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Molybdenum-MCM-41 silica as heterogeneous catalyst for olefin epoxidation

Franca Bigi[a], Calogero Giancarlo Piscopo[a], Giovanni Predieri[a], Giovanni Sartori[a], Roberto Scotti[b], Robertino Zanoni[c], Raimondo Maggi[a,*]

[a] *Clean Synthetic Methodology Group, Dipartimento di Chimica dell'Università, Parco Area delle Scienze 17A, I-43124 Parma, Italy*
[b] *Dipartimento di Scienza dei Materiali, INSTM, Università di Milano-Bicocca, Via R. Cozzi 53, I-20125 Milano, Italy*
[c] *Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le Aldo Moro 5, 00185 Roma, Italy*

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ABSTRACT

MCM-41-supported molybdenum/bis-dithiocarbamate complex can be efficiently utilized, after treatment with *tert*-butylhydroperoxide (TBHP), for the epoxidation of alkenes under solventless conditions. The treatment with TBHP allows the formation of the real catalyst through oxidative decomposition of the complex affording well dispersed Mo(VI) species grafted onto the silica surface through the silanol groups.

Experimental results, catalytic efficiency and spectroscopy data, allow to advance some hypotheses on the molybdenum-grafted catalyst formation.

The grafted catalyst can be reused several times in the model epoxidation of cyclohexene affording the epoxide with very good yield; only during the first run a modest molybdenum leaching is observed.

Both cyclic and linear alkenes can be epoxidized in good to excellent yields and selectivities.

1. Introduction

The conversion of alkenes into epoxides by reaction with a variety of benign oxidants such as oxygen, hydrogen peroxide and alkyl hydroperoxides in combination with cheap, safe and reusable heterogeneous catalysts shows great interest due to the potential applicability to large scale production [1,2].

Furthermore, solid catalysts can be easily utilized in flow processes that give further advantages associated with the specific experimental conditions allowing precise reaction control through rapid heat transfer and mixing [3,4].

Among the great number of heterogeneous catalysts studied in the alkene epoxidation, materials produced by supporting highly active homogeneous catalysts are particularly attractive because of the possibility to combine the advantages of the homogeneous catalysis with those derived from the use of thermally stable, heterogeneous materials such as zeolites, clays, polystyrenic resins and silicas. These solid catalysts can be obtained through tethering or grafting procedures [5]; concerning this last procedure, the Schiff bases are particularly employed. Recently magnetically recyclable nanocomposite catalysts have been also utilized [6].

However, severe troubles are frequently encountered with the attempts to immobilize proven homogenous catalysts; first of all the anchoring of the ligand–metal complex at the solid support could not be chemically robust enough, and both metal and ligand could leach into the solution resulting in catalyst deactivation and contamination of the final products. Thus, improved anchoring techniques combined with detailed catalyst characterization are needed.

The activity of the supported catalysts is, in general, lower than their homogeneous counterparts; however, some species show enhanced selectivity and longer lifetime due to the site isolation that prevents bimolecular catalyst deactivation [7].

Molybdenum-incorporating heterogeneous catalysts have been utilized in a great number of important reactions such as alkane oxidation [8,9], alkene metathesis [10,11] and selective alcohol oxidation [12]. Moreover, molybdenum, such as other metals with low oxidation potential and hard Lewis acidity in their highest oxidation state, has been utilized as active catalyst in the epoxidation of alkenes with hydrogen peroxide or *tert*-butylhydroperoxide: some interesting examples are the use of MoY zeolites [13], molybdenum-polybenzimidazole adduct [14], molybdate-exchanged layered double hydroxides [15] and molybdenum-containing sol–gel materials [16].

In this regard, covalently grafted Mo(VI) complexes with nitrogen donor ligands have been found to be active catalysts or catalyst precursors for olefin epoxidation by using *tert*-butylhydroperoxide

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* Corresponding author. Tel.: +39 521 905411; fax: +39 521 905472.
E-mail address: raimondo.maggi@unipr.it (R. Maggi).

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(TBHP) as oxygen source. Unfortunately, in some cases and particularly for monodentate nitrile and bidentate bipyridyl ligands, the catalysts are unstable towards molybdenum leaching, which accounted for nearly complete loss of activity in the second catalytic run [17,18]. More stable molybdenum catalysts, covalently bound to MCM-41 mesoporous silicas and aluminosilicates, were obtained by grafting chelate complexes of 1,4-diazabutadiene [19] and (2-pyridyl)-1-pyrazolylacetamide [20] ligands with MoO_2Cl_2 and $MoO(O_2)_2$, respectively. They were found to be effective and truly heterogeneous catalysts for olefin epoxidation. More recently, siliceous MCM-41 materials containing highly dispersed MoO_x units, active in olefin epoxidation, were obtained by reaction of Mo(VI) peroxo species and silica precursors such as tetraethylorthosilicate (TEOS) [21].

In the present paper, we report the preparation, characterization and catalytic performance in the olefin epoxidation of molybdenum species grafted on MCM-41 silica; this new preparation involves the tethering of Mo(VI) dithiocarbamate (DTC) complex to mesoporous MCM-41 and successive *in situ* transformation into the silica grafted molybdenum species by oxidative degradation of the ligand. This method allows the use of less expensive and easy-to-handle sodium molybdate, as molybdenum starting material, in place of oxochloro or oxodiperoxo species [22] or the expensive $CpMoCl_2$ [23]. To the best of our knowledge, the only use of molybdenum-DTC complexes to prepare heterogeneous catalysts is that reported by Qian et al. [24] for the hydrodesulfurization process.

2. Experimental

2.1. Materials and equipment

Cyclohexene (≥99.0%, ~0.01% BHT as stabilizer), cyclooctene (≥99.5%), *cis*,*cis*-1,5-cyclooctadiene (≥98.0%), 1-octene (98%) and *trans*-2-hexene (97%) were purchased from Aldrich and used without further purification. The other reagents, solvents, and standards were purchased in the highest purities available and used without further purification: xylene (mixture of isomers), dichloromethane, ethanol, carbon disulfide, ethyl acetate, bromobenzene, cyclohexene oxide, cyclooctene oxide, 1-methylcyclohexene oxide, 1-octene oxide, TBHP (6 M in decane), cetyltrimethylammonium chloride (25 wt% in water), sodium silicate (27% SiO_2, 14% NaOH in water) and sodium molybdate dihydrate ≥99% from Aldrich, 3-(methylamino)propyltrimethoxysilane from Fluka.

Metal elemental analyses were performed by ICP-AES on Ultima 2 Jobin Yvon HORIBA instrument.

FT-IR spectra of all the catalysts (KBr pellets) were recorded on a Nicolet FT-IR Nexus spectrophotometer (resolution $4\,cm^{-1}$) in the range of $4000–400\,cm^{-1}$.

X-ray diffraction analyses were performed on Philips PW1710 instrument.

Gas-chromatographic analyses were accomplished on a TraceGC ThermoFinnigan instrument (FID).

N_2 adsorption-desorption isotherms, obtained at 77 K on a Micrometrics PulseChemiSorb 2705, were used to determine specific surface areas, SA_{BET}. Before each measurement the samples were outgassed at 383 K for 1 h.

XPS spectra were run on a Vacuum Generators ESCALAB spectrometer, equipped with a hemispherical analyser operated in the Fixed Analyser Transmission (FAT) mode, with a pass energy of 20 or 50 eV. Al $K\alpha_{1,2}$ or Mg $K\alpha_{1,2}$ photons ($h\nu = 1486.6$ and 1253.6 eV, respectively) were used to excite photo-emission. The binding energy (*BE*) scale was calibrated by taking the Au $4f_{7/2}$ peak at 84.0 eV. Correction of the energy shift due to static charging of the samples was accomplished by referencing to the C 1s line from the residual pump line oil contamination, taken at 285.0 eV. The accuracy of reported *BEs* was ±0.2 eV, and the reproducibility of the results was within these values. XPS atomic ratios are relative values, intrinsically affected by a ±10% error. The spectra were collected by a DAC PDP 11/83 data system and processed by means of VG 5000 data handling software.

EPR spectra were recorded on a Bruker EMX spectrometer working at the X-band frequency, equipped with an Oxford cryostat. Spectra were recorded at 123 K. Modulation frequency was 100 kHz, modulation amplitude 5 gauss, microwave power 10 mW. The g values were measured by standardisation with 2,2′-diphenyl-1-picrylhydrazyl (DPPH). The amount of Mo paramagnetic centres (espressed as % of the total amount of Mo) was calculated by double integration of the resonance lines referring the area to a calibration curve (area of EPR signal *vs*. concentration) of $Cu(NO_3)_2\ 1/2H_2O$ in frozen ethylene glycol-water solutions.

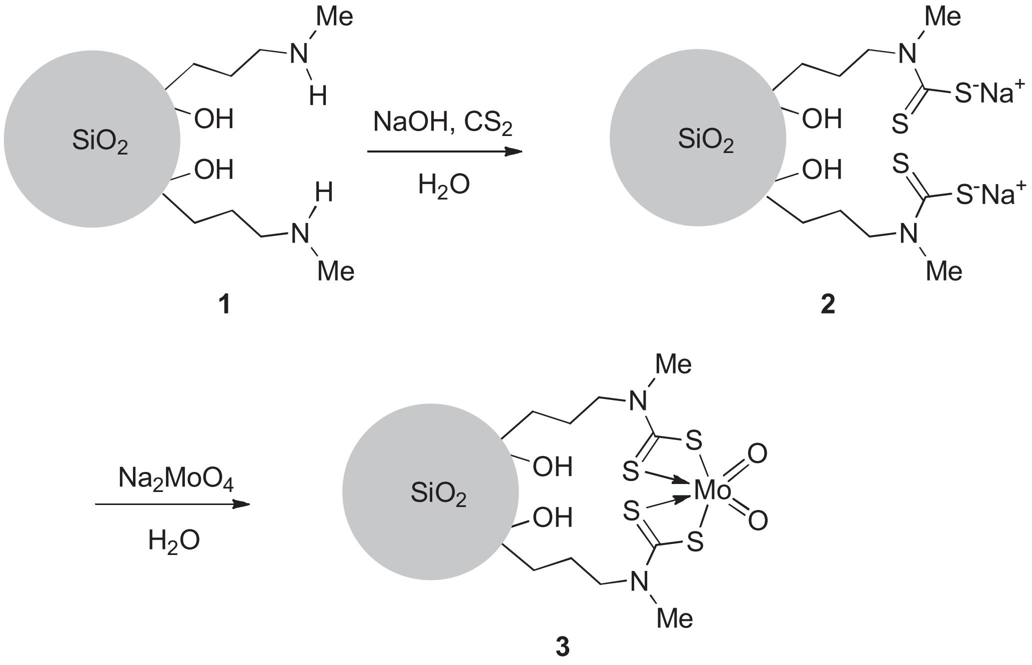
2.2. Catalyst preparation

MCM-41 silica was prepared following a reported procedure [25,26]; its structure was confirmed by XRD analysis (channel dimension: 39 Å), and the BET analysis showed a surface area of $1050\,m^2/g$, a V_{tot} of $1.130\,cm^3/g$ and the following pore volume distribution (cm^3/g): 0–2 nm = 0.007, 2–4 nm = 0.775, 4–10 nm = 0.154, >10 nm = 0.194. The material MCM-41-$(CH_2)_3$-$NHCH_3$ (**1**) was prepared according to a method described in the literature [27] with some adjustments: a mixture of MCM-41 silica (6 g) pre-heated at 300 °C for 16 h, [3-(*N*-methylamino)propyl]trimethoxysilane (6.1 mol, 1.2 g) and xylenes (30 ml) were refluxed under stirring for 15 h. The resulting solid was filtered at rt, washed with hot xylenes (5 × 10 ml) and dried under vacuum [N loading: 1.33 mmol/g (elemental analysis)].

The MCM-41 silica supported oxomolybdenum bis-dithiocarbamate (**3**) (Scheme 1) was prepared by conveniently modifying the procedure early reported for production of molybdenum-dithiocarbamate complexes under homogeneous conditions [28,29] or supported on polystyrene [30]. The MCM-41-$(CH_2)_3NHCH_3$ material (**1**) (500 mg) was dispersed in distilled water (10 ml) with stirring under nitrogen. 0.1 N NaOH aq. solution was added in a 1:1 molar ratio with respect to the supported amine. The mixture was stirred at rt for 10 min. Carbon disulfide was added in 1:1 molar ratio with respect to NaOH and the slurry was stirred for 15 min becoming pale yellow. To the pale yellow slurry an aq. solution of $Na_2MoO_4{\cdot}H_2O$ (1.2:2 molar ratio with respect NaOH) was added and the mixture was stirred for 15 min. 1 M aq. HCl solution was added dropwise until pH < 1 and the slurry turned to brown colour. The powder was filtered on Buchner funnel and washed with ethanol (10 ml) and methylene chloride (10 ml). After washing, the green powder **3** was dried under vacuum [molybdenum loading: 0.26 mmol/g (ICP–MS); surface area: $970\,m^2/g$].

2.3. Catalytic reactions

The catalytic tests for the epoxidation reactions were performed by procedures reported in the notes of table and figures. The general procedure was as follows: in a stirred batch reactor equipped with condenser and thermometer the selected alkene (20 mmol) and the catalyst (0.1 g, corresponding to 0.026 mmol of molybdenum) were mixed together and the mixture was heated at 80 °C under stirring (70 °C for 2-hexene). TBHP (2 mmol, 0.36 mL of 6 M decane solution) was added by a syringe pump during 3 h at the same temperature. Heating and stirring were continued for one additional hour. The reaction mixture was then cooled to rt; ethyl acetate (20 ml) was added and the solid catalyst was removed by filtration, washed with ethyl acetate (10 ml) and dried under vacuum. The reaction mixture was analyzed by high resolution capillary GC with a fused



Scheme 1. Preparation of dioxomolybdenum bis-dithiocarbamate complex tethered on MCM-41 silica.

silica capillary column SPB-20 from Supelco (30 m × 0.25 mm) using decane as internal standard. The products were identified by comparing their spectral data with those reported in the literature.

3. Results and discussion

As described in the Experimental section, the procedure adopted in the preparation of the supported molybdenum-catalyst implies the following steps sketched in Scheme 1:

(i) reaction of MCM-41 silica with [3-(*N*-methylamino)propyl] trimethoxysilane giving material (**1**);
(ii) production of MCM-41 supported DTC (**2**) by reaction of material (**1**) with NaOH/CS_2;
(iii) production of MCM-41 supported Mo(VI)-bis-DTC complex (**3**) by reaction of supported DTC with sodium molybdate.

Regarding the nature of the complex **3** obtained in step (iii), it should have a structure similar to that of complex **4** (Fig. 1), obtained by reacting sodium molybdate with pure diethyldithiocarbamate [28], as **3** shows the characteristics IR bands attributable to C–N (1540 cm^{-1}) and Mo=O (945 and 903 cm^{-1}) stretching modes, slightly shifted with respect to the same bands observed in the homogeneous counterpart **4** (1510, 920 and 880 cm^{-1}) [28,29].

In addition, the EPR spectrum of the as prepared material Mo(VI)-bis-DTC-MCM-41 (**3**) shows an isotropic signal at $g = 1.943$ (Fig. 2(a)), attributed to adventitious Mo(V) species with a d^1 configuration [31–34], whose amount is very small (~1.2×10^{-3}% of the total loaded molybdenum). The isotropic shape of the signal indicates that the paramagnetic species are not magnetically isolated and that a probable exchange interactions within neighbouring Mo(V) centres occurs [34].

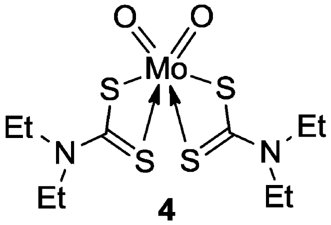


Fig. 1. Structural sketch of bis (*N*,*N*-diethyldithiocarbamate)dioxomolibdenum(VI).

The catalytic activity of material **3** was studied in the model epoxidation of cyclohexene **5** with TBHP (Scheme 2), and the effect of various reaction parameters on the effectiveness of the catalyst was evaluated.

In a first experiment, the reaction was performed without solvent by adding TBHP (2 mmol) in one portion to a mixture of the catalyst (100 mg, corresponding to 0.026 mmol of molybdenum) with a large excess of cyclohexene (20 mmol) previously heated at 80 °C. The reaction mixture was stirred at this temperature for 4 h, cooled to room temperature, filtered to remove the catalyst, and then it was analyzed by GLC. Cyclohexene epoxide **6** was the main reaction product (50% yield). Modest amounts of 2-cyclohexene-1-ol (**7**) and 2-cyclohexene-1-one (**8**) (2–5%) have been also recognized due to the competitive allylic oxidation of cyclohexene.

After this preliminary experiment the catalyst colour turned from green to yellow; this change could be attributable to a variation of the molybdenum oxidation state due to the presence of TBHP. To investigate this behaviour, initially we studied the transformation of the catalyst in the presence of the oxidant: a sample of catalyst **3** (100 mg) was refluxed with TBHP (0.36 mL of a 5.5 M decane solution) in 1,2-dichloroethane (3 mL) for 2 h (as expected during this treatment a change in the colour of the catalyst from green to yellow was observed). The activity of the as prepared and the TBHP-treated catalysts was compared with that of the recovered catalyst after the first run. Reaction profiles are shown in Fig. 3.

The TBHP-treated catalyst (●) showed a slightly higher initial rate with respect to the as prepared (■) and the recovered catalysts (▲).The plateau was, respectively, reached at 50%, 47% and 42% cyclohexene epoxide yield with respect to the added TBHP; the cyclohexene epoxide yields of the 3rd and 4th runs were around 40%. Moreover, the as prepared and the recovered catalysts needed an induction period of about 20 and 50 min, respectively. During this period part of the oxidant is consumed in the oxidative transformation of the catalyst. These results can be, to some

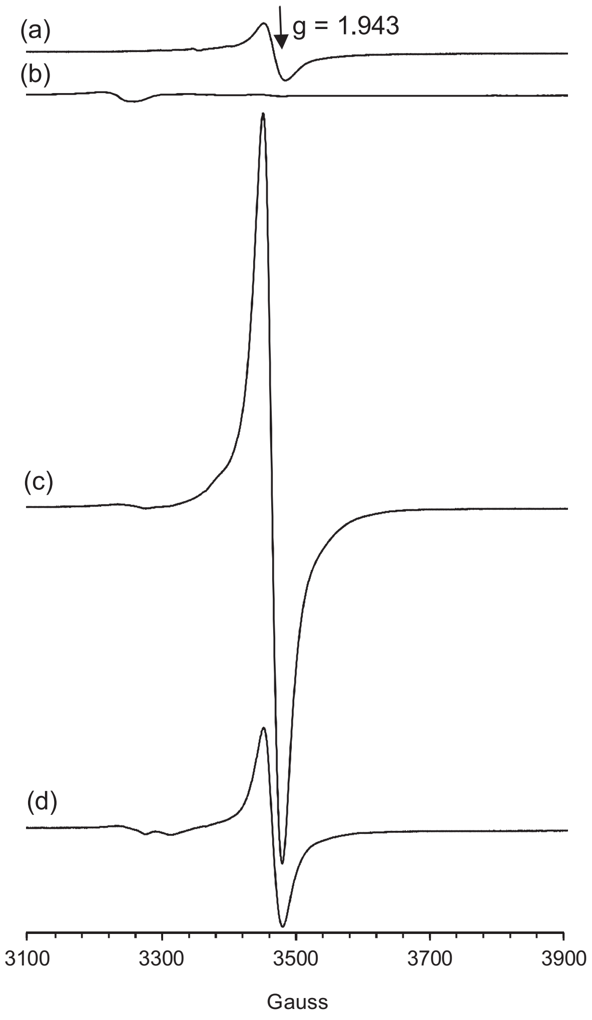
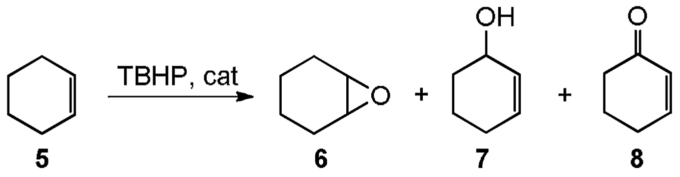


Fig. 2. EPR spectra recorded at 123 K of the MCM-41 silica supported molybdenum catalyst: as prepared catalyst **3** (a), catalyst **3** oxidized with TBHP (b), catalyst **3** after 1st run (c) and after 4th run (d).

extent, rationalized on the basis of spectroscopic studies carried out with the three catalysts. Indeed, in the EPR spectrum the signal at $g = 1.943$ [attributed to traces of paramagnetic Mo(V) species] completely disappears after treatment with TBHP (Fig. 2(b)). However, after the first experiment of cyclohexene epoxidation in the presence of TBHP, EPR spectrum shows again the signal of Mo(V) species at $g = 1.943$ (Fig. 2(c)). Although its intensity is higher than that of the as prepared material, it remains very low ($\sim 8.1 \times 10^{-3}$% of the total loaded Mo) and probably due to undesired redox processes. Oxidation of Mo-MCM-41 silica with TBHP gives rise to the conversion of Mo(V) to the active Mo(VI) species and results in the disappearance of the characteristic intense signal for the paramagnetic Mo(V) centres. It is reasonable to expect that the reoxidation to Mo(VI) species is needed to achieve the maximum efficiency in the successive epoxidation runs.



Scheme 2. Products obtained from cyclohexene oxidation with TBHP.

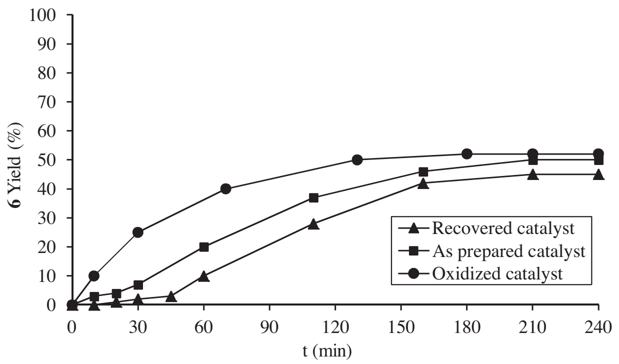


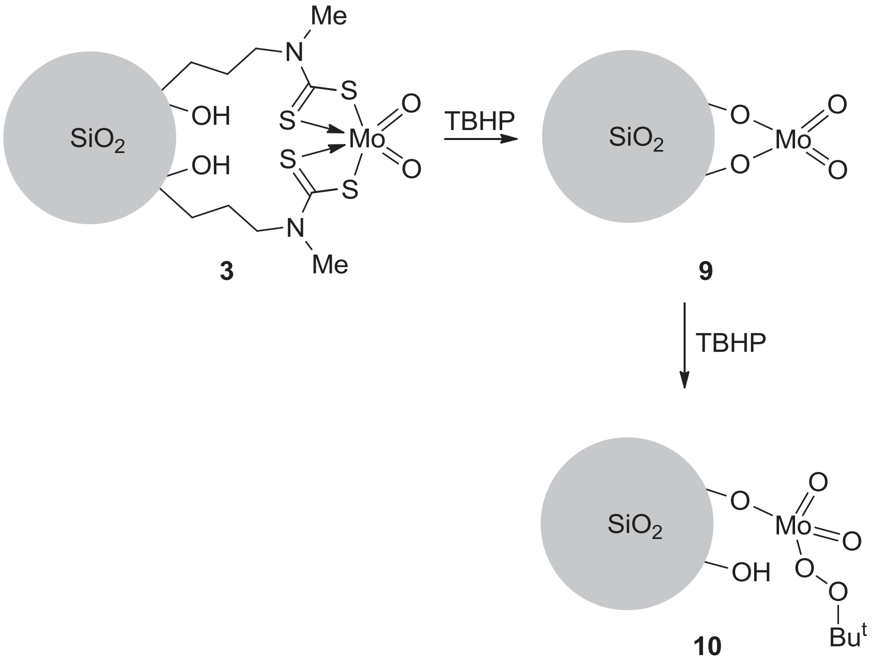
Fig. 3. Reaction profiles for cyclohexene epoxidation with TBHP over Mo-MCM-41 silica catalyst at 80 °C. Reaction conditions: cyclohexene (20 mmol), TBHP (2 mmol), Mo-MCM-41 silica (100 mg corresponding to 0.026 mmol molybdenum). Cyclohexene oxide was the main product accompanied by lower amounts (~2–5%) of 2-cyclohexen-1-ol (**7**) and 2-cyclohexen-1-one (**8**) [yields based on TBHP].

Furthermore, the comparison of the IR spectra of the as prepared and the recovered catalysts shows that the active sites undergo a tremendous transformation in the presence of the oxidant. In fact, whereas the Mo=O stretchings are present before and after oxidation at 945 and 903 cm^{-1}, C–N stretching band a 1540 cm^{-1} disappeared and the band attributed to thiocarbamate group at 1465 cm^{-1} is severely reduced and leaves a new band centred at 619 cm^{-1} ascribable to the sulfate groups (ν_4). This suggests that supported Mo-bis-DTC complex is unstable in the presence of TBHP, the ligand being decomposed by oxidation giving sulfites and sulfates and consequently causing the Mo(VI) species to graft onto the silica surface through the silanol groups, thus initially producing the rest state catalyst **9** that finally is transformed in the real active catalyst **10** by reaction with TBHP (Scheme 3).

During this transformation a portion of the molybdenum ions is leached into solution as evidenced by XPS analysis of the as prepared (Mo/Si atomic ratio = 0.24) and oxidized (Mo/Si atomic ratio = 0.19) catalysts; this lowering of molybdenum content does not affect the catalytic activity in the model epoxidation reaction. Furthermore, the present heterogenisation process based on the "ligand sacrifice" combined with a partial loss of molybdenum, could afford a catalyst with a well dispersed metal centres on the surface of the silica matrix. This transformation promotes the creation of catalysts with unique activities and selectivities by circumventing the oligomerization of the active monomeric species.

Due to the not so high yield (~50%) obtained with the one portion addition of the TBHP, we suspected a possible competitive TBHP decomposition, as already found for homogeneous Mo(VI) epoxidations by Sheldon [35]; in an attempt to overcome this limitation of the present methodology, the model reaction was repeated by slowly adding TBHP during 3 h through a syringe pump to the stirred suspension of the catalyst and cyclohexene heated at 80 °C. The heating was then continued for one additional hour. Under these conditions, the decomposition of TBHP was really inhibited, and the cyclohexene epoxide yield reached 93% (94% selectivity), accompanied by traces of 2-cyclohexen-1-ol and 2-cyclohexen-1-one. This low amount of allylic oxidation products could also be attributed to the positive activity of BHT (0.01% as stabilizer of cyclohexene) that prevents the radical side-reactivity of Mo(VI) catalyst.

The catalyst reusability was then studied under the above optimized conditions: four successive runs were performed and at the end of every run toluene was added and the reaction mixture was filtered at 80 °C, the catalyst was washed with hot toluene and dried under vacuum and finally it was treated with TBHP and reused in the successive run with the following results [yield (selectivity) %]:



Scheme 3. Oxidation of the supported dioxomolybdenum bis-dithiocarbamate complex.

1st: 93 (94), 2nd: 96 (97), 3rd: 97 (98), 4th: 97 (98). It is evident from the results that the catalyst can be used several times in the model reaction with some activity improvement upon the first run despite the observed modest loss of molybdenum in the first run [Mo content in the catalyst (Mo/Si atomic ratio): 1st: 0.19, 2nd: 0.18, 3rd: 0.18, 4th: 0.18].

A possible rationale of this slight catalyst activity improvement upon reuse comes from the comparison of the EPR spectra of the catalyst after the first and the fourth run (Fig. 2(c) and (d)). The amount of the Mo(V) species decreases indeed from $8 \times 10^{-3}\%$ after the first cycle to $2.3 \times 10^{-3}\%$ after the fourth cycle.

The catalyst transformation in the presence of the oxidizing reagent has been also followed by XPS analysis. Table 1 shows the *BE* values (eV) found in the model dithiocarbamate molybdenum complex and in the relevant grafted catalysts; Mo/Si atomic ratio values (AR) are also quoted.

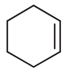
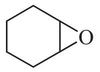
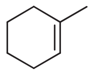
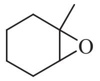
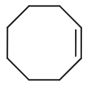
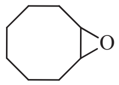
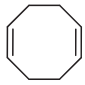
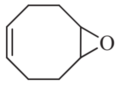
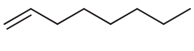
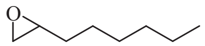
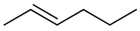
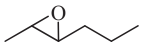
The Mo $3d_{5/2}$ binding energy values exhibited by the reported species are all comparable with that of MoO_3 (232.8 eV) [36]. No other components are detectable in the Mo $3d_{5/2}$ peaks, indicating that the Mo(VI) species are largely predominant. On the other hand, S 2p *BEs* moves from lower value in material **3**, typical of dithiocarbamate species [37], to higher value in the final catalyst **9** and in the reused ones, typical of S(VI) species, as SO_3 and sulphates [32]. It is interesting to note that the Mo/Si atomic ratio undergoes a decrease only in the first oxidation run with TBHP.

Table 1
Binding energy (*BE*) values (eV) and atomic ratios (*AR*) obtained by XPS measurements.

	Catalyst **3**	Catalyst **10**	Catalyst **3** after four catalytic runs
BE (eV)			
Si 2p	103.0	103.2	103.2
S 2p	163.7	169.1	169.3
Mo $3d_{5/2}$	232.9	232.5	232.5
Δ(Mo-S)	69.2	63.4	63.2
AR			
Mo/Si	0.24	0.19	0.18

In order to prove the heterogeneous nature of the catalyst the "hot filtration" test [38] was performed, in which the catalyst was separated from the reaction suspension after 2 h, at approximately 45% cyclohexene epoxide yield through filtration at 80 °C. The reaction progress in the filtrate and in the suspension was further monitored: the filtrate showed a modest increase of cyclohexene conversion after two additional hours (from 45% to 52%), confirming a small active molybdenum species leaching. As expected, addition of cyclohexene and TBHP to the solid catalyst and heating at 80 °C for four hours resulted in 92% cyclohexene epoxide **6** production. The test was repeated with the reused catalyst: in this case the clear filtrate was completely inert even at prolonged reaction time. These experiments allow the conclusion that the present

Table 2
Epoxidation of alkenes with TBHP in the presence of Mo-MCM-41 silica catalyst[a].

Entry	Reagent	Product	Yield [selectivity] (%)
1			93 [94]
2			61 [90]
3			96 [97]
4			51 [70][b]
5			65 [95]
6			80 [97]

[a] Reaction conditions: alkene (20 mmol), TBHP (2 mmol), Mo-MCM-41 silica (0.1 g corresponding to 0.026 mmol molybdenum), 80 °C, 4 h.

[b] The selectivity is lower due to the formation of the bis-epoxide (18% yield).

catalytic system underwent some molybdenum leaching only in the first run, probably due to the loss of molybdenum species not strongly linked to the support surface or partially liberated during the initial oxidative degradation of the ligand. This was also confirmed by XPS analysis of the as prepared, oxidized and recovered catalysts that shows a Mo/Si atomic ratio of 0.24, 0.19 and 0.18, respectively.

Finally the Mo-MCM-41 silica catalyst was used with success for the epoxidation of some alkenes as illustrated in Table 2.

The catalyst was active and selective for small and large molecules: the large pores of the mesoporous support allow the penetration of these molecules. Modest efficiency was, however, observed with 1,5-cyclooctadiene due to the competitive production of different by-products including the bis-epoxide.

4. Conclusion

A good yield of epoxidation of alkenes with TBHP can be achieved by using a molybdenum bis-dithiocarbamate complex supported on MCM-41 silica, provided the solid is suitably treated with TBHP. In the presence of TBHP the ligand of the supported molybdenum complex undergoes oxidative decomposition giving sulfites and sulfates and consequently permitting to graft well dispersed Mo(VI) species onto the silica surface through the silanol groups. This catalyst is more active than the precursor and can be reused several times in the model epoxidation of cyclohexene affording the epoxide with 93–98% yield. A modest leaching of molybdenum is observed only in the first run. The synthetic process can be efficiently applied to both cyclic and linear alkenes affording epoxides with good to excellent yields and selectivities.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.01.028.

References

[1] M. Dusi, T. Mallat, A. Baiker, Catal. Rev. 42 (2000) 213–278.
[2] D.E. De Vos, B.F. Sels, P.A. Jacobs, Adv. Synth. Catal. 345 (2003) 457–473.
[3] A. Nagaki, N. Takabayashi, Y. Tomida, J. Yoshida, Org. Lett. 10 (2008) 3937–3940.
[4] A. Nagaki, H. Kim, J. Yoshida, Angew. Chem. Int. Ed. 47 (2008) 7833–7836.
[5] C. Pereira, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, J. Mol. Catal. 283 (2008) 5–14.
[6] S. Shylesh, J. Schweizer, S. Demeshko, V. Schunemann, S. Ernst, W.R. Thiel, Adv. Synth. Catal. 351 (2009) 1789–1795.
[7] T.J. Terry, G. Dubois, A. Murphy, T.D.P. Stack, Angew. Chem. Int. Ed. 46 (2007) 945–947.
[8] N.F. Chen, W. Ueda, K. Oshihara, Chem. Commun. (1999) 517–518.
[9] A.M. Khenkin, R. Neumann, J. Am. Chem. Soc. 126 (2004) 6356–6362.
[10] H. Aritani, O. Fukuda, T. Yamamoto, T. Tanaka, S. Imamura, Chem. Lett. (2000) 66.
[11] H. Weissman, K.N. Plunkett, J.S. Moore, Angew. Chem. Int. Ed. 45 (2006) 585–588.
[12] G. Ming-Lin, L. Hui-Zhen, Green. Chem. 9 (2007) 421–423.
[13] J. Rack Sohn, J.H. Lunsford, J. Mol. Catal. 32 (1985) 325–332.
[14] S. Leinonen, D.C. Sherrington, A. Sneddon, D. McLoughlin, J. Corker, C. Carnevali, F. Morazzoni, J. Reedijk, S.B.D. Spratt, J. Catal. 183 (1999) 251–266.
[15] F.M.P.R. van Laar, D.E. De Vos, F. Pierard, A. Kirsh-De Mesmaeker, L. Fiermans, P.A. Jacobs, J. Catal. 197 (2001) 139–150.
[16] M. Jia, A. Seifert, W.R. Thiel, J. Catal. 221 (2004) 319–324.
[17] P. Ferreira, I.S. Gonçalves, F.E. Kühn, A.D. Lopes, M.A. Martins, M. Pillinger, A. Pina, J. Rocha, C.C. Romão, A.M. Santos, T.M. Santos, A.A. Valente, Eur. J. Inorg. Chem. (2000) 2263–2270.
[18] C.D. Nunes, A.A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romão, J. Rocha, I.S. Gonçalves, J. Mater. Chem. 12 (2002) 1735–1742.
[19] C.D. Nunes, M. Pillinger, A.A. Valente, A.D. Lopes, I.S. Gonçalves, Inorg. Chem. Commun. 6 (2003) 1228–1233.
[20] M. Jia, A. Seifert, W.R. Thiel, Chem. Mater. 15 (2003) 2174–2180.
[21] P.C. Bakala, E. Briot, L. Salles, J.-M. Brégeault, Appl. Catal., A 300 (2006) 91–99.
[22] M. Jia, W.R. Thiel, Chem. Commun. (2002) 2392–2393.
[23] I.J. Shannon, T. Maschmeyer, R.D. Oldroyd, G. Sankar, J. Meurig Thomas, H. Pernot, J.-P. Balikdjian, M. Che, J. Chem. Soc., Faraday Trans. 94 (1998) 1495.
[24] A. Ishihara, H. Mochizuki, J. Lee, E.W. Qian, T. Kabe, Y. Tatsumi, K. Umehara, J. Jpn. Pet. Inst. 48 (2005) 137–144.
[25] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.W. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834–10843.
[26] A. Maldotti, A. Molinari, G. Varani, M. Lenarda, L. Storaro, F. Bigi, R. Maggi, A. Mazzacani, G. Sartori, J. Catal. 209 (2002) 210–216.
[27] A. Cauvel, G. Renard, D. Brunel, J. Org. Chem. 62 (1997) 749–751.
[28] C.G. Young, J. Chem. Educ. 72 (1995) 751–753.
[29] F.W. Moore, M.L. Larson, Inorg. Chem. 6 (1967) 998–1003.
[30] S. Bhaduri, H. Khwaja, J. Chem. Soc., Dalton Trans. (1983) 415–418.
[31] M. Che, J.C. McAteer, A.J. Tench, J. Chem. Soc., Faraday Trans. 1 F 74 (1978) 2378–2384.
[32] F. Morazzoni, C. Canevali, F. D'Aprile, C.L. Bianchi, E. Tempesti, L. Giuffrè, G. Airoldi, J. Chem. Soc., Faraday Trans. 91 (1995) 3969–3974.
[33] K. Kruczala, S. Schlick, J. Phys. Chem. B 102 (1998) 6161–6168.
[34] A. Brückner, B. Kubias, B. Lücke, Catal. Today 32 (1996) 215–222.
[35] R.A. Sheldon, Recl. Trav. Chim. Pays-Bas 92 (1973) 253–266.
[36] D. Briggs, M.P. Seah, Practical Surface Analysis, 1, second ed., John Wiley & Sons, Chichester, 1990.
[37] A.A. Achilleos, L.R. Gahan, T.W. Hambley, P.C. Healy, D.M. Weedon, Inorg. Chim. Acta 157 (1989) 209–214.
[38] H.E.B. Lempers, R.A. Sheldon, J. Catal. 175 (1988) 62–69.