Incorporation of a (Cyclopentadienyl)molybdenum Oxo Complex in MCM-41 and Its Use as a Catalyst for Olefin Epoxidation

Marta Abrantes,[a] Sandra Gago,[b] Anabela A. Valente,[b] Martyn Pillinger,[b] Isabel S. Gonçalves,*[b] Teresa M. Santos,[b] João Rocha,[b] and Carlos C. Romão*[a]

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The tricarbonyl complex [(η^5-C_5H_4-COOMe)$Mo(CO)_3Cl$]-was prepared from the reaction of sodium (methoxycarbonyl)-cyclopentadienide, (C_5H_4-CO_2Me)Na, with (Bu_4N)[Mo-$(CO)_5I$]. Heating the ester with 3-(triethoxysilyl)propylamine gave the amide derivative {[η^5-C_5H_4-CONH-$C_3H_6Si(OEt)_3$]-$Mo(CO)_3Cl$}. The functionalised tricarbonyl complex was immobilised in the ordered mesoporous silica MCM-41 with a loading of 13 wt.-% Mo (1.4 mmol·g^{-1}) by carrying out a grafting reaction in dichloromethane. Powder X-ray diffraction and nitrogen adsorption–desorption analysis indicated that the structural integrity of the support was preserved during the grafting and that the channels remained accessible, despite significant reductions in surface area, pore volume and pore size. The success of the coupling reaction was confirmed by ^{29}Si and ^{13}C (CP) MAS NMR spectroscopy. A supported dioxo complex of the type [(η^5-C_5H_4R)MoO_2Cl] was subsequently prepared by oxidative decarbonylation of the tethered tricarbonyl complex using *tert*-butyl hydroperoxide (TBHP). The oxidised material is an active catalyst for the liquid phase epoxidation of cyclooctene with TBHP as the oxygen source. Similar catalytic results were obtained using the tethered tricarbonyl complex directly as a pre-catalyst since fast oxidative decarbonylation occurs under the reaction conditions used. For both systems, the desired epoxide was the only product and the initial activities were about 13 mol·mol^{-1}_{Mo}·h^{-1}. The solid catalysts were recycled several times. Some activity was lost between the first and second runs but thereafter tended to stabilise.

Introduction

Molybdenum(VI) complexes are versatile catalysts for the oxidation of organic compounds.[1] The most significant reaction in industry is the epoxidation of propylene to propylene oxide by alkyl hydroperoxides, catalysed with high activity and selectivity by soluble Mo^{VI} compounds.[2] In recent years, complexes of the type [$MoO(O_2)_2(L_1)(L_2)$] and [$MoO_2X_2(L_1)(L_2)$] (X = Cl, Br, CH_3) with different combinations of base ligands L_1 and L_2 have been extensively investigated as catalysts for epoxidation reactions, usually employing *tert*-butyl hydroperoxide (TBHP) as the monooxygen source.[3,4] In contrast, cyclopentadienyl oxo complexes of the type [(η^5-C_5R_5)MoO_2Cl], which are isoelectronic with the [$MoO_2X_2(L_1)(L_2)$] complexes, have been less well studied, even though it was reported in 1991 that the pentamethylcyclopentadienyl complex [Cp*MoO_2Cl] is able to catalyse the olefin epoxidation reaction with TBHP.[5] The lack of a convenient synthesis of [(η^5-C_5R_5)MoO_2X] complexes is one reason why their catalytic potential has not been studied in more detail. However, some of us recently reported a simple entry to (η^5-C_5R_5)chlorodioxomolybdenum(VI) complexes (R = H, CH_3, CH_2Ph) based on the oxidative decarbonylation of the readily available [(η^5-C_5R_5)$Mo(CO)_3Cl$] precursors with TBHP.[6] It was found that the dioxomolybdenum(VI) complexes catalyse the epoxidation of cyclooctene, styrene and 1-octene with TBHP as the oxidising agent. Turnover frequencies (TOF) of up to 21000 mol·mol^{-1}_{Mo}·h^{-1} were found and these even surpass that of the well-known CH_3ReO_3/H_2O_2 system. Preliminary results also indicated that the parent tricarbonyl complexes can be applied directly as catalyst precursors in the olefin epoxidation, without isolation of the dioxo complexes prior to use.

Despite the good results obtained for oxomolybdenum(VI) complexes in homogeneous catalysis, increasing attention is being focussed on studying and developing heterogeneous catalysts since these can be easily separated from a reaction mixture and recycled and this is of significant industrial interest.[7] One approach is to link metal complexes to inorganic oxides by way of Lewis base ligands functionalised with alkylalkoxysilanes. For example, Thiel and co-workers prepared covalently anchored complexes of the type [$MoO(O_2)_2$(L−L)] using the mesoporous silica

[a] Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa,
Quinta do Marquês, EAN, Apt. 127, 2781-901 Oeiras, Portugal
Fax: (internat.) + 351-21-4411277,
E-mail: ccr@itqb.unl.pt
[b] Department of Chemistry, CICECO, University of Aveiro, 3810−193 Aveiro, Portugal
Fax: (internat.) + 351-234-370084,
E-mail: igoncalves@dq.ua.pt

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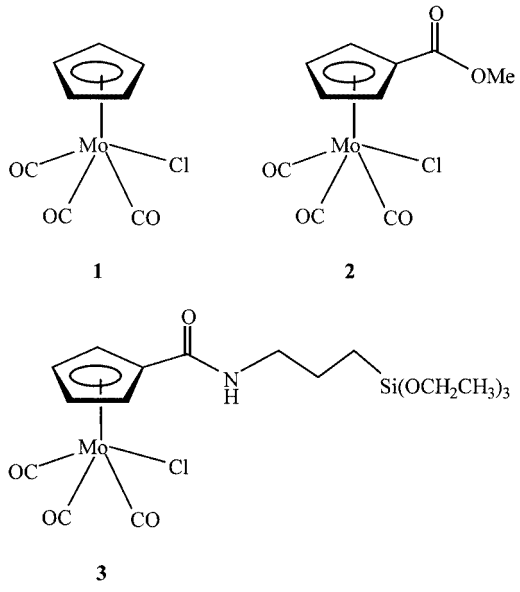
MCM-41 derivatised with a bidentate pyrazolylpyridine ligand.[8] The hybrid system was highly active and truly heterogeneous for the liquid-phase epoxidation of cyclooctene with TBHP as the oxygen source. Molybdenum(VI) complexes of the type $[MoO_2Cl_2(L_1)(L_2)]$ have also been immobilised in MCM-41 derivatised with monodentate nitrile and bidentate bipyridyl ligands.[9] Unfortunately, these catalysts proved to be unstable towards molybdenum leaching which accounted for nearly complete loss of activity in a second reaction cycle. Better results were obtained using 1,4-diazabutadiene ligands covalently linked to the support, although significant catalytic activity was still lost between the first and second runs.[10] In order to obtain more stable catalysts, it would be preferable if the oxomolybdenum fragment was covalently linked to the support, rather than relying on an interaction between the metal centre and a Lewis base ligand. In the present work we set out to prepare an immobilised $[(\eta^5\text{-}C_5R_5)MoO_2Cl]$ complex by oxidative decarbonylation of a monosubstituted $[(\eta^5\text{-}C_5H_4R)Mo(CO)_3Cl]$ precursor covalently anchored to MCM-41. The resultant material has been examined as a catalyst for the epoxidation of olefins using TBHP.

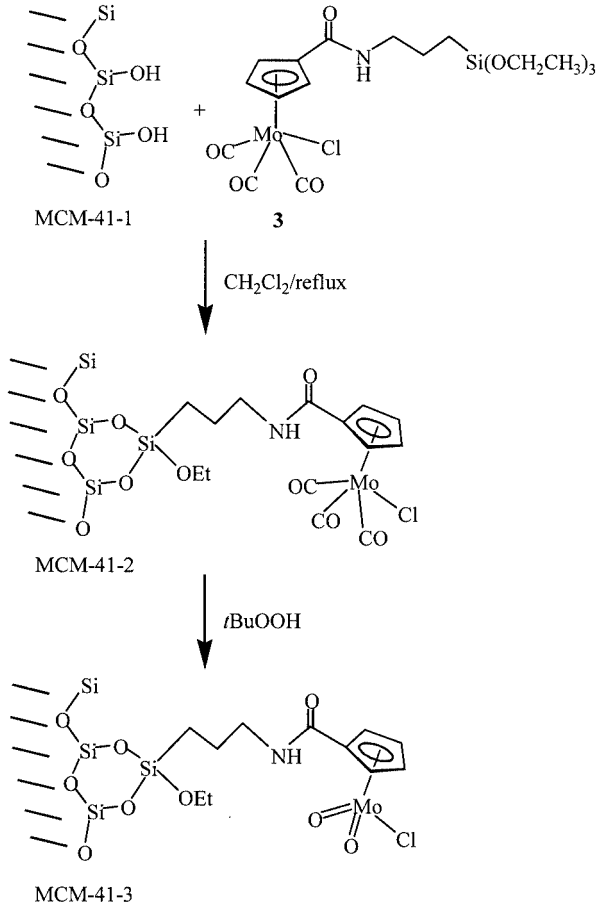
Results and Discussion

Synthesis and Characterisation

The tricarbonyl complex $[(\eta^5\text{-}C_5H_4\text{-}COOMe)Mo(CO)_3Cl]$ (**2**) was prepared from the reaction of sodium (methoxycarbonyl)cylopentadienide, $(C_5H_4\text{-}COOMe)Na$, with $(Bu_4N)[Mo(CO)_5I]$ in THF at reflux. Compound **2** is air sensitive and very insoluble in noncoordinating solvents. As expected, the IR spectrum (KBr) of **2** showed three strong terminal carbonyl absorptions (at 2056, 1990 and 1973 cm^{-1}) and a strong organic carbonyl absorption at 1725 cm^{-1}. For comparison, $[CpMo(CO)_3Cl]$ (**1**) in CCl_4 exhibits three ν_{CO} bands at 2056, 1986 and 1962 cm^{-1}.[11] The ^1H NMR spectrum of **2** contains a pair of pseudo triplets (A_2B_2 pattern) at $\delta = 5.72$ and 6.03 ppm for the cyclopentadienyl protons $H^{3,4}$ and $H^{2,5}$, respectively. A singlet was also observed at $\delta = 3.83$ ppm for the methoxycarbonyl protons ($-OCH_3$). Heating the ester **2** with 3-(triethoxysilyl)propylamine at 120 °C for 3 hours gave the amide derivative $\{[\eta^5\text{-}C_5H_4\text{-}CONH\text{-}C_3H_6Si(OEt)_3]Mo(CO)_3Cl\}$ (**3**) as an oil which was dried under vacuum and used without further purification. A similar method was used by Jia et al. to functionalise a pyrazolylpyridine ligand with (triethoxysilyl)propyl groups.[8] The presence of the amide functional group in **3** was indicated by the IR spectrum which showed the absence of the peak at 1725 cm^{-1} from the starting material and new bands at 3298 (ν_{NH}), 1617 and 1577 cm^{-1} (NHCO). The last two frequencies are similar to those reported for $[(\eta^5\text{-}C_5H_4\text{-}CONH\text{-}R)W(CO)_3CH_3]$ (1641 and 1554 cm^{-1}) and $[(\eta^5\text{-}C_5H_4\text{-}CONH\text{-}R)W(CO)_3I]$ (1642 and 1556 cm^{-1}).[12] Further evidence for the success of the reaction was provided by the ^{13}C spectrum of **3** which contained a weak resonance at $\delta = 163.2$ ppm which was assigned to the carbon atoms of the CONH groups.



Treatment of calcined and dehydrated MCM-41 (MCM-41-1) with a solution of the triethoxysilane compound **3** in dichloromethane at reflux gave the modified material MCM-41-2 containing 13 wt.-% Mo ($1.4\ mmol \cdot g^{-1}$) (Scheme 1). If the surface area is taken as $500\ m^2 \cdot g^{-1}$ (see below), the metal content corresponds to a surface coverage



Scheme 1

of about 1.7 Mo atom per nm^2. This value is similar to experimentally determined values for the concentration of free silanol groups on the surface of pristine MCM-41.[13] Direct evidence for the incorporation of the covalently linked organic system in MCM-41-2 was obtained by recording ^{29}Si MAS NMR spectra (Figure 1). The ^{29}Si MAS NMR spectrum of the parent support MCM-41-1 exhibits two broad resonances at $\delta = -109.9$ and -102.4 ppm, assigned to the species Q^4 and Q^3 of the silica framework, respectively, [$Q^n = Si(OSi)_n(OH)_{4-n}$]. The ^{29}Si CP MAS NMR spectrum shows a marked increase in the relative intensity of the Q^3 peak, confirming that these silicon centres are attached to hydroxy groups. A weak resonance is also present at about -91 ppm corresponding to the Q^2 species. For the grafted material MCM-41-2, both the ^{29}Si MAS and CP MAS NMR spectra clearly show the diminished relative intensity of the Q^2 and Q^3 peaks, indicating the esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atom in the organic ligand. Three additional signals can be observed in the CP MAS spectrum at $\delta = -46.7$, -53.1 and -60.3 ppm, and can be assigned to the T^1, T^2 and T^3 organosilica species, respectively, [$T^m = RSi(OSi)_m(OEt)_{3-m}$]. The presence of residual OEt groups in MCM-41-2 was confirmed by the ^{13}C CP MAS NMR spectrum which contains peaks at $\delta = 23.0$ and 17.6 ppm. Additional peaks were readily assigned to the carbon atoms of the propyl, cyclopentadienyl and CO groups (see Exp. Sect.).

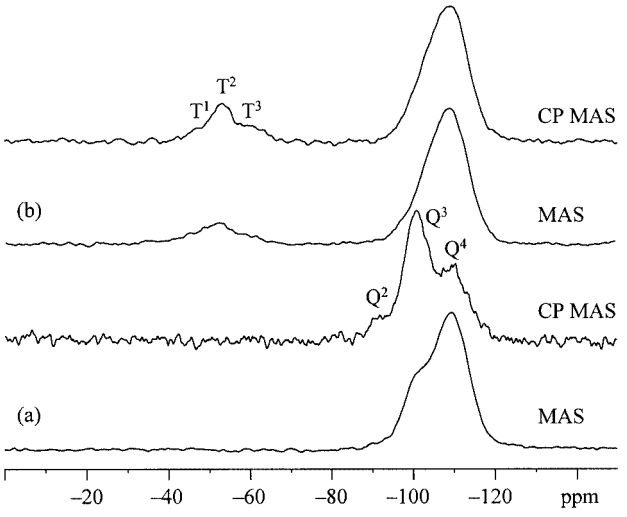


Figure 1. ^{29}Si MAS and CP MAS NMR spectra of (a) MCM-41-1 and (b) MCM-41-Si(OEt)$_n$C$_3$H$_6$NHCOCpMo(CO)$_3$Cl (MCM-41-2)

The powder X-ray diffraction (XRD) pattern of the unmodified MCM-41 sample (MCM-41-1) is typical of a well-ordered mesoporous phase (Figure 2). Several distinct Bragg peaks are present in the range $2\theta = 2-8°$ which can be indexed to different *hkl* reflections for a hexagonal unit cell (using the strongest reflection, d_{100}, $a = 2d_{100}/\sqrt{3} = 41.0$ Å). Upon grafting with **3**, several peaks were still observed indicating retention of the long-range hexagonal symmetry. The significant attenuation of the XRD peak intensities was not interpreted as a loss of crystallinity. Instead, it is likely that there is a reduction in the X-ray scattering contrast between the silica framework and the metal-organic moieties which are located inside the channels of the host.[8b,9b,10a,14] Figure 3 shows the N_2 isotherms of the MCM materials. Unmodified MCM-41 exhibits a reversible type IV adsorption–desorption isotherm, characteristic of a mesoporous solid (pore width between 2 and 50 nm, according to the IUPAC).[15] The values of S_{BET} and V_p are listed in Table 1. A sharp step in the capillary condensation in the primary mesopores can be observed at a relative

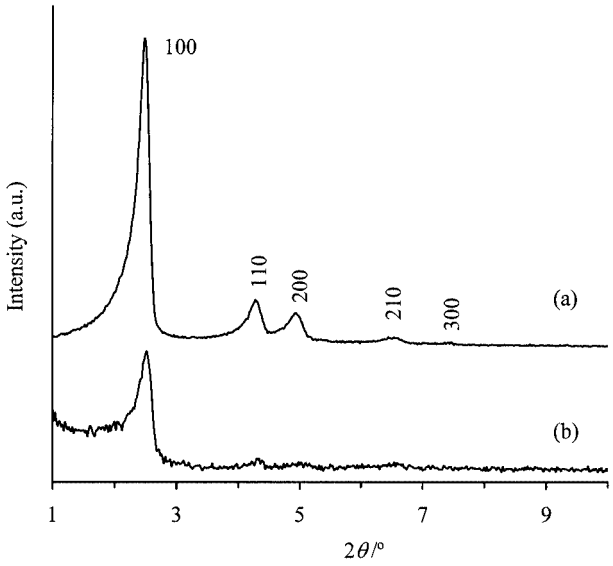


Figure 2. Powder XRD patterns of (a) MCM-41-1 and (b) MCM-41-Si(OEt)$_n$C$_3$H$_6$NHCOCpMo(CO)$_3$Cl (MCM-41-2). The relative intensities for MCM-41-2 have been multiplied by five with respect to those for MCM-41-1

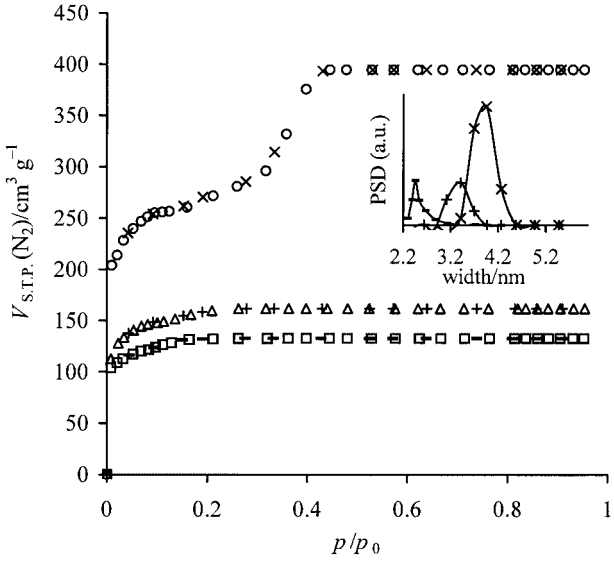


Figure 3. N_2 adsorption (circles: MCM-41-1; squares: MCM-41-2; triangles: MCM-41-3) and desorption (×: MCM-41-1; –: MCM-41-2; +: MCM-41-3) isotherms at 77 K and pore size distribution profiles (inset) of MCM-41-1 (×), MCM-41-2 (–) and MCM-41-3 (+)

pressure of ca. 0.3, indicating a narrow pore size distribution. The adsorption isotherm is flat in the high-pressure region ($p/p_0 > 0.6$) which shows that the material has a low external surface area and insignificant secondary mesoporosity. After modification in the preparation of MCM-41-2, S_{BET} and V_p decreased significantly, suggesting that grafting of the bulky complex on the internal silica surface was accomplished (Figure 3, Table 1). This conclusion is also supported by the decrease in the p/p_0 coordinates of the inflection points of the isotherms upon the post-synthesis treatment.[16] The capillary condensation step becomes less pronounced, suggesting that the pore size distribution of the MCM-41 support was partly affected by the modification. The maximum of the PSD curve for MCM-41 determined by the BJH method, d_{BJH}, decreased by 36% after the tethering procedure.

Table 1. Texture parameters of MCM-41 samples from N_2 isotherms at 77 K

Sample	S_{BET} [$m^2 \cdot g^{-1}$]	ΔS_{BET}[a] (%)	V_P [$cm^3 \cdot g^{-1}$]	ΔV_P[b] (%)	d_{BJH} [nm]
MCM-41-1	1010	–	0.61	–	3.9
MCM-41-2	493	−51	0.21	−66	2.5
MCM-41-3	581	−42	0.25	−59	3.4

[a] Variation of surface area in relation to parent MCM-41-1. [b] Variation of total pore volume in relation to parent MCM-41-1.

Oxidative decarbonylation of the supported metal complex in MCM-41-2 was carried out by treatment of the material with an excess of TBHP (Scheme 1). During the reaction, the material changed colour from brown to pale yellowish-brown. The product, designated as MCM-41-3, was isolated by filtration and the excess TBHP removed by washing with dichloromethane. The presence of an MoO_2 unit in MCM-41-3 was indicated by the IR spectrum which showed two bands for the symmetric (943 cm^{-1}) and asymmetric (911 cm^{-1}) Mo=O stretching vibrations. For comparison, the corresponding stretching frequencies for the complexes (η^5-C_5R_5)chlorodioxomolybdenum(VI) (R = H, CH_3, CH_2Ph) are located at ca. 920/890 cm^{-1} (ν_{sym}/ν_{asym}).[6] In the Raman spectrum of MCM-41-3, bands were observed at 358 and 266 cm^{-1} which can be attributed to symmetric Mo−Cp stretching and MoO_2 wagging modes, respectively (cf. 328 and 261 cm^{-1} for [$CpMoO_2Cl$][6]). The reaction of MCM-41-2 with TBHP was accompanied by some metal leaching, as evidenced by a decrease in the molybdenum content from 13 to 9 wt.-% and a slight increase in the values of S_{BET} and V_p (Figure 3, Table 1).

Catalytic Olefin Epoxidation

The modified materials MCM-41-2 and MCM-41-3 were tested as catalysts or catalyst precursors for the liquid phase epoxidation of cyclooctene with TBHP at 55 °C (Figure 4, Table 2). For comparison, the tricarbonyl complexes **1**−**3** were also tested as homogeneous pre-catalysts for the same reaction. Cyclooctene conversion in the absence of a catalyst or in the presence of the parent MCM-41 sample was negligible after 6 h and the catalytic activity exhibited by the modified mesoporous materials and the tricarbonyl complexes can therefore be attributed to active species containing molybdenum. For all systems, cyclooctene oxide was the only observed reaction product. The kinetic profiles for MCM-41-2 and MCM-41-3 were quite similar (Figure 4). Initially, the reaction is fast but it then slows down somewhat and conversion after 24 hours is far from quantitative (< 63%). Similar kinetic profiles have been reported for complexes belonging to the [$MoO_2X_2(L_1)(L_2)$] family, in which case an auto retardation effect can be observed due to the formation of *tert*-butyl alcohol, a competitive inhibitor for the attack of TBHP at the molybdenum centre.[4e] The initial activity of epoxidation using MCM-41-2, expressed as initial rate per unit weight of solid, is higher than that for MCM-41-3 (Table 2, values in brackets). However, when the initial activities are expressed as initial rate per mol of MCM-41-supported Mo species, the values are practically the same for both samples since MCM-41-2 (13 wt.-% Mo) possesses a higher Mo loading than MCM-41-3 (9 wt.-% Mo). This suggests that the in-situ oxidative decarbonylation of MCM-41-2 by TBHP is fast and probably gives rise to the same type of active metal species present in MCM-41-3 under the catalytic conditions.

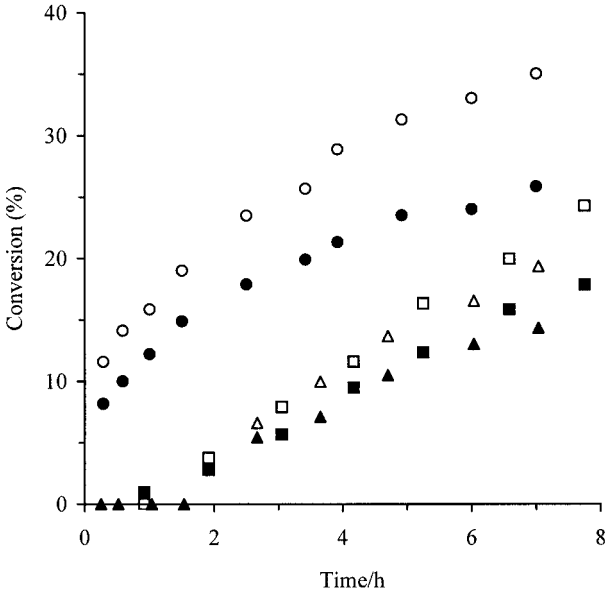


Figure 4. Conversion profiles for the epoxidation of cyclooctene with TBHP at 55 °C using MCM-41-2 (open symbols) or MCM-41-3 (solid symbols): run 1 (circles); run 2 (squares); run 3 (triangles)

The kinetic profile for the homogeneous reaction using the pre-catalyst **3** was similar to that observed using the modified MCM materials (Figure 5). In fact, the initial activities are almost identical (12−13 $mol \cdot mol_{Mo}^{-1} \cdot h^{-1}$). Considerably higher activities were obtained using the tricarbonyl complexes **1** and **2** as precatalysts, particularly in the

Table 2. Catalytic epoxidation of cyclooctene with TBHP at 55 °C using homogeneous (**1**−**3**) and heterogenised (MCM-41-2, MCM-41-3) molybdenum catalysts

Catalyst	Initial activity [mol·mol$_{Mo}^{-1}$·h^{-1}][a]	Conversion[b] (%)
1	140	100
2	40	100
3	13	82
MCM-41-2 (run, 1)	12 (17)[c]	63
MCM-41-2 (run, 2)	−[d]	57
MCM-41-2 (run, 3)	−[d]	51
MCM-41-3 (run, 1)	13 (12)[c]	52
MCM-41-3 (run, 2)	−[d]	46
MCM-41-3 (run, 3)	−[d]	39

[a] Turnover frequency calculated at ca. 18 min. [b] Cyclooctene conversion after 24 h. [c] The values in parentheses are the initial activities expressed per unit weight of catalyst (mmol g_{cat}^{-1}·h^{-1}). [d] An induction period was observed.

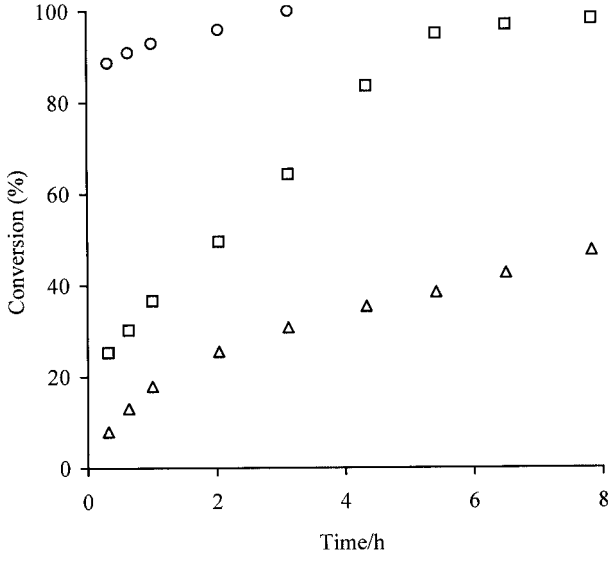


Figure 5. Conversion profiles for the epoxidation of cyclooctene with TBHP at 55 °C using complexes **1** (circles), **2** (squares) and **3** (triangles)

case of the unsubstituted cyclopentadienyl complex (turnover frequency = 140 mol·mol$_{Mo}^{-1}$·h^{-1}). No induction periods were observed using the tricarbonyl complexes **1**−**3** directly, suggesting that the conversion into the corresponding dioxo complexes is quite fast under the applied reaction conditions. Previous studies have shown that the epoxidation of cyclooctene in a homogeneous phase proceeds at practically the same rate in the presence of $CpMo(CO)_3Cl$ or the corresponding $CpMoO_2Cl$ complex and that catalyst/cyclooctene molar ratios as small as 1:10000 give turnover frequencies as high as 21000 mol·mol$_{Mo}^{-1}$·h^{-1} {for [(η^5-C_5Bz_5)MoO_2Cl]}.[6] In the presence of complex **3**, the epoxidation reaction is much slower probably due to the pendant triethoxysilyl groups which may lead to the formation of less reactive dimers/oligomers.

The stabilities of the modified materials MCM-41-2 and MCM-41-3 were studied by recycling the recovered solids twice. Before each reuse, the solid was separated from the reaction solution, thoroughly washed with dichloromethane and dried at room temperature. Some loss of catalytic activity was observed for both samples from the first to the second run but afterwards the activity tended to remain constant (Table 2, Figure 4). After the first run the catalytic results obtained with the two materials were quite similar, suggesting that the materials become much alike after the first run. As mentioned above, the synthesis of MCM-41-3 by treatment of MCM-41-2 with excess TBHP was accompanied by some metal leaching. Hence, one would expect the same to occur when using MCM-41-2 directly under the oxidising catalytic conditions. Indeed, the molybdenum loading after the first run was ca. 83% of the original value which may partly explain the observed catalyst deactivation. In the case of MCM-41-3, no measurable metal leaching occurred during the first run but a significant decrease in activity was nevertheless observed. Both catalyst systems exhibit induction periods of nearly 90 min for the second and third runs, leading to TOFs (calculated for ca. 2.5 h of the third reaction cycle) of 2.5 and 2.0 mol·mol$_{Mo}^{-1}$·h^{-1} for MCM-41-2 and MCM-41-3, respectively. According to studies by Trost and Bergman,[5] the (pentamethyl)cyclopentadienyl analogue [Cp*MoO_2Cl] can react with TBHP to give the peroxo complex [Cp*$MoO(O_2)Cl$] which is inactive as a catalyst for olefin epoxidation.[5] We suspect, therefore, that another reason for the loss of activity between the first and second runs for the systems initially containing MCM-41-2 and MCM-41-3 is because of the formation of supported peroxo complexes. Leaching tests were performed for MCM-41-3 by removing the catalyst from the reaction mixture by hot filtration after 20 minutes. The filtrate was then allowed to react for a further 340 minutes. The conversion of cyclooctene increased by 7%, whereas with the catalyst it increased by 21%. These results suggest that epoxidation in the presence of MCM-41-3 (for the first run) is, to a certain extent, homogeneously catalysed by leached molybdenum species. However, since a sintered glass filter was used it is possible that small catalyst particles were not completely separated by this porous media and that MCM-41-3 is a truly heterogeneous catalyst.[17]

The modified materials MCM-41-2 and MCM-41-3 were tested for the epoxidation of other olefins, namely cyclododecene, *trans*-2-octene and 1-octene. Olefin conversion after 24 hours decreases in the following order for both materials: cyclooctene > cyclododecene > *trans*-2-octene > 1-octene (Figure 6). In the case of *trans*-2-octene the corresponding epoxide is the only product at less than 10% conversion. When the substrate is 1-octene, an unsubstituted and much less reactive olefin, conversion is negligible (< 1%). In the case of cyclododecene, a more bulky substrate, the reaction proceeds to 34−38% conversion after 24 h and the epoxide is the main product, while the corresponding diol is a secondary reaction product obtained in less than 5% yield.

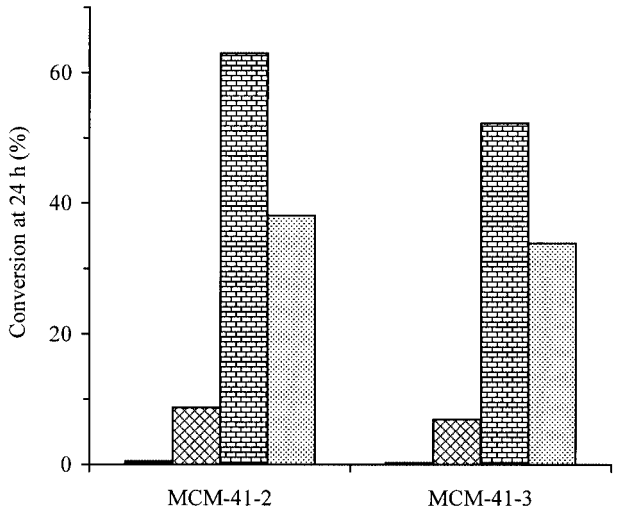


Figure 6. Olefin conversion after 24 h with TBHP at 55 °C using MCM-41-2 or MCM-41-3: 1-octene (solid); *trans*-2-octene (diamonds); cyclooctene (bricks); cyclododecene (dots)

Conclusions

A method has been presented for the immobilisation of a monosubstituted cyclopentadienyltricarbonylchloro molybdenum complex in mesoporous silica. The material can be used as a pre-catalyst for the reaction of *tert*-butyl hydroperoxide and cyclooctene to yield the corresponding epoxide. Upon recycling, some activity is lost between the first and second runs but thereafter it tends to remain constant. According to the leaching test carried out for MCM-41-3, it is possible that epoxidation (in the first run) also occurs in a homogeneous phase. Although the selectivity to the epoxide is very high, the activities are moderate paralleling that observed for the precursor complex (containing the triethoxysilyl group) in a homogeneous phase. We have also noted in this work that the methoxycarbonyl-substituted complex [(η^5-C_5H_4-COOMe)$Mo(CO)_3Cl$] can be used as a pre-catalyst for the olefin epoxidation reaction but the observed activity is much lower than that obtained when the unsubstituted [$CpMo(CO)_3Cl$] is used. These results indicate that a more effectively supported catalyst might be possible by preparing a precursor complex of the type [(η^5-C_5R_5)$Mo(CO)_3X$] where the ligand X terminates in a trialkoxylsilyl group.

Experimental Section

Materials and Methods: All preparations and manipulations were performed using standard Schlenk techniques under oxygen-free and water-free nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone ketyl; CH_2Cl_2 and NCMe over CaH_2), distilled under nitrogen and used immediately (THF) or kept over 4-Å molecular sieves (3-Å for NCMe). Microanalyses for C, H, N were performed at the ITQB (C. Almeida) and Mo was determined by ICP-AES at the Central Laboratory for Analysis, University of Aveiro (E. Soares). Room-temperature powder XRD data were collected with a Philips X'pert diffractometer with a curved graphite monochromator (Cu-K_α radiation) in a Bragg−Brentano para-focusing optics configuration. Samples were step-scanned in 0.02 °2θ steps with a counting time of 2 s per step. The values of the BET specific surface area (S_{BET}, determined in the p/p_0 range 0.03−0.13) and specific total pore volume, V_p, were estimated from N_2 adsorption isotherms measured at 77 K, as described previously.[18] The pore size distributions (PSD) were calculated by the BJH method using the modified Kelvin equation with a correction for the statistical film thickness on the pore walls.[19] The statistical film thickness was calculated using the Harkins-Jura equation in the p/p_0 range 0.1−0.95. IR spectra were measured with a Mattson 7000 FT-IR spectrometer using KBr pellets. Raman spectra were recorded with a Bruker RFS100/S FT instrument (Nd:YAG laser, 1064 nm excitation, InGaAs detector). NMR spectra in solution were recorded with Bruker CXP-300 (^1H) and Bruker AMX-300 (^{13}C) spectrometers. Room temperature ^{29}Si and ^{13}C solid state NMR spectra were recorded at 79.49 and 100.62 MHz, respectively, with a Bruker Avance 400P spectrometer. ^{29}Si MAS NMR spectra were recorded with 40° pulses, spinning rates of 5.0−5.5 kHz and 60 s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 5.5 μs ^1H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were acquired with a 3.5 μs 90° proton pulse and 2 ms contact time with spinning rates of 7−8.5 kHz and 4 s recycle delays. ^{13}C spectra were also recorded in the solid state at 125.76 MHz with a Bruker Avance 500 spectrometer. Chemical shifts are quoted in ppm relative to TMS.

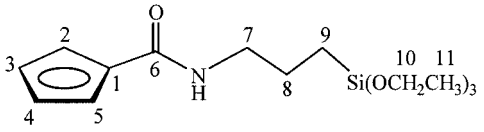
The liquid-phase oxidation of a variety of olefins was carried out at 55 °C under air (atmospheric pressure) in a micro reaction vessel equipped with a magnetic stirrer which was loaded with complex (0.036 mmol) or MCM-catalyst (43.8 mg), olefin (1.8 mmol) and TBHP (2.8 mmol, 5.5 M in decane). Samples were withdrawn periodically and analysed using a gas chromatograph (Varian 3800) equipped with a capillary column (SPB-5, 20 m × 0.25 mm × 0.25 μm) and a flame ionization detector. Undecane was used as an internal standard added after the reaction.

Published procedures were used to prepare the compounds (C_5H_4-COOMe)Na,[20] (Bu_4N)[$Mo(CO)_5I$][21] and [$CpMo(CO)_3Cl$] (**1**).[6] Pure siliceous MCM-41 (MCM-41-1) was synthesised hydrothermally at 100 °C under basic conditions using [($C_{14}H_{29}$)NMe_3]Br as the templating agent and sodium silicate solution as the silica source.[9b] The calcined product (540 °C/6 h) was dehydrated prior to use by heating at 180 °C for 2 h under vacuum.

[(η^5-C_5H_4-COOMe)$Mo(CO)_3Cl$] (2): A solution of (Bu_4N)[$Mo(CO)_5I$] (0.96 g, 1.60 mmol) in THF (20 mL) was mixed with a solution of (C_5H_4-COOMe)Na (0.28 g, 1.9 mmol) in THF (20 mL) and heated to reflux overnight (18 h). The THF was removed from the resultant yellow-brown solution affording an oily residue. Diethyl ether (20 mL), distilled water (20 mL) and acetic acid (0.1 mL) were then added and, after stirring for 20 min, CCl_4 (5 mL) was added and the colour of the emulsion turned red. The mixture was stirred for a further 20 min. The ether phase was then separated and the remaining aqueous phase extracted five times with 20 mL aliquots of diethyl ether. After evaporation of the solvent from the combined ether extracts a red residue was obtained. This was redissolved in acetone (20 mL) and activated charcoal and anhydrous Na_2SO_4 were added. After stirring for 30 min the mixture was filtered. Evaporation of the red filtrate gave an orange solid which was thoroughly washed with water and cold hexane. Yield: 0.22 g, 41%. Selected IR (KBr): $\tilde{\nu}$ = 3114 (m), 2958 (m), 2056 (vs, ν_{CO}), 1990 (vs, ν_{CO}), 1973 (vs, ν_{CO}), 1725 (s, ν_{CO}), 1476 (m), 1434 (m), 1372 (m), 1283 (s), 1194 (m), 1144 (s), 961 (m), 772 (m), 557 (m), 525 (m), 469 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS):

δ = 3.83 (s, 3 H, $-OCH_3$), 5.72 (t, 2 H, $H^{3,4}$), 6.03 (t, 2 H, $H^{2,5}$) ppm. $C_{10}H_7ClMoO_5$ (338.56): calcd. C 35.48, H 2.08; found C 35.53, H 2.22.

{[η^5-C_5H_4-CONH-$C_3H_6Si(OEt)_3$]Mo(CO)$_3$Cl} (3): One equivalent of 3-triethoxysilylpropylamine was added to [(η^5-C_5H_4-COOMe)-Mo(CO)$_3$Cl] (**2**) (2.27 g, 6.7 mmol) and the mixture stirred at 120 °C for 3 h. After this, low boiling volatiles were removed in vacuo at 50 °C. The resultant brown oil was used without further purification. Selected IR (neat): $\tilde{\nu}$ = 3298 (sh, ν_{NH}), 3108 (w), 2975 (m), 2928 (m), 2886 (m), 2044 (vs, ν_{CO}), 1965 (vs, ν_{CO}), 1926 (vs), 1617 (m, CONH), 1577 (m, CONH), 1470 (m), 1443 (m), 1390 (m), 1280 (m), 1237 (w), 1102 (s), 1077 (s), 958 (s), 786 (vs), 596 (m), 540 (m) cm^{-1}. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.8 (C^9), 18.4 (C^{11}), 24.3 (C^8), 46.6 (C^7), 59.4 (C^{10}), 94.9 (C^{1-5}), 95.1, 97.3, 163.2 (C^6), 218 (CO) ppm.



MCM-41-2: A solution of {[η^5-C_5H_4-CONH-$C_3H_6Si(OEt)_3$]Mo-(CO)$_3$Cl} (**3**) (5.0 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of MCM-41-1 (2 g) in toluene (15 mL) and the mixture stirred under reflux for 44 h. The suspension was filtered and the brown powder washed several times with CH_2Cl_2, before drying under vacuum at 40 °C. Selected IR (KBr): $\tilde{\nu}$ = 3419 (br), 3246 (sh, ν_{NH}), 2982 (m), 2939 (sh), 1979 (w, ν_{CO}), 1624 (m, CONH), 1484 (m), 1444 (m), 1393 (m), 1237 (s), 1082 (vs), 954 (br), 797 (s), 564 (br), 454 (vs) cm^{-1}. ^{13}C CP MAS NMR: δ = 8.4 (C^9), 17.6 (C^{11}), 23.0 (C^8), 42.6 (C^7), 58.3 (C^{10}), 86.3 (br., C^{1-5}), 166.7 (C^6) ppm. Elemental analysis found C 16.63, H 3.23, N 1.97, Mo 13.0.

MCM-41-3: MCM-41-2 (0.3 g) was suspended in CH_2Cl_2 (10 mL). Under continuous magnetic stirring, *tert*-butyl hydroperoxide solution (4.1 mmol, 5.0−6.0 M in *n*-decane, 10 equiv.) was added dropwise and the mixture stirred at room temperature for 4 h. The resultant light brown powder was filtered, washed several times with CH_2Cl_2 and dried under vacuum at room temperature. Selected IR (KBr): $\tilde{\nu}$ = 3431 (br), 3262 (sh, ν_{NH}), 2982 (w), 2938 (sh), 1629 (m, CONH), 1508 (w), 1469 (w), 1445 (w), 1384 (w), 1364 (w), 1237 (vs), 1080 (vs), 943 (m, ν_{sym} Mo=O), 911 (m, ν_{asym} Mo=O), 799 (m), 739 (sh), 568 (w), 454 (vs) cm^{-1}. Selected Raman: 2962, 2932, 2895, 1590, 1455, 1321, 1045, 967, 942, 915, 358, 266 cm^{-1}. Elemental analysis found C 11.9, H 2.80, N 1.96, Mo 9.0.

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