ORIGINAL PAPER



Surface modification of magnetite nanoparticles with molybdenum-dithiocarbamate complex: a new magnetically separable nanocatalyst

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Received: 1 July 2016/Accepted: 13 February 2017 © Springer-Verlag Wien 2017

Abstract Surface modification of silica-coated magnetite nanoparticles (SCMNPs) by anchoring of molybdenumdithiocarbamate complex resulted in the preparation of a new magnetically separable nanocatalyst for the epoxidation of olefins. The prepared nanocatalyst was characterized by various physicochemical techniques which indicated that the molybdenum complex is successfully supported on the SCMNPs support. This heterogeneous catalyst exhibited good catalytic activity and high selectivity in the epoxidation of olefins with tertbutyl hydroperoxide as oxidant under mild reaction conditions. It can be easily recovered by an external magnetic field and reused up to three times without noticeable deactivation.

Graphical abstract



Keywords Magnetite · Molybdenum · Dithiocarbamate · Immobilization · Epoxidation

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Introduction

Recently, easy separation and reuse of homogeneous transition metal catalysts via their immobilization on the surface of solid supports while maintaining their catalytic performance has attracted great interest in catalytic researches [1-4]. Various support materials such as polymers [2, 3], zeolites [4, 5], and mesoporous materials [6-8]have been used due to their high surface areas and welldefined structures. However, most of this type of supported catalysts suffers from reduced catalytic efficiency mainly as a result of diffusion limitations. One of the most useful methods for easy recovery and reuse of the catalysts is the use of functionalized magnetic nanoparticles as catalyst support. Separation by external magnetic field is a hopeful method in comparison to conventional filtration or centrifugation methods to attain improved reusability [9–11]. On the other hand, as the accessible surface area of the magnetic nanoparticles is external, they have no the internal diffusion limitations of porous materials. To preserve the magnetite nanoparticles from probable chemical reactions and agglomeration, their outer surface may be coated with a silica layer which also provides an inert barrier between the magnetite core and surface functional groups.

In this context, magnetite nanoparticles (MNPs) have attracted much attention due to their unique properties such as high stability, low toxicity, relatively high surface area, and easy recovery. They have been used in many fields such as catalysis of organic reactions [10–14], metal ion separations [15–20], magnetic resonance imaging (MRI) [21–24], and biomedical applications [25–28].

Several types of transition metal homogeneous catalysts have been immobilized on the surface of MNPs and have exhibited excellent catalytic efficiencies in various

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reactions including hydrolysis [29], carbon–carbon crosscoupling reactions [30–33], polymerization [34], hydrogenation [35, 36], hydroformylation [37, 38], and olefin epoxidation [39–42].

In an extension of our previous researches on the immobilization of homogeneous molybdenum catalysts on various supports [40-44] we investigate, for the first time, the immobilization of molvbdenum-dithiocarbamate complex on the surface of silica-coated magnetite nanoparticles to achieve a heterogenized molybdenum catalyst for the epoxidation of olefins. Furthermore, we discuss about full characterization of the prepared catalyst such as its microstructure, magnetic behavior, and surface area as well as its nitrogen adsorption-desorption isotherms. Finally, the catalytic activity of the prepared catalyst will be illustrated in the epoxidation of olefins and allylic alcohols with tert-butyl hydroperoxide as oxidant. The benefits of this system are the easy recycling of the catalyst at the end of reaction as well as high activity, selectivity, and stability.

Results and discussion

Preparation of Mo-dtc-SCMNPs nanomaterial

The involved steps in the immobilization of molybdenumdithiocarbamate complex on the surface of magnetite nanoparticles have been illustrated in Fig. 1. The first step includes the preparation of magnetite nanoparticles (MNPs). In the next step, the outer surface of magnetite nanoparticles was coated with a silica layer to obtain SCMNPs. Then, treatment of silanol groups of SCMNPs with aminopropyltriethoxysilane (Amp) achieved AmpSCMNPs. Condensation of ethoxy groups of the silylating agent with the silanol groups of SCMNPs leads to the formation of stable siloxane (Si–O–Si) bonds through which the aminopropyl groups have been attached covalently to the surface of SCMNPs. Next addition of carbon disulfide to the resulted nanomaterial gives the dithiocarbamate ligand supported on the surface of silica-coated magnetite nanoparticles (dtc-SCMNPs). In this step, nucleophilic attack of amine groups of Amp-SCMNPs to carbon disulfide as electrophile forms -NH-CS₂- groups supported on the surface of silica-coated magnetite nanoparticles. Finally, reaction of MoO₂(acac)₂ with supported dithiocarbamate ligand produces the molybdenum-dithiocarbamate complex immobilized on the surface of magnetite nanoparticles, Mo-dtc-SCMNPs.

Characterization of the prepared Mo-dtc-SCMNPs nanomaterials

Figure 2 shows the FT-IR spectra of SCMNPs, Amp-SCMNPs, dtc-SCMNPs, and Mo-dtc-SCMNPs. The characteristic peaks of the Fe–O bonds in the magnetite core of the prepared nanomaterials are observed at around $450-590 \text{ cm}^{-1}$ [45]. The strong and broad absorption band at about 1000–1100 cm⁻¹ is due to the stretching vibrations of Si–O–Si bonds which confirmed the presence of silica layer on the outer surface of MNPs. The observed band at 2800–2900 cm⁻¹ is assigned to C–H stretching vibrations and verifies the presence of aminopropyl chain in Amp-SCMNPs (Fig. 2b). In the FT-IR spectrum of dtc-SCMNPs (Fig. 2c), the bands at 1465 and 678 cm⁻¹ are assigned to N–CS₂ and C–S vibrations, respectively [46, 47]. Also, the appearance of the bands at 910 and 935 cm⁻¹ in the FT-IR spectrum of Mo-dtc-SCMNPs



Fig. 1 Schematic representation of the preparation of Mo-dtc-SCMNPs

Fig. 2 FT-IR spectra of *a* SCMNPs, *b* Amp-SCMNPs, *c* dtc-SCMNPs, and *d* Mo-dtc-SCMNPs



Wavenumber / cm⁻¹

(Fig. 2d) is characteristic of cis-MoO₂ group [48] which confirms the complexation of supported dithiocarbamate ligand with molybdenum in the final nanomaterial.

The amounts of supported aminopropyl group and dithiocarbamate ligand were determined from CHNS analyses of the materials and are given in Table 1. Molybdenum content of the soxhlet extracted Mo-dtc-SCMNPs was found to be 0.19 mmol g^{-1} from the inductively coupled plasma-optical emission spectroscopy (ICP-OES) chemical analysis and further confirmed the

Table 1 Elemental analysis of the prepared nanomaterials

Sample	N content/ mmol g^{-1}	S content/ mmol g^{-1}	Mo content/ mmol g^{-1}	$\frac{S_{\text{BET}}}{\text{m}^2 \text{g}^{-1}}$
MNPs	0.02	_	_	6
Amp-SCMNPs	0.41	_	_	nd
dtc-SCMNPs	0.37	0.58	_	nd
Mo-dtc-SCMNPs	0.30	0.45	0.19	73
Mo-dtc-SCMNPs ^a	nd	nd	0.18	nd

nd not determined

^a First recovered catalyst

attachment of molybdenum complex on the surface of MNPs.

The XRD pattern of the Mo-dtc-SCMNPs nanomaterial has been shown in Fig. 3. Diffraction peaks in this pattern can be indexed according to diffraction planes of inverse cubic spinel structure (JCPDS No. 19-0629). This indicates that the crystalline structure of the MNPs support has maintained after the immobilization of molybdenum complex. The broadness of the peaks is due to the nanocrystalline nature of the prepared nanomaterial.

The magnetic properties of MNPs, Amp-SCMNPs, and Modtc-SCMNPs were investigated by using vibrating sample magnetometry (Fig. 4). As can be seen in Fig. 4, the magnetization curves of all nanomaterials showed no hysteresis loop and they exhibited superparamagnetic properties. The saturation magnetization of the nanomaterials decreases successively (from 60 emu/g in MNPs to 30 emu/g in Mo-dtc-SCMNPs) with surface modification of the magnetite core.

The superparamagnetic property of the catalyst is important for its employment in catalytic applications. Despite the decrease in the saturation magnetization in comparison with parent MNPs, the Mo-dtc-SCMNPs can be recovered in the presence of external magnetic field and







redispersed rapidly without aggregation when the magnetic field is removed.

As the surface area and textural properties of the heterogeneous catalysts are important parameters in determining their catalytic performance, the nitrogen adsorption–desorption isotherms of MNPs and Mo-dtc-SCMNPs were studied (Fig. 5). As can be seen in Fig. 5, adsorption–desorption isotherms for both materials exhibited the type II isotherm [49]. The small hysteresis loops encountered in the case of Mo-dtc-SCMNPs indicates the presence of some mesoporosity in this material. The observed mesoporosity may be caused by some aggregation of individual nanoparticles due to van der Waals forces.

Total surface areas (S_{BET}) of MNPs and Mo-dtc-SCMNPs (given in the Fig. 5) were obtained based on the Brunauer–

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Emmet–Teller (BET) method. Interestingly, it was found that the surface area of Mo-dtc-SCMNPs is greater than that of MNPs. This can be explained by considering the aggregation in these nanomaterials. Aggregation of the nanoparticles decreases the available external surface area of the nanoparticles. So, in the case of Mo-dtc-SCMNPs, the decrease in the aggregation of the nanoparticles due to the presence of functional groups results in greater surface area in this nanomaterial. The results reveal that the Mo-dtc-SCMNPs material possesses adequate surface area after the immobilization of molybdenum-dithiocarbamate complex on the surface of MNPs.

Figure 6 shows the SEM and TEM images of the prepared Mo-dtc-SCMNPs nanomaterial. The SEM image illustrates that the prepared Mo-dtc-SCMNPs nanomaterial is composed of spherical nanoparticles. Aggregation results in



Fig. 5 Nitrogen adsorption-desorption isotherms of MNPs and Modtc-SCMNPs



Fig. 6 The SEM (top) and TEM (bottom) images of prepared Modtc-SCMNPs

increasing the size of the nanoparticles as seen in the SEM image. Also, the TEM image of the prepared nanomaterial shows that most of the nanoparticles are aggregated. As can be seen nm in the edges of the aggregated nanoparticles, their particle size can be estimated about 15 nm.

Catalytic epoxidation of olefins and allylic alcohols in the presence of Mo-dtc-SCMNPs

Catalytic efficiency of the prepared Mo-dtc-SCMNPs was evaluated in the epoxidation of some olefins and allylic alcohols with *tert*-butyl hydroperoxide (TBHP) as oxidant. The results are given in Tables 2 and 3. Also, the epoxidation of cyclooctene in the presence of parent SCMNPs as well as blank (no catalyst) test was investigated to clarify the catalytic effect of the prepared Mo-dtc-SCMNPs (Table 4). As can be seen in this table, the epoxidation reactions do not proceed significantly in the absence of the Mo-dtc-SCMNPs.

Moreover, we found that the catalytic efficiency of the prepared Mo-dtc SCMNPs nanomaterial is comparable to

 Table 2
 Results of catalytic epoxidation of some olefins with TBHP

 in presence of Mo-dtc-SCMNPs

Run no.	Olefins	Time/h	Conversion/%	Selectivity/%
1	1-Hexene	8	42	>99
		24	89	>99
2	1-Octene	8	29	>99
		24	59	>99
3	1- Decene	8	22	>99
		24	52	>99
4	Cyclooctene	8	99	>99
		24	99	>99
5	Cyclohexene	8	83	>99
		24	92	>99

Reaction conditions: 50 mg catalyst, 4 mmol olefin, 0.75 cm 3 TBHP, 5 cm 3 refluxing chloroform

 Table 3 Results of catalytic epoxidation of some allylic alcohols

 with TBHP in presence of Mo-dtc-SCMNPs

Run no.	Olefins	Time/h	Conversion/%	Selectivity/%
1	3-Methyl-2-buten-1-ol	8	89	>99
		24	99	>99
2	Trans-2-hexen-1-ol	8	81	>99
		24	96	>99
3	1-Octen-3-ol	8	69	>99
		24	82	>99

Reaction conditions: 50 mg catalyst, 4 mmol allylic alcohol, 0.75 cm^3 TBHP, 5 cm³ refluxing chloroform

Run no.	Time/h	Conversion/%	Selectivity ^a /%
1 ^b	12	14	41
2^{c}	12	16	36
3 ^d	2	84	>99
	24	86	>99

 Table 4 Results of the epoxidation of cyclooctene with TBHP in different conditions

Reaction conditions: 50 mg catalyst, 4 mmol cyclooctene, 0.75 cm^3 TBHP, 5 cm^3 refluxing chloroform

^a Selectivity toward epoxycyclooctane

^b Reaction in the absence of catalyst

^c Reaction in the presence of SCMNPs

^d Results after filtering the catalyst

that of our previous catalysts based on large surface area mesoporous materials [50–53]. This observation may be explained by taking to account the fact that compared to earlier catalysts with greater surface area but small pore size, the Mo-dtc-SCMNPs has not diffusion limitations as all of the surface area of the Mo-dtc-SCMNPs nanomaterial is external. Also, it seems that the presence of S-donor dithiocarbamate ligand in the catalyst increases its catalytic activity in comparison with similar catalysts immobilized on the surface of SCMNPs [40–42].

The Mo-dtc-SCMNPs catalyst can be recycled easily by using a permanent magnet compared to other catalysts supported on mesoporous networks which needs a time consuming filtration of reaction mixture.

Results of Tables 2 show that reactivities of the olefins with internal double bond are higher than that of terminal ones. This can be interpreted by considering the proposed mechanism of the olefin epoxidation in the presence of molybdenum catalysts [54–57]. In the first step, the TBHP is coordinated to the molybdenum center to give molybdenum-alkyl peroxide species. Then, the peroxidic oxygen would have electrophilic character and the catalytic epoxidation proceed through electrophilic oxygen transfer from the resulted molybdenum-alkyl peroxide to the olefin as nucleophilic reagent (Fig. 7). Hence, olefins with higher electron density have more nucleophilic character and show higher reactivities in comparison with terminal ones.

The Mo-dtc-SCMNPs catalyst was reused for the epoxidation of cyclooctene to investigate the reusability and stability of the catalyst. The results are presented in Fig. 8 and show that the activity and selectivity do not decrease significantly for at least three recycles.

To examine the stability of the surface-attached molybdenum complex, filtration test was conducted in the epoxidation of cyclooctene which after 2 h the Mo-dtc-SCMNPs catalyst was separated magnetically at the reaction temperature. The solution was transferred into another flask and further refluxed for 22 h to investigate whether conversion resulted from solubilized molybdenum complex leached from the MNPs or supported molybdenum catalyst. The conversions and selectivities were determined after 2 and 24 h (Table 4). It was found that the conversion increased slightly (2%) and then remains constant. So, it can be concluded that the epoxidation reaction proceeds mostly by the heterogeneous Mo-dtc-SCMNPs catalyst. Moreover, after separating the Mo-dtc-SCMNPs catalyst, no considerable leaching of molybdenum was detected as indicated by ICP-OES (Table 1). Thus, from these results it can be concluded that the molybdenum-dithiocarbamate complex is tightly anchored to the surface of SCMNPs and the prepared heterogeneous catalyst is stable in the reaction conditions.





Fig. 8 Results of the epoxidation of cyclooctene with TBHP in the presence of recycled Mo-dtc-SCMNPs. Reaction conditions: 50 mg catalyst, 4 mmol olefin, 0.75 cm³ TBHP, 5 cm³ refluxing chloroform

 Table 5
 Comparison of the results obtained for cycooctene epoxidation catalyzed by various molybdenum-based catalysts

Run No.	Catalyst	Time /h	Conversion /%	Selectivity ^a /%	Reference
1	Mo-dtc-SCMNPs	8	99	>99	This work
2	MoO ₂ pyprMCM- 41	7	98	>99	[51]
3	Mo-POM	8	99	>99	[58]
4	Mo-AMP- CuBTC	8	99	>99	[59]
5	$MoO_2(acac)_2$	4	99	>99	This work

^a Selectivity toward epoxycyclooctane

Furthermore, Table 5 compares the efficiency of the prepared Mo-dtc-SCMNPs catalyst with some of the previously reported heterogeneous catalysts as well as $MoO_2(acac)_2$ as homogeneous one. It can be seen that the catalytic activity of the Mo-dtc-SCMNPs catalyst is comparable to that of other molybdenum catalysts.

Conclusion

Molybdenum-dithiocarbamate complex was immobilized on the surface of silica-coated magnetite nanoparticles. The external surface of SCMNPs was functionalized with aminopropyl group and then dithiocarbamate ligand. Then, complexation of the supported dithiocarbamate ligands with molybdenum complex gave a magnetically recoverable molybdenum catalyst. Physicochemical characterizations showed superparamagnetic properties as well as relatively high surface area of the prepared catalyst. This recoverable catalyst was active in the epoxidation of olefins with high activity and excellent selectivity. In addition, it could be readily removed from the reaction mixture by an external magnetic field and reused for three times without considerable loss of its catalytic efficiency.

Experimental

FT-IR spectra of the samples were provided on Perkin-Elmer Spectrum RXI FT-IR spectrometer in the wavenumber range of $400-4000 \text{ cm}^{-1}$, using pellets of the nanomaterials diluted with potassium bromide. Molybdenum content of the catalyst was measured by Varian Vista-MPX ICP-OES spectrometer. CHNS analysis of the samples was performed on Thermo Finnigan (Flash 1112 Series EA) Analyzer. X-ray diffraction (XRD) patterns of the prepared nanomaterials were recorded with a SIEFERT XRD 3003 PTS diffractometer using Cu K α radiation ($\lambda = 0.154$ nm). Measurement of magnetic susceptibilities were done using a vibrating sample magnetometer (BHV-55, Riken, Japan) in the magnetic field range of -8000 to 8000 Oe at room temperature. Scanning electron microscopy (SEM) analyses of the samples were performed with ZEISS-DSM 960A microscope. Nitrogen adsorption-desorption analyses were performed using Quanta chrome Nova 2200, Version 7.11 Analyzer at liquid nitrogen temperature (77 K). Before the adsorption analysis the samples were outgassed at 383 K. The analysis of epoxidation products were conducted by a gas chromatograph (HP, Agilent 6890N) equipped with capillary column (HP-5) using helium as carrier gas. GC-MS of the products was provided using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

Preparation of modified SCMNPs with dithiocarbamate ligand (dtc-SCMNPs)

Aminopropyl-modified silica-coated magnetite nanoparticles (Amp-SCMNPs) were synthesized according to our previous report [40]. The prepared Amp-SCMNPs (1.0 g) were suspended in 50 cm³ of 0.1 M sodium hydroxide with sonication and then 5 cm³ carbon disulfide in 10 cm³ isopropanol were added. The mixture was stirred for 4 h at room temperature. The solid was collected with a permanent magnet and repeatedly washed with ethanol. The resultant solid (named as dtc-SCMNPs) was dried under vacuum at 353 K.

Immobilization of molybdenum complex on the surface of magnetite nanoparticles (Mo-dtc-SCMNPs)

First, 2 mmol of $MoO_2(acac)_2$ (prepared according to literature method [60]) was dissolved in 50 cm³ ethanol. The prepared dtc-SCMNPs (1.0 g, dried in vacuum oven at

353 K) was then added to this solution with sonication and the mixture was refluxed for 24 h under nitrogen atmosphere. The product was separated with a permanent magnet and washed with ethanol. The obtained Mo-dtc-SCMNPs nanomaterial was soxhlet extracted with methanol to remove unreacted reagents and was dried under vacuum at 353 K.

Catalytic epoxidation of olefins and allylic alcohols in the presence of Mo-dtc-SCMNPs

The catalytic tests for the epoxidation reactions were performed in the presence of Mo-dtc-SCMNPs as catalyst and *tert*-butyl hydroperoxide (TBHP, 80% in di-*tert*-butyl peroxide) as oxidant. The general procedure was as follows: to a mixture of 50 mg catalyst and 4 mmol olefin or allyl alcohol in 5 cm³ chloroform was added 0.75 cm³ TBHP and the mixture was refluxed under nitrogen atmosphere for appropriate time. Samples were withdrawn in given times and were analyzed using GC analysis.

Acknowledgements The authors gratefully acknowledge financial support from the Iran National Science Foundation (INSF) (Grant No. 93009193).

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