Heterogenization of Organometallic Molybdenum Complexes with Siloxane Functional Groups and their Catalytic Application

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Dedicated to Prof. Dr. Richard Schrock on the occasion of his 60th birthday

Abstract: η^5-$CpMo(CO)_3R$ complexes containing siloxane functional groups [$(CH_2)_3Si(OMe)_3$ or $(CH_2)Si(OEt)_3$] attached to either the cyclopentadiene ligand or directly to Mo were grafted on the mesoporous materials MCM-41 and MCM-48 by reaction of the OR (R = Me, Et) moieties in the silane ligand and surface silanol groups (Si-OH). For the sake of comparison mesoporous materials modified with silane groups were reacted with $Na^+[CpMo(CO)_3]^-$. The XRD, N_2 adsorption-desorption, and TEM analyses provide strong evidence that the mesoporous structure of the supporting material retains its long-range ordering throughout the grafting process, despite significant reductions in surface area, pore volume and pore size. The appearance of strong IR bands around 2016 and 1956 cm^{-1} on the grafted samples also shows that the η^5-$CpMo(CO)_3R$ complexes have been successfully grafted. Elemental analysis reveals that the grafted samples contain 0.3–3.5 wt % Mo. ^{29}Si CP MAS-NMR spectra give clear evidence for a reduction in the numbers of the Q_3 and Q_2 sites. The formation of new peaks around −49.8, −57.9, and −66.2 ppm (T_1, T_2, and T_3) indicates esterification of silanol groups by the alkoxy groups of the silane ligand. Both the *in situ* and *ex situ* prepared samples show good catalytic activity for the epoxidation of cyclooctene.

Keywords: catalysis; epoxidation; grafting; molybdenum; siloxane

Introduction

Various molybdenum(VI) complexes are known to be versatile catalysts for the oxidation of organic substrates.[1] Molybdenum-based catalysts have been applied for the industrial epoxidation of propylene, utilizing *tert*-butyl hydroperoxide (TBHP) as oxidizing agent since the late 1960 s.[2] A lot of work has been dedicated to the understanding of the involved catalytic reactions in subsequent years in order to improve both yields and selectivities.[3] During the last decade several well defined homogeneous epoxidation catalysts have been developed and described.[4] Recently cyclopentadienylmolybdenum complexes of the formula $Cp'MoO_2Cl$ were found to be efficient homogeneous catalysts for the epoxidation of alkenes with TBHP as the oxidant.[5] Furthermore, it became clear that the direct application of their carbonyl precursor compounds of the formula $CpMo(CO)_3Cl$ leads to equally efficient catalysts, since the carbonyl complexes are *in situ* oxidized – also by TBHP – to their oxo congeners. The carbonyl precursor compounds can be stored for long time without any problems while the oxides are somewhat more sensitive.[5] Additionally, $Cp'Mo(CO)_3R$ complexes (R = alkyl) and their oxidized congeners are also known and have already been successfully utilized as homogeneous catalysts or catalyst precursors.[6] However, industrial interest is still to a significant degree focused on heterogeneous catalysts due to their advantages, e.g., easier product/catalyst separation.[7] Among the various supporting materials studied, the mesoporous silicates known as MCM-41 and MCM-48[8] 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.[9]

Different approaches have been used in order to obtain heterogeneous molybdenum catalysts for olefin ep-

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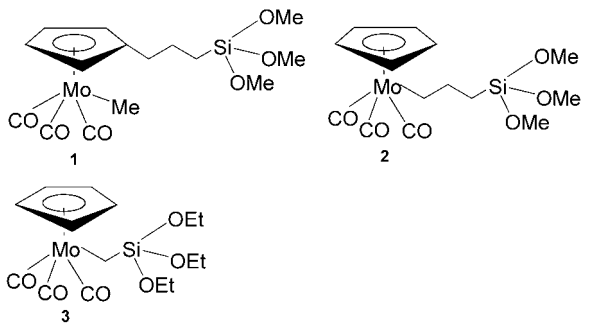


Figure 1. Formulae of complexes **1** –**3**.

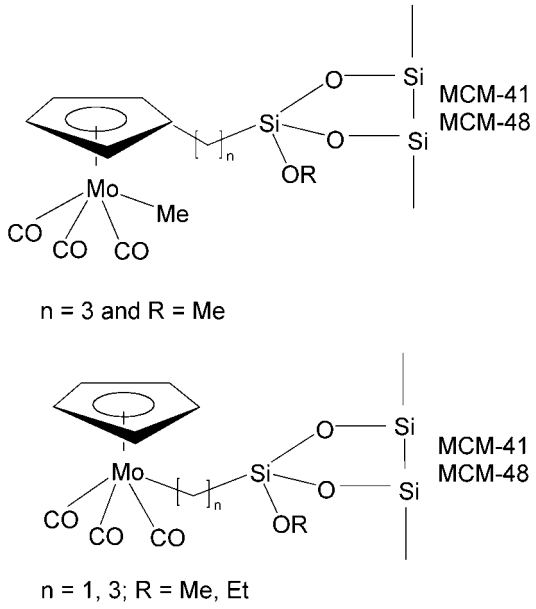
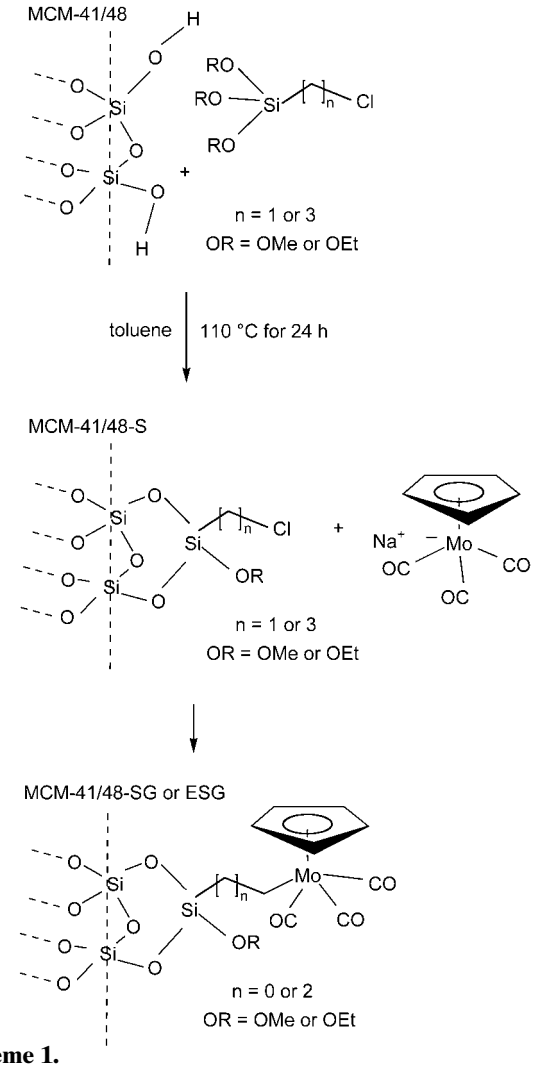


Figure 2. Formulae of the heterogenized complexes.



Scheme 1.

oxidation. A general problem is that Mo(VI) cannot easily be incorporated into the tetrahedral positions of the silicate framework of molecular sieves owing to its large ionic size and charge.[10] Polymer supported Mo(VI) complexes, however, have been reported to be active and recyclable catalysts for olefin epoxidation with TBHP.[11] Nevertheless, in the latter case problems are reported 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 a hybrid material.[12] Recently, modified MCM-41 and MCM-48 materials were synthesized by grafting MoO_2X_2 (X = Cl, Br) and $CpMo(CO)_3Cl$, the latter being quite efficient homogeneous epoxidation catalysts.[13] Additionally, surface-fixed bidentate Lewis bases have been used to bind catalytically Mo(VI) complexes as described by Gonçalves et al.[14] and, independently, by Thiel et al.[15] Silylation using Me_3SiCl to remove residual Si–OH groups, which were considered to be favourable for the catalytic reaction on the surface of the mesoporous material,[12] reduced the catalyst leaching significantly.[15]

During the last decades organometallic complexes with silane functional groups, either attached directly to the metal centre or to a cyclopentadienyl ligand have been reported.[16] These functional groups often contributed a considerable kinetic stabilization to the resulting complexes.[16] The introduction of an alkoxysilane 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.[5,14–16] Recently, we have successfully synthesized and characterized a series of cyclopendadienyl-molybdenum complexes containing a siloxane functional group.[17] In this work such complexes (compounds **1**–**3**, see Figure 1) are reported to be turned into 'surface organometallic catalysts' by fixing them to MCM-41 and MCM-48 (Figure 2).

Additionally, the *in situ* synthesis of surface fixed $CpMoR(CO)_3$ by functionalization of the mesoporous framework with $Cl(CH_2)_3Si(OMe)_3$ or $ClCH_2Si(OEt)_3$ followed by the reaction of $Na^+[CpMo(CO)_3]^-$ with the chloride ion of the silane functional group on MCM-41 and MCM-48 is presented (Scheme 1).

Results and Discussion

Synthesis and Textural Characterization

The compounds **1–3** are prepared as described previously.[17] They are slightly air sensitive and very well soluble both in non-polar (e.g., *n*-hexane) and polar (e.g., THF) solvents. The IR spectra (KBr) of compounds **1–3** show strong absorption bands at 2016, 1956 and 1963 cm^{-1}, respectively, from terminal carbonyl groups. The ^1H, ^{13}C and ^{29}Si NMR spectra as well as elemental analysis confirm the purity of the complexes.[17] The treatment of the complexes **1–3** with calcined and dehydrated MCM-41 and MCM-48 leads to the modified materials which are respectively designated as SM-41CpSG, SM-48CpSG, SM-41MoSG, SM-48MoSG, SM-41MoESG and SM-41MoESG (see Figure 2). The *in situ* grafting of the CpMo complexes is carried out by silylation of MCM-41 and MCM-48 followed by treatment with $Na^+[CpMo(CO)_3]^-$ (see Scheme 1) which are represented as SM-41SG, SM-48SG, SM-41ESG and SM-48ESG.

The powder XRD patterns of the parent MCM-41 (Figure 3 a), and the corresponding grafted Mo samples (SM-41CpSG, SM-41MoSG, SM-41MoESG, SM-41SG and SM-41ESG) are depicted in Figure 3 b – f. In each case all four reflections are observed in the 2 θ range 2–8°, with an indexing corresponding to a hexagonal cell showing the (100), (110), and (200) and (210) planes. Figure 3A – F show the XRD patterns of the parent MCM-48 and the corresponding samples with the grafted Mo complexes (SM-48CpSG, SM-48MoSG, SM-48MoESG, SM-48SG and SM-48ESG), which exhibit 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 sextet pattern observed between the 2θ angles 3° – 6°, are characteristic of a cubic mesoporous MCM-48 structure. Compared to parent MCM-41 and MCM-48, the grafted samples show a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher 2 θ values. These changes originate from a contraction of the unit cells of the grafted samples, because of the im-

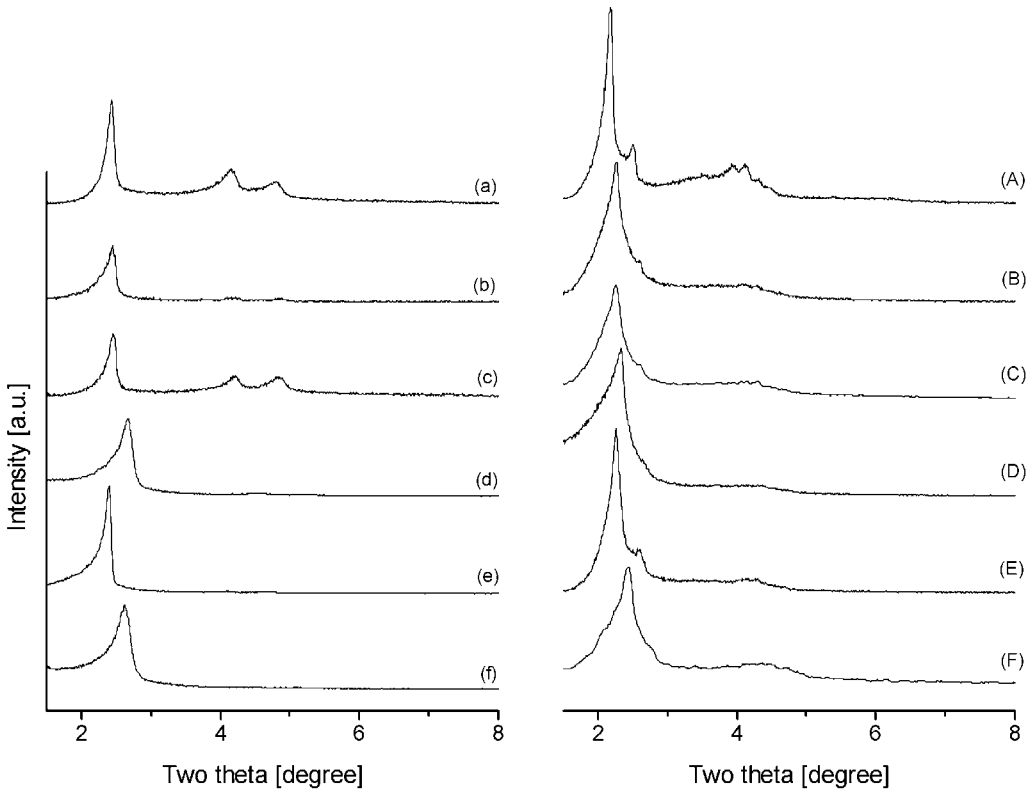


Figure 3. Powder XRD pattern of (a, A) SM-41, SM-48; (b, B) SM-41CpSG, SM-48CpSG; (c, C) SM-41MoSG, SM-48MoSG; (d, D) SM-41MoESG, SM-48MoESG; (e, E) SM-41SG, SM-48SG and (f, F) SM-41ESG, SM-48ESG.

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

Sample	Mo [wt %]	Interplane distance [nm][a]	Unit cell parameter [nm][b]	BET surface area [$m^2 g^{-1}$]	Pore diameter [nm]
MCM-41	–	3.80	4.39	839	2.74
SM-41CpSG	2.3	3.62	4.18	620	2.5–3.1
SM-41MoSG	1.7	3.60	4.16	640	2.3–3.1
SM-41MoESG	0.3	3.31	3.82	–	–
SM-41SG	1.03	3.69	4.26	726	1.9–2.1
SM-41ESG	0.94	3.37	3.89	–	–
MCM-48	–	3.97	9.72	1043	2.41
SM-48CpSG	3.41	3.90	9.55	790	2.24–3.5
SM-48MoSG	1.83	3.92	9.60	680	2.27–3.5
SM-48MoESG	0.4	3.81	9.33	–	–
SM-48SG	1.18	3.90	9.55	840	2.1
SM-48ESG	1.27	3.65	8.94	–	–

[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.

mobilization of the bulky organosilane groups on the channels of MCM-41 and MCM-48 by reaction with surface silanol (Si-OH) groups.[14] The intensity reduction is mainly due to contrast matching between the silicate framework and organic moieties located inside the channels of the mesoporous molecular sieves.[14] The results clearly indicate that the structure of the mesoporous materials remains intact through the grafting procedure.

The low temperature N_2 adsorption/desorptions isotherm of parent MCM-41 and MCM-48 are of type (IV) according to the IUPAC[18] and characteristic for mesoporous solids. A well-defined sharp inflection is observed between the relative pressure (p/p_0) of 0.3–0.4 due to capillary condensation of nitrogen inside the primary mesoporous channels. Compared to parent mesoporous samples, the modified samples (Figure 4) exhibit a decrease in N_2 uptake due to the presence of bulky organometallic complexes grafted on the mesoporous channels. The calculated textural parameters using XRD and adsorption/desorption isotherms are summarized in Table 1. 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 distribution and display also a decrease in surface area and unit cell volume. The decrease of the unit cell value and the broad distribution of pore size evidences that the organometallic complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials.[14]

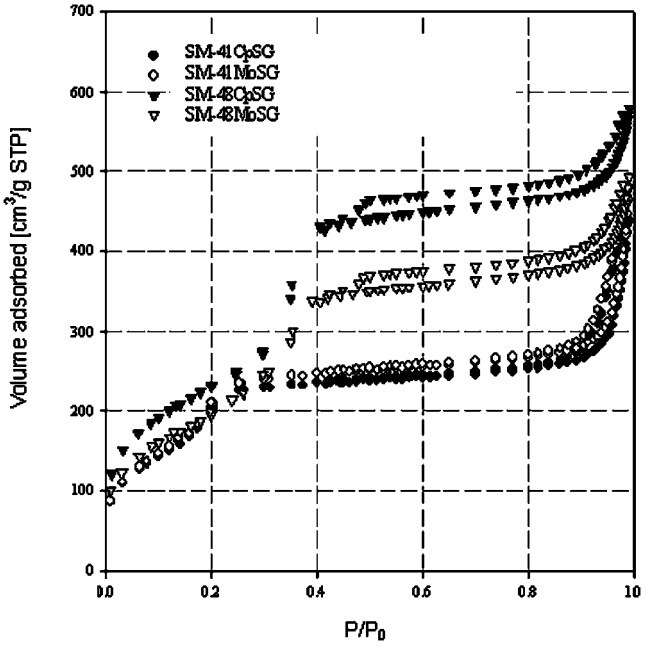


Figure 4. N_2 adsorption/desorption isotherms of complexes **1** and **2** grafted on MCM-41 and MCM-48.

The TEM images (Figure 5) of the grafted samples provide 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 grafted samples shows the reflection of the (100) and the (110) planes, which further support the presence of long-range ordering in the samples. Elemental analyses (EAs) of the grafted samples of compounds **1**–**3** reveal (Table 1) an Mo loading of 0.3–3.5 wt %. The complexes containing methoxysilane units enable somewhat higher Mo complex loading on the surfaces than the complex containing ethoxy ligands. This may be due to the higher reactivity of the methoxy groups with silanol moieties in the mesoporous channels in comparison to the ethoxy groups. Furthermore, it is evident that direct grafting is more efficient and leads to higher Mo complex loading on the surface than *in situ* grafting. EA further confirms clearly the decrease of Cl on the SM-41SG and SM-48 SG samples in

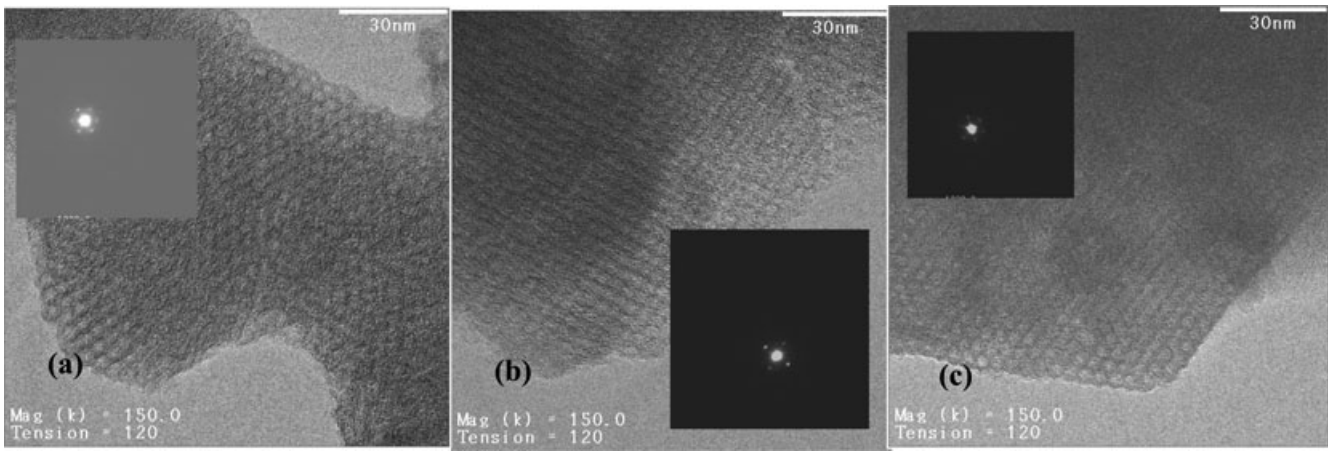


Figure 5. TEM images of (a) SM-48CpSG, (b) SM-48MoSG (c) SM-41MoESG.

comparison to the SM-41S and SM-48S samples. Therefore, it is clear that a considerable amount of Cl is utilized for the reaction with the $Na^+[CpMo(CO)_3]^-$ salt.

Figure 6 depicts the FT-IR spectra of parent calcined mesoporous MCM-41, MCM-48 and grafted samples. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si–O–Si). New, comparatively small bands around 2016 and 1956 cm^{-1} can be assigned to terminal carbonyl (CO) group vibrations of the grafted compounds. Additional bonds appear in the range of 2949 and 2853 cm^{-1} due to C–H stretching vibrations, originating from the CH_2 groups present in the silane ligand. In order to transfer the Mo precursor in the formal oxidation state +II to the catalytically active species in the formal oxidation state +VI, the SM-41CpSG and SM-41MoSG samples are treated with TBHP. The FT-IR spectra recorded prior to and after oxidation are shown in Figure 7. 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, indicating the oxidative conversion of the Mo–CO groups into Mo=O species[5,13,19]. The oxidative decarbonylation method has already been successfully applied for the oxidation of $Cp'Mo(CO)_3X$ and $Cp'Mo(CO)_3R$ complexes, both in homogeneous[5,6] and heterogeneous phase.[13]

The parent MCM-41 and the grafted samples were 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_5 species of the silica framework, respectively, $[Q_n = Si(OSi)_n(OH)_{4-n}]$ (Figure 8).[14] A weak shoulder is also observed at $\delta = -94.5$ ppm for the Q_2 species. The grafting of complexes **1**–**3** and the *in situ* grafting of η^5-CpMo complexes on mesoporous materials result 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.[14] However, Figure 8 also shows considerable unreacted silanol groups remaining after the grafting. The ^{29}Si CP MAS NMR spectra also exhibit two additional signals at $\delta = -49.8$ and -57.9 ppm assigned to T_1 and T_2 organosilica species, respectively, $[T_m = RSi(OSi)_m(OR)_{3-m}]$. A weak, broad signal at $\delta = -66.2$ ppm can be assigned to a T_3 environment. The amounts of T_1 and T_2 are much higher in the case of SM-41MoSG than in the case of SM-41CpSG, which suggests that the Mo loading is much higher in the former case than in the later. This observation is in good agreement with the EAs (Table 1).

Catalytic Applications

The grafted samples are tested as heterogeneous catalysts in olefin epoxidation, with cyclooctene being the substrate and TBHP as the oxidizing agent. The results are summarized in Table 2. The SM-41SG and SM-48SG materials show about 65–68% cyclooctene conversion with nearly 100% epoxide selectivity after 24 h reaction time. In the cases of SM-41CpSG, SM-41MoSG, SM-48CpSG, and SM-48MoSG 95–100% conversion and about 100% selectivity are obtained. The initial activities (based on the TOFs) are highest for SM-41CpSG, SM-41MoSG, SM-48CpSG and SM-48MoSG. These materials have longer hydrocarbon bridges between the Mo atoms and the surface Si–O groups than the ESG-materials, thus reducing the influence of the electron donor abilities of the surface on the Lewis acidity of the catalytic centres (see Figure 1 and Scheme 1). The slightly more pronounced steric bulk of the remaining ethoxy groups (after the heterogenization reaction) in the case of the ESG materials may also contribute to the generally somewhat lower initial activ-

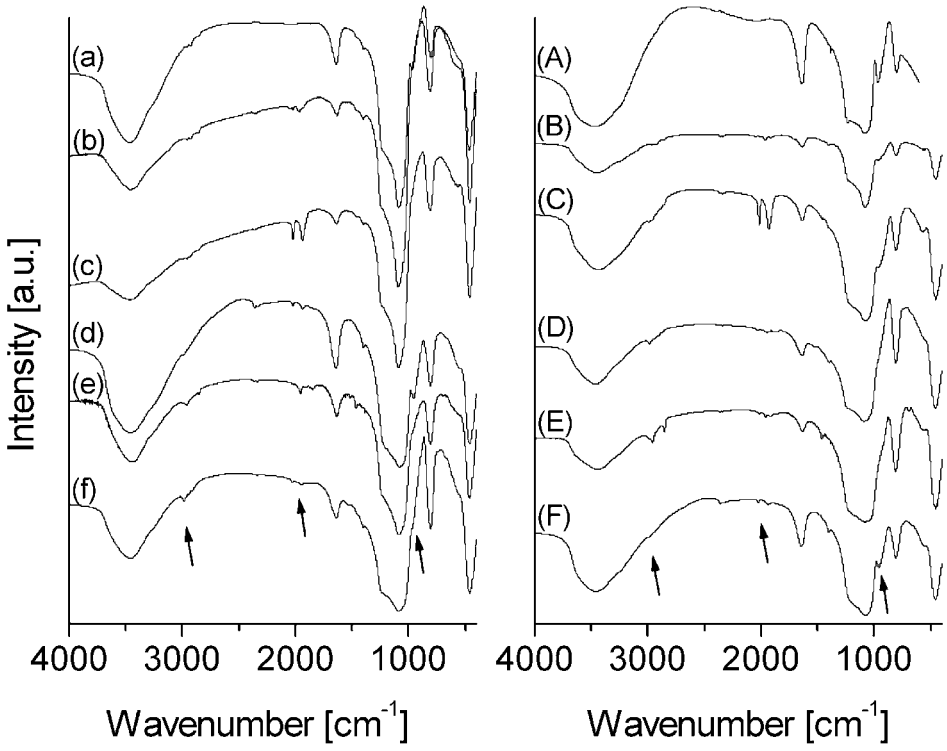


Figure 6. FT-IR spectrum of (a, A) SM-41, SM-48; (b, B) SM-41MoSG, SM-48MoSG; (c, C) SM -41CpSG, SM-48CpSG; (d, D) SM-41MoESG, SM-48MoESG; (e, E) SM-41SG, SM-48SG and (f, F) SM-41ESG, SM-48ESG.

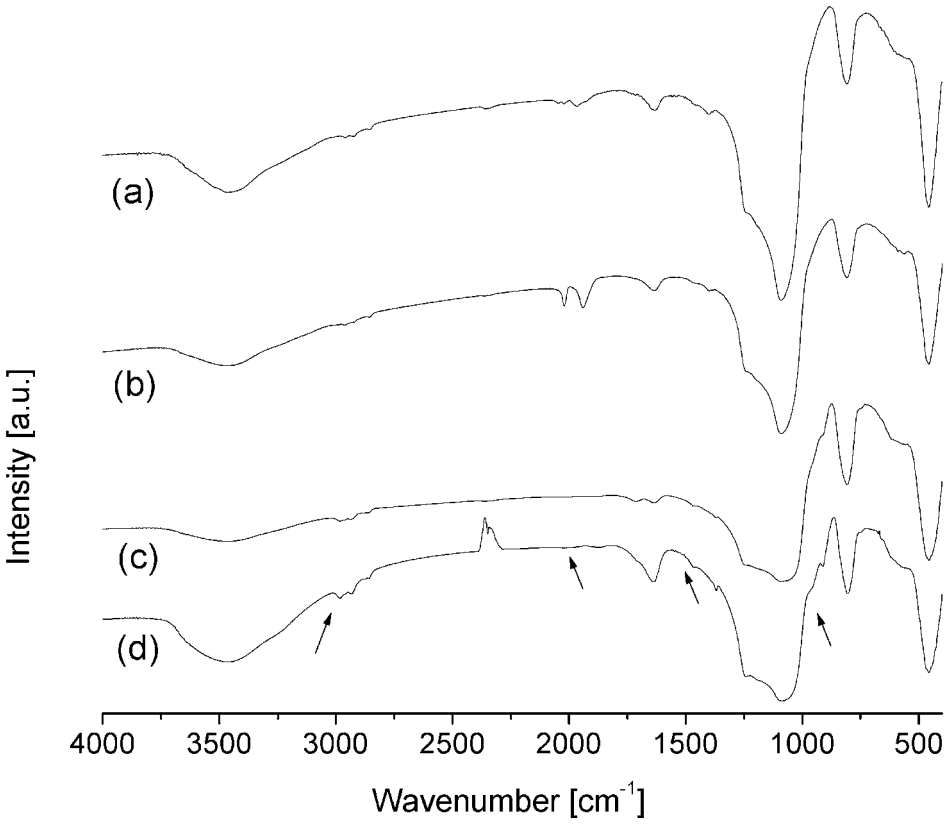


Figure 7. FT-IR spectrum of (a) SM-41MoSG, (b) SM -41CpSG, (c) SM-41MoSG-TBHP treated and (d) SM-41CpSG-TBHP treated samples.

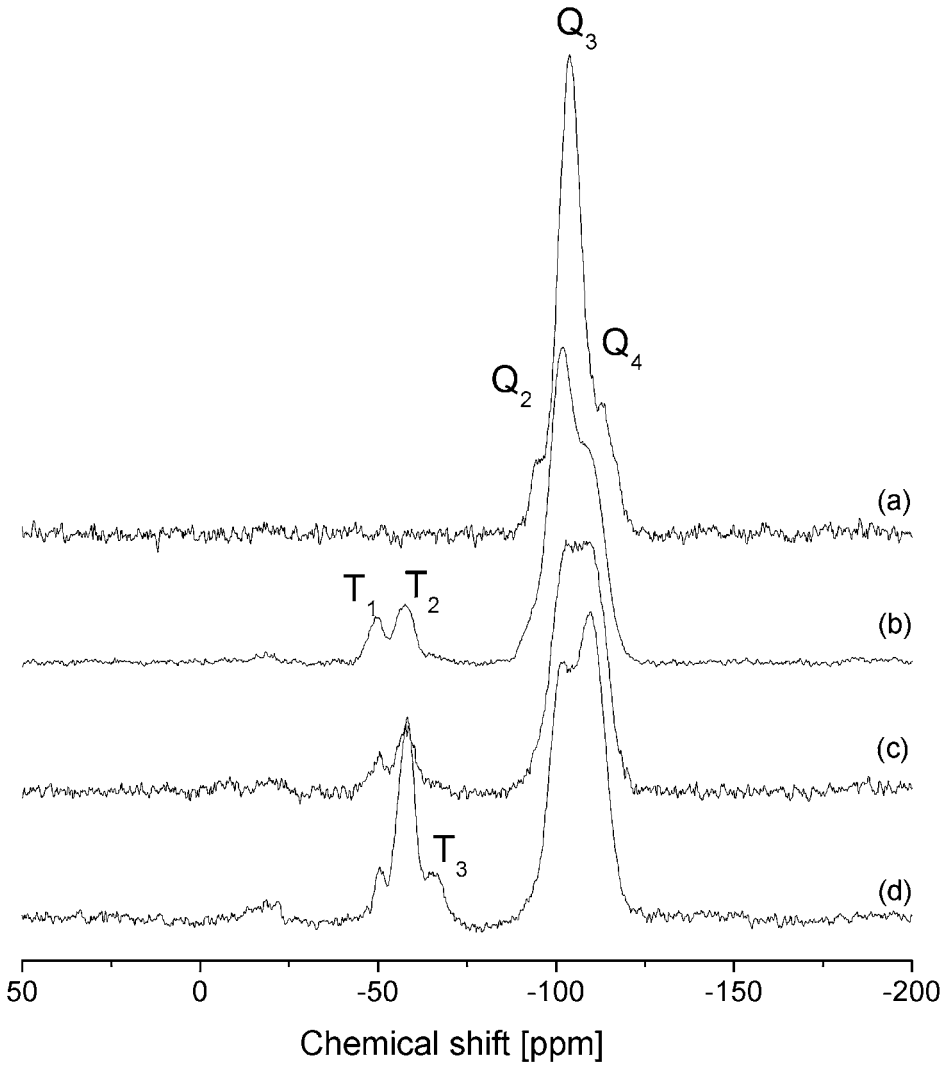


Figure 8. [29]Si CP MAS NMR spectrum of (a) SM-41; (b) SM-41CpSG; (c) SM -41MoSG and (d) SM-41SG.

ity of these catalysts. The prehistory (heterogenization method) of the complexes, however, seems also to have a certain impact on the catalytic activities (the MoSG and MoESG materials are more active than the SG and ESG materials). The reasons for this observation, however, are not yet completely understood and are still under investigation. All the catalysts, however, show TOFs in the same order of magnitude as the respective homogeneous catalysts **1**–**3**, thus indicating that the reaction is not diffusion limited. This is in good agreement with the results obtained by TEM and BET analyses where the pore channels are found to remain accessible after grafting with the complexes **1** to **3**. After the first catalytic run the catalyst was washed several times with dichloromethane to remove physisorbed molecules and the reaction was repeated several times. The catalysts are found to be active even after several catalytic runs, however, the catalytic activity decreases. The observed decrease in activity is very likely due to the chemisorptions of organic molecules on the surface, as such preventing the access of substrate and oxidant molecules to the active Mo species. This was confirmed by TG-MS analysis of SM-48MoSG before and after reactions (Figure 9). The TG-mass spectrum of SM-48MoSG before reaction shows about 10% weight loss up to 1000 °C, due to decomposition of complex **2** present in the channels of the mesoporous molecular sieves. However, SM-48MoSG after reaction displays a weight loss of about 23%, being 13% higher than that of the original sample. This increase in weight is attributed to a considerable amount of chemisorbed coke present on the grafted samples after reaction. In order to avoid the thermal destruction of the active Mo complex, the (chemisorbed organic) cokes are not removed by calcination. In order to examine the extent of leaching, which could also account for the activity loss, control experiments were performed. The catalytic reaction is interrupted after a 50% conversion of the substrate, the

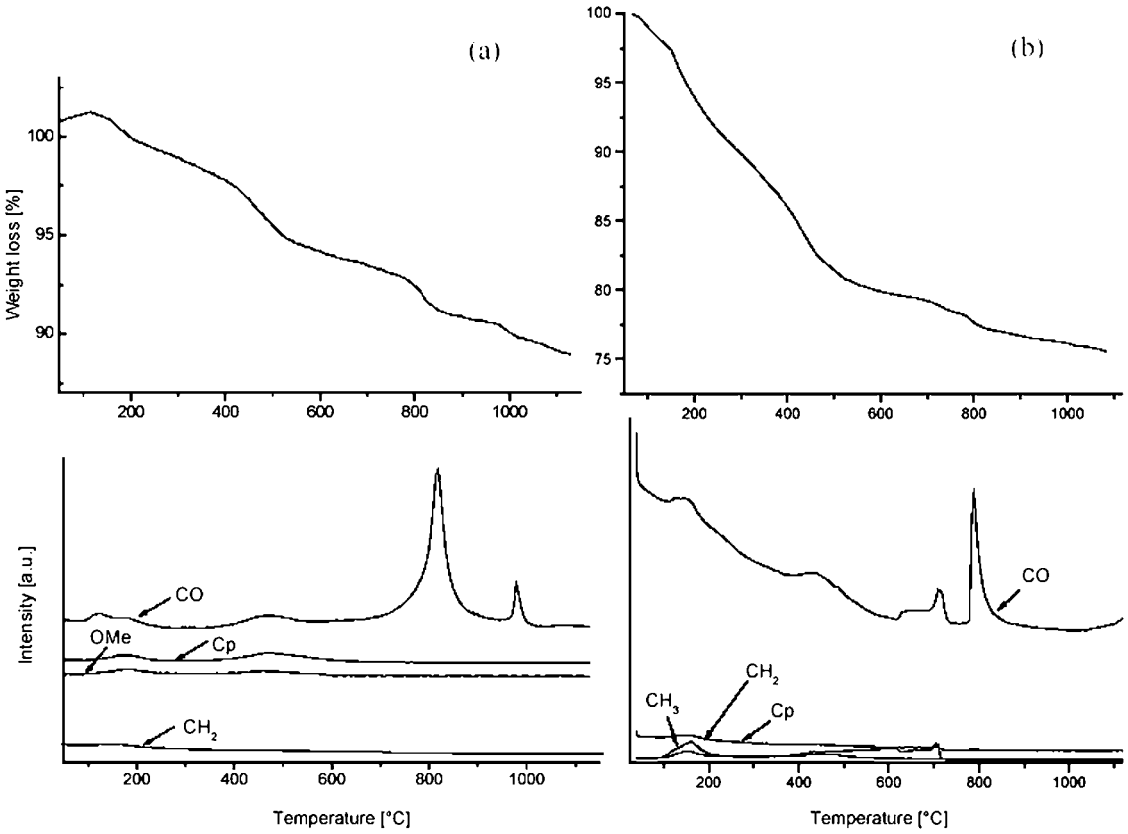


Figure 9. TG-mass spectrum of SM-48MoSG (a) before reaction and (b) after reaction.

solution is filtered off at reaction temperature and the filtrate is examined for its catalytic activity. This activity, however, is negligible ($<5\%$ epoxide yield (i.e., within the measurement error) in the 24 h after filtration), thus demonstrating that catalyst leaching does not play a significant role.

Conclusions

Successful grafting of the complexes **1–3** by the utilization of a metal- or ligand-attached siloxane group on the mesoporous molecular sieves MCM-41 and MCM-48 is achieved without significant loss of ordering. The *in situ*

Table 2. Oxidation of cyclooctene with various CpMo complexes grafted on MCM-41/MCM-48.

Catalysts	1st run				3rd run				TOF[a]
	4 h		24 h		4 h		24 h		
	Con.	Sel.	Con.	Sel.	Con.	Sel.	Con.	Sel.	
SM-41SG	36	98	68	100	13	50	31	44	2800
SM-48SG	32	88	66	99	8	100	33	80	4850
SM-41ESG	13	100	35	82	14	71	28	64	2900
SM-48ESG	13	97	63	92	17	64	47	64	3150
SM-41CpSG	66	58	95	79	17	100	46	98	10100
SM-48CpSG	88	82	100	100	21	100	73	90	8100
SM-41MoSG	50	39	95	87	24	85	57	91	8400
SM-48MoSG	97	100	100	100	25	61	80	70	10200
SM-41MoESG	11	53	33	73	7	100	27	89	4900
SM-48MoESG	21	45	46	78	10	100	29	95	6300

[a] TOFs are calculated after 5 min reaction time of the first catalytic run.

and *ex situ* grafted samples are active and highly selective catalysts for the cyclooctene epoxidation with the oxidizing agent TBHP. The samples **1** and **2**, containing methoxysilane display both higher complex loadings on the surfaces and higher catalytic activity in the epoxidation reaction owing to the higher reactivity of the methoxy functional groups with the siloxane groups of the surface. Catalyst leaching seems not to be a pronounced problem, but significant activity losses occur after several runs, very likely due to coke formation and chemisorption of organic molecules on the surface.

Experimental Section

Synthetic Procedures

Mesoporous molecular sieves are synthesized following the procedures described earlier[9] with molar gel compositions of SiO_2 : 0.2 NaOH : 0.27 TMAOH : 0.27 CTABr : 60 H_2O for MCM-41, and 5.0 SiO_2 : 2.5 NaOH : 0.87 CTABr : 0.13 Brij30 : 400 H_2O for MCM-48 respectively. Solvents were dried by standard procedures (THF, with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under argon and kept over 4 Å molecular sieves. The homogeneous catalysts **1**–**3** were synthesized as published previously.[17]

Synthesis of Complex 1

$Mo(CO)_6$ was added to a deep orange solution of sodium (trimethoxysilylpropyl)cyclopentadienyl in 30 mL THF. After refluxing for 18 h, the obtained deep orange solution of the sodium salt, $NaMo(CO)_3C_5(CH_2)_3Si(OCH_3)_3H_4$ was cooled to room temperature and methyl iodide was then added dropwise. After stirring at room temperature for 12 h, the solvent was removed from the reaction mixture in oil pump vacuum at room temperature until a sticky, deep brown residue remained. This residue was extracted with *n*-hexane three times and the obtained orange red solution chromatographed on Florisil (60–100 mesh) with *n*-hexane as solvent. The yellow fraction was eluted with *n*-hexane and diethyl ether (1:1) and collected. After removal of all solvents, compound **1** was obtained as a brown yellow oil.

The complexes **2** and **3** were synthesized using a solution of $NaMo(CO)_3C_5H_5$ in 30 mL THF, which was treated with 3-iodopropyltrimethoxysilane or iodomethyltriethoxysilane. After stirring the reaction mixture at room temperature for 12 h, the solvent was removed in oil pump vacuum at room temperature until a sticky deep brown residue remained, the residue was extracted with *n*-hexane three times and the obtained orange red solution chromatographed on Florisil (60–100 mesh) with *n*-hexane as solvent. The yellow fraction was eluted with *n*-hexane and diethyl ether (1:1) and collected. After removal of all solvents, compounds **2** and **3** were obtained as brown yellow oils.

Grafting and Characterization Methods

Grafting experiments were carried out using standard Schlenk techniques under an argon atmosphere with the following procedure: First the mesoporous molecular sieves MCM-41/48 were pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. The activated sample was treated with 0.2 mmol of complexes **1**–**3** in 30 mL dry THF under an argon atmosphere. The mixture was stirred at 339 K for 24 h. The resulting solution was filtered off and the pale orange solid was washed repeatedly with CH_2Cl_2 until all physisorbed Cp complex was removed from the surface. The washed samples were dried under vacuum at room temperature. The materials prepared from the complexes **1**–**3** on MCM-41 and MCM-48 are designated as SM-41CpSG, SM-48CpSG, SM-41MoSG, SM-48MoSG, SM-41MoESG and SM-48MoESG, respectively.

The *in situ* grafting (Scheme 1) was carried out according to the following procedure: first the mesoporous molecular sieve (MCM-41 or MCM-48, respectively) was silylated with chloropropyltrimethoxy- and chloromethyltriethoxysilane using dry toluene (30 mL) as solvent under an argon atmosphere at 383 K for 24 h. Then excess silane was removed by filtration followed by washing several times with dichloromethane. The resulting solid was dried under vacuum at room temperature. The samples silylated with chloropropyltrimethoxysilane and chloromethyltriethoxysilane are designated as SM-41S, SM-48S, SM-41ES and SM-48ES, respectively. After drying, the silylated samples were treated with 2 mmol of $Na^+[CpMo(CO)_3]^-$ salt in 30 mL dry THF under an argon atmosphere. The mixture was again stirred for 24 h at 339 K. The *in situ* grafted sample was filtered off and the resulting orange solid was washed repeatedly with CH_2Cl_2 to remove all physisorbed CpMo salt. The washed samples were dried under vacuum at room temperature. The samples prepared by the *in situ* method are named SM-41SG, SM-48SG, SM-41ESG, and SM-48ESG.

Microanalyses were performed at the Mikroanalytisches Laboratorium of the Technische Universität München (M. Barth and co-workers). IR spectra were measured with a Unican Mattson Model 7000 FTIR spectrometer using KBr pellets. Powder XRD data were collected with a Phillips X'pert diffractometer using Cu-Kα radiation filtered by Ni. Nitrogen adsorption-desorption measurements were 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 was degassed at 723 K overnight to a residual pressure of *ca.* 10–24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the N_2 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) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron micrographs (TEM) were recorded on a JEOL JEM 2010 microscope operated at 120 kV. Thermogravimetric mass spectra analysis (TG-MS) measurements were conducted with a Netzsch TG209 system; typically about 10 mg of sample were heated from 300 to 1473 K at 10 K min^{-1} under argon. ^{29}Si CP MAS NMR spectra were recorded

at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with 5.5 μs ^{1}H 90^{0} pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded at 75.468 MHz with 2.8 μs ^{1}H 90^{0} pulses, 8 ms contact time, a spinning rate of 8 kHz and 5 s recycle delays.

Catalytic Reactions

The catalytic behaviour of the grafted samples (*ca.* 175 mg) was tested by examining the oxidation of cyclooctene (0.8020 g; 8 mmol) at 328 K in a liquid-phase batch reactor with TBHP (5.5 M in *n*-decane; 16 mmol) as the oxidizing agent. A catalyst:oxidant:substrate ratio of 0.0063 : 2 : 1 was applied. The samples were analyzed every 30 min for 4 h and the reaction was terminated after 24 h. The analyses were carried out using a gas chromatograph (HP 5890) using an FID detector. The yields and conversions were calculated according to calibration curves ($r^2 = 0.999$) determined prior to reaction course.

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