The enhanced catalytic activity and stability of oxodiperoxomolybdenum-modified mesoporous organosilicas in selective epoxidation reactions†

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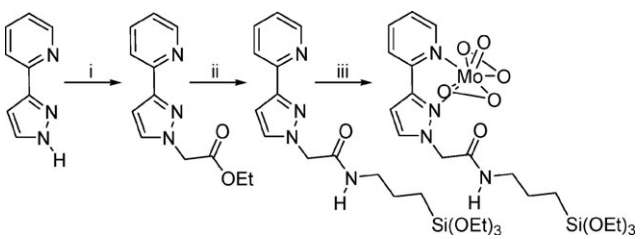
Complexes of the type (L–L)MoO(O$_2$)$_2$ heterogenized on phenylene-bridged mesoporous organosilicas show a 10-fold increase in catalytic activity and a high stability in liquid phase epoxidation reactions, with H$_2$O$_2$ as the oxidant, compared to the corresponding MCM-41-derived systems.

Selective olefin epoxidation generates valuable starting materials for further functionalization, and opens up access to industrially important products such as polyethers, epoxy resins and surfactants.[1] A whole series of homogeneous catalysts have been identified as being active in this reaction. Among them, molybdenum- and tungsten-based catalytic systems play an important role.[2] However, the regeneration of the homogeneous catalyst from reaction mixtures causes cost and waste problems. It is therefore worthwhile developing innovative approaches for the heterogenization of the homogeneous catalysts for this reaction using environmentally benign oxidants.

Catalyst heterogenization on solid supports with high surface areas is a convenient method, since the unique textural features of porous materials allow high catalyst loadings and the uniform dispersion of active sites.[3] Recently, we verified the application of molybdenum complexes of the type (L–L)MoO(O$_2$)$_2$ (L–L = pyrazolylpyridine ligand) grafted onto mesoporous MCM-41 for the epoxidation of cyclooctene, with ^{t}BuOOH as the oxidizing agent.[4] We proved that removing the residual Si–OH groups on the support by silylation enhanced the stability of the material and facilitated the regeneration of the catalyst due to the increased surface hydrophobicity.[4b] However, such systems still show only poor catalytic activity with H$_2$O$_2$ as the oxidant. It therefore seemed to be beneficial to investigate the heterogenization of such complexes on so-called 'periodic mesoporous organosilicas' (PMOs). PMOs are available *via* a template-directed condensation of bifunctional precursors of the type (RO)$_3$Si–X–Si(OR)$_3$. They have a homogeneous distribution of organic fragments and silica moieties in the framework. It is known that hydrophobic surfaces can improve the catalytic activity and stability of active sites in inclusion chemistry.[5]

For this purpose, catalysts of the type (L–L)MoO(O$_2$)$_2$ were tethered onto hydrophobic PMOs derived from phenylene (–C$_6$H$_4$–, **B**)- and ethylene (–CH$_2$CH$_2$–, **E**)-bridged organosilicas. PMOs **B** and **E** were prepared from their corresponding bifunctional silsesquioxane precursors. Molecular organization in the walls is an outstanding feature of **B** since, in this case, hydrophobic arene and hydrophilic silica layers are alternatively arranged with a periodicity of 7.6 Å.[6] The molybdenum-containing precursors were synthesized as outlined in Scheme 1.[4] Mesoporous catalysts **BMo**, **EMo** and **MMo** (catalyst on conventional MCM-41) were prepared by following a post-synthetic grafting method in dry toluene using supports **B**, **E** and **M**.†

The success of the grafting procedure could be demonstrated spectroscopically.† All the heterogenized catalysts showed ^{13}C CP-MAS NMR spectra similar to those of their free congener. Typically, the resonances of the two carbon atoms of the ethoxide groups (57.7 and 14.9 ppm) decreased in intensity due to condensation with the surface Si–OH groups and liberation of EtOH.[4] Besides, the ^{13}C CP-MAS NMR spectra of **BMo** (**EMo**) showed sharp peaks at 133.7 (5.3) ppm, corresponding to the –Si–C$_6$H$_4$–Si– (–Si–CH$_2$–CH$_2$–Si–) groups in the framework walls. The ^{29}Si MAS NMR spectrum of **BMo** displayed three signals, which could be assigned to the T^2 and T^3 silicon centres bound to phenylene (−81.4 and −71.6 ppm), and to the linker unit of the molybdenum complex (−71.6 and −63.5 ppm).[7] **EMo** showed two peaks: one at −58 ppm (T^2: C(OH)*Si*(OSi)$_2$) and the other at −67 ppm (T^3: C*Si*(OSi)$_3$). There were no resonances typical of Q^n species (Q^n = Si(OSi)$_n$(OH)$_{4-n}$, n = 2–4),[8] which means that no silicon–carbon bond cleavage occurred during the synthesis of the supports and the subsequent high temperature grafting process. The ^{29}Si MAS NMR spectrum of **MMo**, as expected, showed signals at −110 to −90 ppm (Q sites) and



Scheme 1 Synthesis of oxodiperoxo{(3-triethoxysilylpropyl)-[3-(2-pyridyl)pyrazol-1-yl]acetamide}molybdenum; i: THF, NaH, BrCH$_2$COOEt, ii: NH$_2$(CH$_2$)$_3$Si(OEt)$_3$, iii: CH$_2$Cl$_2$, (dmf)$_2$MoO(O$_2$)$_2$.

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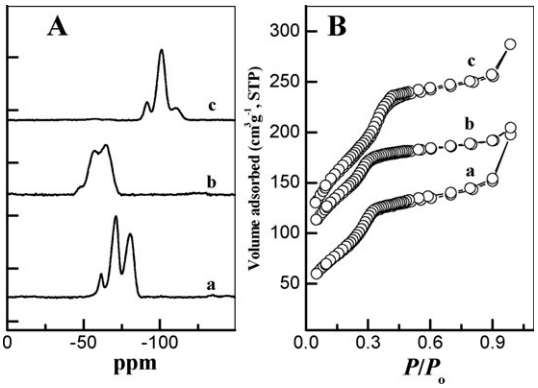

Fig. 1 (A) ^{29}Si CP-MAS NMR spectra and (B) N_2 adsorption/desorption isotherms at 77 K of (a) **BMo**, (b) **EMo** and (c) **MMo** samples.

weak resonances at −70 to −60 ppm (T sites), which originated from the low loading of the silylating agents (Fig. 1A). N_2 adsorption/desorption experiments gave type IV isotherms, with a sharp capillary condensation step at P/P_o = 0.3–0.4 for all samples, typical of mesoporous materials having a uniform mesopore structure (Fig. 1B). The measured BET surface areas and BJH pore sizes of the **BMo**, **EMo** and **MMo** samples were 613, 595 and 634 $m^2\ g^{-1}$, and 2.5, 2.4 and 2.4 nm, respectively. Furthermore, the catalyst loading of all the mesoporous materials, determined by their nitrogen content, was found to be nearly 0.4 mmol g^{-1}.

Powder XRD patterns of **BMo**, **EMo** and **MMo** showed typical peaks at low angles related to the hexagonal mesoporous structure.[9] Additional peaks appeared for **BMo** in the range $10^\circ < 2\theta < 50^\circ$ that could be assigned to a periodicity with a spacing of 7.6 Å in the framework walls (Fig. 2).[6]

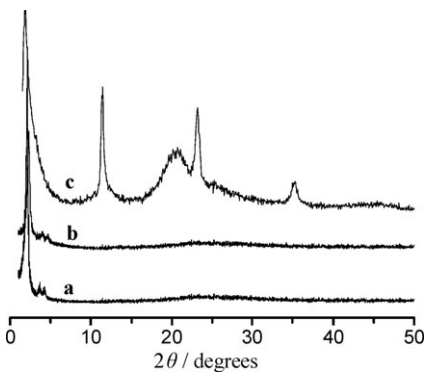

Fig. 2 Powder XRD patterns of (a) **MMo**, (b) **EMo** and (c) **BMo**.

The molybdenum-containing samples were tested in the epoxidation reaction of cyclooctene at 60 °C, in the presence of 1 mol% of catalyst, with different solvents ($CHCl_3$, toluene, CH_3CN) and oxidizing agents (70% ^{t}BuOOH in H_2O, H_2O_2). As expected, the yield of the reaction was both solvent- and oxidant-dependent; a combination of $CHCl_3$ and ^{t}BuOOH gave the best conversions, with nearly 100% selectivity for epoxycyclooctane,† corroborating with our observations of homogeneous epoxidation catalysis using complexes of the type (L–L)$MoO(O_2)_2$.[10] However, under identical reaction conditions, **BMo** showed a much higher activity than **EMo** or **MMo**, although the catalyst loading was similar for all samples (Fig. 3).

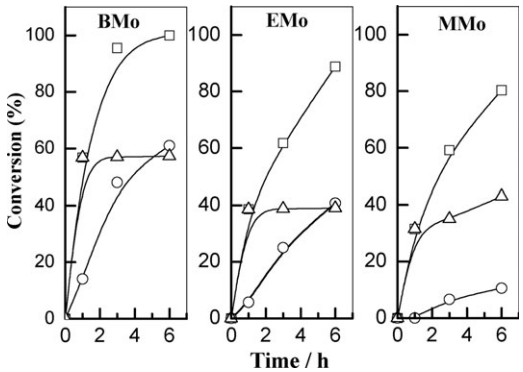

Fig. 3 □: Kinetic profiles for the epoxidation of cyclooctene with 70% ^{t}BuOOH in H_2O. △: Heterogeneous reaction check by continuing the reaction after removing the catalyst after 1 h. ○: Kinetic profile with H_2O_2 as the oxidizing agent.

Furthermore, we recently reported that homogenous (L–L)$MoO(O_2)_2$ catalysts, as well as MCM-41-grafted samples, show only poor cyclooctene conversion with 30% H_2O_2 as the oxidizing agent.[4] In contrast, **BMo**/H_2O_2 converts cyclooctene in about 60% yield after 6 h, while **EMo** gives only 30% and **MMo** shows an almost negligible conversion of 6%. Therefore, the nature of the support is responsible for a 10-fold enhancement of the catalytic activity. This effect, which is also observed for 70% ^{t}BuOOH in H_2O, can, in our opinion, be assigned to the increased hydrophobicity of the framework walls due to the presence of phenylene bridges in defined positions. The unique hydrophobic pores facilitate the adsorption of olefins close to the active sites, and/or reduce the adsorption of the more polar epoxide and by-products (^{t}BuOH or H_2O). Encouraged by the results with cyclooctene, the epoxidation of a series of other olefins was investigated under optimized reaction conditions (Table 1). Similar to cyclooctene, **BMo** converts these olefins to their corresponding epoxides in good to excellent yields, showing again the novelty of the present catalytic system.

Additionally, the catalytic properties of (L–L)$MoO(O_2)_2$ grafted onto hydrophobic PMOs remained unchanged upon reuse. The materials turned out to be recyclable up to four times, while samples with conventional MCM-41 show a continuous decrease in catalytic activity after each run. Experiments where the solid catalysts were removed at the

Table 1 The epoxidation reaction of different olefins catalysed by **BMo**[a]

		Yield of epoxide (%)[b]	
Entry	Substrate	^{t}BuOOH	H_2O_2
1	Cyclooctene	100	62
2	Cycloheptene	96	55
3	Cyclohexene	85	49
4	Styrene	83	48
5	1-Octene	73	34

[a] Reaction conditions: 1 mmol alkene, 1.2 mmol oxidant, 1 mol% **BMo**, 5 mL $CHCl_3$, 6 h, reflux. [b] Yields were determined by GC-MS with respect to an internal standard (n-decane).

reaction temperature after 1 h support this conclusion (Fig. 3). After this time, there was no catalytic activity in the solutions for **BMo** and **EMo** (with 70% ^{t}BuOOH in H_2O), while for **MMo**, leaching of the catalyst had taken place. We assign this behavior to the coordinatively-inert framework walls, which make the ligand–molybdenum interaction become dominant.

In summary, the present studies show the first example of the catalytic activity and stability tuning of a heterogenized epoxidation catalyst by the nature of its support. Compared to conventional MCM-41 or its surface silylated analogs, hydrophobic mesoporous organosilica materials give an outstanding activity, along with high stability and selectivity, even in the presence of cheap and environmentally benign aqueous oxidants. The results further confirm that the use of structurally well-defined PMOs as supports allows the reuse of the catalysts without any loss of activity, which is of special importance for expensive noble metals and/or chiral ligands. Further investigations of the surface properties of these materials is currently under way to understand their relationship with the catalytic properties.

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Experimental section

Synthesis of (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]-acetamide

0.93 g (4.02 mmol) of [3-(2-pyridyl)-1-pyrazolyl]acetic acid ethyl ester was mixed with 0.89 g (4.02 mmol) of 3-triethoxy-silylpropylamine and heated to 150 °C for 2 h. All volatiles were then removed *in vacuo*, resulting in an oily residue in quantitative yield.

Synthesis of oxodiperoxo{(3-triethoxysilylpropyl)-[3-(2-pyridyl)pyrazol-1-yl]acetamide}molybdenum-modified mesoporous materials BMo, EMo and MMo

A portion of 0.03 g of oxodiperoxo{(3-triethoxysilylpropyl)-[3-(2-pyridyl)pyrazol-1-yl]acetamide}molybdenum dissolved in 5 mL of dry chloroform was added to a suspension of 0.30 g of the appropriate mesoporous support (**B**, **E** or **M**) in 30 mL of dry toluene. The mixture was stirred under an atmosphere of nitrogen for 12 h at 90 °C. The solid was filtered off, washed with $CHCl_3$ and dried *in vacuo* to obtain the mesoporous supported hybrid materials.

Powder X-ray diffraction patterns were obtained on a Siemens D5005 diffractometer with Cu-K_α radiation (30 kV, 30 mA). Nitrogen adsorption/desorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 sorption analyzer after evacuation of the samples at 150 °C overnight. Solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra were recorded at 100.6 and 79.49 MHz, respectively, using a Bruker AVANCE 400 spectrometer.

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