Hybrid Mesoporous Materials with a Uniform Ligand Distribution: Synthesis, Characterization, and Application in Epoxidation Catalysis

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A novel mesoporous MCM-41-type of hybrid material was synthesized by co-condensation of tetraethyl orthosilicate and the chelate ligand (3-trimethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (**1**) in the presence of cetyltrimethylammonium bromide as template. Surfactant extraction produced hybrid mesoporous materials with uniform mesoscale channels, large pore volumes, and high specific surface areas. The preservation of the chelate ligand structure during the hydrothermal synthesis and the acid extraction process was confirmed by ^{13}C CP-MAS NMR spectroscopy. Solid epoxidation catalysts can be obtained by introducing oxodiperoxomolybdenum species $MoO(O_2)_2$ into the hybrid materials via a ligand exchange reaction. All molybdenum-containing catalysts showed high activity for the liquid-phase epoxidation of cyclooctene with ^tBuOOH and stability against leaching of active molybdenum species. The excellent stability of these catalysts indicated that almost all the incorporated chelate ligands are chemically accessible for the coordination of the catalytically active $MoO(O_2)_2$ moieties.

Introduction

Due to the outstanding properties of mesoporous materials such as MCM-41,[1,2] such highly ordered silicas have widely been used as supports for catalytically active sites.[3] Simple impregnation from solution or deposition by (MO)CVD processes are just two methods for introducing naked metal ions or clusters to the surface. However, structurally well-defined catalysts are only rarely accessible this way. The search for mechanistic linkages between heterogeneous and homogeneous catalysis has thus enforced investigations on how to generate catalytically active sites in a defined environment on a solid support. This is possible by covalently grafting catalysts developed from homogeneous systems to the surface. Again mesoporous materials are an excellent choice for such experiments, since they offer not only extremely high specific surface areas, large and defined pore sizes, defined surface acidity, and excellent mechanical stability but also a high concentration of surface Si−OH groups for the binding of the catalyst.[2,4] All these properties can be tuned in some extent during the process of material synthesis.

Postsynthetic grafting is the most popular way to anchor organic groups in a specific manner to the surface, which finally results in hybrid organic−inorganic materials.[4,5] However, there are some drawbacks related to this procedure: the distribution of the organic group is generally not uniform all over one channel[5a,b] and the loading with larger and sterically demanding organic functionalities is often low, mainly constrained by diffusion limitations. An alternative way to overcome these problems would be to prepare *hybrid* mesoporous materials by a template-directed synthesis, which is usually based on the co-condensation of organosilane precursors with other silica reagents (e.g., tetraalkoxysilanes) in a templating environment. Mann et al. pioneered this strategy by incorporating phenyl and *n*-octyl functionalities into mesoporous MCM-41-type materials.[6] Later, this approach was extended by other research groups to a number of different func-

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tional groups including mercaptopropyl, amine, epoxide, imidazole, vinyl, methacrylate, cyclodextrin moieties, and many more.[5,7] However, it still is a challenge to obtain hybrid mesoporous materials containing a specific organic functional group in a one-step synthesis. This would be of high relevance for an application in catalysis. The main difficulty related to this is to control the preparation conditions in a way that a hybrid material with uniform distributions of organic functional groups and a highly ordered channel system is obtained. Additionally, the organic precursor has to be stable throughout the hydrothermal synthesis of the material and has to survive the surfactant removal process.[5b]

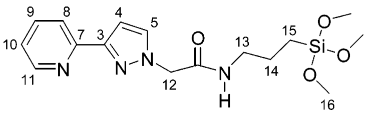
Recently, our interest in hybrid materials has focused on the incorporation of oxodiperoxomolybdenum complexes $[(L-L)MoO(O_2)_2]$ (L−L = pyrazolylpyridine chelate ligand) into mesoporous MCM-41 materials for application in epoxidation catalysis. Currently, heterogeneous epoxidation is a very active topic in the field of catalysis due to the significant industrial interest.[8] However, it is known from heterogenized chromium, vanadium, and molybdenum catalysts coordinated to monodentate ligands that they usually undergo leaching of the active species into solution, especially in the presence of protic agents such as alcohols or organoperoxides.[8a,8b] We therefore chose a chelating system that offers high coordinative stability for the heterogenization and that we have investigated in detail as epoxidation catalysts in solution before.[9] By a postgrafting procedure, we could obtain a hybrid mesoporous MCM-41 material containing the oxodiperoxomolybdenum complexes, which is active and truly heterogeneous for the catalytic epoxidation of cyclooctene with ^tBuOOH as oxygen source.[10]

Here, we report a direct incorporation strategy for the synthesis of a hybrid mesoporous material by co-condensation of tetraethyl orthosilicate (TEOS) and the chelate ligand (3-trimethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (**1**) in the presence of cetyltrimethylammonium bromide (CTAB) as template. The surfactant-extracted materials were characterized by elemental analysis, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption, solid-state CP-MAS NMR spectroscopy (^{13}C and ^{29}Si), and infrared spectroscopy (IR). Molybdenum-containing catalysts were obtained by introducing oxodiperoxomolybdenum species $MoO(O_2)_2$ into the hybrid materials with a ligand exchange reaction. The catalytic properties were investigated on the molybdenum-containing catalysts for the liquid-phase epoxidation of cyclooctene with ^tBuOOH.

Experimental Section

Synthetic Procedures. (a) (3-Trimethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (1). 2-(3-Pyrazolyl)pyridine (10 mmol, 1.45 g) was added to a suspension of NaH (10 mmol, 0.24 g) in THF (50 mL) under stirring. When the evolution of H_2 ceased, methyl bromoacetate (10 mmol, 1.53 g) was added and the resulting solution was refluxed for 4 h. After removing the solvent in a vacuum, the product was extracted with diethyl ether and recrystallized to obtain [3-(2-pyridyl)-1-pyrazolyl]acetic acid methyl ester. A mixture of the ester (4.0 mmol, 0.87 g) and 3-trimethoxysilylpropylamine (4.0 mmol, 0.74 g) was heated to 150 °C for 2 h. Then all volatiles were removed in a vacuum resulting **1** as an oily residue. The numbering scheme for NMR spectra assignments is given in the Chart 1: ^1H NMR (250.13 MHz, 25 °C, $CDCl_3$) δ 8.62 (d, J 4.0 Hz, H^{11}), 7.91 (d, J 8.1 Hz, H^8), 7.70 (dt, J 7.9 Hz, J 1.7 Hz, H^9), 7.52 (d, J 2.4 Hz, H^5), 7.22 (m, H^{10}), 6.96 (d, H^4), 6.31 (br, NH), 4.85 (s, H^{12}), 3.47 (s, H^{16}), 3.21 (t, J 6.8 Hz, H^{13}), 1.54 (m, H^{14}), 0.52 (m, H^{15}); $^{13}C\{^1H\}$ NMR (62.89 MHz, 25 °C, $CDCl_3$) δ 166.3 (C=O), 151.9 (C^7), 151.0 (C^3), 148.5 (C^{11}), 135.7 (C^9), 132.0 (C^5), 121.8 (C^{10}), 119.3 (C^8), 104.3 (C^4), 54.3 (C^{12}), 49.5 (C^{16}), 41.0 (C^{13}), 21.7 (C^{14}), 5.4 (C^{15}).

Chart 1. Assignment of the NMR Spectra for Ligand 1



(b) Synthesis of Hybrid Mesoporous Materials (2a−2c). An aqueous solution of ethylamine was added to a stirred aqueous solution of CTAB. Then a mixture of TEOS and **1** with methanol was added dropwise, leading to a composition in molar ratio of 1.0:x:0.14:2.4:2.0:100 SiO_2/**1**/CTAB/$EtNH_2$/methanol/H_2O ($x = 0.028$ for **2a**, 0.055 for **2b**, and 0.083 for **2c**). The reaction mixture was stirred for a further 4 h at room temperature before being heated to 100 °C for 24 h. The product was recovered by filtration, washed thoroughly with distilled water, and air-dried under ambient conditions. The surfactant (CTAB) was extracted by twice stirring 3.0 g of the synthesized hybrid material in 250 mL of methanol and 6.0 g of an aqueous solution of HCl (36%) at 50 °C for 6 h. The resulting solid (**2a**, **2b**, or **2c**) was then filtered, washed with methanol, and dried in air at 150 °C. Elemental analysis for **2a**: C, 6.09; H, 1.58; N, 1.45. **2b**: C, 9.69; H, 1.98; N, 3.33. **2c**: C, 12.66; H, 2.22; N, 4.37.

(c) Preparation of the Molybdenum-Containing Catalysts (3a−3c). Catalysts containing oxodiperoxomolybdenum species were obtained by stirring 0.50 g of the hybrid materials of **2a, 2b,** or **2c** with different amounts of $MoO(O_2)_2 \cdot (DMF)_2$ (0.037 g for **2a**, 0.086 g for **2b**, 0.113 g for **2c**) in 40 mL of $CHCl_3$ at room temperature for 24 h. Then the resulting catalysts **3a**, **3b,** or **3c** were filtered off, washed, Soxhlet-extracted with $CHCl_3$, and dried in a vacuum at room temperature.

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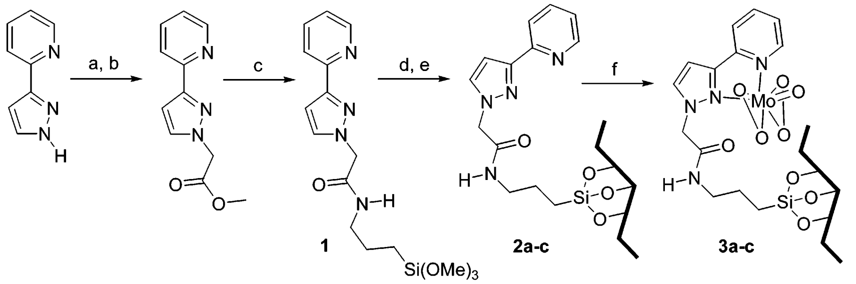
Scheme 1[a]



[a] Conditions: (a) NaH, THF; (b) $BrCH_2COOMe$, reflux, 4 h; (c) $H_2N(CH_2)_3Si(OMe)_3$, 150 °C, 2 h; (d) $EtNH_2$, $[CH_3(CH_2)_{15}N(CH_3)_3]Br$ in water, $Si(OEt)_4$, MeOH; (e) MeOH/HCl; (f) $MoO(O_2)_2{\cdot}(DMF)_2$, $CHCl_3$.

Characterization. XRD measurements were performed with a Seifert-FPM XRD7 diffractometer with Cu Kα radiation at 40 kV and 36 mA. TEM images were recorded on a Philips CM20FEG microscope operating at 200 kV with Gatan GIF imaging filter model 678. Nitrogen adsorption/desorption isotherms were measured at the liquid nitrogen temperature, using a Sorptomatic 1990 analyzer. Samples were degassed at 140 °C 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 the desorption branches of the 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. IR spectra were obtained from KBr pressed pellets using a Perkin-Elmer Spectrum 1000 FTIR spectrometer.

Catalytic Reactions. The catalytic epoxidation of cyclooctene was carried out as described in the literature.[10b] In a standard procedure, 1.00 g of cyclooctene (9.07 mmol), 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), and 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 were evaluated by the conversion of cyclooctene to epoxycyclooctane.

Leaching experiments were carried out in order to prove the heterogeneous character of the reactions. In a duplicate reaction, the solid catalyst was removed at the reaction temperature by filtration at ~50% of conversion of cyclooctene. The filtrate was then heated to reaction temperature again and monitored for continuing reactions.

Results and Discussion

Synthesis and Characterization. Chelate ligand **1** bearing the $Si(OMe)_3$ group was synthesized according to the procedure for the synthesis of (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide.[10b] The hybrid mesoporous products **2a**, **2b**, and **2c** were obtained as outlined in Scheme 1. A main feature of this route is to use the weak organic base $EtNH_2$ instead of the conventionally applied strong base NaOH, which avoids incorporation of Na^+ ions into the mesoporous material.[11] To prevent phase separation, TEOS and **1** were first dissolved in a small volume of methanol before adding this mixture to the surfactant solution. It was reported that the presence of a suitable amount of methanol in the system may increase the degree of order of the mesoporous materials compared with a purely aqueous system.[7e,12]

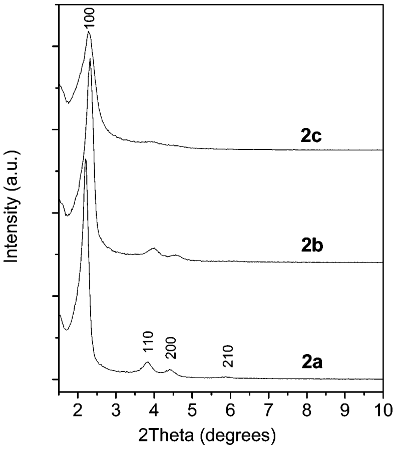


Figure 1. Powder XRD patterns of surfactant-extracted hybrid materials.

After the hydrothermal synthesis, the template was removed by treating the materials with a solution of MeOH/aqueous HCl.[7c] The powder XRD patterns of the three template extracted hybrid materials are shown in Figure 1. Samples **2a** shows four peaks, which can be indexed as the (100), (110), (200), and (210) reflections of the hexagonal symmetry lattice of MCM-41 material.[2] The relative intensities of higher angle peaks slightly decrease for **2b**. Sample **2c** exhibits the prominent diffraction peak (100) clearly, but the other peaks decrease to a very low level and are thus nearly undetectable. These results suggest the presence of periodic arrangement of hexagonal geometry channels in all the three hybrid materials. The reduction in diffraction intensity upon increasing the loading with **1** can be partly assigned to a decrease in the mesoscopic order of the materials and may also be partly due to the contrast matching resulting from the presence of the large amounts of organic moieties inside the pore channels of the materials.[5a,7f,10b]

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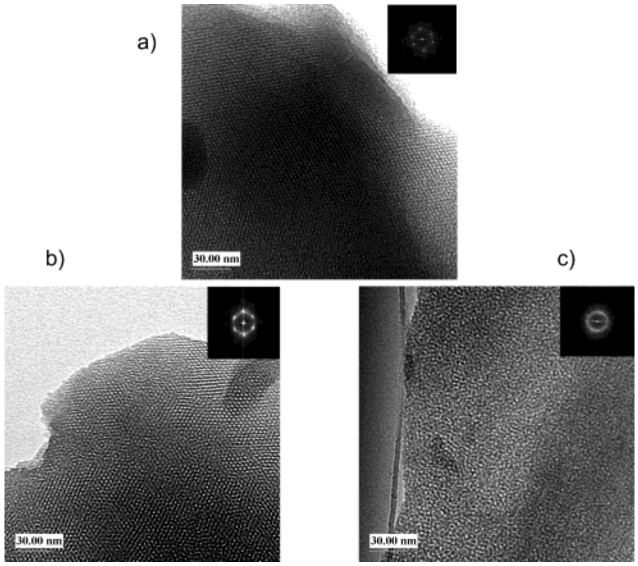

Figure 2. TEM images of surfactant-extracted hybrid materials of (a) **2a**, (b) **2b**, and (c) **2c**. The inset shows the electron diffraction pattern from the selected region.

High-resolution TEM images are consistent with the XRD results, showing clearly the hexagonal symmetry in the arrangement of the channels of the hybrid materials (Figure 2). The sample **2a** is highly ordered with long-range, hexagonal arrangement of the channels. While the overall order is slightly reduced for **2b**, the ordering of **2c** is considerably decreased, which is also confirmed by the electron diffraction patterns of the materials (see inlets in Figure 2), probably caused by the higher concentration of **1** in the reaction mixture. However, the pore channels of **2c** still appear to be uniform at the mesoscale.

The mesoporous structure of the hybrid materials can be further confirmed by N_2 adsorption/desorption isotherms (Figure 3). All the three samples exhibit type IV isotherms (definition by IUPAC),[13] which is characteristic for mesoporous materials (pore diameters 2−50 nm). Compared to **2a** and **2b**, the uptake of N_2 for **2c** is lower. **2c** shows a relative broad pore size distribution, indicating the lowered order of this material. However, the pore size distributions of **2a** and **2b** are much narrower than that of an analogous system obtained by postsynthetic grafting.[10b] This may be explained by a stabilization of the micelles (formed during the gelation process) by the presence of the chelate ligand **1**. Relevant data of the surfactant-extracted hybrid mesoporous materials **2a**−**2c** is shown in Table 1.

^{29}Si CP-MAS NMR spectra confirm that the organic−inorganic moieties are the basic structure units of the hybrid mesoporous materials (Figure 4). Three signals at −112, −103, and −93 ppm correspond to Q^4 [$(SiO)_4$*Si*], Q^3 [$(SiO)_3$*Si*(OR)] (R = H, Me), and Q^2 [$(SiO)_2$*Si*$(OR)_2$] species of the inorganic silica framework.[10b,14] A major resonance centered at −67 ppm can be assigned to organosilica T^3 species [C-*Si*$(OSi)_3$].[10b] Only a very small amount of T^2 species [C-*Si*$(OSi)_2$(OMe)] is present in these materials as evidenced by a weak resonance at around −57 ppm (overlapped partly with the T^3 signal).[10b] The intensities of the resonances for organosilicon species increase with the increase of the loading of the chelate ligand. The fact that T^3 sites are the major organosilica species suggests that the hydrolysis/condensation of **1** during the preparation process is nearly complete, indicating a strong linkage (three Si−O−Si covalent bonds) between the organic ligand and the silica matrix.

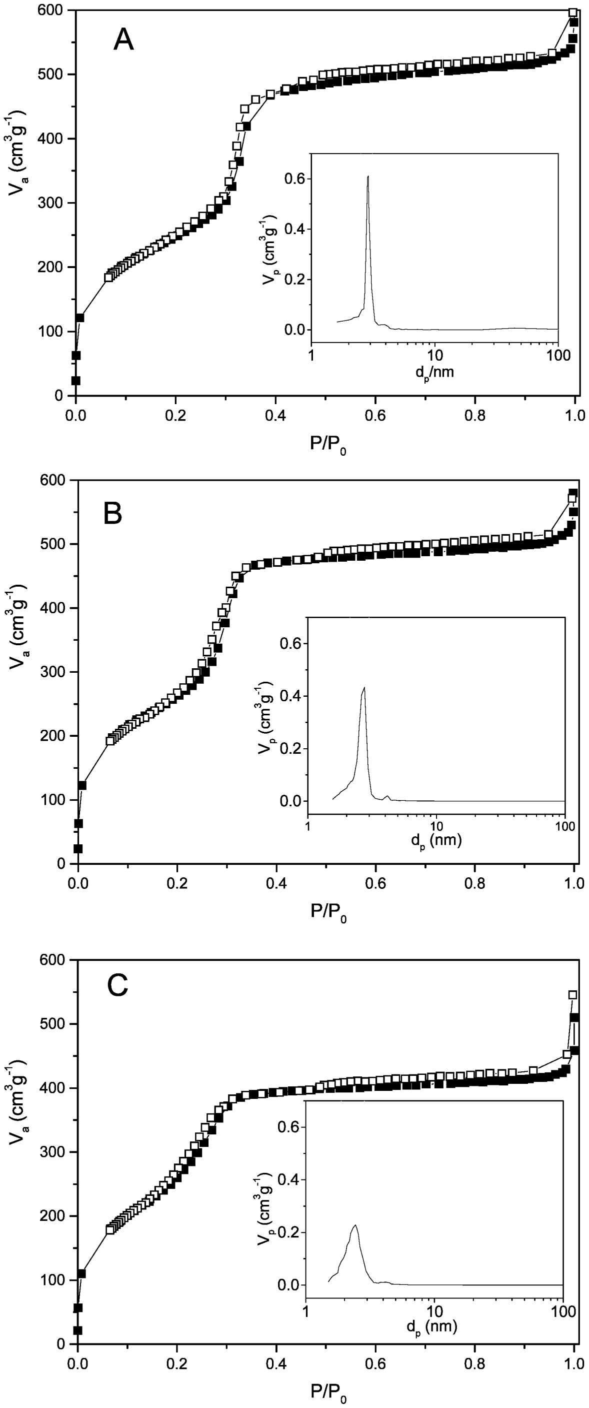

Figure 3. N_2 adsorption−desorption isotherms at 77 K and pore size distribution profiles (inset) of surfactant-extracted hybrid materials. A, **2a**; B, **2b**; C, **2c**.

To prove the preservation of the chelate ligand structure during the hydrothermal synthesis and the acid extraction process, ^{13}C CP-MAS NMR spectroscopy

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Table 1. Characteristic Data of Surfactant-Extracted Hybrid Mesoporous Materials

hybrid materials	content of ligand **1**[a]		yield[b] (%)	surface area (m^2/g)	pore vol (mL/g)	mean pore diam (nm)
	mmol/g	wt %				
2a	0.26	7.6	89.4	906	0.90	2.9
2b	0.60	17.6	90.0	972	0.90	2.9
2c	0.78	23.0	90.8	948	0.66	2.5

[a] Calculated according to the content of nitrogen (CHN elemental analysis). [b] Based on complete condensation of ligand **1** and TEOS.

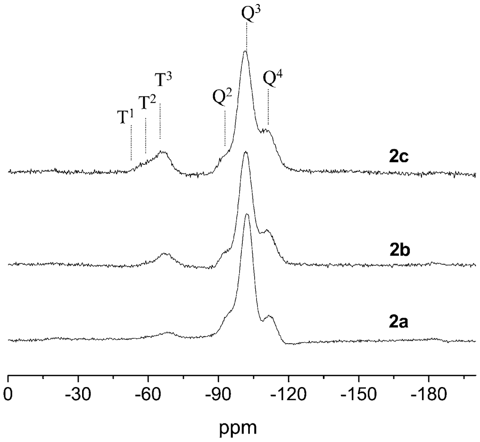

Figure 4. ^{29}Si CP-MAS NMR spectra of surfactant-extracted hybrid materials **2a**, **2b**, and **2c**.

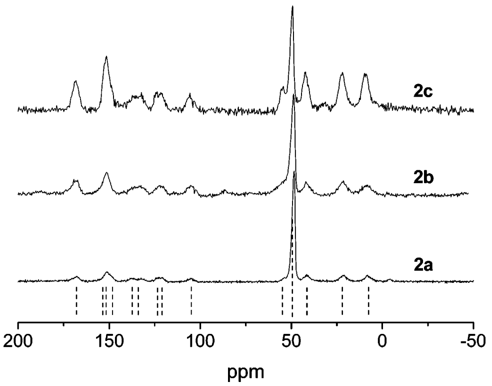

Figure 5. ^{13}C CP-MAS NMR spectra of surfactant-extracted hybrid materials **2a**, **2b**, and **2c**, compared with the resonances of the free ligand **1** (NMR in solution, dashed lines assigning the relative intensities).

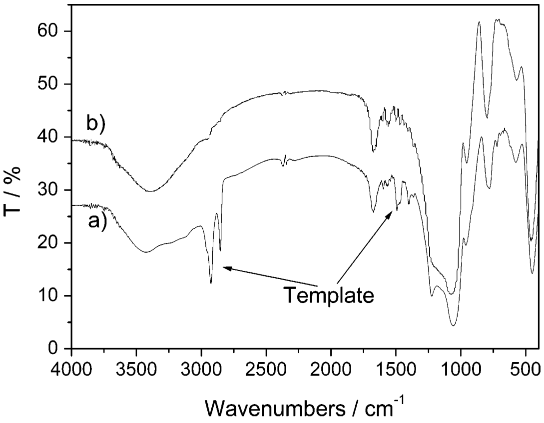

Figure 6. FTIR spectra of hybrid materials **2c**: (a) as-synthesized and (b) after template extraction with a methanol/HCl mixture.

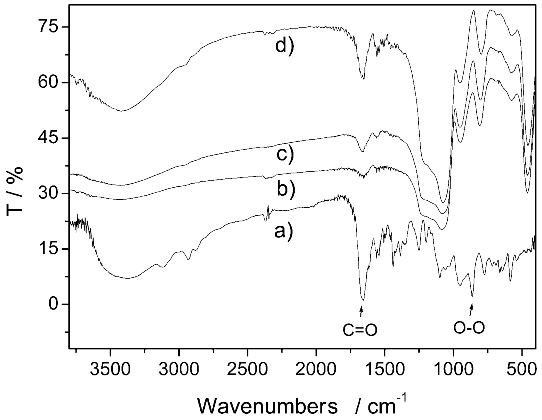

Figure 7. FTIR spectra of (a) the free complex $MoO(O_2)_2$·**1**, as well as the three Mo-containing catalysts (b) **3a**, (c) **3b**, and (d) **3c**.

is the method of choice as shown in Figure 5. All three template extracted hybrid materials show spectra similar to that of chelate ligand **1**. The strong resonance at 49 ppm is observed for all hybrid materials. It can be mainly assigned to organosilica C−SiO*C*H_3 groups. This may indicate that the hydrolysis/condensation of **1** is not fully complete during the template-directed synthesis process. Besides, no carbon signal belonging to the CTAB surfactant is present in ^{13}C CP-MAS NMR spectra, suggesting a complete removal of the surfactant from the hybrid mesoporous materials by the acid extraction process, which can be further confirmed by the FTIR spectra (Figure 6).

In comparison with the NMR spectra of the grafted mesoporous MCM-41 materials,[10b] there is a considerably higher content of organosilica species in **2b** and **2c**, indicating a high loading with the chelate ligand, which corroborates with the elemental analyses (Table 1). The loading of the chelate ligand in **2c** is 23.0 wt % material, thus more than twice the content of the samples obtained by postsynthetic grafting procedure (∼10 wt %).

An additional advantageous feature of **2a**−**2c** is the strong linkage between the organic ligand and the silica matrix via three covalent bound Si−O−Si groups (see discussion above). In the corresponding sample obtained by postsynthetic grafting, the organic ligand is tethered to the surface in average via two Si−O−Si units.[10b]

Treatment of **2a**−**2c** with $MoO(O_2)_2$·$(DMF)_2$ in $CHCl_3$ solution gave the three catalysts **3a**−**3c**. FTIR spectra of the three Mo-containing catalysts and the free complex $MoO(O_2)_2$·**1** are given in Figure 7. It is clear that **3c** shows the relative high peak intensities corresponding to the organic compound. This gave further evidence of the high loading of the chelate ligand in this material. Besides, the poor resolution for the introduced ligand in the hybrid materials should be due to the strong IR absorbance of the siliceous base materials in a similar region.

Catalytic Properties in Epoxidation of Cyclooctene. Three Mo-containing catalysts **3a**−**3c** were

Table 2. Activity of Molybdenum-Containing Catalysts for the Epoxidation of Cyclooctene[a]

catalysts	Mo loading mmol/g	Mo loading wt %	Mo/ligand **1** (mol ratio)	conversion[b] (%)	TOF[c]
3a	0.22	2.1	0.9:1	34	102
3b	0.49	4.7	0.9:1	60	83
3c	0.62	6.0	0.9:1	66	71

[a] All reactions were performed with 9.1 mmol of cyclooctene, 9.6 mmol of TBHP (5.5 M in decane) in 25 mL of $CHCl_3$, and 100 mg of catalyst at 61 °C. [b] Conversion of cyclooctene to epoxycyclooctane determined by GC/MS after 1.35 h. [c] Turnover frequencies (TOF) determined after 1.35 h, which are expressed in $\text{mol(cyclooctene)}\cdot\text{mol(Mo)}^{-1}\cdot\text{h}^{-1}$.

examined for the epoxidation of cyclooctene, the standard substrate for studying the olefin epoxidation. As expected, all catalysts are active for this reaction with nearly 100% of selectivity to epoxycyclooctane (Table 2), which is consistent with the MCM-41 system obtained by grafting method[10] and the corresponding homogeneous catalysts we previously reported.[9] Under the reaction conditions applied, **3c** showed the highest activity due to the highest loading of active molybdenum sites. However, comparing the specific activity (TOF), **3a** turns out to be the most active system (TOF).

To investigate leaching of the active species into the liquid phase under operating conditions, the solid catalysts were filtered at the reaction temperature of 61 °C at ~50% conversion of cyclooctene. Then the filtrate was investigated for continuing activity at the reaction temperature, which was found to be almost undetectable (not shown here). This gives very strong evidence for a really heterogeneous catalysis, indicating the very high stability against leaching of these catalysts.

We should not forget to mention that besides coordination to a chelate ligand, the oxodiperoxomolybdenum species may also interact with the surface Si−OH groups of the silica material, which was modeled using organosilanols as ligands.[15] We recently have confirmed that $MoO(O_2)_2$ species can be adsorbed by porous silica gels or mesoporous MCM-41 materials even in the absence of a ligand.[16] These adsorbed molybdenum species cannot be removed by Soxhlet extraction with $CHCl_3$, which means that the metal−supported system is stable under the preparation conditions. However, such Mo-containing materials are not stable under the reaction conditions of the cyclooctene epoxidation; serious leaching of active molybdenum species into solution is observed, suggesting that the silica-adsorbed oxodiperoxomolybdenum species are unstable in the presence of highly polar and/or protic reagents such as ^{t}BuOOH and ^{t}BuOH. For the catalysts discussed here, coordination of $MoO(O_2)_2$ to Si−OH groups of the support can be avoided by controlling the stoichiometry. Therefore, the ratio $MoO(O_2)_2$/ligand is kept at 0.9:1.0 for all catalysts. This certainly requires the prerequisite that almost every chelate ligand in the materials must be accessible for the coordination of $MoO(O_2)_2$, which is confirmed by the leaching experiments. The high accessibility of the chelate ligands in the hybrid materials may be assigned to a stabilizing influence of the rigid molecular structure (two linked heteroaromatic rings and the amide group of **1**, acting as a covalently bonded structure template in the condensation process) during the formation of the micelles.[17] We suppose that, due to its special structural features, **1** reduces the mobility of the long alkyl side chain of CTAB and thus stabilizes the micelles. Obviously this effect is strongly concentration dependent. Then the covalently bonded template ligand is copolymerized with the monomer TEOS to form a highly cross-linked matrix. After MeOH/HCl extraction process, the noncovalently bonded template (CTAB) can be removed from hybrid materials to create mesoporous cavities, while the covalently linked ligand is kept. The functional part of the ligand is exposed, resulting in very high chemical accessibility of the ligands.

Conclusion

New organic−inorganic hybrid mesoporous MCM-41-type materials have been synthesized successfully by co-condensation of TEOS and chelate ligand (3-trimethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide in the presence of CTAB template. This method allows the introduction of high concentrations of chelate ligands/catalysts, with the preservation of uniform mesoscale channels, large pore volumes, and high specific surface areas. Almost all the incorporated chelate ligands are chemically accessible for the coordination of the catalytically active $MoO(O_2)_2$ moieties, which results in the formation of highly active heterogenized catalysts for the liquid-phase epoxidation of cyclooctene with ^{t}BuOOH with excellent stability against leaching. Further work is currently in progress to investigate the catalytic properties of these hybrid catalysts for other olefins and the attempt to use H_2O_2 instead of ^{t}BuOOH as the oxidizing agent. In addition, further characterization of these materials by EXAFS is underway to obtain more information about the specific coordination mode between the oxodiperoxomolybdenum species and the hybrid mesoporous materials.

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