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Oxodiperoxo molybdenum modified mesoporous MCM-41 materials for the catalytic epoxidation of cyclooctene†

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A hybrid heterogeneous catalyst system, which has been synthesized by covalently anchoring oxodiperoxo molybdenum chelate complexes onto the surface of mesoporous MCM-41, is highly active and truly heterogeneous for the liquid-phase epoxidation of cyclooctene with ^{t}BuOOH as the oxygen source.

Catalytic olefin epoxidation in the liquid-phase is an important topic for the synthesis of fine chemicals.[1] A whole series of soluble metal salts or complexes has found to be active in this reaction during the last few decades. Among them, Mo(VI) complexes have widely been reported.[2,3] However, increasing attention is drawn to studying and developing heterogeneous catalysts since they can easily be separated from a reaction mixture and recycled, which is of significant industrial interest.[4]

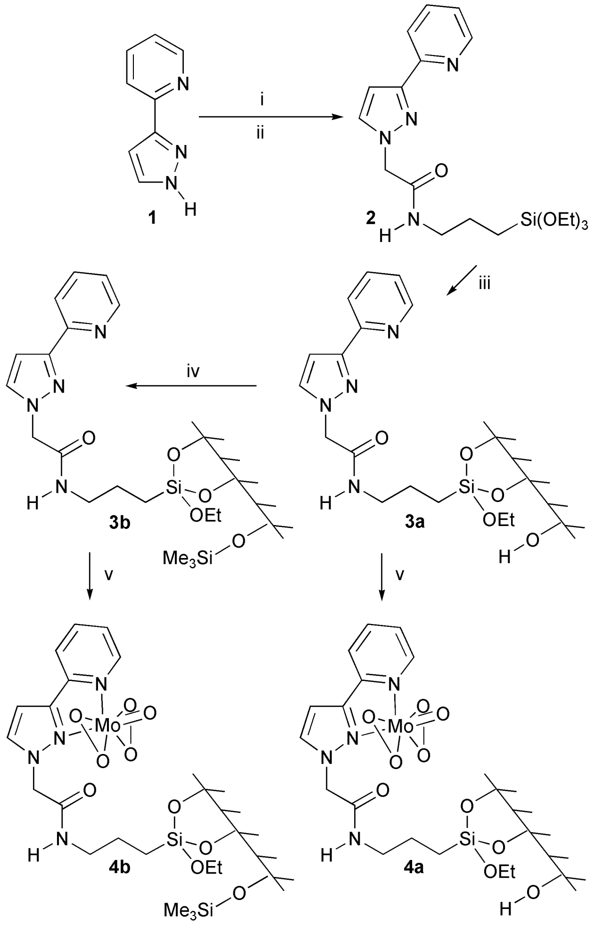
Different approaches have been used in order to obtain heterogeneous molybdenum catalysts for olefin epoxidation. A general problem is, that Mo(VI) can not easily be incorporated into the tetrahedral positions of the silicate framework of molecular sieves.[5] Sherrington *et al.* reported that polymer-supported Mo(VI) complexes are active and recyclable catalysts for olefin epoxidation with ^{t}BuOOH.[6] A new strategy for the confinement of metal centers in mesoporous silicates is the covalent attachment of organometallic or coordination compounds to form a hybrid material.[7] In contrast to organic polymers, inorganic mesoporous materials do not swell or dissolve in organic solvents, they have large and defined pore sizes and high specific surfaces as well as excellent mechanical and thermal stabilities. Recently, Rocha *et al.* synthesized modified MCM-41 and MCM-48 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 use the corresponding MoO_2Cl_2 supported material as 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.

Previously, we reported oxodiperoxo molybdenum complexes of the type (L–L)$MoO(O)_2$ with bidentate 2-(1-alkyl-3-pyrazolyl)pyridine ligands L–L to be highly active and stable homogeneous catalysts for olefin epoxidation.[10,11] Here we present an efficient approach to a covalent anchoring of this type of complex onto mesoporous MCM-41 under mild conditions. The resulting functionalized materials are active and truly heterogeneous catalysts for cyclooctene epoxidation.

The supported catalysts were synthesized from MCM-41 materials[12] as outlined in Scheme 1.

3a was further silylated using Me_3SiCl in order to remove the residual Si–OH groups on the surface of the mesoporous material, which were supposed to be unfavorable for the catalytic reaction. Zhao and Lu found that the adsorption characteristics of MCM-41 for polar molecules greatly depend on the concentrations of surface silanol groups.[13] Modification of MCM-41 by silylation with Me_3SiCl makes the surface more hydrophobic. Besides, Tatsumi *et al.* showed that trimethylsilylation of MCM-41 and MCM-48 improves their stability against moisture and mechanical compression.[14]

The success of the synthesis is confirmed by the solid state ^{13}C CP/MAS NMR spectrum. Both **4a** and **4b** present spectra similar to **2·MoO(O$_2$)$_2$**. However, the peaks corresponding to the OEt groups (δ = 57.7 and 10.4) are decreased in intensity due to the grafting on MCM-41. The solid state ^{29}Si CP/MAS NMR spectra provide direct evidence for the incorporation of the covalently linked organic system (Fig. 1). The spectrum of the unmodified MCM-41 support shows three signals at −108, −102 and −90 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].[13,15] The Q^3 sites are associated with the isolated Si–OH groups, and the Q^2 sites correspond to the geminal silanols. For the modified sample **4a**, three additional broad and overlapping signals appeared at −70, −60 and −53 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 and T^3 being the major organosilica species. Supporting the ligand leads to a decrease of the intensities of the Q^2 resonances and an increase of the Q^4



Scheme 1 *Reagents*: i, THF, NaH, $BrCH_2COOEt$, 4 h, refl.; ii, $H_2N(CH_2)_3Si(OEt)_3$, 2 h, 150 °C; iii, MCM-41, toluene, 9 h, 100 °C; iv, Me_3SiCl, 24 h, RT; v, $CHCl_3$, $MoO(O_2)_2·(DMF)_2$, 24 h, RT.

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† Electronic supplementary information (ESI) available: experimental data. See http://www.rsc.org/suppdata/cc/b2/b207645d/

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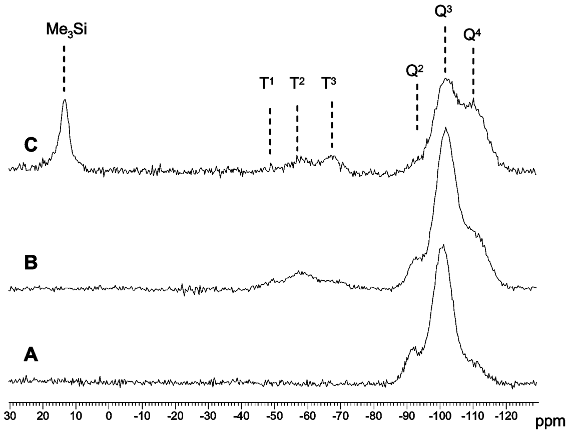

Fig. 1 ^{29}Si CP/MAS NMR spectra of MCM-41 (A) and the modified samples **4a** (B) and **4b** (C).

resonances with respect to Q^3. However, silylation with Me$_3$SiCl makes the Q^2 resonances disappear, decreases the intensity of the Q^3 resonances and increases the Q^4 resonances while a sharp peak at 13 ppm is assigned to the silicon nuclei of the Me$_3$Si groups. The 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 silylation. Further characterization of the catalyst was performed by N$_2$ adsorption and XRD.

4a and **4b** catalysts were tested for the epoxidation of cyclooctene with ^{t}BuOOH at 61 °C (see Fig. 2A). As expected, both samples showed good activities and high selectivities (almost 100% to epoxycyclooctene), which is consistent with the homogeneous system we previously reported.[11] Under our conditions, **4b** showed higher reaction rates than **4a** although the loading with active sites is the same. This might be due to the higher hydrophobicity of **4b**, which could reduce the adsorption abilities for the more polar epoxide and ^{t}BuOH. Besides, the higher hydrophobicity is also believed to be advantageous for the adsorption of the olefin.

The most remarkable result is the high stability of these catalysts against leaching of the active species into the liquid phase under the given reactive conditions. In the duplicate reaction over **4a** (see Fig. 2), it was found that cyclooctene can just be converted at a very low rate in the solution after removing the catalyst by filtration at the reaction temperature, which means only trace active species have been leached from the mesoporous host. For **4b**, there is almost no detectable subsequent conversion in the filtrate. This is a very strong evidence for a real heterogeneous catalysis and indicates that the undesired slight leaching of the catalyst can be inhibited by the further silylation by Me$_3$SiCl.

The excellent stability of our modified materials 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 the MoO(O$_2$)$_2$ unit and the chelating ligand. Further surface modification by Me$_3$SiCl can also have a positive influence on the stability against leaching by increasing the hydrophobicity of the mesoporous materials. The recyclability of **4a** and **4b** was studied by using the catalysts in a second reaction run. We found that the catalytic properties of these materials can be almost fully recovered by filtration, washing the solid with chloroform and finally drying at 70 °C under vacuum for a few hours. These results suggest that these catalysts are recyclable by selecting suitable treatment conditions. Investigations on the influence of the polarity of the framework (including Al-containing mesoporous material) on the catalytic activities and stabilities are underway.

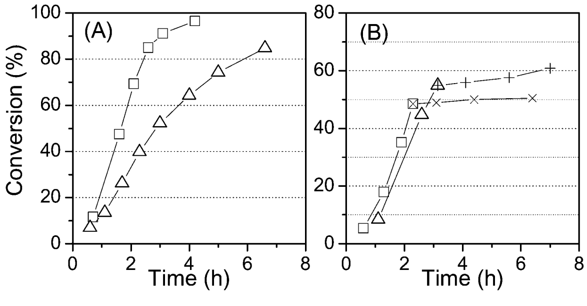

Fig. 2 (A) Kinetic profiles of epoxidation of cyclooctene with ^{t}BuOOH over **4a** (△) and **4b** (□). (B) Heterogeneous reaction check for **4a** (△) and **4b** (□), by continuing the reaction after removing the catalysts **4a** (+) and **4b** (×) by filtration at reaction temperature. Reaction conditions: the suspension, which contained 9.1 mmol cyclooctene, 9.6 mmol ^{t}BuOOH (5.5 M in decane) and 100 mg of catalyst (3.3 wt% Mo) in 25 mL CHCl$_3$, was stirred and heated to reflux temperature (61 °C).

Additionally to cyclooctene, 1-octene was tested as a substrate for heterogeneous epoxidation. As expected, this less activated olefin requires a higher reaction temperature (toluene, 111 °C) to be transferred to the corresponding epoxide. This has also been found for [2-(1-alkyl-3-pyrazolyl)pyridine]oxodiperoxo molybdenum(VI) complexes under homogeneous conditions.[11b]

In summary, our work presents a successful example of an active, truly heterogeneous modified mesoporous MCM-41 system obtained by covalent grafting of a chelate ligand. The presented method also provides a general approach to the synthesis of a large family of supported heterogeneous catalysts containing *N*,*N*′-chelating ligands.

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Notes and references

1 *Transition Metals for Fine Chemicals and Organic Synthesis*, ed. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 1998, **vol. 2**, p. 261ff.

2 Halcon Int., J. Kollar, U.S. Pat. 3,351,635, 1967.

3 (*a*) K. A. Jørgensen, *Chem. Rev.*, 1989, **89**, 431–458; (*b*) *Catalytic Oxidations with Hydrogen Peroxides as Oxidant*, ed. G. Strukul, Kluwer, Rotterdam, 1992.

4 (*a*) A. Corma, M. Domine, J. A. Gaona, J. L. Jorda, M. T. Navarro, F. Rey, J. Perez-Pariente, J. Tsuji, B. McCulloch and L. T. Nemeth, *Chem. Commun.*, 1998, 2211–2212; (*b*) J.-Y. Piquemal, E. Briot, M. Vennat, J.-M. Brégeault, G. Chottard and J.-M. Manoli, *Chem. Commun.*, 1999, 1195–1196; (*c*) D. Hoegaerts, B. F. Sels, D. E. De Vos, F. Verpoort and P. A. Jacobs, *Catal. Today*, 2000, **60**, 209–218; (*d*) M. Sasidharan, P. Wu and T. Tatsumi, *J. Catal.*, 2002, **205**, 332–338.

5 (*a*) R. A. Sheldon, I. W. C. E. Arends and H. E. B. Lempers, *Collect. Czech. Chem. Commun.*, 1998, **63**, 1724–1742; (*b*) R. A. Sheldon, I. W. C. E. Arends and H. E. B. Lempers, *Catal. Today*, 1998, **41**, 387–407.

6 (*a*) S. Leinonen, D. C. Sherrington, A. Sneddon, D. McLoughlin, J. Corker, C. Canevali, F. Morazzoni, J. Reedijk and S. B. D. Spratt, *J. Catal.*, 1999, **183**, 251–256; (*b*) M. M. Miller and D. C. Sherrington, *J. Chem. Soc., Chem. Commun.*, 1994, 55–56; (*c*) M. M. Miller, D. C. Sherrington and S. Simpson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2091–2096; (*d*) J.-H. Ahn and D. C. Sherrington, *Chem. Commun.*, 1996, 643–644.

7 (*a*) R. Anwander, *Chem. Mater.*, 2001, **13**, 4419–4438; (*b*) A. Stein, B. J. Melde and R. C. Schroden, *Adv. Mater.*, 2000, **12**, 1403–1419.

8 P. Ferreira, I. S. Goncalves, F. E. Kühn, A. D. Lopes, M. A. Martins, M. Pillinger, A. Pina, J. Rocha, C. C. Romao, A. M. Santos, T. M. Santos and A. A. Valente, *Eur. J. Inorg. Chem.*, 2000, 2263–2270.

9 C. D. Nunes, A. A. Valente, M. Pillinger, A. C. Fernandes, C. C. Romao, J. Rocha and I. S. Gonçalves, *J. Mater. Chem.*, 2002, **12**, 1735–1742.

10 (*a*) W. R. Thiel, M. Angstl and T. Priermeier, *Chem. Ber.*, 1994, **127**, 2373–2379; (*b*) W. R. Thiel and T. Priermeier, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1737–1738.

11 (*a*) W. R. Thiel and J. Eppinger, *Chem. Eur. J.*, 1997, **3**, 696–705; (*b*) W. R. Thiel, M. Angstl and N. Hansen, *J. Mol. Catal. A: Chem.*, 1995, **103**.

12 W. Y. Lin, Q. Cai, W. Q. Pang and Y. Yue, *Chem. Commun.*, 1998, 2473–2474.

13 X. S. Zhao and G. Q. Lu, *J. Phys. Chem. B*, 1998, **102**, 1556–1561.

14 T. Tatsumi, K. A. Koyano, Y. Tanaka and S. Nakata, *Stud. Surf. Sci. Catal.*, 1998, **117**, 143–150.

15 F. de Juan and E. Ruiz-Hitzky, *Adv. Mater.*, 2000, **12**, 430–432.