

In situ grafting of cyclopentadienyl-molybdenum complexes on mesoporous materials: The reaction of $[\eta^5\text{-CpMo}(\text{CO})_3]^- \text{Na}^+$ with surface fixed iodo-benzyl siloxane

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Abstract

$\text{Na}^+[\eta^5\text{-CpMo}(\text{CO})_3]^-$ is grafted on aromatic silane (iodo-benzyl trimethoxy silane) modified surfaces of MCM-41 and MCM-48 molecular sieves. The XRD, N_2 adsorption–desorption, and TEM analysis provide strong evidence that the mesoporous structure of the supporting materials retains its long range ordering after the grafting process, despite significant reductions of the surface area, pore-volume and pore size. The appearance of strong IR bands around 2016 and 1956 cm^{-1} as well as 3010 cm^{-1} on the grafted samples showing the presence of carbonyl as well as aromatic functional groups, evidences the successful grafting of the $\eta^5\text{-CpMo}(\text{CO})_3$ complexes. Elemental analysis reveals 6.4 and 8.3 wt% Mo on the SM-41ASG and SM-48ASG samples, respectively. The appearance of new ^{29}Si CP MAS-NMR peaks around -61.4 , and -69.6 ppm (T_2 and T_3) indicates the esterification of silanol groups by the methoxy group of the silane ligand. The samples prepared by this in situ method show high loading of Mo and also good catalytic activity and selectivity for olefin-epoxidation.

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1. Introduction

A variety of molybdenum (VI) complexes are known to be versatile catalysts for the oxidation of organic substrates [1–9]. Molybdenum based catalysts were applied for the industrial epoxidation of propylene, utilizing *t*-butyl hydroperoxide (TBHP) as oxidizing agent since the late 1960s [10,11]. A lot of work was dedicated to the understanding of the involved catalytic reactions in subsequent years in order to improve both yields and selectivities [12–15]. During the last decade several well defined homogeneous epoxidation catalysts were described [16–22]. Recently, cyclopentadienyl molybdenum

complexes of formula $\text{Cp}'\text{MoO}_2\text{Cl}$ ($\text{Cp} = \text{C}_5\text{R}_5$; $\text{R} = \text{H}$, CH_3) were found to be efficient homogeneous catalysts for epoxidation of alkenes with TBHP as the oxidant [23–26]. Furthermore, it became clear that the direct application of their carbonyl precursor compounds of formula $\text{CpMo}(\text{CO})_3\text{Cl}$ leads to equally efficient catalysts, since the carbonyl complexes are in situ oxidized – also by TBHP – to their oxo and/peroxo congeners [23–26]. The carbonyl precursor compounds can be stored for long times without any problems while the oxides are somewhat more sensitive [23–26]. Additionally, $\text{Cp}'\text{Mo}(\text{CO})_3\text{R}$ complexes ($\text{R} = \text{alkyl}$) and their oxidized congeners are also known and already successfully utilized as homogeneous catalysts or catalyst precursors [27]. However, industrial interest is still to a significant degree focused on heterogeneous catalysts due to their advantages, e.g., easier product/catalyst separation

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[28–30]. Among the various supporting materials studied, the mesoporous silicates known as MCM-41 and MCM-48 [31] with regular pore size, large surface areas, large number of surface silanol groups, and high chemical and thermal stability, are potential and promising candidates as both catalysts and catalyst supports [32,33].

Different approaches were used in order to obtain heterogeneous molybdenum catalysts for olefin epoxidation. A general problem is that Mo(VI) can not easily be incorporated into the tetrahedral positions of the silicate framework of molecular sieves owing to its large ionic size and charge [34]. Polymer supported Mo(VI) complexes, however, have been reported to be active and recyclable catalysts for olefin epoxidation with TBHP [35–38]. Nevertheless, in the latter case problems are described to have occurred during the catalytic reactions, such as swelling or leaching of the active species in the organic solution phase. Another strategy for the confinement of metal centres in mesoporous silicates is the covalent attachment of organometallic or coordination compounds to form hybrid materials [39–43]. Recently, modified MCM-41 and MCM-48 materials were synthesized by grafting MoO_2X_2 ($\text{X} = \text{Cl}, \text{Br}$) and $\text{CpMo}(\text{CO})_3\text{Cl}$, the latter being quite efficient homogeneous epoxidation catalysts [23–26,43]. Additionally, surface-fixed bidentate Lewis bases have been used to bind Mo(VI) complexes as described by Gonçalves et al. [44–48] and, independently, by Thiel et al. [49–51] Silylation using Me_3SiCl to remove residual Si–OH groups, which was considered to be favourable for the catalytic reaction

on the surface of the mesoporous material [39–42], reduced the catalyst leaching significantly [49–51].

During the last decades organometallic complexes with silane functional groups, either attached directly to the metal centre or to a cyclopentadienyl ligand were reported [52–57]. These functional groups often contributed a considerable kinetic stabilization to the resulting complexes [52–57]. The introduction of an alkoxy silane group in the organometallic complexes has received additional attention, owing to the ease of heterogenization of these transition metal complexes by using organic or inorganic supports [43–57]. Recently we have successfully synthesized and characterized a series of cyclopentadienyl molybdenum complexes containing a siloxane functional group, and heterogenized these compounds on the surface of mesoporous materials such as on MCM-41 and MCM-48 leading to ‘surface organometallic catalysts’ [58,59]. However, these organometallic compounds with siloxane functionalities are quite sensitive and their handling during the heterogenization process is somewhat difficult. An alternative is modifying the surface of the mesoporous materials by using linkers with a siloxane functional group, and then fixing organometallic groups by in situ reactions.

In the present study, we are using *p*-(iodomethyl)phenyltrimethoxysilane to modify the surface of the mesoporous materials MCM-41 and MCM-48. Then the modified mesoporous materials are applied to graft η^5 -CpMo(CO)₃ moieties by in situ reaction of $\text{Na}^+[\eta^5\text{-CpMo}(\text{CO})_3]^-$ with an iodo-group, attached into the mesoporous surface via the silane functional groups as shown in Chart 1.

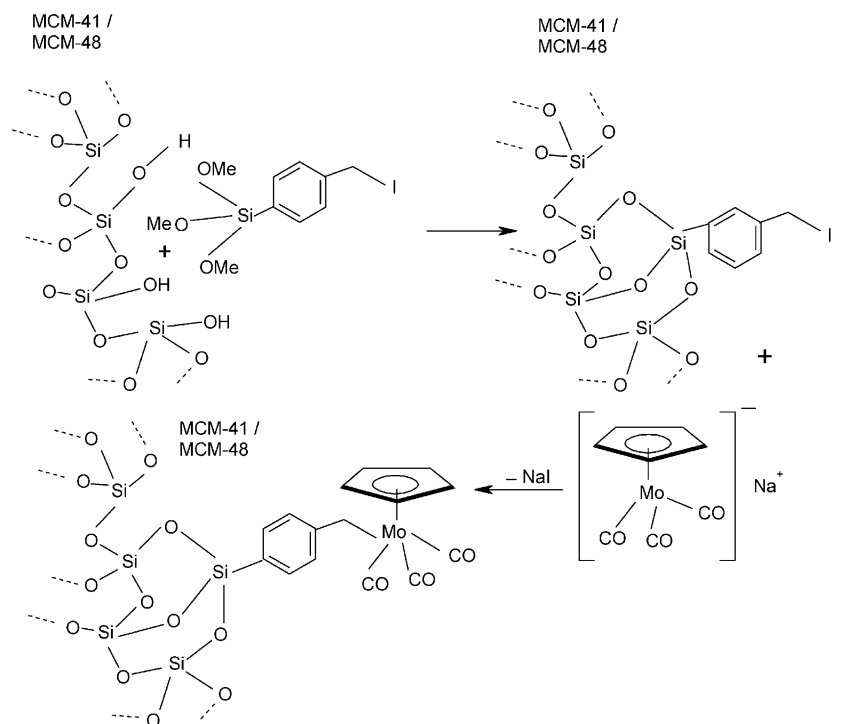


Chart 1.

2. Experimental

2.1. Synthetic procedure

Mesoporous molecular sieves are synthesized following the procedures described earlier [32,33] with molar gel compositions of 1.0 SiO₂:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H₂O for MCM-41, and 5.0 SiO₂:2.5 NaOH:0.87 CTABr:0.13 Brij30:400 H₂O for MCM-48, respectively. Solvents are dried by standard procedures (THF, toluene with Na/benzophenone ketyl; CH₂Cl₂ with CaH₂), distilled under argon and kept over 4 Å molecular sieves. Grafting experiments are carried out using standard Schlenk techniques under argon atmosphere with the following procedure: The mesoporous molecular sieves MCM-41/48 are pre-activated at 473 K under vacuum (10⁻³ mbar) for 4 h to remove physisorbed water. Then the activated mesoporous molecular sieve (MCM-41 or MCM-48) is silylated with *p*-(iodomethyl)phenyltrimethoxysilane using dry toluene (30 ml) as solvent under an argon atmosphere at 383 K for 24 h. Then excess silane is removed by filtration followed by repeated washing with dichloromethane. The resulting solid is dried under vacuum at room temperature. After drying, the silylated samples are treated with 2 mmol of Na⁺[CpMo(CO)₃]⁻ in 30 ml dry THF under argon atmosphere. The mixture is again stirred for 24 h at 339 K. The in situ grafted samples are filtered off and the resulting orange solid is washed repeatedly with CH₂Cl₂ to remove all physisorbed Mo complexes. The washed samples are dried under vacuum at room temperature. The samples synthesized applying MCM-41 and MCM-48 as carrier materials are designated as SM-41ASG and SM-48ASG, respectively.

2.2. Characterization methods

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). IR spectra are measured with a Unicam Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data are collected with a Philips X'pert diffractometer using Cu K α radiation filtered by Ni. Nitrogen adsorption–desorption measurements are carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 is degassed at 723 K overnight to a residual pressure of ca. 10–24 mbar. A lower degassing temperature of 413 K is used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) are determined by the BET method. The total pore volume (VP) is estimated from the N₂ uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 g cm⁻³. The pore size distribution curves (PSD),

the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) are computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) is recorded on a JEOL JEM2010 operated at 120 kV. Thermo gravimetric mass spectra analysis (TG-MS) measurements are conducted with a Netzsch TG209 system; typically about 10 mg of sample was heated from 300 to 1473 K at 10 K min⁻¹ under argon. ²⁹Si CP MAS NMR spectra are recorded at 59.62 MHz, with a (7.1 T) Bruker AV 300 spectrometer, with 5.5 μ s ¹H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays.

2.3. Catalytic applications

The catalytic behavior of selected amounts of the grafted samples (22–175 mg; see Table 3 for the molar ratios) is tested by examining the oxidation of cyclooctene (0.802 g; 8 mmol) at 328 K in a liquid phase batch reactor with TBHP (5.5 M in decane; 16 mmol) as the oxidizing agent. The samples are analyzed after 5 min and every 30 min for 4 h and the reaction is terminated after 24 h. The analyses are carried out using a gas chromatograph (HP 5890) equipped with a FID detector. Runs with pure carrier material, as well as runs performed with the silylated, but not Mo-grafted material show no catalytic activities for cyclooctene epoxidation under the above mentioned reaction conditions.

3. Results and discussion

The powder XRD pattern of the in situ grafted Mo samples (SM-41ASG and SM-48ASG) are depicted in Fig. 1. Fig. 1(a) shows the XRD pattern of SM-41ASG. The main reflection corresponding to a hexagonal unit cell is observed at a 2 θ range of 2.76°, with three

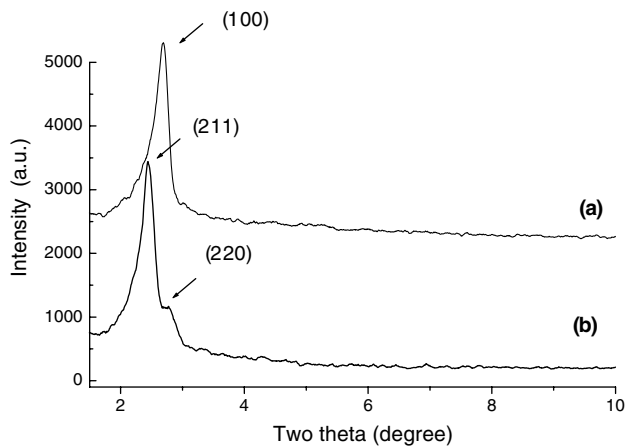


Fig. 1. Powder X-ray diffraction pattern of: (a) SM-41ASG and (b) SM-48ASG.

Table 1
Textural properties of the MCM-41/MCM-48 and the grafted samples

Sample	Mo (wt%)	Interplane distance (nm) ^a	Unit cell parameter \bar{a} (nm) ^b	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
MCM-41	–	3.80	4.39	839	0.8
SM-41ASG	6.4 (1 atom/nm ²)	3.16	3.65	407	0.3
MCM-48	–	3.97	9.72	1043	1.2
SM-48ASG	8.3 (1 atom/nm ²)	3.26	7.98	577	0.4

^a d_{100} for MCM-41 and d_{211} for MCM-48.

^b $\bar{a} = 2d_{100}/\sqrt{3}$ for MCM-41; $\bar{a} = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ for MCM-48.

other weak reflections in the 2θ range of 3–8°. The indexing shows the (110), and (200) and (210) planes. Fig. 1(b) shows the XRD pattern of SM-48ASG, which exhibits a main reflection corresponding to the (211) plane along with a shoulder peak derived from the (220) plane, typical for cubic cells. These peaks together with the weak sextet pattern observed between the 2θ angles at 3–6°, are characteristic for a cubic mesoporous MCM-48 structure. The calculated textural parameters using XRD and adsorption/desorption isotherms are summarized in Table 1. Compared to parent MCM-41 and MCM-48 [43], the grafted samples show a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher 2θ values (Table 1). These changes originate from a contraction of the unit cells of the grafted samples, because of the grafting of the bulky organosilane groups on the channel surfaces of MCM-41 and MCM-48 by reaction with surface silanol (Si–OH) groups [44–48]. The intensity reduction is mainly due to contrast matching between the silicate framework and the organic moieties located inside the channels of the mesoporous molecular sieves [44–48]. The results clearly indicate that the structures of the mesoporous materials remain intact throughout the grafting procedure.

The low temperature N₂ adsorption/desorption isotherm is of type (IV) according to the IUPAC [60] and characteristic for mesoporous solids. However, compared to parent mesoporous samples [43], the samples bearing grafted Mo complex (Fig. 2) exhibit a drastic decrease in N₂ uptake and surface area (50%; Table 1) due to both the presence of quite large amounts of the comparatively bulky organometallic molecules and to bridging silane moieties on the surface of the mesoporous channels. Further, the parent MCM-41 and MCM-48 samples exhibit narrow pore size distributions with average pore diameters of 2.7 and 2.4 nm, respectively. The grafted materials exhibit a broader pore size (1.6–2.3 nm) distribution and display also a decrease in surface area and unit cell volume compared to parent MCM-41 and MCM-48 [43]. The decrease of the unit cell value and the broad pore size distribution evidences that the organometallic complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials [44–48].

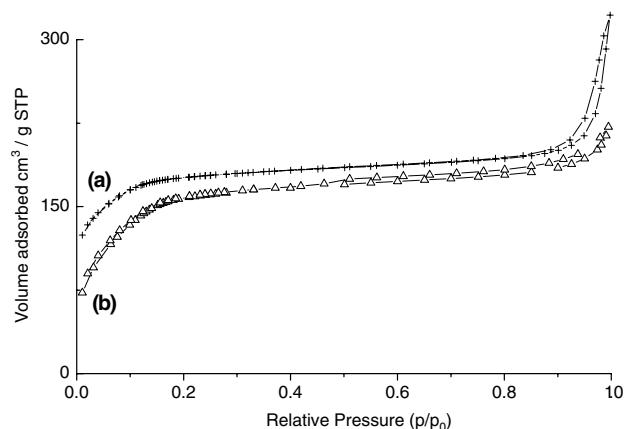


Fig. 2. N₂ adsorption/desorption isotherms of: (a) SM-41ASG and (b) SM-48ASG.

The TEM images (see Fig. 3) of the grafted samples are providing strong evidence that the mesoporous structure of the support retains long range ordering [8,9] throughout the grafting process and that the channels remain accessible. The ED pattern of the grafted samples shows the reflection of the (100) and the (110) planes, which further supports the presence of long range ordering in the samples.

FT-IR spectra of parent calcined mesoporous MCM-41, MCM-48 and grafted samples show bands at 1206, 1060, and 794 cm⁻¹, attributable to stretching vibrations of the mesoporous framework (Si–O–Si). New bands around 2016 and 1956 cm⁻¹ are observed on the grafted

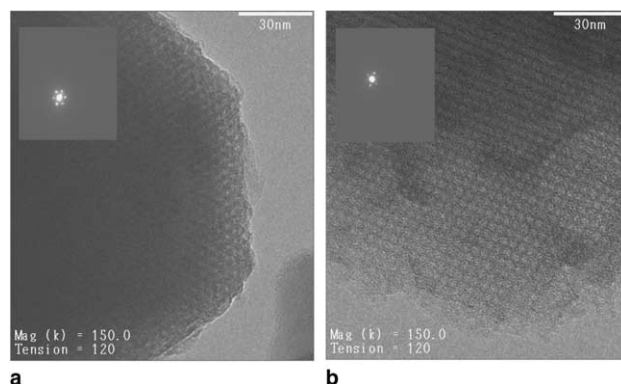


Fig. 3. TEM images of: (a) SM-41ASG and (b) SM-48ASG.

samples, and can be assigned to terminal carbonyl (CO) group vibrations of the grafted compounds. Additional bands around 1580 s (aryl) and two bands around 2949 and 2853 cm^{-1} arise from C–H stretching vibrations, originating from CH_2 groups. The presence of these bands after the heterogenization process further confirms the presence of silane ligands as well as of the $\eta^5\text{-CpMo}(\text{CO})_3$ complexes on the channels of the mesoporous materials. In order to transfer the Mo precursor from the formal oxidation state +II to the catalytic active species with a formal oxidation state of +VI, the SM-41ASG and SM-48ASG are treated with TBHP. FT-IR spectra were recorded prior to and after oxidation. After the treatment with TBHP the bands around 2016 and 1956 cm^{-1} disappear and new bands around 914 and 964 cm^{-1} are formed, due to the oxidative conversion of the Mo–CO groups into Mo=O species [20–26,43,61]. The oxidative decarbonylation method was successfully applied already previously for the oxidation of $\text{Cp}'\text{Mo}(\text{CO})_3\text{X}$ and $\text{Cp}'\text{Mo}(\text{CO})_3\text{R}$ complexes, both in homogeneous [23–27] and heterogeneous phase [43]. The corresponding changes in the IR spectra were observed and CpMoO_2X compounds could be isolated and fully characterized [23].

The parent MCM-41 and the grafted samples are examined by solid-state ^{29}Si CP MAS NMR spectroscopy. The parent MCM-41 exhibits two broad elaborate resonances in the ^{29}Si CP MAS NMR spectrum at $\delta = -113.0$ and -103.8 ppm, assigned to Q_4 and Q_3 species of the silica framework, respectively, [$Q_n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$] [44–51]. A weak shoulder is also observed at $\delta = -94.5$ ppm for the Q_2 species. The in situ grafting of $(\text{MeO})_3\text{Si}(\text{C}_6\text{H}_4)\text{CH}_2\text{I}$ results in the reduction of the Q_2 and Q_3 resonances, and a concurrent increase of the Q_4 resonance. This is consistent with an esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atom in the organic ligand [44–51]. The ^{29}Si CP MAS NMR spectra also exhibit two additional signals at $\delta = -61.4$ and -69.6 ppm assigned to T_2 and T_3 organosilica species, respectively, [$T_m = \text{RSi}(\text{OSi})_m(\text{OR})_{3-m}$]. The observed signals for organosilica in the present case (T_2 and T_3) compared to signals recorded in earlier studies (T_1 and T_2 signals) evidence that the aromatic silane is more effectively silylated on the surface of the mesoporous materials. However, as expected, the silylated but not Mo-containing and the Mo-containing grafted samples show (nearly) identical ^{29}Si CP MAS NMR signals, thus indicating that during the in situ grafting process there is no significant change in the silicon environment (see Fig. 4). The observed changes in the ^{29}Si CP MAS NMR spectra arise only during the silylation procedure using the aromatic silane.

Elemental analyses (EAs) of the grafted samples show Mo loadings of 6.4 and 8.3 wt% for SM-41ASG and SM-48ASG, respectively. Compared to SM-41ASG,

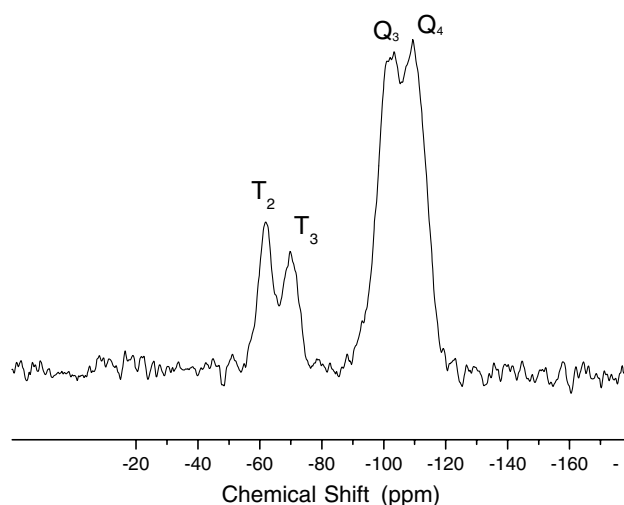


Fig. 4. ^{29}Si CP MAS-NMR spectrum of SM-41ASG sample.

the observed higher Mo loading on SM-48ASG is due to three dimensional pore openings of the mesoporous structure of MCM-48 in comparison to the one dimensional pore openings of MCM-41 being accordingly accessible only from one direction. Furthermore, compared to earlier grafting methods [43,58] the use of an aromatic silane linker leads to a particularly high amount of CpMo complex on the surface. This may be due to the fact that the mesoporus surface is silylated to a higher degree (see ^{29}Si Cp MAS-NMR) and thus a high Mo loading is reached. EA confirms the absence of iodide ions (I^-) on the SM-41ASG and SM-48ASG surface.

The grafted samples are tested as heterogeneous catalysts in olefin epoxidation, with cyclooctene being the substrate and TBHP as the oxidizing agent. The SM-41ASG and SM-48ASG materials show about 90–95% cyclooctene conversion with nearly 100% epoxide selectivity after 24 h reaction time. The initial activities (reflected by the TOFs) are somewhat higher for SM-48ASG than for SM-41ASG, owing probably to the three dimensional pore opening of the former compared to the one dimensional pore access of the later. However, both catalysts show TOFs about one order of magnitude lower than the respective homogeneous catalysts of formula $(\eta^5\text{-CpMoR}(\text{CO})_3)$ [23–27], thus indicating that diffusion limitation plays, not unexpectedly for heterogeneous systems, a certain role.

After the first catalytic run the catalyst is washed several times with dichloromethane to remove physisorbed molecules and the reaction is repeated several times. The catalysts are found to be active even after several catalytic runs (see Table 2). However, the catalytic activities and selectivities decrease somewhat in all cases over several runs. Particularly small amounts of diol can be observed after several runs as by-product. Catalyst leaching seems to play not a important role, however,

Table 2
Oxidation of cyclooctene over grafted materials^a

Catalysts	Conversion (%)	Selectivity (%)
SM-41ASG	91	100
2nd run	87	80
3rd run	85	76
SM-48ASG	95	100
2nd run	92	71
3rd run	91	72

^a Temperature = 328 K, time = 24 h, catalyst:substrate molar ratio = 18×10^{-3} .

in the presented heterogeneous system. This was found by filtrate experiments. The solid catalyst was removed at the reaction temperature after 50% conversion had been reached from the solution phase and the further conversion of the filtrate within an additional 24 h reaction time was recorded. The solution showed no appreciable conversion (less than 4%). A possible explanation for the observed decrease in activity and selectivity occurring from one catalytic runs to the next may be a combination of small amounts of residual *t*-BuOH remaining in the materials, some coke formation during the reactions from the organic materials deposited in the pores on the catalytic sites and some leaching of catalytically inactive Mo species. These effects, despite each in itself not very pronounced sum up to 5–8% conversion reduction and selectivity losses of ca. 25% after three runs.

Additionally, the reaction was carried out with different catalyst/substrate ratios and the results are depicted in Table 3. Both SM-41ASG and SM-48ASG show good initial activities, particularly when low catalyst amounts are applied. The observed TOFs (110–520 1/h), are higher than the TOFs of η^5 -CpMo(CO)₃Cl systems directly grafted on a mesoporous surface when applied under similar conditions. The higher activity in the case examined here is very likely due to the longer distance of the Lewis acidic Mo center from the surface. Close proximity of the electron deficient Mo atom in

Table 3
Oxidation of cyclooctene at different catalysts:substrate ratios^a

$M(\text{cat.})/$ $M(\text{subst.})^b \times 10^{-3}$	Conversion (%)			TOF ^c (1/h)
	5 min	4 h	24 h	
SM-41ASG	16	15	52	91
	8	12	48	89
	5.5	9	45	77
SM-48ASG	2	8	30	68
	20	22	69	95
	10	19	65	92
	5	15	53	85
	2.3	10	39	77

^a Temperature = 328 K.

^b Substrate = cyclooctene.

^c Determined after 5 min reaction time.

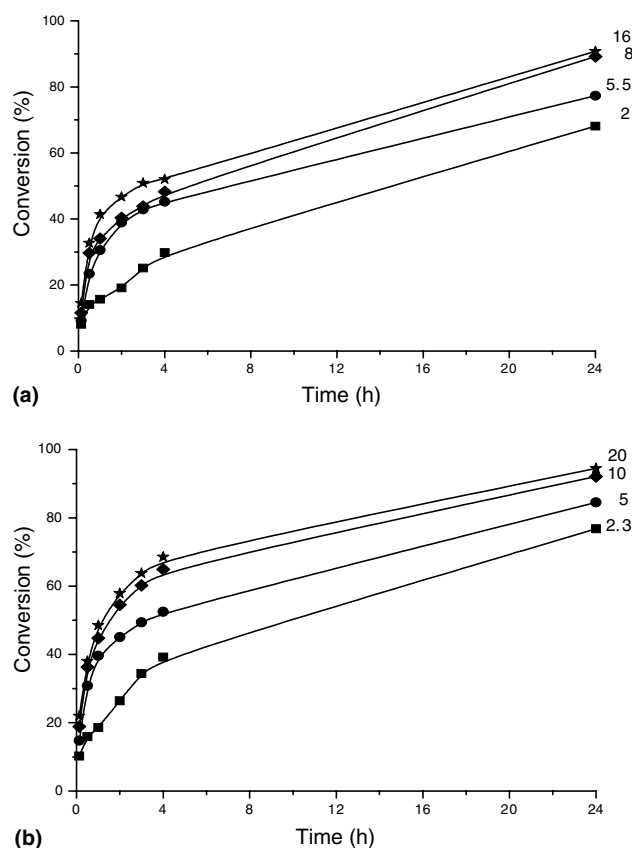


Fig. 5. Kinetics profiles for the epoxidation of cyclooctene over: (a) SM-41ASG and (b) SM-48ASG at different $M(\text{catal.})/M(\text{subst.}) \times 10^{-3}$ (see in the figure).

the active catalyst species to strong electron donors, such as silane moieties usually reduce the catalytic activity as has been noted already [48,58,59]. Initial TOFs of ca. 10–20 1/h for heterogeneous systems [48] and ca. 10–400 1/h for homogeneous Cp'Mo(CO)₃R-based systems [48,59] bearing electron donating ligands either on the Cp'-moiety or as Mo-bound R-groups have been reported.

Kinetic profiles of the grafted materials at different catalyst/substrate ratios are depicted in Fig. 5. In all the reactions the velocity slows down during the course of the reaction. This behavior is assigned to the interaction of the catalyst with the by-product butyl alcohol, which is formed during the reaction from the oxidant and is able to coordinate to the Mo compounds to a certain degree, when it is present in great excess [20–26].

4. Conclusions

A η^5 -CpMo(CO)₃ type complex is in situ grafted on mesoporous materials by means of a linking benzylsiloxane ligand, which was fixed on the surface of a mesoporous (MCM-41 and MCM-48) molecular sieve in a

previous reaction step. The supported materials retain long range ordering throughout the grafting process. The grafted samples are quite active and highly selective for olefin epoxidation. The kinetic profile shows good initial activities (TOF) for the chosen reactions. Furthermore, the leaching of Mo during the course of the reaction is found to be not very significant and the catalysts can be reused several times without pronounced loss of activity and selectivity.

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