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

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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.

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## 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

(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