Received: 15 June 2017 | Revised: 2 August 2017 | Accepted: 4 August 2017
DOI: 10.1002/aoc.4064

FULL PAPER

WILEY Applied Organometallic Chemistry

Click functionalization of magnetite nanoparticles: A new magnetically recoverable catalyst for the selective epoxidation of olefins

Majid Masteri-Farahani | Samaneh Shahsavarifar

Faculty of Chemistry, Kharazmi University, Tehran, Islamic Republic of Iran

Correspondence
Majid Masteri-Farahani, Faculty of Chemistry, Kharazmi University, Tehran, Islamic Republic of Iran.
Email: mfarahany@yahoo.com

A new magnetically recoverable heterogeneous molybdenum catalyst was developed by means of a click chemistry approach. First, silica-coated magnetite nanoparticles were functionalized using a bidentate ligand via thiol–ene click reaction of mercaptopropyl-modified magnetite nanoparticles with acrylic acid. Then, a molybdenum complex was covalently supported on the surface of the clicked silica-coated magnetite nanoparticles. The prepared catalyst was characterized using Fourier transform infrared and inductively coupled plasma optical emission spectroscopies, X-ray diffraction, vibrating sample magnetometry and transmission electron microscopy. The catalytic performance of the prepared heterogeneous catalyst was investigated in the epoxidation of olefins with *tert*-butyl hydroperoxide as oxidant. This catalyst could be reused for five runs without significant loss of activity and selectivity.

KEYWORDS
click chemistry, epoxidation, heterogeneous catalysis, magnetite, molybdenum

1 | INTRODUCTION

Catalytic reactions have a critical role in promoting the development of the chemical industry.[1,2] Since many catalysts are expensive and pollute the environment, the development of well-planned processes for reusing catalysts is essential from an economic point of view. One way to address this problem is to employ solid supports for the immobilization of homogeneous catalysts.[3,4] The selection of support is critical, as it affects catalytic efficiency.[5–8]

Recent studies have indicated that magnetite nanoparticles with superparamagnetic behaviour are appropriate supports for immobilizing catalysts and may facilitate isolation of catalysts from reaction mixtures with an external magnetic field. Functionalization of the surface of magnetite nanoparticles is a well-known method for the preparation of magnetically recyclable heterogeneous catalysts. Homogeneous catalysts can be immobilized with the aid of appropriate linkers or ligands on the surface of magnetite nanoparticles.[9–15]

One of the efficient methods for the covalent functionalization of solid supports is the application of the click chemistry approach introduced by Sharpless and co-workers.[16] Because of their interesting benefits, click reactions are robust tools for combining various groups to afford new functional materials.[17] Among the various click processes, the thiol–ene click reactions have attracted considerable attention in materials science.[18–21] Thiol–ene click reactions involve the reaction of S—H groups with C=C double bonds which proceeds by a radical mechanism.

Although several efforts have been made for the immobilization of molybdenum complexes onto various solid supports,[8,22–26] the use of the click chemistry approach as a new and efficient method for preparing heterogenized molybdenum catalysts has not been reported so far. The special and interesting magnetic

https://doi.org/10.1002/aoc.4064

properties encouraged us to employ the thiol–ene click reaction on the surface of magnetite nanoparticles for the design of a new heterogenized molybdenum catalyst for the epoxidation of olefins.

In this paper, modification of the surface of magnetite nanoparticles with mercaptoacetic acid via a thiol–ene click reaction and immobilization of a molybdenum complex is reported. The prepared magnetically recoverable molybdenum catalyst showed high catalytic activity and excellent selectivity (100%) in the epoxidation of olefins and allylic alcohols with *tert*-butyl hydroperoxide (TBHP) as oxidant. As one advantage, the catalyst can be easily recovered by magnetic separation. Also, the catalyst can be reused several times without considerable loss of catalytic activity and showed high stability under the reaction conditions.

2 | EXPERIMENTAL

2.1 | Materials and instrumentation

Chemicals were provided by Merck and were of high purity. All of the solvents were distilled and purified using standard procedures.

Fourier transform infrared (FT-IR) spectra were acquired using a PerkinElmer Spectrum RXI FT-IR spectrometer. Chemical analysis of the prepared catalyst was done using a Varian VISTA-MPX inductively coupled plasma optical emission spectrometry (ICP-OES) instrument. Transmission electron microscopy (TEM) images were recorded using a Philips EM 208S instrument with an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) images were obtained with a Zeiss DSM 960A microscope. Magnetic susceptibility analyses were done using a vibrating sample magnetometer (BHV-55, Riken, Japan) at room temperature. X-ray diffraction (XRD) patterns were acquired using Cu Kα radiation (λ = 1.54 Å) with a Siefert XRD 3003 PTS diffractometer. The progress of the catalytic epoxidation of olefins was determined using a gas chromatograph (Agilent 6890 N) equipped with an HP-5 capillary column and flame ionization detector.

2.2 | Preparation of mercaptopropyl-modified silica-coated magnetite nanoparticles (SCMNPs-SH)

Silica-coated magnetite nanoparticles (SCMNPs) were prepared according to a reported method.[27] SCMNPs (1 g) were dispersed in toluene (50 ml) with an ultrasonic homogenizer and then 3-mercaptopropyltrimethoxysilane (1 ml) was added to the mixture. The mixture was refluxed for 24 h under nitrogen atmosphere and, after cooling to room temperature, the solid was magnetically separated, washed several times with methanol to remove the unreacted residue of silylating reagent and then vacuum-dried at 80 °C.

2.3 | Click reaction of SCMNPs-SH with acrylic acid

To a solution of acrylic acid (2 mmol) in chloroform (30 ml) was added SCMNPs-SH (1 g) under dry nitrogen atmosphere. After 15 min, benzoyl peroxide (0.1 mmol) was added and the mixture was refluxed for 2 h. The prepared SCMNPs-S-COOH was then magnetically separated, washed with chloroform to remove the unreacted reagents and then vacuum-dried at 80 °C.

2.4 | Immobilization of molybdenum complex on surface of SCMNPs-S-COOH

A solution of $MoO_2(acac)_2$ (4 mmol, prepared according to a literature method[28]) in ethanol (50 ml) was added to SCMNPs-S-COOH (2 g, dried in a vacuum oven at 80 °C) and, after sonication, the mixture was refluxed for 12 h under nitrogen atmosphere. The product was separated with an external magnet and washed with methanol to remove unreacted $MoO_2(acac)_2$. The obtained SCMNPs-S-COO-MoO_2 catalyst was then dried under vacuum at 80 °C.

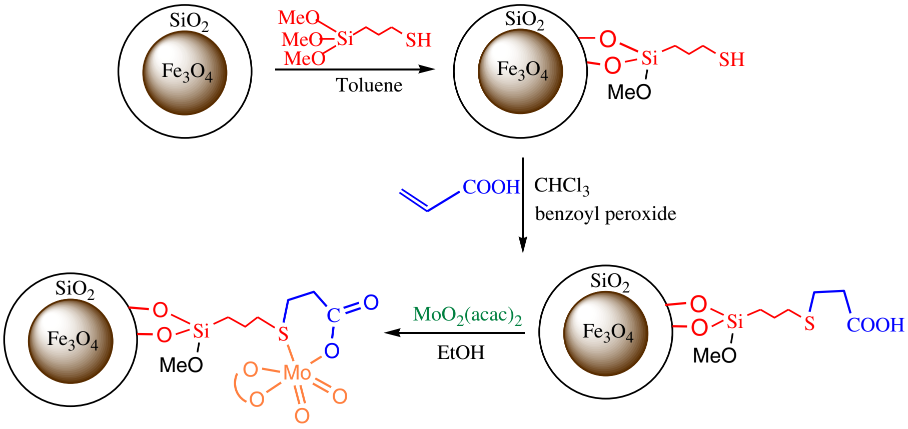
2.5 | Catalytic epoxidation of olefins in presence of SCMNPs-S-COO-MoO_2

In a typical experiment for the epoxidation reaction, 100 mg of SCMNPs-S-COO-MoO_2 catalyst was added to a solution of olefin (8 mmol) in chloroform (10 ml). After addition of TBHP (80% in di-*tert*-butyl peroxide; 14 mmol) the mixture was refluxed under nitrogen atmosphere. Samples were collected at given times and were analysed using GC to determine the conversion and selectivity of the epoxidation reaction. At the end of each epoxidation reaction, the catalyst was magnetically separated, washed with chloroform and then dried under vacuum. The catalyst was reused five times in the epoxidation of cyclooctene under the same experimental conditions.

3 | RESULTS AND DISCUSSION

3.1 | Preparation of SCMNPs-S-COO-MoO_2 catalyst

The details of the synthetic pathway adopted for the construction of the molybdenum catalyst are illustrated in Scheme 1. Initially, SCMNPs were prepared according to



SCHEME 1 Procedure for construction of SCMNPs-S-COO-MoO_2

an earlier report.[27] Then, the surface of SCMNPs was modified with thiol groups via treatment of surface silanol (Si—OH) groups with 3-mercaptopropyltrimethoxysilane to produce SCMNPs-SH nanomaterial. In the next step, the thiol–ene click reaction was conducted between unsaturated C═C bonds of acrylic acid and thiol functional groups of SCMNPs-SH in the presence of benzoyl peroxide as radical initiator to afford SCMNPs-S-COOH, as a bidentate ligand for the subsequent immobilization of molybdenum species. Eventually, complexation of SCMNPs-S-COOH was carried out with an excess of $MoO_2(acac)_2$ to give the SCMNPs-S-COO-MoO_2 catalyst. Afterwards, Soxhlet extraction of the product was done to remove the physically adsorbed molybdenum species from the final catalyst.

3.2 | Characterization of SCMNPs-S-COO-MoO_2 catalyst

In order to confirm the modification of the surface of SCMNPs in each step, the FT-IR spectra of the obtained materials were acquired and are shown in Figure 1. The bands at around 450–590 and 1000–1100 cm^{-1} in the spectra of all the materials are due to the stretching vibrations of Fe—O and Si—O in the SCMNPs core.[29] The tethering of mercaptopropyl groups on the surface of SCMNPs can be established by the observation of C—H stretching vibration band appearing at about 2928 cm^{-1} and a weak band at 2298 cm^{-1} due to the S—H stretching vibration in the FT-IR spectrum of SCMNPs-SH.[30] In the FT-IR spectrum of SCMNPs-S-COOH, the observed new band at

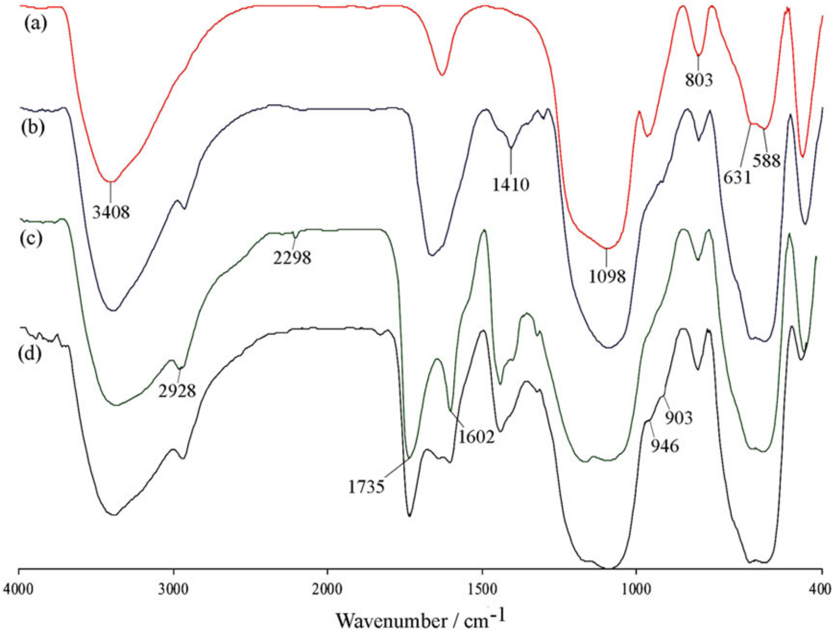


FIGURE 1 FT-IR spectra of (a) SCMNP, (b) SCMNP-SH, (c) SCMNP-S-COOH and (d) SCMNP-S-COO-MoO_2

1735 cm^{-1} can be assigned to C═O stretching vibration of supported carboxyl group and confirms the successful click reaction between S—H group of SCMNPs-SH and C═C bond of acrylic acid. The presence of *cis*-MoO_2 group in SCMNPs-S-COO-MoO_2 can be deduced from the appearance of two bands at 903 and 946 cm^{-1} due to the stretching vibrations of the *cis*-MoO_2 fragment.[31]

According to the ICP-OES results, the molybdenum content of SCMNPs-S-COO-MoO_2 catalyst was found to be 0.06 mmol g^{-1} which further indicated the functionalization with the molybdenum complex.

In order to reveal the crystal phase of the prepared SCMNP-S-COO-MoO_2, powder XRD analysis was conducted. The XRD pattern of SCMNPs-S-COO-MoO_2 (Figure 2) was found to be in accordance with standard XRD data (JCPDS card number 19–0629) for reverse spinel structure of magnetite.[32] As can be seen in the XRD pattern, there are six characteristic Bragg peaks corresponding to the (220), (311), (411), (422), (511) and (440) crystallographic planes of magnetite.

The broadness of the peaks is a consequence of the nanocrystalline nature of the prepared catalyst. The resultant catalyst exhibited only the diffraction peaks of magnetite nanoparticles which indicate that, during the functionalization steps, the crystal phase of the magnetite core is maintained. Moreover, there is no additional peak due to the molybdenum complex which reveals the good dispersion of the molybdenum complex on the surface of SCMNPs.

The particle size and morphology of the SCMNPs-S-COO-MoO_2 catalyst were explored by means of SEM and TEM. The SEM image (Figure 3a) of SCMNPs-S-COO-MoO_2 revealed the smooth surface of the nearly spherical nanoparticles with diameters of about 15 nm. The TEM image (Figure 3b) also confirmed that the diameters of SCMNPs-S-COO-MoO_2 nanoparticles are about 15–20 nm.

The magnetization behaviours of MNPs, SCMNPs and SCMNPs-S-COO-MoO_2 were studied using vibrating sample magnetometry. Superparamagnetic behaviour can be seen for all of the prepared nanomaterials as both their magnetization and demagnetization curves pass through the origin and there is no any hysteresis loop in these curves (Figure 4). Also, the saturation magnetization values decreased with the progress of functionalization of SCMNPs. However, in spite of a lower magnetization value, the net magnetism exhibited by SCMNP-S-COO-MoO_2 is enough for its efficient isolation from dispersed mixtures with employment of a permanent magnet.

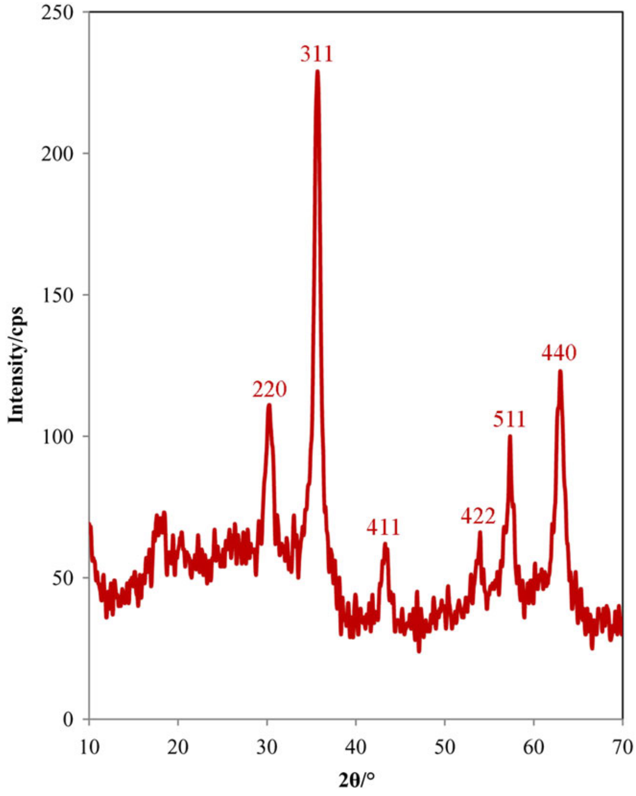


FIGURE 2 XRD pattern of as-prepared SCMNP-S-COO-MoO_2 catalyst

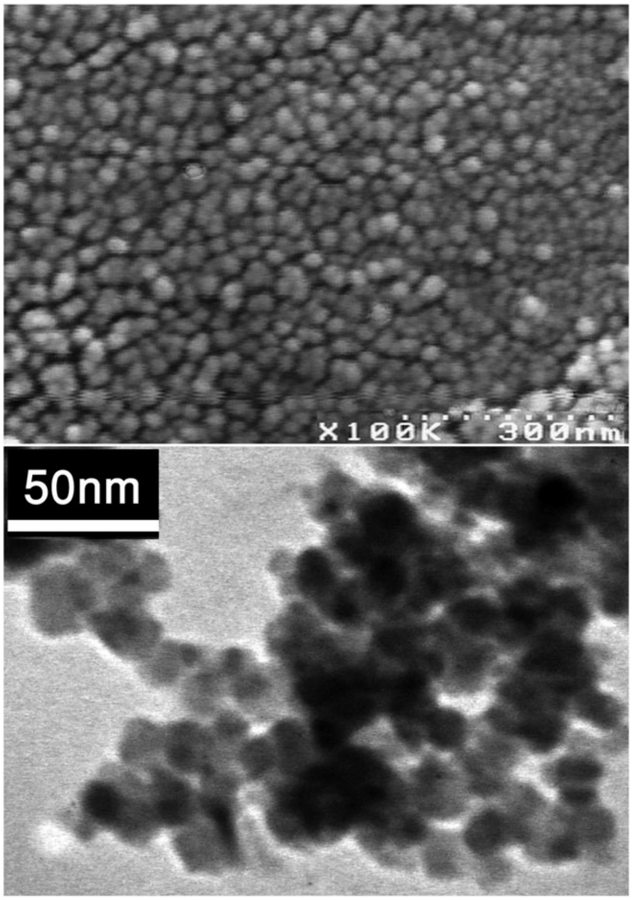


FIGURE 3 (a) SEM and (b) TEM images of as-prepared SCMNP-S-COO-MoO_2 catalyst

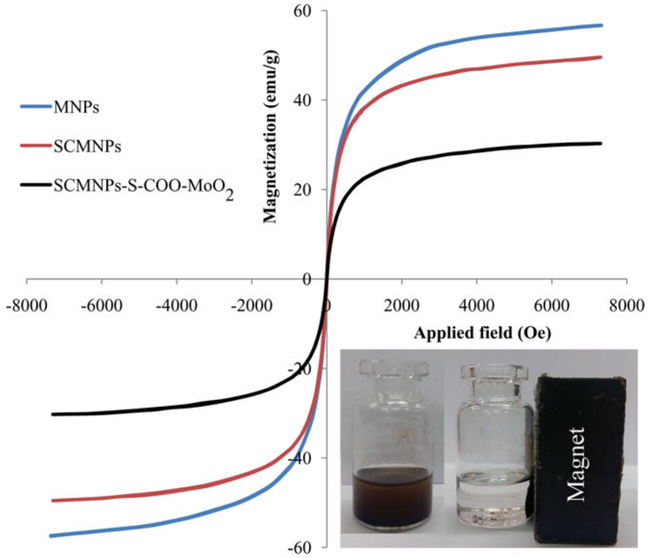


FIGURE 4 Magnetization curves of MNPs, SCMNPs and SCMNP-S-COO-MoO_2 (inset: Magnetic separation of SCMNPs-S-COO-MoO_2 with permanent magnet)

3.3 | Catalytic epoxidation of olefins in presence of SCMNPs-S-COO-MoO_2 catalyst

The prepared SCMNPs-S-COO-MoO_2 catalyst was employed in the catalytic epoxidation of olefins and allylic alcohols with TBHP as oxidant. The results are shown in Figure 5. It was found that the olefins were selectively (>99%) converted to their corresponding epoxides. Examination of the results reveals that the activity of the catalytic system is olefin-dependent, with cyclic olefins exhibiting higher conversions. The sequence of decreasing reactivities based on conversions is: cyclooctene > cyclohexene > 1-hexene > 1-octene > 1-decene. To account for this trend, two governing factors, i.e. electronic and steric effects, should be taken into consideration. As indicated in our earlier works,[10,12] the mechanism of the epoxidation reaction with alkyl hydroperoxides in the presence of molybdenum compounds is electrophilic addition of electron-deficient peroxidic oxygen to the olefin C═C double bond as nucleophile (Figure 6). Thus, increasing the electron donation ability of C═C double bond in cyclic olefins is expected to promote the rate of the epoxidation reaction in comparison with terminal olefins.

In order to reveal the important role of the catalyst in this reaction, two experiments were carried out in which cyclooctene was reacted with TBHP in the absence of the catalyst or in the presence of SCMNPs and the results are given in Table 1. As can be seen, no significant reaction occurred in the absence of the catalyst. The significant decrease of olefin conversion in the absence of the catalyst clearly shows the importance of the catalyst in the epoxidation reaction.

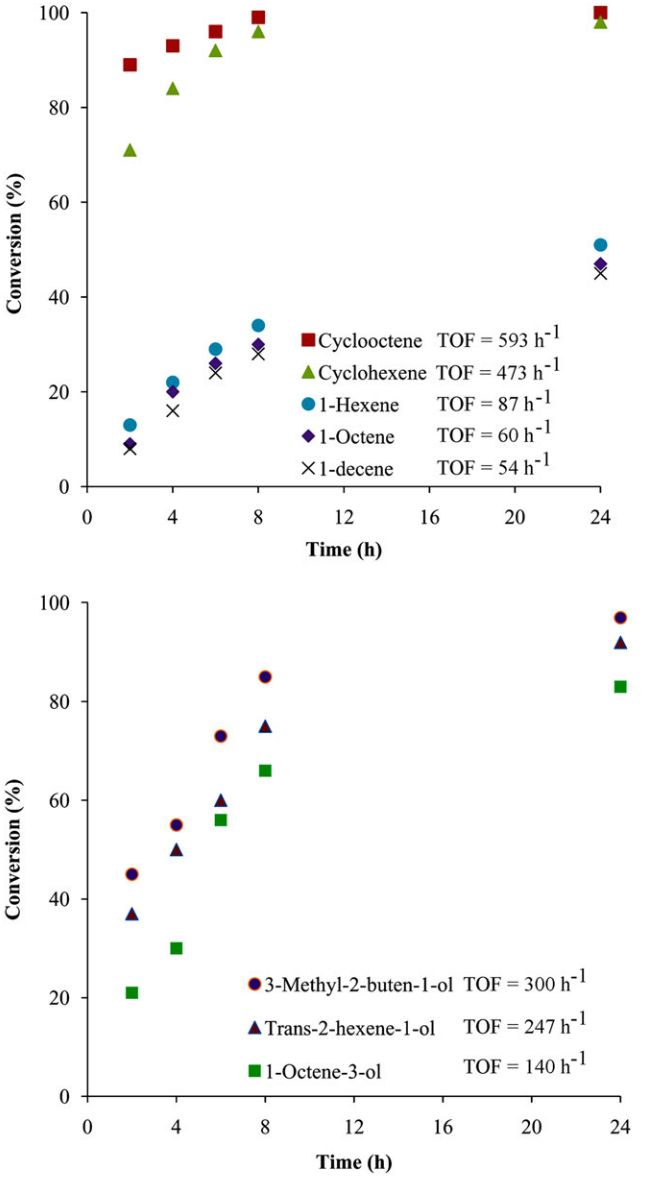


FIGURE 5 Results of epoxidation of olefins (top) and allylic alcohols (bottom) with TBHP in the presence of catalyst (selectively > 99%). Reaction conditions: Catalyst (100 mg), olefin (8 mmol), TBHP (14 mmol), refluxing chloroform (10 ml)

At the end of each reaction, the SCMNPs-S-COO-MoO_2 catalyst could be easily isolated from the mixture by applying an external magnetic field. The inset of Figure 4 obviously shows that the reaction mixture quickly becomes transparent after applying an external magnet.

Also, the reusability of SCMNPs-S-COO-MoO_2 as catalyst was explored by its reuse in the successive epoxidation of cyclooctene with TBHP under the same reaction conditions. In each cycle, the SCMNPs-S-COO-MoO_2 was magnetically isolated, washed with methanol and dried at 80 °C under vacuum. As is evident from Table 2,

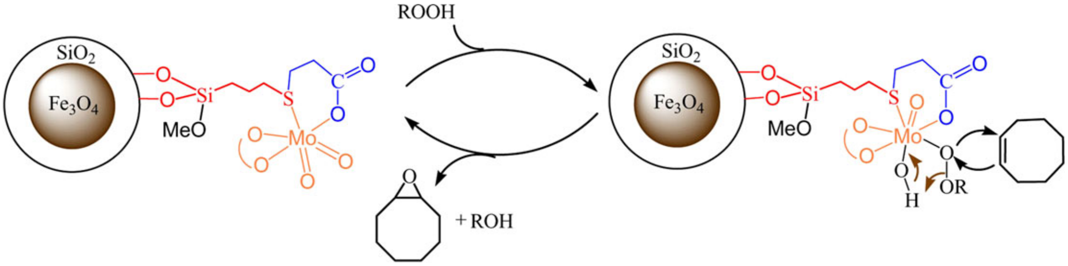


FIGURE 6 Mechanism of epoxidation of cyclooctene with TBHP in the presence of SCMNPs-S-COO-MoO_2

TABLE 1 Epoxidation of cyclooctene with TBHP in the absence of catalyst

Entry	Time (h)	Conversion (%)	Selectivity (%)[a]
1[b]	8	9	35
2[c]	8	5	39

Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (14 mmol), refluxing chloroform (10 ml).

[a] Selectivity to epoxycyclooctane.

[b] Reaction carried out in the presence of SCMNPs.

[c] Reaction carried out in the absence of catalyst.

TABLE 2 Epoxidation of cyclooctene with TBHP in the presence of recycled catalyst and ICP-OES analysis of recycled catalyst

Run	Conversion (%)	Selectivity (%)[a]	Mo content (mmol g^{-1})
1	97	>99	0.06
2	95	>99	0.06
3	94	>99	0.05
4	90	>99	0.05
5	89	>99	0.05

Reaction conditions: catalyst (100 mg), cyclooctene (8 mmol), TBHP (14 mmol), refluxing chloroform (10 ml), 24 h.

[a] Selectivity to epoxycyclooctane.

the catalyst could be recycled up to five times without notable loss of activity and selectivity in successive runs. Also, ICP-OES analyses of the recycled catalyst show no significant loss of the molybdenum content after five sequential catalytic cycles. Altogether, these results indicate the stability of the prepared catalyst under the reaction conditions.

4 | CONCLUSIONS

In summary, we have designed a novel magnetically recoverable heterogeneous molybdenum catalyst by means of facile click chemistry approach, which can be used for the epoxidation of olefins with high activity and selectivity. The prepared catalyst can be readily recovered by magnetic decantation and used for epoxidation of olefins and allylic alcohols for up to five times without loss of activity and selectivity.

ACKNOWLEDGEMENT

The authors are grateful to Kharazmi University for financial support.

ORCID

Majid Masteri-Farahani http://orcid.org/0000-0001-9770-9566

REFERENCES

[1] J. G. de Vries, S. D. Jackson, *Catal. Sci. Technol.* **2012**, *2*, 2009.

[2] Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, *Chem. Soc. Rev.* **2014**, *43*, 3480.

[3] R. B. Nasir Baig, R. S. Varma, *ACS Sustain. Chem. Eng.* **2014**, *2*, 2155.

[4] R. Y. Parapat, O. H. I. Saputra, A. P. Ang, M. Schwarze, R. Schomacker, *RSC Adv.* **2014**, *4*, 50955.

[5] J. M. Fraile, J. I. Garcia, C. I. Herrerias, J. A. Mayoral, E. Pires, *Chem. Soc. Rev.* **2009**, *38*, 695.

[6] J. Hong, F. Zaera, *J. Am. Chem. Soc.* **2012**, *134*, 13056.

[7] A. Fihri, M. Bouhrara, U. Patil, D. Cha, Y. Saih, V. Polshettiwar, *ACS Catal.* **2012**, *2*, 1425.

[8] A. Tadjarodi, S. Mirzakhani, M. Masteri-Farahani, *React. Kinet., Mech. Catal.* **2017**, *120*, 593.

[9] A. Rezaeifard, P. Farshid, M. Jafarpour, G. K. Moghaddam, *RSC Adv.* **2014**, *4*, 9189.

[10] M. Masteri-Farahani, N. Tayyebi, *J. Mol. Catal. A* **2011**, *348*, 83.

[11] P. Veerakumar, I. P. Muthuselvam, C. T. Hung, K. C. Lin, F. C. Chou, S. B. Liu, *ACS Sustain. Chem. Eng.* **2016**, *4*, 6772.

[12] M. Mohammadikish, M. Masteri-Farahani, S. Mahdavi, *J. Magn. Magn. Mater.* **2014**, *354*, 317.

[13] M. B. Gawande, P. S. Branco, R. S. Varma, *Chem. Soc. Rev.* **2013**, *42*, 3371.

[14] V. Polshettiwar, R. Luque, A. Fihri, H. B. Zhu, M. Bouhrara, J. M. Bassett, *Chem. Rev.* **2011**, *111*, 3036.

[15] A. Pourjavadi, S. H. Hosseini, M. Doulabi, S. M. Fakoorpoor, F. Seidi, *ACS Catal.* **2012**, *2*, 1259.

[16] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

[17] O. E. Hutt, X. Mulet, G. P. Savage, *ACS Comb. Sci.* **2012**, *14*, 565.

[18] V. K. Tiwari, B. B. Mishra, K. B. Mishra, N. Mishra, A. S. Singh, X. Chen, *Chem. Rev.* **2016**, *116*, 3086.

[19] V. Castro, H. Rodriguez, F. Albericio, *ACS Comb. Sci.* **2016**, *18*, 1.

[20] Y. Shi, X. Cao, H. Gao, *Nanoscale* **2016**, *8*, 4864.

[21] S. Li, L. Wang, F. Yu, Z. Zhu, D. Shobaki, H. Chen, M. Wang, J. Wang, G. Qin, U. J. Erasquin, L. Ren, Y. Wang, C. Cai, *Chem. Sci.* **2017**, *8*, 2107.

[22] S. Abednatanzi, A. Abbasi, M. Masteri-Farahani, *J. Mol. Catal. A* **2015**, *399*, 10.

[23] M. Najafi, A. Abbasi, M. Masteri-Farahani, V. H. Rodrigues, *Inorg. Chem. Commun.* **2014**, *46*, 251.

[24] M. Mirzaee, B. Bahramian, A. Amoli, *Appl. Organometal. Chem.* **2015**, *29*, 593.

[25] S. Shylesh, J. Schweizer, S. Demeshko, V. Schunmann, S. Ernst, W. R. Thiel, *Adv. Synth. Catal.* **2009**, *351*, 1789.

[26] K. Leus, Y.-Y. Liu, M. Meledina, S. Turner, G. Van Tendeloo, P. Van Der Voort, *J. Catal.* **2014**, *316*, 201.

[27] C. Huang, B. Hu, *Spectrochim. Acta B* **2008**, *63*, 437.

[28] G. J. Chen, J. W. Mc Donald, W. E. Newton, *Inorg. Chem.* **1976**, *15*, 2612.

[29] X. Q. Liu, Z. Y. Ma, J. M. Xing, H. Z. Liu, *J. Magn. Magn. Mater.* **2004**, *270*, 1.

[30] D. Pavia, G. M. Lampman, G. S. Kriz, *Introduction to Spectroscopy*, 3rd ed., Western Washington University **2006**.

[31] J. Topich, *Inorg. Chem.* **1981**, *20*, 3704.

[32] A. Hu, G. T. Yee, W. Lin, *J. Org. Chem.* **2005**, *127*, 12486.

How to cite this article: Masteri-Farahani M, Shahsavarifar S. Click functionalization of magnetite nanoparticles: A new magnetically recoverable catalyst for the selective epoxidation of olefins. *Appl Organometal Chem*. 2017;e4064. https://doi.org/10.1002/aoc.4064