Grafting of η^5-Cp(COOMe)MoCl(CO)$_3$ on the surface of mesoporous MCM-41 and MCM-48 materials

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Abstract

η^5-Cp(COOMe)MoCl(CO)$_3$ is grafted on the surface of mesoporous MCM-41 and MCM-48 materials through available silanol groups. The structural intactness of the supporting materials is confirmed by powder XRD and N$_2$ adsorption analysis. The presence of the Mo complex on the surface is confirmed by FT-IR and elemental analysis. The catalysts are successfully applied for cyclooctene epoxidation.

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1. Introduction

Several molybdenum complexes are applied as versatile catalysts for the oxidation of organic substrates and therefore of significant current interest [1–7]. Molybdenum based catalysts are applied for the industrial epoxidation of propylene with *t*-butyl hydroperoxide (TBHP) since the late 1960s [8,9]. Thus, considerable efforts were dedicated in the following decades to the understanding of the involved catalytic reactions in order to reach even better yields and selectivities [10–26]. Recently it has been shown that Cp′Mo(CO)$_3$Cl (Cp′ = Cp or ring substituted Cp derivatives) can be used as olefin epoxidation catalyst precursors – being in situ oxidized to the Mo(VI) compounds of formulae Cp′MoO$_2$Cl and Cp′MoO(O$_2$)Cl – and present advantages over the direct application of the Mo(VI) species Cp′MoO$_2$Cl [15–17]. The carbonyl precursor of the above mentioned compounds can be stored for long times without any problems, while the oxides are somewhat more sensitive [15–25]. Both Cp′Mo(CO)$_3$R complexes (R = alkyl) and their oxidized congeners are successfully utilized as homogeneous catalyst precursors

or catalysts [15–17]. Recently we and several other groups have successfully heterogenized various siloxane functionalized Mo based catalysts and some mixed metal carbonylate salts on recently developed [26–28] mesoporous solids (MCM-41 and MCM-48) by various methodologies and found that the resulting heterogeneous materials can be utilized as active and relatively stable catalysts [29–39]. However, these organometallic compounds with siloxane functionalities are very sensitive and their handling during the heterogenization process is somewhat difficult [40].

In the present study the complex η^5-Cp(COOMe)-MoCl(CO)$_3$ (**1**) has been directly grafted by the reaction of the available silanol groups on the surfaces of the mesoporous materials (MCM-41 and MCM-48) with a –COOMe group present in complex **1**. The grafted materials were systematically characterized and applied for cyclooctene epoxidation reactions.

2. Experimental

2.1. Synthetic procedure

The following materials, colloidal silica (SiO$_2$), fumed silica (SiO$_2$), hexadecyl-trimethyl ammonium bromide

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(CTABr), polyoxyethylen(4)-laurylether (Brij-30), tetramethyl ammonium hydroxide (TMAOH, 25 wt%), and sodium hydroxide (NaOH) are used without purification for the synthesis of the mesoporous materials.

η^5-Cp(COOMe)MoCl(CO)$_3$ (**1**) is synthesized via a procedure described earlier [35]. Mesoporous molecular sieves are synthesized following published procedures [32] with molar gel compositions of 1.0 SiO$_2$:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H$_2$O for MCM-41, and 5.0 SiO$_2$:2.5 NaOH:0.87 CTABr:0.13 Brij30:400 H$_2$O for MCM-48, respectively. Solvents are dried by standard procedures (CH$_2$Cl$_2$ with CaH$_2$), 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 treated with 2 mmol of complex **1** in 30 ml dry dichloromethane under argon atmosphere. The mixture is stirred for 24 h at 339 K. The grafted samples are filtered off and the resulting pale orange solid is washed repeatedly with CH$_2$Cl$_2$ to remove all physisorbed Mo complexes. The washed samples are dried under vacuum at room temperature. The samples synthesized by MCM-41 and MCM-48 are designated as SM-41CpCOMo and SM-48CpCOMo, respectively.

2.2. Characterization methods

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). IR spectra were measured with an Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data are collected with a Phillips X'pert diffractometer using Cu Kα 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 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) are computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls.

2.3. Catalytic applications

The catalytic behaviour of the grafted samples (equivalent to 0.02 mmol of Mo, based on elemental analysis) 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 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.

3. Results and discussion

FT-IR spectra of grafted materials (SM-41CpCOMo and SM-48CpCOMo) show bands around 1206, 1060, and 794 cm^{-1}, attributable to stretching vibrations of the mesoporous framework (Si–O–Si). New weak bands around 2016 and 1956 cm^{-1} are observed for the grafted samples, and can be assigned to terminal carbonyl (CO) group vibrations of the grafted compounds. Elemental analyses (EAs) of the grafted samples show Mo loadings of 0.3 wt%, which correspond to about 1% complex loading on both SM-41CpCOMo and SM-48CpCOMo. Furthermore, the presence of equimolar amounts of Cl found by elemental analyses is evidencing that grafting occurs through the available silanol group in the mesoporous materials and the ester group (COOMe) of complex **1**. The powder XRD pattern of the parent calcined MCM-41 and MCM-48 are in full agreement with reported patterns [29–33]. Several distinct Bragg peaks are observed in the $2\theta = 2$–8° range, which can be indexed to different hkl reflections for a hexagonal symmetry (using the strongest reflection, d_{100}) and a cubic symmetry (using the strongest reflection, d_{211}), respectively. After the grafting processes the higher angle (2θ) peaks are still observed, indicating the retention of long-range hexagonal and cubic symmetry (see Fig. 1).

The low temperature N$_2$ adsorption/desorption isotherms of parent MCM-41 and MCM-48 are of type (IV) according to the IUPAC [41] and characteristic for mesoporous solids. A well-defined sharp inflection is observed
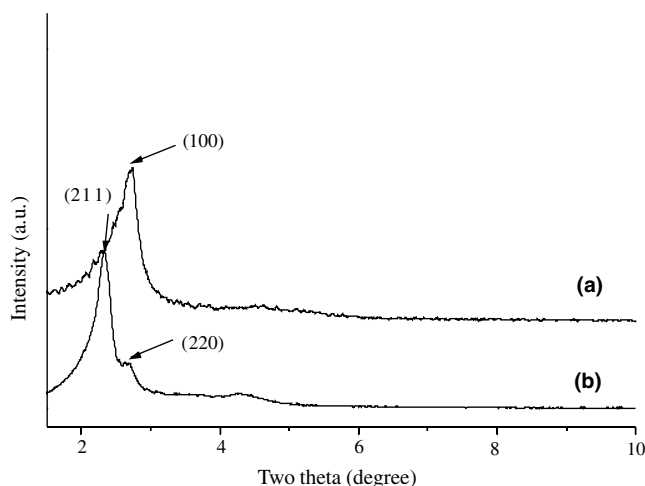

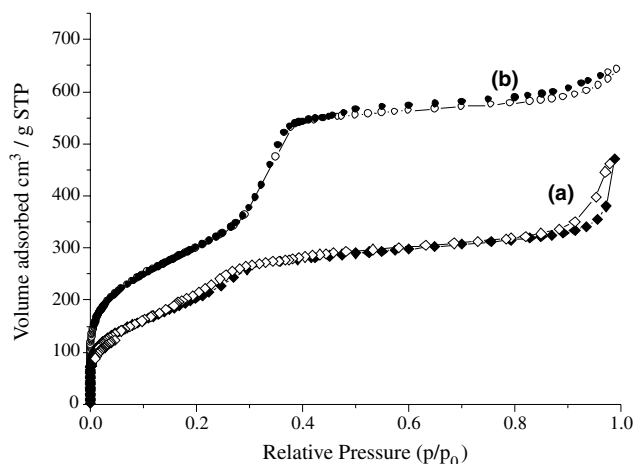Fig. 1. Powder X-ray pattern of: (a) SM-41CpCOMo and (b) SM-48CpCOMo.

Fig. 2. N$_2$ adsorption/desorption analysis of: (a) SM-41CpCOMo and (b) SM-48CpCOMo.

Table 2
Oxidation of cyclooctene over SM-41CpCOMo and SM-48CpCOMo materials in repeated runs[a]

No. of runs	SM-41CpCOMo		SM-48CpCOMo	
	Conversion (%)	Epoxide selectivity (%)[b]	Conversion (%)	Epoxide selectivity (%)[b]
1st run	58	97	64	100
2nd run	53	96	60	100
3rd run	51	89	56	96

[a] Temperature = 328 K, Time = 24 h.
[b] Cyclooctane-diol as the remaining products.

between the relative pressure (p/p_0) of 0.3–0.4 due to capillary condensation of nitrogen inside the primary mesopores. Compared to the parent mesoporous samples, the modified samples (Fig. 2) exhibit a decrease in N$_2$ uptake due to the presence of the organometallic complexes grafted on the surface of the mesoporous channels. The parent MCM-41 and MCM-48 samples exhibit narrow pore size distributions with average pore diameters of 2.7 and 2.44 nm, respectively, compared to the grafted materials SM-41CpCOMo and SM-48CpCOMo (see Table 1). These grafted materials exhibit a broader pore size distribution (1.9–2.6 nm) and display also a decrease in surface area (814–920 m^2 g^{-1}) and unit cell volume (0.8 and 0.9 m^3 g^{-1}), compared to the parent samples (MCM-41 and MCM-48), which show higher surface areas (840 and 1040 m^2 g^{-1}) and unit cell volumes (0.9 and 1.1 m^3 g^{-1}). The decrease of the unit cell parameters 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 [30–33,35–38]. However, the observed sharp reflection on the adsorption/desorption curve of the grafted samples gives strong evidence that the mesoporous structure of the support retains long-rang ordering [29–33,35–38] throughout the grafting process and that the channels remain accessible.

The oxidation of cyclooctene in the presence of the grafted samples as heterogeneous catalysts yields cyclooc-tene epoxide as the major product and a minor amount of cycloocten-diol is formed (see Table 2). The details concerning the catalytic reaction are given in the experimental part. Blank runs show that no significant amount of epoxide is formed in the absence of catalyst. The kinetics of SM-41CpCOMo and SM-48CpCOMo show high initial activity (Fig. 3), however the reaction velocity slows down during the course of the reaction. This behaviour has been assigned to the interaction of the catalyst with the by-product *tert*-butyl alcohol [30–33], which is formed during the course of the reaction from the spent oxidant TBHP. The SM-41CpCOMo and SM-48CpCOMo materials show about 58–64% cyclooctene conversion with 95–100% epoxide selectivity after 24 h reaction time. Further, SM-48CpCOMo showed marginally higher catalytic efficiency than SM-41CpCOMo. The observed higher catalytic efficiency of SM-48CpCOMo compared to SM-41CpCOMo is due to the three dimensional pore openings in the case of SM-48CpCOMo compared to one dimensional pore openings of SM-41CpCOMo. Furthermore, the catalytic activities of the present heterogeneous systems are found to be comparable or even better than those of related systems described earlier [35].

The catalysts are found to be active still after several catalytic runs, however, the catalytic activity slightly decreases during the second run. The observed small decrease in activity is very likely also due to the coordination of *tert*-butyl alcohol on the active Mo species [29–33]. In order to examine the heterogeneity of the catalyst samples, control filtrate experiments were performed. The catalytic reaction is interrupted after a 50% conversion of the substrate, the solution is filtered off at reaction temperature and the filtrate is examined for its catalytic activity. This activity,

Table 1
Textural properties of 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	0.89
SM-41CpCOMo	0.3	3.23	3.73	814	0.8
MCM-48	–	3.97	9.72	1043	1.2
SM-48CpCOMo	0.3	3.78	9.25	920	0.9

[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.
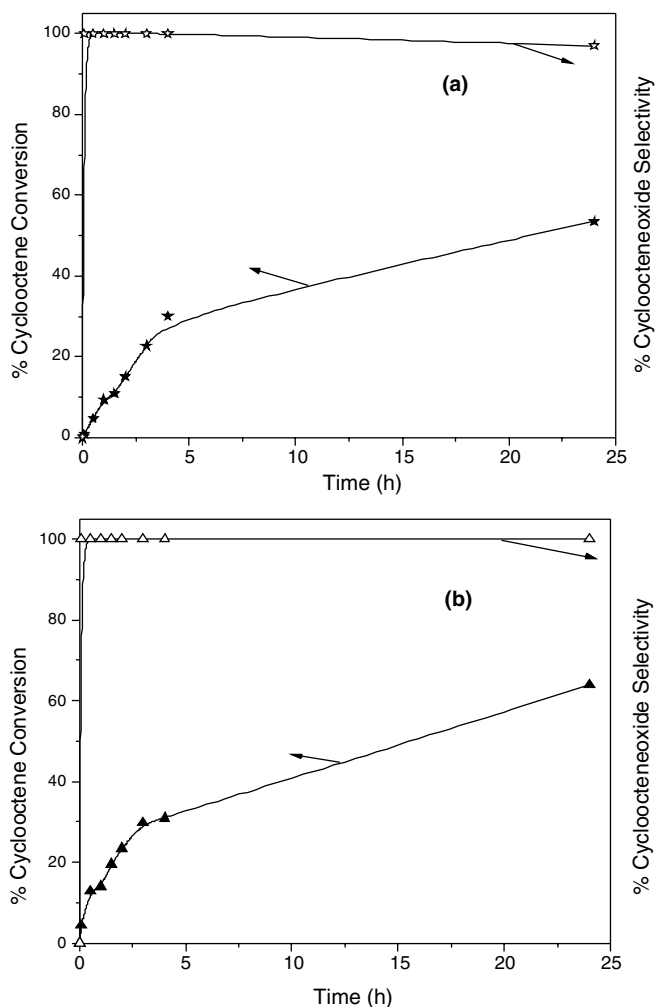
Fig. 3. Kinetics profiles of cyclooctene epoxidation over: (a) SM-41CpCOMo and (b) SM-48CpCOMo.

however, is minor (6–8% product yield), thus demonstrating that catalyst leaching is of minor importance. This observation is further confirmed by elemental analyses of the used catalysts, which shows ca. 0.25 wt% of Mo remaining in both materials.

4. Conclusion

η^5-Cp(COOMe)MoCl(CO)$_3$ is successfully heterogenized on the surface of MCM-41 and MCM-48 materials through available silanol groups. The grafted materials retain long-range ordering and the catalysts are active for cyclooctene epoxidation. Leaching is minor and the catalysts are reusable for several runs without much change in catalytic activity.

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