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Mesoporous MCM-41 Materials Modified with Oxodiperoxo Molybdenum Complexes: Efficient Catalysts for the Epoxidation of Cyclooctene

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An organic−inorganic hybrid heterogeneous catalyst system was synthesized by covalently anchoring oxodiperoxo molybdenum complexes $[(L{-}L)MoO(O_2)_2]$ (L−L = (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide) onto the mesoporous silica MCM-41 (Si−MCM-41) and aluminosilicate MCM-41 (Al−MCM-41) materials. Characterization of the functionalized materials by powder X-ray diffraction (XRD), N_2 adsorption, and solid-state CP-MAS NMR spectroscopy (^{13}C and ^{29}Si) demonstrates that the oxodiperoxo molybdenum complexes are grafted successfully into the mesoporous MCM-41 materials. The structures of both the mesoporous materials and the molybdenum complex are preserved during the grafting process. All the hybrid materials are active and truly heterogeneous catalysts for the liquid-phase epoxidation of cyclooctene with ^tBuOOH as the oxygen source. The catalytic properties (activity and recyclability) of the supported materials can be improved by their further silylation using Me_3SiCl, which can be explained by the increase of hydrophobicity of the mesoporous surface due to removal of residual Si−OH groups. The modified aluminosilicate MCM-41 materials show higher activities than the corresponding siliceous materials, which might be due to the incorporation of Lewis acidic centers.

1. Introduction

The discovery of mesoporous MCM-41 materials[1,2] has given an enormous stimulus to research in heterogeneous catalysis, selective adsorption, and novel functional materials.[3,4] This is due to their outstanding advantages such as extremely high surface areas, combined with large and defined pore sizes of mesoporous materials, compared with other solid supports. The presence of a large number of silanol (Si−OH) groups on the inner surface provides the opportunity to support or anchor various functional groups by different postsynthetic modification methods, such as silylation, esterification, and chemical depositions.[4−7] Among them, the surface silylation reaction is becoming the most popular way to alter the surface reactivity or to tune other surface properties such as polarity, hydrophobicity, or hydrophilicity of such materials.[6,7]

Recently, some attempts to prepare molybdenum modified mesoporous materials have been published[8,9] since homogeneous molybdenum complexes have been widely reported as highly active catalysts for the liquid-phase epoxidation of olefins.[10−13] Rocha et al. synthesized modified MCM-41 and MCM-48 materials by grafting MoO_2X_2 (X = Cl, Br) and found that these materials are active in the epoxidation of cyclooctene.[8] Gonçalves et al. described another attempt to graft 2,2′-bipyridine covalently to MCM-41 and used the corresponding MoO_2Cl_2 supported material as an epoxidation catalyst.[9] However, in both publications, the authors confirmed that at least a part of the observed activity is due to leached molybdenum species in solution. In fact, leaching is a particular problem for heterogeneous catalysts in liquid-phase oxidation catalysis owing to the strong complexing and solvolytic properties of oxidants and products.[14]

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Very recently, we reported a hybrid heterogeneous catalyst system,[15] which is synthesized by covalently anchoring oxodiperoxo molybdenum chelate complexes onto the surface of a mesoporous Si−MCM-41 material. This material is highly active and truly heterogeneous for the liquid-phase epoxidation of cyclooctene with ^{t}BuOOH as the oxygen source. The excellent stability of these catalysts can be attributed to the covalent grafting between the organic ligand system and the inorganic mesoporous material, the mild reaction conditions during the generation of the grafted system, and the strong binding between the $MoO(O_2)_2$ unit and the chelating ligand. The latter feature was examined in a series of experiments with related homogeneous oxodiperoxo molybdenum(VI) catalysts.[12,13]

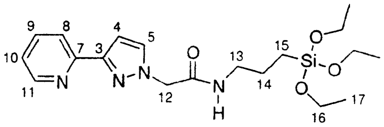
In the present work, two different mesoporous materials, Si−MCM-41 and Al−MCM-41, were used to anchor catalytically active oxodiperoxo molybdenum sites via the silylated ligand (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide. Further surface silylation with Me_3SiCl was carried out in a postsynthetic procedure with the ligand-supported mesoporous siliceous or aluminosilicate materials in order to improve the catalytic properties by changing the surface properties. Different methods of characterization, such as elemental analysis, powder X-ray diffraction (XRD), N_2 adsorption, and solid-state CP-MAS NMR spectroscopy (^{13}C and ^{29}Si) were applied to obtain information about structural features, as well as surface information. Additionally, the influence of the surface modification with Me_3SiCl and the change of the polarity (Lewis acid−base) of the framework on the catalytic properties (activity, stability, and recyclability) were investigated for the liquid-phase epoxidation of cyclooctene with ^{t}BuOOH.

2. Experimental Section

2.1. Synthetic Procedures. *Mesoporous Si−MCM-41 (**Si-1**) and Al−MCM-41 (Si/Al = 40) (**Al-1**).* Mesoporous **Si-1** and **Al-1** were prepared as described in the literature.[16] A typical procedure was as follows: 15.46 g of an aqueous solution of ethylamine (70%, 240 mmol ethylamine) were added to a stirred solution of distilled water (175 mL), 5.10 g (14 mmol) of cetyltrimethylammonium bromide (CTAB), and 0.34 g (2.5 mmol) of $AlCl_3 \cdot 6H_2O$ (only in the case of **Al-1**). After this, 20.80 g (100 mmol) of tetraethyl orthosilicate (TEOS) was added dropwise, leading to a composition of 1.0:x:0.14:2.4:100 SiO_2/Al_2O_3/CTAB/$EtNH_2$/H_2O ($x = 0$ for **Si-1** or 0.125 for **Al-1**). The reaction mixture was stirred for further 4 h at room temperature before being heated to 110 °C for 1−3 days. The product was recovered by filtration and washed with distilled water, dried at ambient temperature, and then calcined at 580 °C in air for 7 h.

*(3-Triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (**3**).* [3-(2-pyridyl)-1-pyrazolyl]aceticacid ethylester (**2**)[12a,17] (0.93 g, 4.02 mmol) was mixed with 0.89 g (4.02 mmol) of 3-triethoxysilylpropylamine and heated to 150 °C for 2 h under an atmosphere of argon. After this, all volatiles were removed in vacuum, resulting in **3** as an oily residue in quantitative yield. The numbering scheme for NMR spectra assignments is given in Scheme 1. ^{1}H NMR (250.13 MHz, 25 °C, $CDCl_3$) δ 8.49 (d, J 5.0 Hz, H^{11}), 7.80 (d, J 7.9 Hz, H^8), 7.57 (dt, J 7.9 Hz, J 1.8 Hz, H^9), 7.47 (d, J 2.4 Hz, H^5), 7.09 (m, H^{10}), 6.82 (d, H^4), 6.65 (br, NH), 4.78 (s, H^{12}), 3.62 (q, J 7.0 Hz, H^{16}), 3.13 (q, J 6.2 Hz, H^{13}), 1.45 (m, H^{14}), 1.04 (t, H^{17}), 0.38 (m, H^{15}). $^{13}C\{^1H\}$ NMR (62.89 MHz, 25 °C, $CDCl_3$) δ 166.7 (C=O), 152.7 (C^7), 151.2 (C^3), 148.9 (C^{11}), 136.1 (C^9), 132.2 (C^5), 122.2 (C^{10}), 119.7 (C^8), 104.9 (C^4), 57.7 (C^{16}), 54.8 (C^{12}), 41.3 (C^{13}), 23.3 (C^{14}), 17.8 (C^{17}), 7.0 (C^{15}).

Scheme 1. Assignment of the NMR Spectra for Ligand 3 and Free Complex 4



*Oxodiperoxo{(3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide} Molybdenum(VI) (**4**).* Compound **3** (0.61 g, 1.50 mmol) and 0.48 g (1.50 mmol) of $MoO(O_2)_2 \cdot (DMF)_2$[18] were dissolved in 30 mL of dry $CHCl_3$ and stirred for 4 h at room temperature. The solvent was removed in vacuum, and the resulting yellow solid **4** was washed with diethyl ether and dried in a vacuum. Yield: 90%. ^{1}H NMR (250.13 MHz, 25 °C, $CDCl_3$) δ 9.32 (d, J 5.0 Hz, H^{11}), 8.28 (t, J 7.8 Hz, H^9), 7.97 (d, H^8), 7.71 (t, J 7.8 Hz, H^{10}), 7.57 (d, J 2.6 Hz, H^5), 6.91 (br, NH), 6.74 (d, H^4), 4.75 (s, H^{12}), 3.77 (q, J 7.0 Hz, H^{16}), 3.17 (q, J 6.0 Hz, H^{13}), 1.60 (m, H^{14}), 1.18 (t, H^{17}), 0.57 (m, H^{15}). $^{13}C\{^1H\}$ NMR (62.89 MHz, 25 °C, CD_3CN) δ 165.9 (C=O), 155.4 (C^{11}), 151.4 (C^7), 150.2 (C^3), 144.8 (C^9), 136.4 (C^5), 127.1 (C^{10}), 124.8 (C^8), 105.9 (C^4), 59.0 (C^{16}), 54.8 (C^{12}), 42.8 (C^{13}), 23.6 (C^{14}), 18.7 (C^{17}), 8.1 (C^{15}).

*Preparation of the Supported Ligand/Si−MCM-41 (**Si-5**) and Ligand/Al−MCM-41 (**Al-5**) Materials.* A 0.130 g portion of **3** (0.32 mmol) dissolved in 4 mL of dry chloroform was added to a suspension of 0.70 g of the mesoporous support **Si-1** (or **Al-1**) in 40 mL of dry toluene. The mixture was stirred under an atmosphere of argon for 9 h at 100 °C. Then the solids were filtered and washed by $CHCl_3$, and dried in vacuum at 160 °C to obtain the hybrid materials **Si-5** and **Al-5**. Anal. Found in **Si-5**: C, 7.58; H, 1.37; N, 2.04. Anal. Found in **Al-5**: C, 7.21; H, 1.52; N, 2.23.

*Silylation of **Si-5** and **Al-5** To Prepare **Si-6** and **Al-6**.* In a typical silylation experiment, 0.70 g of a dried and degassed sample of **Si-5** or **Al-5** was soaked in a solution of 30 mL of toluene with 1.00 g (9.2 mmol) of Me_3SiCl at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone and diethyl ether, and dried at 150 °C to obtain **Si-6** and **Al-6**, respectively. Anal. Found in **Si-6**: C, 9.94; H, 1.85; N, 1.75. Anal. Found in **Al-6**: C, 9.61; H, 2.00; N, 2.03.

*Preparation of the Oxodiperoxo Molybdenum Modified Mesoporous MCM-41 Materials **Si-7** and **Al-7**.* Compound **Si-5** or **Al-5** (0.70 g) was stirred with 0.096 g (0.30 mmol) of $[MoO(O_2)_2 \cdot (DMF)_2]$ dissolved in 60 mL of $CHCl_3$ at room temperature for 24 h. The resulting samples were filtered, Soxhlet-extracted with $CHCl_3$ to remove untethered species, and dried in vacuum. Anal. Found in **Si-7**: C, 6.58; H, 1.44; N, 1.89. Anal. Found in **Al-7**: C, 7.13; H, 1.59; N, 1.97.

*Preparation of the Silylated Oxodiperoxo Molybdenum Modified Mesoporous MCM-41 Materials **Si-8** and **Al-8**.* **Si-8** and **Al-8** were obtained from the silylated precursors **Si-6** and **Al-6**, respectively, using the same procedure as described above. Anal. Found in **Si-8**: C, 9.53; H, 1.85; N, 1.72. Anal. Found in **Al-8**: C, 8.58; H, 1.81; N, 1.77.

The loading of molybdenum in all the four samples is 3.3 wt %, which can be calculated according to the amount of dissolved $[MoO(O_2)_2 \cdot (DMF)_2]$, because the bright yellow chloroform solution (originating from the Mo complex) turned to colorless after the addition and filtration of the solid support. This means that all molybdenum species underwent coordination with the supported chelate ligands.

2.2. Characterization of the Catalysts. XRD measurements were performed with a SEIFERT-FPM XRD7 diffractometer with Cu Kα radiation at 40 kV and 36 mA. Nitrogen

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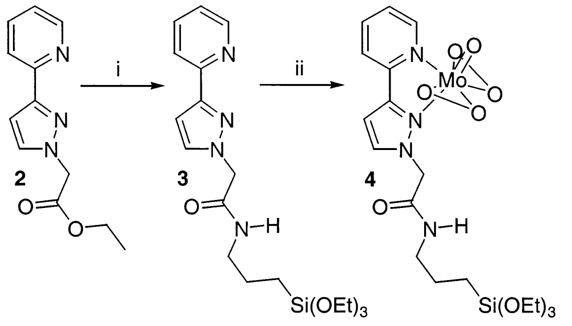
adsorption/desorption isotherms were measured at the liquid nitrogen temperature, using a SORPTOMATIC 1990 analyzer. Samples were degassed at 413 K overnight before measurements. Specific surface areas were calculated using the BET model. Pore volumes were estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the BJH model. Solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra were recorded at 100.61 and 79.49 MHz, respectively, using a Bruker AVANCE 400 spectrometer.

2.3. Catalytic Reactions. The catalytic epoxidation of cyclooctene was carried out in a two-necked 100-mL flask equipped with a reflux condenser and a Quickfit septum adapter. In the standard procedure, 1.00 g of cyclooctene (9.07 mmol), 1.00 g of dibutyl ether (7.75 mmol, internal standard), 100 mg of the solid catalyst, and 25 mL of $CHCl_3$ were added to the flask. The suspension was stirred and heated to reflux temperature (61 °C), then 1.70 mL of a 5.5 M solution of ^tBuOOH in decane was added to start the reaction. The course of the reaction was monitored by quantitative GC analysis. The catalytic activity for the epoxidation of cyclooctene was evaluated by the conversion of cyclooctene to cyclooctene epoxide.

3. Results and Discussion

3.1. Synthesis and Characterization. Ligand **3** was obtained as outlined in Scheme 2 according to a procedure published for octadecyl[3-(2-pyridyl)-1-pyrazolyl]acetamide by simply heating the ester **2** with one equivalent of 3-triethoxysilylpropylamine.[12a] It reacts with $MoO(O_2)_2·(DMF)_2$ in dry $CHCl_3$ to give the free complex **4**, which was synthesized to provide spectroscopic data (IR and NMR) for comparison with the supported mesoporous materials.

Scheme 2[a]



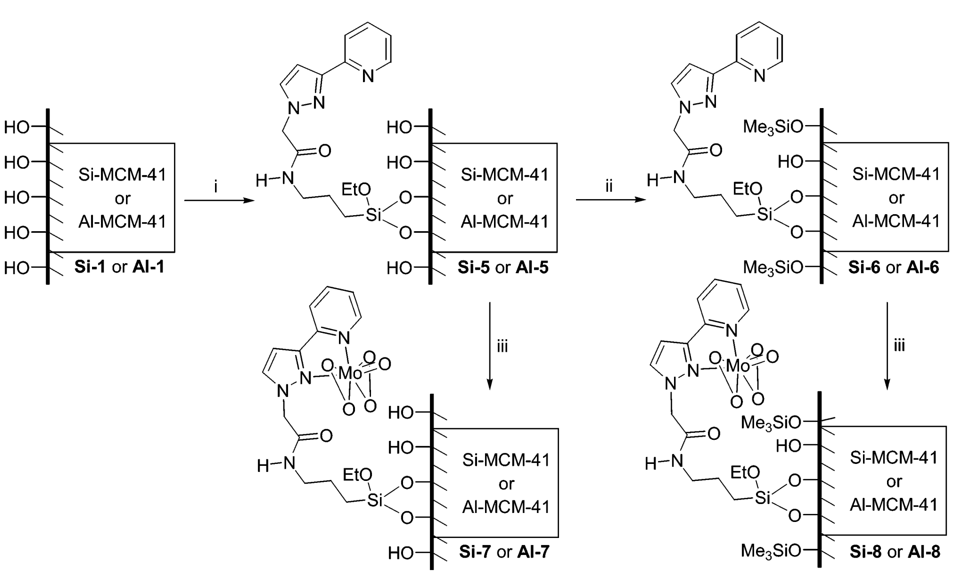
[a] (i) $H_2N(CH_2)_3Si(OEt)_3$, 2 h, 150 °C; (ii) $CHCl_3$, $MoO(O_2)_2·(DMF)_2$, 24 h, RT.

The oxodiperoxo molybdenum modified mesoporous MCM-41 materials were synthesized as outlined in Scheme 3. Postsynthetic silylation using Me_3SiCl was carried out to remove the residual silanol groups on the surface of the mesoporous MCM-41 material, which are supposed to be unfavorable for the catalytic reaction. Therefore, modification of MCM-41 by silylation with Me_3SiCl will make the surface more hydrophobic. Recently Zhao and Lu reported that the adsorption characteristics of MCM-41 for polar molecules greatly depend on the concentrations of surface silanol groups.[7] Additionally, Tatsumi et al. showed that trimethylsilylation of MCM-41 and MCM-48 improves their stability against moisture and mechanical compression.[19]

Figure 1 shows the XRD patterns for the parent siliceous MCM-41 material **Si-1** and the modified materials **Si-7** and **Si-8**. **Si-1** is a well-ordered mesoporous phase which can be indexed according to a hexagonal lattice characteristic of MCM-41.[1,2] For **Si-7**, the relative intensities of higher angles peaks decreased after introduction of the molybdenum complex. Silylation with Me_3SiCl (**Si-8**) leads to a further considerable decrease in the intensities of these reflections, but the main reflections of the XRD pattern can still be observed. According to related references,[20−22] the intensity reduction may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicate that the structure of the mesoporous materials remains intact through the grafting procedure. Similar results have also been observed for the modified aluminosilicate MCM-41 systems (not shown here).

Figure 2A shows the N_2 isotherms of **Si-1** and the ligand modified samples **Si-5** and **Si-6** recorded at 77 K. The Mo-containing samples were not tested by this

Scheme 3[a]



[a] (i) Ligand **3**, Toluene, 9 h, 100 °C; (ii) Me_3SiCl, 24 h, RT; (iii) $CHCl_3$, $MoO(O_2)_2·(DMF)_2$, 24 h, RT.

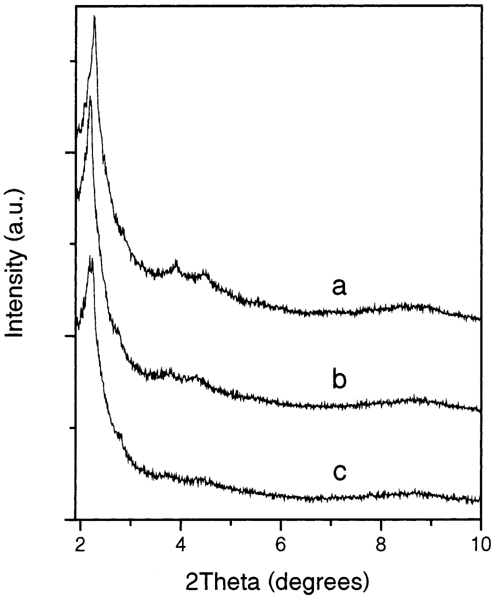


Figure 1. Powder XRD patterns of **Si-1** (a), **Si-7** (b), and **Si-8** (c).

means because the outgassing temperature of 413 K, applied before the N_2 adsorption measurements, will lead to a decomposition of the peroxo complexes. **Si-1** gave a type IV isotherm[23] (definition by IUPAC) with a small hysteresis, which is characteristic for mesoporous materials possessing pore diameters between 2 and 50 nm. A sharp increase in the adsorption of N_2 between the relative pressures of 0.3 and 0.4 can be assigned to capillary condensation.[7] The hysteresis above the relative pressures of 0.4 can be attributed to the capillary condensation within interparticles and/or some impurity phases.[7,24,25] Compared to **Si-1**, the modified samples **Si-5** and **Si-6** exhibit a decreased uptake of N_2 owing to the incorporation of the ligand (**Si-5**) and the further silylation with Me_3SiCl (**Si-6**). The ligand modified Al−MCM-41 samples show results similar to those of the corresponding siliceous materials (Figure 2B). From Figure 2 it can be also seen that the parent solids **Si-1** and **Al-1** exhibit narrow pore size distributions with average pore diameters of about 2.7 nm. But for the modified materials, broad and lower pore size distributions were obtained, which might imply that the chelating ligand and the Me_3Si- groups are not uniformly distributed through the MCM-41 channel surface in these samples. It was reported that organic groups in a grafted mesoporous sample are mainly located on internal surfaces close to the pore windows.[21]

The BET specific surface areas of the two parent materials Si−MCM-41 (**Si-1**) and Al−MCM-41 (**Al-1**) were calculated to 947 and 1018 m^2g^{-1}, respectively (Table 1). The ligand modified samples obviously exhibit lower specific surfaces than the parent solids due to the introduction of the organic moieties (ligands and/or Me_3-Si groups), which is also responsible for a reduction of pore volumes and pore diameters (Table 1).

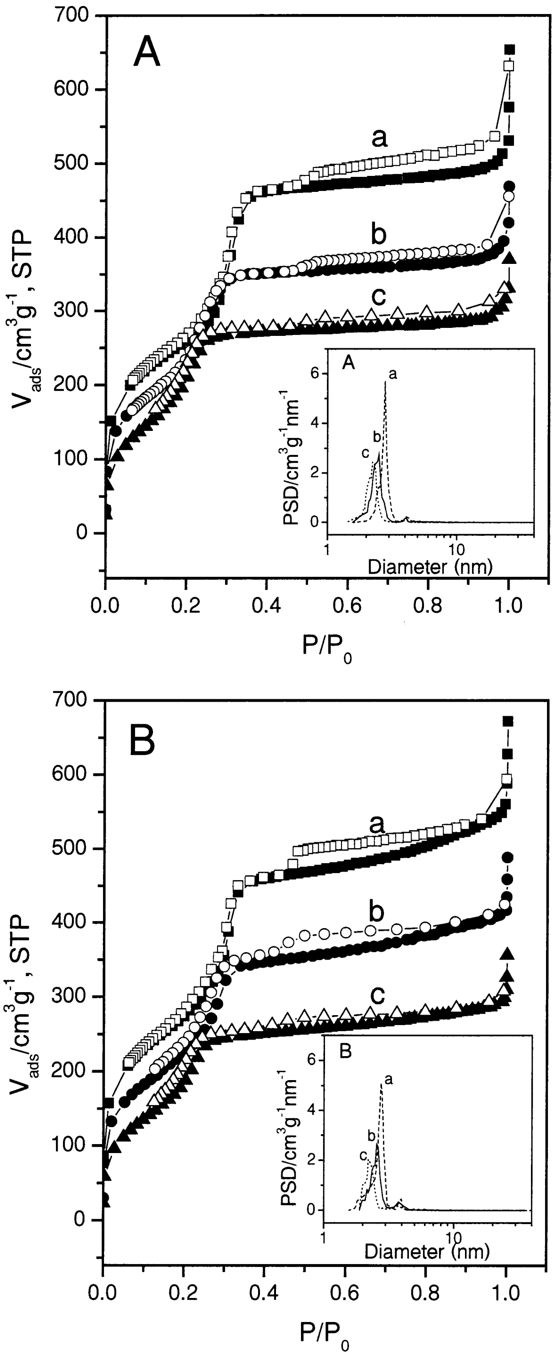


Figure 2. N_2 adsorption−desorption isotherms at 77 K and pore size distribution profiles (inset) of various materials. A: **Si-1** (a); **Si-5** (b); **Si-6** (c). B: **Al-1** (a); **Al-5** (b); **Al-6** (c).

The success of the synthesis of Mo-containing mesoporous MCM-41 materials was confirmed by ^{13}C CP-MAS NMR spectroscopy (Figure 3). **Si-7** presents a spectrum similar to that of the free complex **4** (dashed lines giving relative intensities). The resonances corresponding to the two different carbon atoms of the ethoxide groups (δ = 57.7 and 14.9) are decreased in intensity compared to those of **4**, which suggests that a condensation reaction to form covalent Si−O−Si cou-

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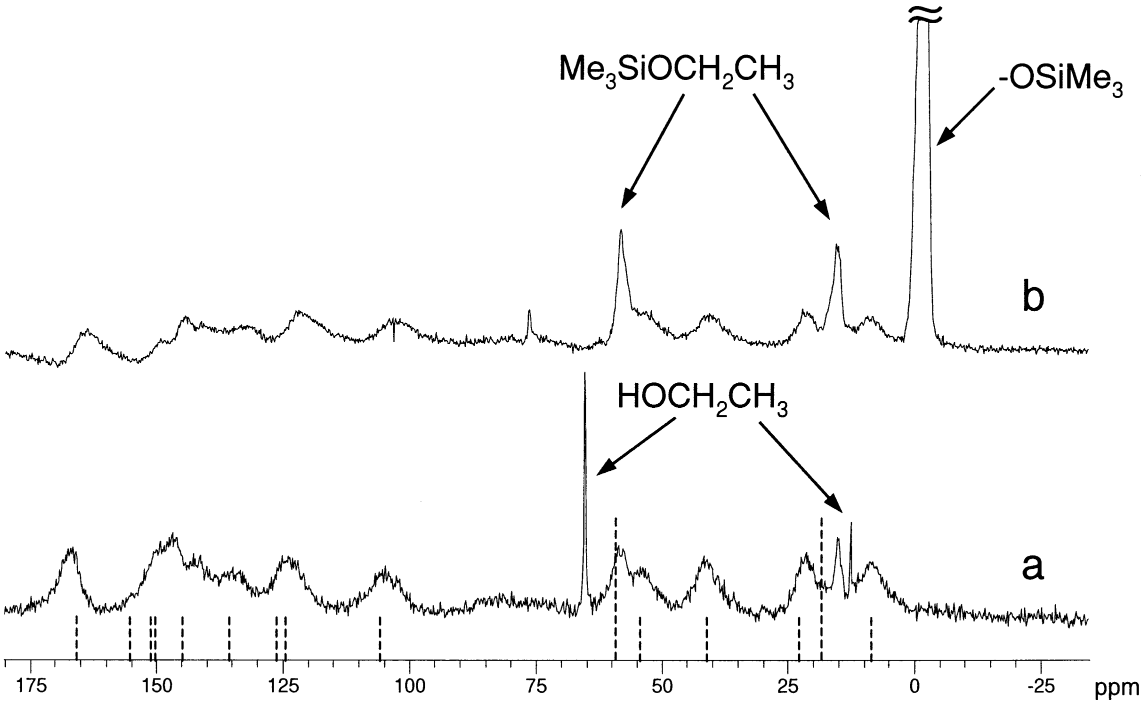

Figure 3. ^{13}C CP-MAS NMR of the modified mesoporous materials **Si-7** (a) and **Si-8** (b) compared with the resonances of the free complex **4** (dashed lines give relative intensities).

Table 1. Textural Parameters of Parent MCM-41 and Ligand Modified Materials from N_2 Isotherms at 77 K

sample	BET surface area (m^2/g)	pore vol (mL/g)	BJH pore diameter (nm)
Si-1	947	1.06	2.7
Si-5	842	0.81	2.5
Si-6	729	0.51	2.2
Al-1	1018	1.06	2.7
Al-5	854	0.71	2.5
Al-6	663	0.51	2.2

pling between the chelating ligand and the surface silanol groups of MCM-41 has occurred during the ligand grafting process. Additionally, two sharp signals at 65.3 and 12.5 ppm can be assigned to free ethanol formed as a side product of this reaction. **Si-8** shows nearly the same spectrum suggesting that the structure of the ligand system is preserved after silylation of unreacted Si−OH groups with Me_3SiCl. Besides, a very strong resonance at −1.9 ppm can be assigned to the methyl groups of the introduced Me_3Si moieties.[26] The resonances corresponding to free ethanol have disappeared, while two strong peaks appearing at 58.5 and 15.5 ppm (overlapping with the ethoxide groups of ligand **3**) can be attributed to the ethoxide groups of $Me_3Si-OC_2H_5$, formed by the reaction between Me_3SiCl and free ethanol on the surface of the mesoporous material. A small resonance at 76.6 ppm originates from traces of the solvent $CHCl_3$.

^{29}Si CP-MAS NMR spectra provide direct evidence for the incorporation of the covalently linked organic system (Figure 4). The spectrum of the unmodified mesoporous MCM-41 support **Si-1** shows three signals at −110, −101, and −92 ppm corresponding to Q^4, Q^3, and Q^2 species of the silica framework [$Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2-4$].[7,26] The Q^3 sites are associated with isolated Si−OH groups, and the Q^2 sites correspond to geminal silandiols. For the modified sample **Si-7**, three additional broad and overlapping signals appear at −67, −58, and −49 ppm, which can be assigned to T^3, T^2, and T^1 organosilica species [$T^m = RSi(OSi)_m(OEt)_{3-m}$, $m = 1-3$], respectively,[8] with T^2 as the major system. Parallely, the relative intensity of the Q^2 resonances decreases with a slight increase of Q^4. For **Si-8**, grafting of the trimethylsilane groups to MCM-41 further decreases the intensity of the Q^2 resonances (almost to the detection limit) and drastically increases the intensity of the Q^4 silicon atoms, while a sharp peak at 13 ppm can be assigned to the silicon nuclei of the trimethylsilyl (Me_3Si-) groups. Changes in the relative intensities of the Q^4, Q^3, and Q^2 signals can be explained by the redistribution of the silicon sites during surface silylation.[7] The Al-containing mesoporous materials (**Al-1**, **Al-7**, and **Al-8**) show ^{29}Si CP-MAS spectra very similar to those of the corresponding siliceous materials (not shown here).

3.2. Catalytic Properties in Epoxidation of Cyclooctene. The modified Mo-containing MCM-41 materials were tested as catalysts for the epoxidation of cyclooctene with ^tBuOOH as the oxygen source at a reaction temperature of 61 °C (Figure 5). All the samples showed good activities, and high selectivities (nearly 100%) to cyclooctene epoxide. These results are consistent with the homogeneous system we previously reported,[13] which indicates that the coordinative environment surrounding the active Mo species in the modified materials should be analogous to that of the homogeneous complexes. Under the reaction conditions applied, **Si-8** showed higher reaction rates than **Si-7** although the loading with active molybdenum sites is the same. Similar results were also found for the Al-containing mesoporous samples, with **Al-8** showing higher catalytic activity than **Al-7**.

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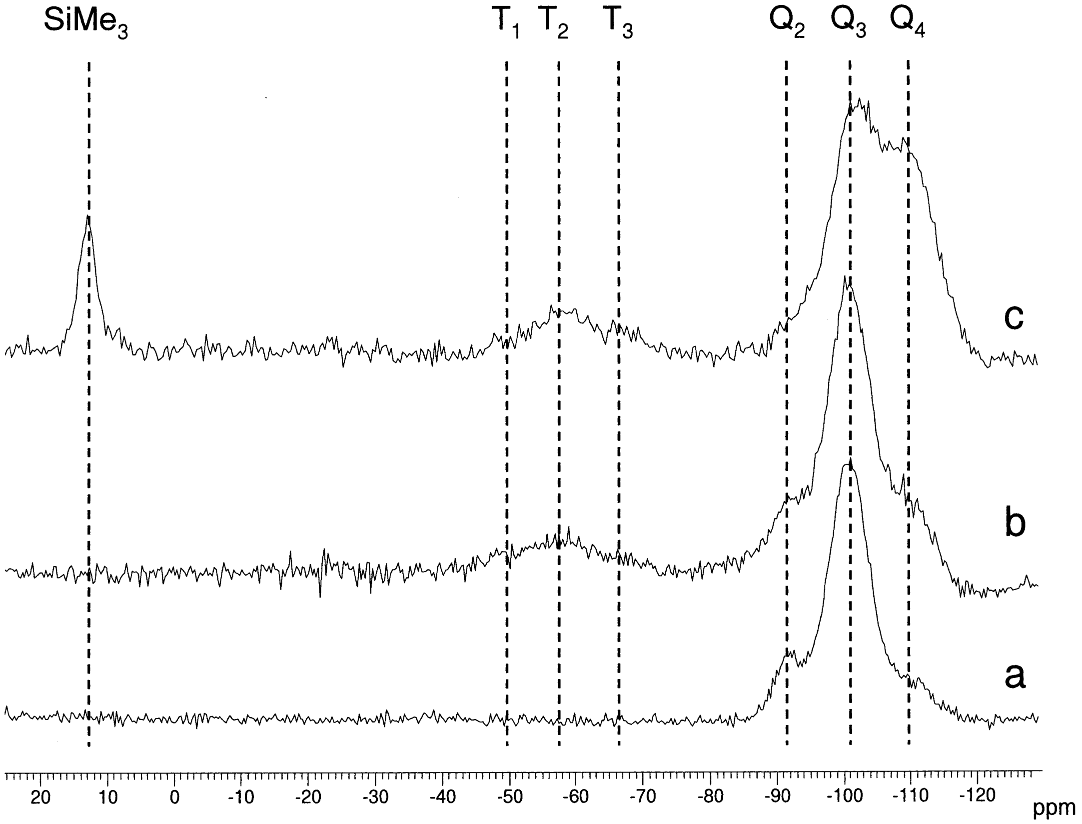

Figure 4. ^{29}Si CP-MAS NMR spectra of **Si-1** (a) and the modified samples **Si-7** (b) and **Si-8** (c).

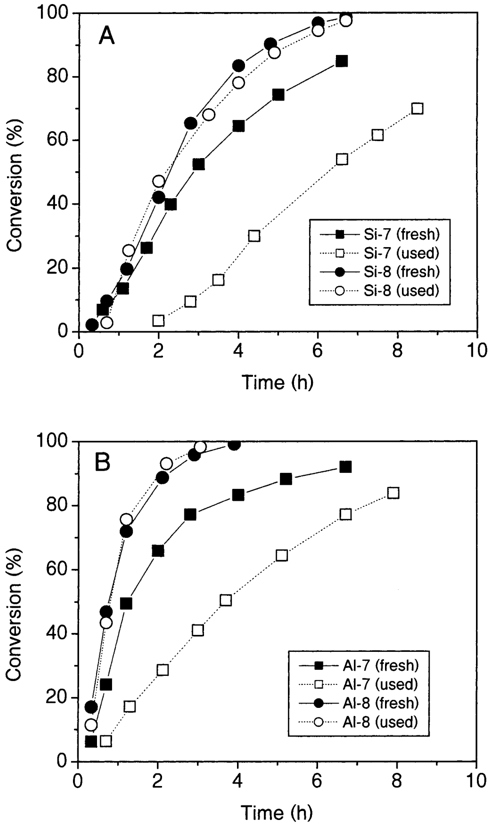

Figure 5. Kinetic profiles of epoxidation of cyclooctene with ^{t}BuOOH over various catalysts.

The recyclability of the modified catalysts was examined by reusing them in a second reaction run. Before reuse, the catalyst was separated from the reaction mixture by filtration at the reaction temperature, washed with $CHCl_3$, and dried at room temperature. For the recycled catalysts **Si-7** and **Al-7**, the induction period, already observed in the first run, increased obviously while the reaction rate decreased slightly compared with that of the fresh samples. Interestingly, the catalytic activities, as well as the induction periods, of recycled **Si-8** and **Al-8** did not change significantly in the second run indicating the excellent stability and recyclability of these systems.

The results presented above suggest that the activity and recyclability of the modified mesoporous material can clearly be improved by decrease of the number of surface Si−OH groups using Me_3SiCl as the silylating agent. As only a small part of the Si−OH groups are consumed during the introduction of the ligand system, the remaining Si−OH groups will provide centers for the adsorption of organic compounds (^{t}BuOOH, ^{t}BuOH, epoxide) by hydrogen bonding, which will hinder the diffusion to and away from the catalytically active centers in the mesoporous cavities and therefore decrease the overall activity of the catalyst. Our NMR spectroscopic investigations prove that reacting the surface with Me_3SiCl converts quite a part of the Si−OH groups into Si−O−$SiMe_3$ groups and therefore increases the hydrophobicity, which will reduce adsorption effects.

It should be pointed out here that the Al-containing catalysts **Al-7** and **Al-8** show higher activities than the corresponding neat siliceous samples **Si-7** and **Si-8**. This seems to be in contrast to the increase of activity by silylation of surface Si−OH groups, since it is known that the implementation of Al into the silicate framework increases both Brønsted and Lewis acidic sites in the surface. Besides, a direct calcination in air can partially dealuminate the mesoporous sample, then create new Lewis acidic sites due to the formation of extraframework Al.[16,27−30] Therefore, in our opinion there are at least two possible explanations for this feature: on one hand, Al sites near the complex could activate ^{t}BuOOH for proton transfer to a $Mo(O_2)$ unit, which we proved to be the first step in the activation of the organo peroxide.[13c] On the other hand, a Lewis acidic site in close proximity to the tethered catalyst could undergo coordination to the carbonyl group of the amide fragment. This would reduce the donor strength of the pyrazole molybdenum bond and lead to an increase of catalytic activity.[12a,13a]

As reported previously,[15] our modified materials showed very high stability against leaching of the active species into the liquid phase under the given reactive conditions. This feature, which is important for a heterogeneous oxidation catalyst system, is mainly caused by the relatively strong interaction between the chelating ligand and the molybdenum center and to the covalent grafting between the organic ligand system and the inorganic mesoporous material. It is known from heterogenized chromium, vanadium, and molybdenum catalysts bearing monodentate ligands that they undergo leaching of the active species into solution, especially in the presence of protic agents such as alcohols or organo peroxides.[14] We therefore focused on stable chelate complexes of the type $(L{-}L)MoO(O_2)_2$ bearing bidentate 2-(1-alkyl-3-pyrazolyl)pyridine ligands L−L, which we have investigated in detail as catalysts in solution and from which we have an almost complete mechanistic insight of the oxygen transfer process.[12,13] From our data it is probable that surface modification by Me_3SiCl should have an additional positive influence on the stability against leaching.

In addition to ^{t}BuOOH, H_2O_2 can be used as the oxygen source for the epoxidation of cyclooctene. However, the reaction rates measured under identical conditions are lower than those with ^{t}BuOOH (about 34% conversion in 15 h), while the selectivity for the epoxide does not change at all. An analogous behavior was observed when pyrazolylpyridine oxodiperoxo molybdenum complexes are applied in homogeneous solution.[12a] At present, we are carrying out further work on the catalytic oxidiation properties (activity, stability, recyclability, etc.) of our compounds with H_2O_2.

4. Conclusions

Our work presents a successful example of an active, truly heterogeneous modified mesoporous MCM-41 catalyst for olefin epoxidation obtained by covalent grafting of an oxodiperoxo molybdenum chelate complex. The excellent stability of these catalysts can be attributed to the covalent grafting between the organic ligand system and the inorganic mesoporous material, to the mild reaction conditions during the generation of the grafted system, and to the strong binding between $MoO(O_2)_2$ unit and the chelating ligand.

The catalytic properties (activity and recyclability) of the supported materials can be improved by further silylation with Me_3SiCl to remove residual Si−OH groups from the mesoporous surface. Modified aluminosilicate MCM-41 materials show better activity than the corresponding siliceous materials, which might be due to the higher Lewis acidity of Al−MCM-41 caused by the incorporation of the aluminum into the mesoporous material. Further work may be required to test the catalytic properties of these modified materials for other olefins. Also, characterization work on the surface properties (hydrophobicity and polarity) of these materials is underway in order to get a clear picture of the relationship with the catalytic properties.

The presented method also provides a general approach to the synthesis of a large family of supported heterogeneous catalysts containing N,N′-chelating ligands. We believe that, besides this oxodiperoxo Mo species, other metal species can be introduced into these hybrid materials for special application in catalysis or in the material field.

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Note Added after ASAP

This paper was released ASAP on 4/29/03 with an error in Schemes 2 and 3. It was reposted on 5/08/03 with the correct structures in these schemes and with the reaction conditions moved to scheme footnotes.

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