio-SCMNPs}$

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 MoO₂-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



Fig. 1. The sequence of events in the preparation of MoO₂-thio-SCMNPs.

silanol (Si-OH) groups of SCMNPs with aminoropropyltrimethoxvsilane afforded aminoropropylated silica coated magnetite nanoparticles (AmpSCMNPs). During this reaction, the silylating reagent reacts with the Si-OH groups on the surface of SCMNPs to form a stable Si-O-Si bond through which the aminopropyl chain was attached to the surface of SCMNPs. The next step involves Schiff base condensation reaction of amino groups in AmpSCMNPs with carbonyl groups of terephthaldehyde to yield the tereph-SCMNPs [46]. Binding of thiosemicarbazide molecules to modified magnetite nanoparticles is achieved through the next Schiff base condensation reaction between remained carbonyl group in the tereph-SCMNPs and the amine groups of the thiosemicarbazide molecules. In the final step, complexation of the thio-SCMNPs was performed with excess of MoO₂(acac)₂ to afford MoO₂-thio-SCMNPs. Soxhlet extraction of the product was carried out subsequently in order to remove the unreacted $MoO_2(acac)_2$ from the resultant nanomaterial.

3.2. Characterization of the prepared MoO₂-thio-SCMNPs nanomaterial

In order to verify the functionalization of the magnetite surface, the FT-IR spectra of the prepared thio-SCMNPs and MoO_2 -thio-SCMNPs nanomaterials were obtained and have been shown in Fig. 2. The observation of two broad bands at around 450–590 cm⁻¹ indicates the characteristic absorption bands of the Fe-O bonds in the magnetite core of the prepared nanomaterials [47].



Fig. 2. FT-IR spectra of (a) thio-SCMNPs and (b) MoO₂-thio-SCMNPs nanomaterials.

The strong and broad absorption band at about $1000-1100 \text{ cm}^{-1}$ revealed the presence of Si-O-Si and Si-O-H stretching vibrations and confirmed the presence of silica shell on the surface of magnetite nanoparticles. The presence of anchored propyl chain was confirmed by C-H stretching vibrations appearing at about 2923 cm⁻¹). In the FT-IR spectrum of thio-SCMNPs, the bands observed at 3256 and 3423 cm⁻¹ were assigned to N-H vibrations

which indicate that the ligand remained in the thione form. The possibility of thione–thiol tautomerism in the ligand was ruled out as no band around $2700–2500 \text{ cm}^{-1}$, characteristic of the thiol



Fig. 3. XRD pattern of the prepared MoO₂-thio-SCMNPs.

group, was observed in the FT-IR spectrum. The bands at 1522 and 1601 cm⁻¹ can be assigned to C=N stretching vibrations, and some weak bands at 1400–1500 cm⁻¹ assigned to stretching vibrations of aromatic rings of thio-SCMNPs were observed that were not present in parent SCMNPs. The appearance of two adjacent bands at 904 and 937 cm⁻¹ in the FT-IR spectrum of complexed material is characteristic of the presence of cis-MoO₂ group [48] and formation of MoO₂–thio-SCMNPs nanomaterial.

Molybdenum content of the prepared nanomaterial was found to be 0.064 mmol g^{-1} on the basis of ICP-AES chemical analysis and further confirmed the presence of molybdenum complex in the final product.

Fig. 3 depicts the XRD pattern of the MoO_2 -thio-SCMNPs nanomaterial. The diffraction peaks can be assigned to the planes of inverse cubic spinel structured Fe₃O₄ (JCPDS no. 19-0629). The broad peaks indicate the nanocrystalline nature of the prepared MoO_2 -thio-SCMNPs nanomaterial.

To study the magnetic properties of magnetite nanoparticles before and after modifications the hysteresis loops of magnetite and functionalized magnetite nanoparticles were investigated at room temperature using vibrating sample magnetometry (VSM).



Fig. 4. Magnetization curves of (a) MNPs, (b) AmpSCMNPs, and (c) MoO₂-thio-SCMNPs.



Fig. 5. TGA curves of the prepared MoO2-thio-SCMNPs.

Magnetization curves of prepared materials are shown in Fig. 4. The magnetization curve of MNPs exhibited no remanence effect (superparamagnetic property) with saturation magnetization of about 60 emu/g. Also, the aminoprpylated silica coated magnetite nanoparticles (AmpSCMNPs) showed superparamagnetic behavior with decreased saturation magnetization of about 42 emu/g. The MoO₂-thio-SCMNPs nanomaterial exhibited superparamagnetic properties with saturation magnetization of about 20 emu/g. The superparamagnetic properties of the prepared MoO₂-thio-SCMNPs nanomaterial are critical for its application, which prevent aggregation and enables it to redisperse rapidly when the magnetic field is removed.

The thermal behavior of the MoO₂-thio-SCMNPs was investigated by thermogravimetric analysis. Fig. 5 shows the TGA, DTG and DTA curves for the prepared MoO₂-thio-SCMNPs. The TGA and DTG curves indicate only one stage of mass reduction as a function of temperature. Due to the hydrophobic nature of the prepared nanomaterial, the amount of adsorbed water below 200 °C was only 2 wt%. The main weight loss at about 300–450 °C was assigned to the combustion of organic compounds which is in good agreement with exothermic DTA peak in this region.

Fig. 6a shows the FE-SEM image of the prepared nanomaterial. The FE-SEM image indicates that the obtained product is composed of spherical nanoparticles. Aggregation gives rise to increase in the size of observed nanoparticles as seen in the FE-SEM image.

Transmission electron micrograph of the prepared nanomaterial has been shown in Fig. 6b. As can be seen, most of the nanoparticles are aggregated. The particle size is about 15 nm in the edges of the aggregated nanoparticles.

3.3. Catalytic epoxidation of olefins and allyl alcohols in the presence of MoO₂-thio-SCMNPs

The catalytic activity of the MoO₂-thio-SCMNPs nanomaterial was evaluated in the epoxidation of some olefins and allyl alcohols with TBHP and CHP as oxidants, and the results are presented in Figs. 7–9. It was found that the MoO₂-thio-SCMNPs nanomaterial can act as an active catalyst and selectively yielded the corresponding epoxides. It is worth noting that the MoO₂-thio-SCMNPs has comparable catalytic activity to our previous catalysts heterogenized on the surface of large surface area MCM-41 [25-29]. This can be interpreted by considering the fact that compared to the those catalysts with higher surface area but narrow pore size, the MoO₂-thio-SCMNPs has no diffusion limitations, as all of the molybdenum active sites are located on the external surface area of SCMNPs. On the other hand, it seems that the presence of Sdonor Schiff base ligand in the final structure of catalyst increases the catalytic activity of the present catalyst in comparison with similar catalysts immobilized on the surface of SCMNPs.

A noticeable point when comparing the results of the epoxidation reactions is the more reactivities of the olefins and allyl alcohols in the presence of TBHP in comparison with CHP. This can be explained with more electrophilic character of the peroxidic oxygen in TBHP. On the basis of previously reports it has been indicated that the epoxidation of olefins in the presence of cisdioxomolybdenum(VI) complexes involves the coordination of TBHP to the Lewis acidic molybdenum center in the first step [49]. The peroxidic oxygen would have electrophilic character and the catalytic epoxidation goes through electrophilic oxygen atom transfer from molybdenum alkyl peroxide to the olefin.



Fig. 7. Results of epoxidation of allyl alcohols with (a) TBHP, and (b) CHP in the presence of MoO_2 -thio-SCMNPs. Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (1.6 ml, 14.4 mmol), refluxing chloroform (10 ml).



Fig. 6. (a) FE-SEM and (b) TEM images of prepared MoO₂-thio-SCMNPs.



Fig. 8. Results of epoxidation of olefins with (a) TBHP, and (b) CHP in the presence of MoO_2 -thio-SCMNPs. Reaction conditions: catalyst (100 mg), olefin (8 mmol), CHP (14.4 mmol), refluxing chloroform (10 ml).



Fig. 9. Results of epoxidation of 3-methyl-2-butene-1-ol with TBHP in the presence of recycled MoO₂-thio-SCMNPs.

Furthermore, allyl alcohols are more reactive than simple olefins. This is probably due to the participation of hydroxyl group in approaching the double bond to the electrophilic oxygen center.

The results of epoxidation of cyclooctene in the absence of the catalyst are included in Table 1 in order to clear up the catalytic effect of the prepared MoO₂-thio-SCMNPs. As can be seen, no significant reaction occurred in the absence of the catalyst.

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Results of the epoxidation of cyclooctene with TBHP.

Entry	Time (h)	Conversion (%)	Selectivity ^a (%)
1 ^b	12	16	36
2 ^c	12	14	41
3 ^d	2	31	> 99
	24	36	99

Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml). ^a Selectivity toward epoxycyclooctane.

^b Reaction was carried out in the presence of SCMNPs.

^c Reaction was carried out in the absence of catalyst.

^d Result after filtering the catalyst.

Recovery test was performed on the prepared nanocatalyst to evaluate whether the catalysis was occurring via surface bound nanocatalyst. In a separate test epoxidation of cyclooctene was allowed to proceed 2 h (ca. 31% cyclooctene conversion, Table 1). The MoO_2 -thio-SCMNPs was then recovered magnetically at the reaction temperature to avoid re-adsorption of the solubilized species and the solution was decanted into a clean 25 ml flask. The solution was refluxed for 24 h to elucidate whether conversion resulted from homogeneous catalyst leached from the support or surface bound molybdenum catalyst. The conversions and selectivities were determined after 2 and 24 h and it was found that the conversion only slightly increased to 36% and then remains constant (Table 1).

After using MoO₂-thio-SCMNPs as catalyst, no molybdenum was detected in the solution by ICP-AAS. On the other hand, the recovered nanocatalyst was reused for the epoxidation of 3-methyl-2-butene-1-ol and the reaction results are presented in Fig. 9. The results show that the activity and selectivity do not decrease significantly for at least two uses of the catalyst. So, from these results it can be concluded that molybdenum species is strongly bonded to the surface of SCMNPs and the prepared nanocatalyst is stable in the reaction conditions and that the epoxidation reaction is truly heterogeneous.

4. Conclusion

In conclusion, the use of modified magnetite nanoparticles to design an efficient magnetically recoverable nanocatalyst for epoxidation of olefins has been demonstrated. First, the external surface of silica coated magnetite nanoparticles were modified with aminopropyltriethoxy silane and terephthaldehyde. Afterwards, Schiff base condensation reaction resulted in immobilization of thiosemicarbazide molecules on the surface of modified magnetite nanoparticles. Subsequent complexation of the supported ligands with molybdenum precursor afforded a magnetically recoverable truly heterogenized molybdenum nanocatalyst which is active and selective in catalytic epoxidation of olefins and allylic alcohols. No contribution from homogeneous catalysis by molybdenum species leached into reaction mixture during the course of the reaction was detected.

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