Mesoporous Silicas Modified with Dioxomolybdenum(VI) Complexes: Synthesis and Catalysis

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The dioxomolybdenum(VI) fragment MoO_2X_2 has been confined within the ordered mesopores of pure siliceous hexagonal MCM-41 and cubic MCM-48 molecular sieves either by direct grafting (solvent impregnation) with $MoO_2X_2(THF)_2$ or by using a spacer ligand [$L = NC(CH_2)_2Si(OEt)_3$]. The materials have been characterised by elemental analysis, powder X-ray diffraction, N_2 adsorption, IR spectroscopy, and magic-angle spinning NMR spectroscopy (^{13}C, ^{29}Si). All catalysts, homogeneous and heterogenised, are active in the epoxidation of cyclooctene with *tert*-butyl hydroperoxide.

Introduction

Homogeneous molybdenum(VI) (Halcon[1]) and heterogeneous titanium(IV)/SiO_2 (Shell[2]) catalysts are the basis of important industrial processes for the epoxidation of propylene, with alkyl hydroperoxides as the oxygen source. The high selectivities and (for a heterogeneous catalyst) high activities of the Ti^{IV}/SiO_2 catalyst prompted the design of novel shape-selective catalysts based on the concept of confinement of redox active metal centres in microporous and mesoporous oxides.[3] This strategy has been particularly successful in the case of titanium silicate materials.[4] Effective catalysts were obtained by incorporating titanium atoms into the framework sites of medium-pore silicalite I and II (TS-1 and TS-2, 5.5 Å pore size),[5] large-pore zeolite β (7 Å),[6] and mesoporous MCM-41 (typically 25−30 Å).[7] In a different approach, isolated tetrahedral Ti^{IV} species were grafted onto the surface of MCM-41 and MCM-48 by reaction of the pendant silanol (Si−OH) groups with titanocene dichloride precursors, followed by calcination.[8] Ti-MCM materials are important as catalysts as they are capable of oxidising relatively bulky reactants.

MCM-41 and MCM-48 are members of the M41S family of ordered mesoporous siliceous materials, formed by surfactant templating methods.[9] They both have very high surface areas (1000 $m^2\,g^{-1}$), high pore volumes (1 $cm^3\,g^{-1}$) and very narrow pore size distributions, tuneable in the range 16−100 Å. Despite the fact that MCM-48 and MCM-41 possess very different surfaces, it is evident that both materials behave similarly in grafting reactions with organometallics and coordination complexes, as observed for example in the case of derivatisation with the *ansa*-bridged ferrocene (1,1′-ferrocenediyl)dimethylsilane.[10] The structure of MCM-41 can be described as a hexagonal arrangement of cylindrical pores embedded in a matrix of amorphous silica. MCM-48 possesses a three-dimensional pore structure, with a silica interface that can be modelled by a minimal surface of the gyroid type.[11] MCM-48 therefore has some advantages over MCM-41 as a catalyst support material.

Early Mo^{VI}/SiO_2 catalysts were not as successful as Ti^{IV}/SiO_2 catalysts due to the rapid leaching of the metal ion. Recently, the synthesis of MoS-1 and MoS-2 has been described.[12] These would be expected to consist of the $Mo^{VI}O_2$ species attached to the framework defect sites. MoS-1 was reported to be an active catalyst for the chemoselective oxidation of thioethers to the corresponding sulfoxides, and MoS-2 was reported to be active in the oxidative dehydrogenation of ethanol to acetaldehyde. Isolated Mo^{VI} active sites have also been grafted onto the inner surfaces of MCM-41, via a molybdenocene dichloride precursor in a manner analogous to that mentioned above for titanium, to generate a catalyst which was tested for the oxidative dehydrogenation of methanol.[13] Another useful strategy for the confinement of metal centres in molecular sieves is the covalent attachment of coordination complexes via a spacer ligand (tethering). The tethering of chiral dioxomolybdenum(VI) complexes to the internal surface of a mesoporous USY-zeolite afforded a catalyst for the asymmetric epoxidation of allylic alcohols.[14]

We recently reported on the synthesis of *cis*-MoO_2^{2+} complexes of the type $MoO_2X_2L_n$ (X = Cl, Br) by reaction of solvent substituted $MoO_2X_2(Solv)_n$ complexes (Solv =

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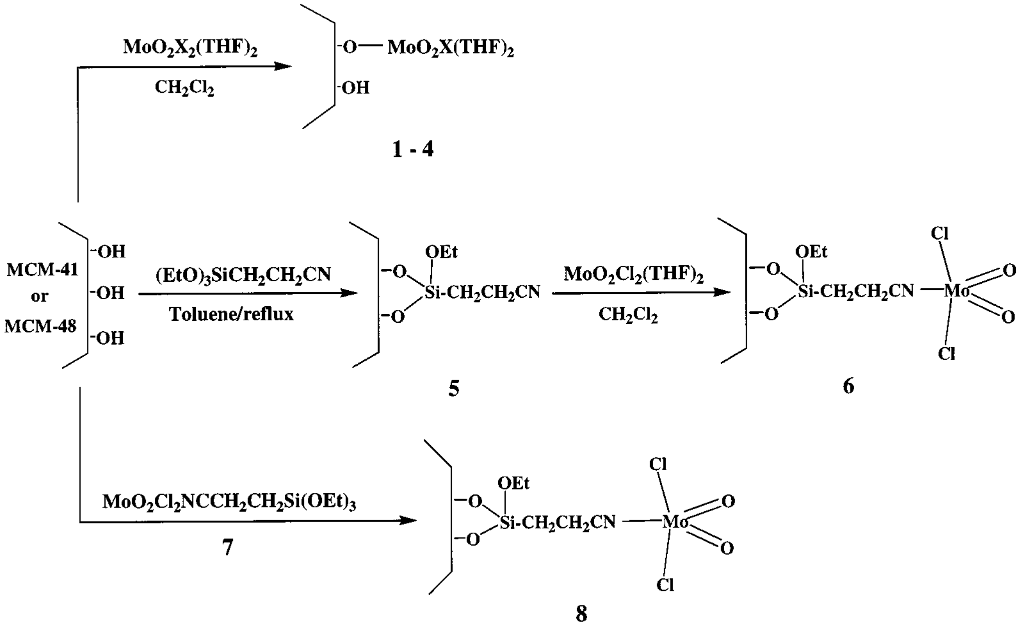
THF, CH_3CN, other nitrile molecules) with mono- and bidentate nitrogen and oxygen ligands.[15] The activity of the dissolved complexes as catalysts in olefin epoxidation with *tert*-butyl hydroperoxide (TBHP) was tested. In this article we report on the heterogenisation of the MoO_2X_2 fragment in MCM-41 and MCM-48 by either direct grafting with $MoO_2X_2(THF)_2$ or by using a spacer ligand [L = $NC(CH_2)_2Si(OEt)_3$]. The materials have been characterised by elemental analysis, powder X-ray diffraction (XRD), N_2 adsorption, IR spectroscopy, and magic-angle spinning (MAS) NMR spectroscopy (^{13}C, ^{29}Si). Preliminary experiments have been carried out to test the behaviour of the materials as catalysts for the epoxidation of cyclooctene with TBHP.

Results and Discussion

The supported materials MCM-41-MoO_2X_2 [X = Cl (**1**); X = Br (**2**)] and MCM-48-MoO_2X_2 [X = Cl (**3**); X = Br (**4**)] were prepared by diffusion of an excess of $MoO_2X_2(THF)_2$ (X = Cl, Br) into calcined and dehydrated MCM-41/MCM-48, in dry dichloromethane. The powders were washed repeatedly with dichloromethane to remove the unchanged oxides, and dried in vacuum at room temperature for several hours. Convenient and improved preparations of MCM-41-(spacer ligand)-MoO_2Cl_2 (**6**)/(**8**) were also developed by reacting MCM-41 with an excess of the nitrile with a triethoxysilyl group [$NC(CH_2)_2Si(OEt)_3$] in toluene, producing MCM-41-$Si(OEt)_nCH_2CH_2CN$ (**5**). This was followed by the addition of $MoO_2Cl_2(THF)_2$, or by the reaction of a solution of $MoO_2Cl_2NC(CH_2)_2Si(OEt)_3$ (**7**) with MCM-41. The products were isolated by filtration and washed thoroughly with ether to remove the unchanged oxide before drying in vacuum at room temperature. The molybdenum complex $MoO_2Cl_2NC(CH_2)_2Si(OEt)_3$ (**7**) was prepared by using a ligand exchange procedure,[15] in which the ligand was reacted with $MoO_2Cl_2(THF)_2$ in CH_2Cl_2 at room temperature. The resulting complex was isolated in excellent yield. The IR spectrum contained two bands assigned to Mo=O stretching modes (947, 916 cm^{-1}) as well as a band belonging to the nitrile ligand [$\nu(N\equiv C)$ = 2258 cm^{-1}]. This C≡N stretching mode is shifted to higher wavenumbers with respect to the free nitrile [$\nu(N\equiv C)$ = 2248 cm^{-1}] due to the coordination to the metal centre, and supports the presence of only one coordinating nitrile ligand.[15a] This unexpected result is not due to the steric bulk of the nitrile ligand but rather due to the fact that one of the ethoxide groups is directed towards the free coordinating position, *cis* to the position occupied by the nitrile group. A general summary of the reactions of these materials with the oxides is presented in Scheme 1.

The successful synthesis of the supported catalysts is confirmed by elemental analysis. The four initial materials **1**−**4** and **6** contained between 0.5 and 1.0 mass-% Mo, which is more than adequate for catalytic applications.[14] In compounds **1**−**4** the IR spectra do not clearly show bands for the two *cis*-Mo=O stretching modes, due to the small percentage of Mo. The products were pale blue powders and not visibly air-sensitive after exposure to air for several hours. Material **8** contained approximately 3.5 mass-% Mo. This is consistent with a coverage of molybdenum atoms of 4.6×10^{-25} mol/nm^2 (0.27 Mo atoms per nm^2). The IR spectra for the supported catalysts **6** and **8** provided evidence for the retention of the nitrile ligand [$\nu(N\equiv C) \approx$ 2260 cm^{-1}].

The powder XRD patterns of the parent calcined (pristine) MCM-41 and MCM-48 can be indexed on a hexagonal unit cell (using the strongest reflection, d_{100}, a = 40.37 Å) and a cubic unit cell (using the strongest reflection, d_{211}, a = 82.38 Å), respectively,. The pattern for MCM-41 also displays a broad secondary feature at $2\theta \approx 4.6°$ where



Scheme 1

(110) and (200) reflections would be expected for a hexagonally ordered material such as MCM-41 (Figure 1). The absence of resolved peaks indicates that any structural order of the material did not extend over a long range. A very similar result was obtained by Schmidt et al. for a purely siliceous MCM-41 prepared as in this work using the surfactant $[(C_{14}H_{29})NMe_3]Br$.[16] The data for the Mo-modified MCM materials are consistent with the retention of the hexagonal and cubic mesoporous structures throughout the grafting process (Figure 1).

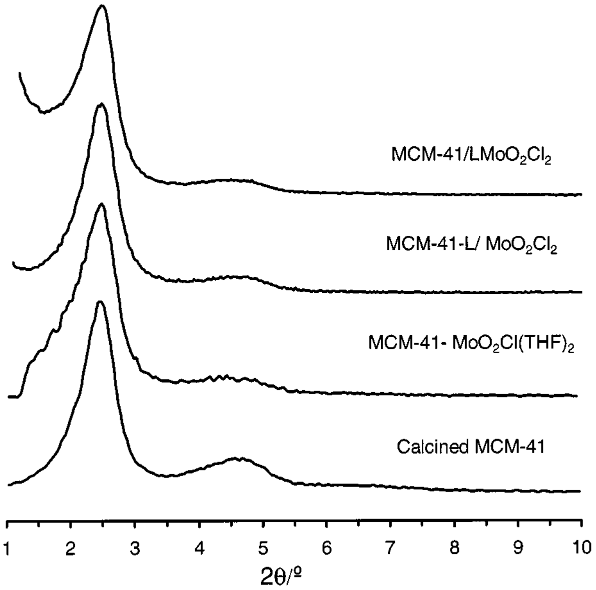


Figure 1. Powder XRD patterns of calcined (pristine) MCM-41 and functionalised samples

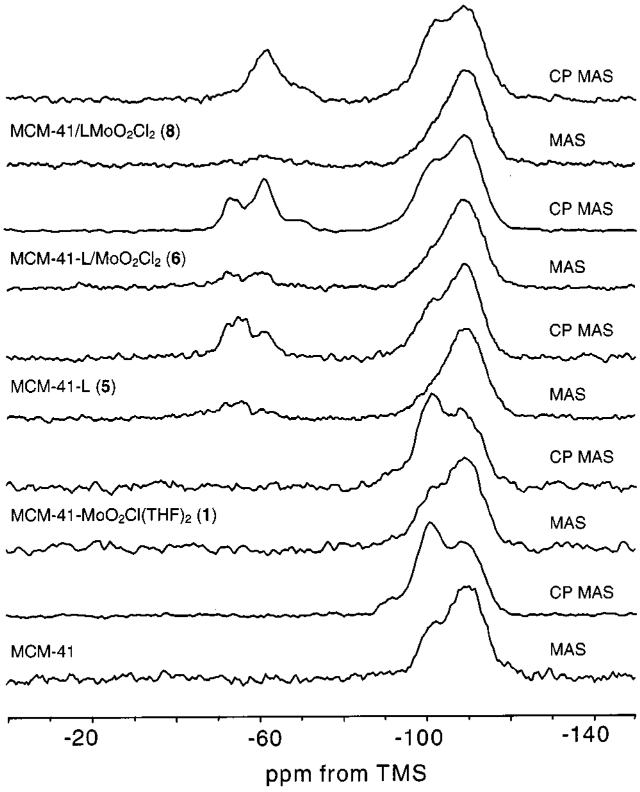


Figure 2. ^{29}Si MAS and CP MAS NMR spectra of calcined (pristine) MCM-41 and functionalised samples

The ^{29}Si CP MAS NMR spectra of MCM-41/MCM-48 functionalised with $MoO_2X_2(THF)_2$ (X = Cl, Br, **1−4**) exhibit two broad overlapping peaks at δ = −108 and −101 assigned to the Q^4 and Q^3 units of the silica framework, respectively, where $Q^n = \mathit{Si}(OSi)_n(OH)_{4-n}$, $n = 2-4$ (Figure 2, for material **1**). A small amount of Q^2 environments is also present (faint peak at δ = −91). The ^{29}Si CP MAS and MAS NMR spectra both show that the relative intensity of the Q^3 (and Q^2) peak changes only slightly upon functionalisation. This is consistent with the low metal loading (≤ 1% Mo) and perhaps also with a weak interaction (monopodal anchoring) of the molybdenum complexes with the surface.

For materials **5**, **6** and **8** the incorporation of the covalently linked organic group is confirmed by ^{29}Si CP MAS and MAS NMR spectroscopy, which shows distinct resonances for the organosilica species [$T^m = R\mathit{Si}(OSi)_m(OEt)_{3-m}$, $m = 1-3$] and for the silica network (Figure 2). For material MCM-41-$Si(OEt)_nCH_2CH_2CN$ (**5**), grafting of the surface with the triethoxysilyl group [$NC(CH_2)_2Si(OEt)_3$] gives additional peaks between δ = −60.8 and −52.8, assigned to the T^1 and T^2 centres. The liquid-state ^{29}Si NMR spectrum for neat $NC(CH_2)_2Si(OEt)_3$ exhibits one resonance at δ = −49.8. As expected, the grafting process also shows a decrease in the relative intensity of the Q^3 resonance and a concomitant increase in the intensity of the Q^4 resonance. This is consistent with the IR spectrum which shows characteristic absorption bands for the covalently linked organic groups [ν(N≡C) = 2257 cm^{-1}].

After addition of the fragment MoO_2Cl_2 to material **5** to give material **6**, significant changes are observed in the region of the ^{29}Si CP MAS NMR spectrum corresponding to the organosilica centres. Three broad overlapping signals are observed at δ = −52.7, −60.7 and −70, assigned to the T^1, T^2 and T^3 environments, respectively. The relative intensities of the T^2 and T^3 resonances are noticeably enhanced in the spectrum of **6** relative to that of **5**, which suggests that the nitrile ligand underwent further condensation on the silica surface during the reaction. MCM-41/$Si(OEt)_nCH_2CH_2CNMoO_2Cl_2$ (**8**) presents a broad resonance at δ = −61.9 assigned mainly to the T^2 centres, $R\mathit{Si}(OSi)_2(OEt)$, and also a faint broad resonance at −70.1, assigned to the T^3 centres, $R\mathit{Si}(OSi)_3$. In comparison, the complex **7** exhibits only one well-defined resonance at δ = −62.5 in the ^{29}Si MAS NMR spectrum.

The ^{13}C CP MAS NMR spectrum of MCM-41-$Si(OEt)_nCH_2CH_2CN$ (**5**) exhibits one faint peak at δ = 120 assigned to N*C*R, two peaks at δ = 58.6 and 10.4 assigned to the ethoxide group, and two well-defined peaks at δ = 16.6 and 7.7 assigned to NC−$\mathit{C}H_2$− and −$\mathit{C}H_2$−Si, respectively. The ^{13}C CP MAS NMR spectrum of MCM-41−$Si(OEt)_nCH_2CH_2CN/MoO_2Cl_2$ (**6**) is similar, except that the peaks corresponding to the ethoxide group (δ = 57.7 and 10.4) are not as intense as the peaks corresponding to the NC−CH_2−CH_2−Si fragment. Also, the resonance at δ = 128 assigned to N≡*C* is shifted downfield slightly compared with **5** as a result of coordination to the MoO_2Cl_2 fragment. Material **8** presents a similar spectrum with δ = 128.6, 120.2 (*C*≡N), 59.0 (O−*C*H₂−), 15.9 (NC−*C*H₂−), 9.4 (−*C*H₃, −*C*H₂−Si) (Figure 3).

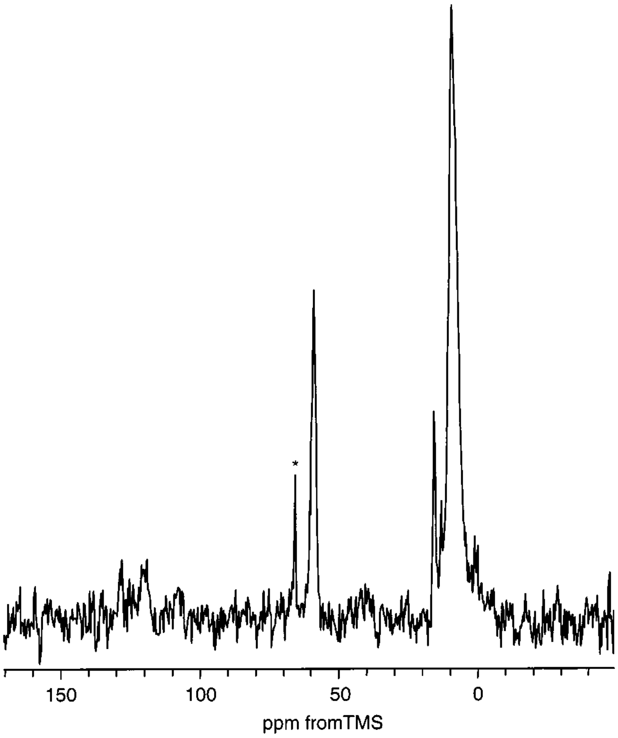


Figure 3. ^{13}C CP MAS NMR spectrum of MCM-41/$LMoO_2Cl_2$ (**8**), L = $NCCH_2CH_2Si(OEt)_n$; * denotes solvent

The N_2 adsorption-desorption isotherms of the solids recorded at 77 K are shown in Figure 4. The isotherms of the MCM-41 and MCM-48 materials are of Type IV according to the IUPAC, characteristic of mesoporous solids (intermediate pore size).[17] The physisorption process consists of monolayer-multilayer adsorption followed by capillary condensation of N_2 in the mesopores, below the expected condensation pressure of N_2. With the exception of MCM-41 and MCM-41/ $LMoO_2Cl_2$ (**8**), which show small hysteresis of adsorption and desorption (Figure 4), all samples have reversible N_2 adsorption isotherms.

The textural parameters determined from the isotherms are given in Table 1. The results for the parent MCM-41 and MCM-48 materials are in agreement with published values.[18,19] With direct grafting of $MoO_2X_2(THF)_2$ on MCM-41 (**1** and **2**), the N_2 adsorption isotherms of the modified and parent samples are very similar. The values of the BET specific surface areas (S_{BET}) and the specific total pore volumes (V_P) of the parent MCM-41 solid decrease between 4 and 7%. By changing the support to cubic mesoporous MCM-48, with the exception of the S_{BET} value for MCM-48-$MoO_2Br(THF)_2$ (**4**), no significant changes of the textural parameters are observed, and are negligible for MCM-48-$MoO_2Cl(THF)_2$ (**3**).

The N_2 adsorption isotherms of the functionalised MCM-41 materials **6** and **8** are different from that of the parent calcined MCM-41, demonstrating a lower uptake (Figure 4). On reaction of $MoO_2Cl_2(THF)_2$ with MCM-41-L (**5**) to give **6**, or on direct grafting of MoO_2Cl_2L (**7**) to give **8**, the values of S_{BET} decrease by 10.6 and 21.2%, respectively, and the values of V_P decrease by 45.1 and 39.0%, respectively (Table 1). These changes in adsorption properties can be attributed to successful grafting of the MoO_2Cl_2 fragment and/or to the tethering ligand $NCCH_2CH_2Si(OEt)_3$. The lower P/P_0 coordinates of the inflection points and the less sharp step of the isotherms in the region of capillary condensation of N_2 in the mesopores of the functionalised materials relative to that of the parent MCM-41 solid, may be assigned to changes in pore size distribution due to derivatisation of the internal silica surface of the mesoporous host. Brunel et al. observed similar changes in the features of the isotherms of MCM-41 upon grafting of functional molecules.[20]

The homogeneous and heterogenised Mo-complexes were tested for the epoxidation of cyclooctene with TBHP as the oxygen source at 55 °C. Typical catalytic runs are shown in Figure 5 and 6, and selectivities and total activities are given in Table 2 (calculated after 120 min reaction time). Reactions were also performed with pure calcined MCM-41/48 and, as expected, no significant epoxide formation was observed under these conditions. Pure calcined MCM-41 was previously found to be inactive in cyclohexene epoxidation with TBHP.[21]

For MCM-41-$MoO_2Cl(THF)_2$ (**1**), 31% conversion was observed after 2 h reaction with 100% selectivity to the epoxide (Figure 5, Table 2). Similar results were obtained for MCM-48-$MoO_2Cl(THF)_2$ (**3**). By contrast, the reaction with MCM-41-$MoO_2Br(THF)_2$ (**2**) was slow and the selectivity to cyclooctene oxide was very low (17% conversion of cyclooctene after 2 h with 56% selectivity to the oxide). This difference in activity between chlorodioxomolybdenum complexes and their bromo analogues has been noted recently by Kühn et al. for the homogeneous catalytic epoxidation of cyclooctene with complexes of the type $MoO_2X_2L_n$ (L = mono- and bidentate nitrogen and oxygen ligand).[15b] The time-dependent curves for MCM-41-$MoO_2X(THF)_2$ are of the same type as that reported recently for the catalytic activity of dissolved $MoO_2Br_2(CH_3CN)_2$ in cyclooctene epoxidation.[15a] This indicates that both reactions take place through the same mechanism, without any significant change in the reaction pathway. The appearance of these curves does not indicate the transformation of the original catalyst to another species during the reaction time and does not show an observable induction period. Similar results were obtained for the material prepared by reacting $MoO_2Cl_2(THF)_2$ with the ligand-grafted MCM-41-L. Indeed, the total activity, calculated after 2 h reaction and expressed as mols of cyclooctene produced per mol of molybdenum atoms per hour, is very similar for MCM-41-$MoO_2Cl(THF)_2$ (**1**) and MCM-41-L/MoO_2Cl_2 (**6**) (Table 2).

The kinetic profiles for the epoxidation of cyclooctene catalysed by homogeneous and heterogenised $MoO_2Cl_2NC(CH_2)_2Si(OEt)_3$ (**7**) are similar (Figure 6).

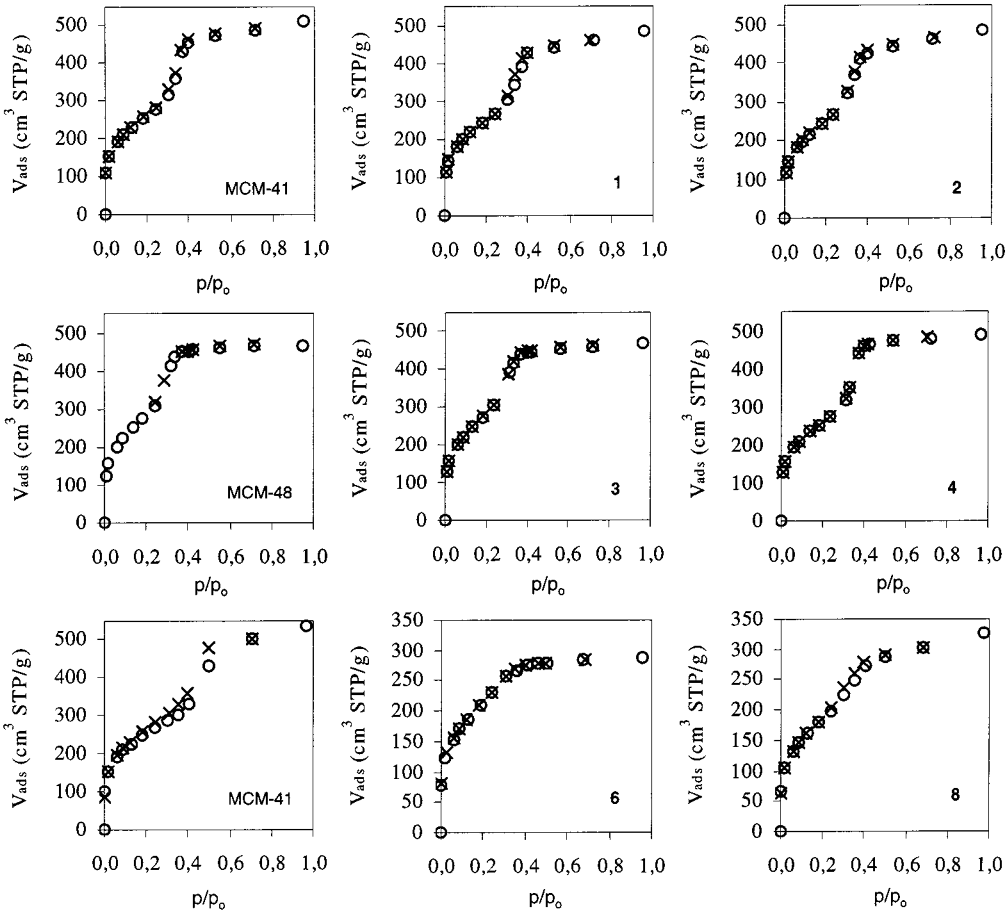


Figure 4. Nitrogen adsorption isotherms measured at 77 K of MCM solid materials before and after grafting/tethering of MoO_2X_2 complexes; open circle: adsorption; ×: desorption

Table 1. Textural parameters of MCM samples from N_2 isotherms at 77 K

	S_{BET} [m^2g^{-1}]	ΔS_{BET}[a] (%)	V_P [cm^3g^{-1}]	ΔV_P[b] (%)
MCM-41[c]	970.2	–	0.79	–
MCM-41-$MoO_2Cl(THF)_2$ (**1**)	916.0	−5.6	0.74	−6.6
MCM-41-$MoO_2Br(THF)_2$ (**2**)	926.2	− 4.5	0.75	−6.6
MCM-48	1095.4	–	0.75	–
MCM-48-$MoO_2Cl(THF)_2$ (**3**)	1083.9	−1.0	0.72	−4.0
MCM-48-$MoO_2Br(THF)_2$ (**4**)	982.1	−10.3	0.75	–
MCM-41[d]	893.4	–	0.82	–
MCM-41-L/MoO_2Cl_2 (**6**)	798.5	−10.6	0.45	−45.1
MCM-41/LMoO_2Cl_2 (**8**)	704.0	−21.2	0.50	−39.0

[a] Variation of surface area in relation to parent MCM material. – [b] Variation of total pore volume in relation to parent MCM material. – [c] MCM-41 sample used to prepare **1** and **2**. – [d] MCM-41 sample used to prepare **6** and **8**.

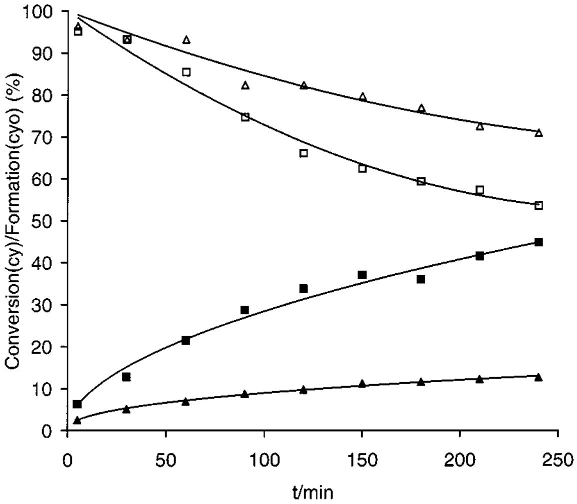


Figure 5. Kinetic profile for the epoxidation of cyclooctene with MCM-41-$MoO_2Cl(THF)_2$ (**1**) (solid square, open square) and MCM-41-$MoO_2Br(THF)_2$ (**2**) (solid triangle, open triangle) at 55 °C (solid symbols represent cyclooctene oxide formation and open symbols represent cyclooctene conversion); see text and Experimental Section for reaction details

After a very quick increase in the yield within the first 5 min the reaction velocities slow down. Thus, for the complex in solution, the yield of cyclooctene oxide formed was about 70% after 30 min, increasing by only a further 3% up to 4 h. A possible explanation for this sudden decrease in activity is the reaction of the active Mo complex in solution with *tert*-butyl alcohol. It has previously been reported that the epoxidation of 1-octene by a TiO_2-on-SiO_2 catalyst and TBHP in benzene at 80 °C exhibits marked autoretardation, attributed to the formation of *tert*-butyl alcohol during the epoxidation process.[22] For the MCM-41-supported complex, the yield of cyclooctene oxide formed was about 28% after 5 min, increasing to about 50% after 4 h. The total

Table 2. Selectivities and total activity (of cyclooctene oxide formed after 120 min reaction) of homogeneous and MCM-41/48-heterogenised dioxomolybdenum catalysts, with or without spacer ligand L = $NCCH_2CH_2Si(OEt)_n$

	Total activity (of cyo formed) [mols mol_{Mo}^{-1}, h^{-1}]	Selectivity (%)
MCM-41-$MoO_2Cl(THF)_2$ (**1**)	128	100
MCM-41-$MoO_2Br(THF)_2$ (**2**)	57.0	56
MCM-48-$MoO_2Cl(THF)_2$ (**3**)	83.2	99
MCM-48-$MoO_2Br(THF)_2$ (**4**)	47.1	52
MCM-41-L/MoO_2Cl_2 (**6**)	122	100
MoO_2Cl_2L (**7**)	38.1	90
MCM-41/$LMoO_2Cl_2$ (**8**)	38.9	93

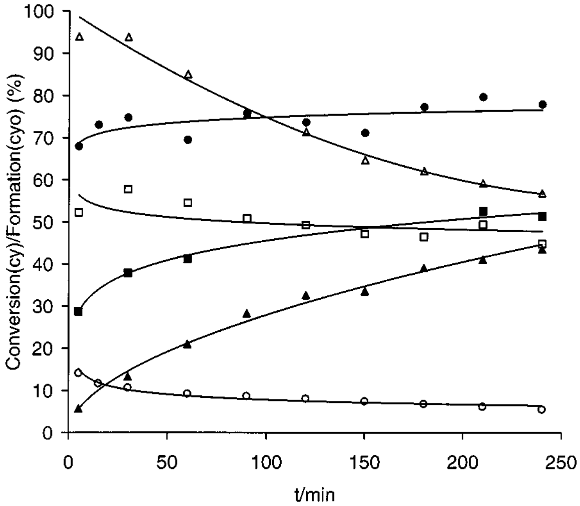


Figure 6. Kinetic profile for the epoxidation of cyclooctene with MCM-41-L/MoO_2Cl_2 (**6**) (solid triangle, open triangle), MCM-41/$LMoO_2Cl_2$ (**8**) (solid square, open square) and MoO_2Cl_2L (**7**) (solid circle, open circle) at 55 °C (solid symbols represent cyclooctene oxide formation and open symbols represent cyclooctene conversion); see text and Experimental Section for reaction details

activity achieved after 2 h reaction was very similar to that for the complex in solution, when the conversion per Mo is considered (Table 2). An initial turnover frequency of 3.5 mmol cyclooctene oxide per g of catalyst per min could be achieved, or 9.5 mol cyclooctene oxide per mol molybdenum atoms per min. These values are of a similar magnitude to those reported for the catalytic oxidation of cyclohexene with surface-grafted Ti-MCM-41[8a] and Ti-ITQ-2[23] catalysts (ITQ-2 is a crystalline layered silica). In a duplicate reaction with MCM-41/$LMoO_2Cl_2$ (**8**), the reaction mixture was filtered at the reaction temperature after 60 min, and then the filtrate was continued to be tested for activity at the reaction temperature. It was found that cyclooctene continued to be converted at a low rate, similar to that observed for the unfiltered reaction. This indicates that leaching may have occurred during the reaction, and that after 60 min at least part of the observed activity was due to the molybdenum in solution. More detailed studies are required to ascertain if the initial catalytic activity (up to 1 h) was mainly heterogeneous in nature.

Experimental Section

General: All preparations and manipulations were performed using standard Schlenk techniques under oxygen-free and water-free nitrogen. Commercial grade solvents were dried and deoxygenated by refluxing at least 24 h over appropriate drying agents under nitrogen, and were freshly distilled prior to use. − Powder XRD data were collected with a Phillips X'pert diffractometer using Cu-K_α radiation filtered by Ni. − Microanalyses were performed at the TU Munich. − Infrared spectra were recorded with a BIORAD FTS 575 C spectrometer with 1000 scans, and KBr and PE windows for mid and far infrared, respectively. − ^{29}Si and ^{13}C NMR spectra were recorded at 79.49 and 100.62 MHz, respectively, with a (9.4 T) Bruker MSL 400P spectrometer. ^{29}Si magic-angle-spinning (MAS) NMR spectra were recorded with 40° pulses, spinning rates 5.0−5.5 kHz and 60 s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 5.5 ms ^{1}H 90° pulses, 8 ms contact time, a spinning rate of 4.5 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million with respect to TMS. ^{13}C CP MAS NMR spectra were recorded with a 4.5 μs ^{1}H 90° pulse, 2 ms contact time, a spinning rate of 8 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million with respect to TMS. − Nitrogen adsorption data were recorded gravimetrically using a CI electronic MK2-M5 microbalance. Equilibrium at each data point was monitored using CI electronics Labweigh software and the pressure was monitored with an Edwards Barocel pressure sensor. The parent calcined MCM-41 and MCM-48 solids were degassed at 723 K whereas the modified samples were degassed at a lower temperature of 413 K to further minimise the destruction of their functionalities. All samples were kept constant at the degassing temperature, overnight (> 14 h), to give a residual pressure of ca. 10^{-2} Pa, and then cooled to room temperature prior to the adsorption measurements. The BET specific surface areas (S_{BET}) were calculated using the BET equation for relative pressures, in the range P/P_0 = 0.05−0.3, taking the cross-sectional area of a nitrogen molecule as 16.2 $Å^2$. The specific total pore volumes (micropore plus mesopore, V_P) were estimated from the nitrogen uptake at $P/P_0 \approx 0.95$, using the density of N_2 in its normal liquid state (ρ = 0.8081 g cm^{-3}). − The hexagonal channel host MCM-41 was synthesised using $[(C_{14}H_{29})NMe_3]Br$ according to published procedures.[9] After calcination (540 °C/6 h), the material was characterised by powder XRD, N_2 adsorption and FTIR spectroscopy. − The cubic channel host MCM-48 was synthesised using $[(C_{16}H_{33})NMe_3]Cl$ according to published procedures.[24] After calcination (540 °C/6 h), the material was characterised by powder XRD, N_2 adsorption and FTIR spectroscopy. − The precursors MoO_2Br_2,[25] MoO_2Cl_2,[25] and $MoO_2X_2(THF)_2$ (X = Cl, Br)[26] were prepared as described previously. − ^{13}C MAS NMR spectroscopy of $MoO_2X_2(THF)_2$ (25 °C): δ = 74.3 (THF), 25.9 (THF).

Preparation of Materials of General Formula MCM-41/48-$MoO_2X(THF)_2$ (X = Cl, Br): Calcined MCM-41/48 (0.5 g) was activated at 180 °C in vacuum (10^{-2} Pa) for 3 h and treated with excess of $MoO_2X_2(THF)_2$ (X = Cl, Br) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 2 d. The solution was filtered and the pale blue solid washed three times with 15-mL portions of CH_2Cl_2, before drying in vacuum at room temperature for several hours.

MCM-41-$MoO_2Cl(THF)_2$ (1): Anal. found Mo 1.10. − ^{29}Si MAS NMR spectrum exhibits one broad resonance at δ = −109.4 and a shoulder at δ = −101.3. ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at δ = −101.1 (Q^3) and δ = −108.2 (Q^4), and a faint peak at δ = −91.8 (Q^2).

MCM-41-$MoO_2Br(THF)_2$ (2): Anal. found Mo 0.7. − ^{29}Si MAS NMR spectrum exhibits one broad resonance at $\delta = -108.5$ and a shoulder at $\delta = -100.8$. ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at $\delta = -100.6$ (Q^3) and $\delta = -108.7$ (Q^4), and a faint peak at $\delta = -91.2$ (Q^2).

MCM-48-$MoO_2Cl(THF)_2$ (3): Anal. found Mo 0.7. − ^{29}Si MAS NMR spectrum exhibits one broad resonance at $\delta = -108.5$ and a shoulder at $\delta = -101.7$. ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at $\delta = -101.7$ (Q^3) and $\delta = -108.8$ (Q^4), and a faint peak at $\delta = -91.2$ (Q^2).

MCM-48-$MoO_2Br(THF)_2$ (4): Anal. found Mo 0.5. − ^{29}Si MAS NMR spectrum exhibits one broad resonance at $\delta = -108.8$ and a shoulder at $\delta = -101.4$. ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at $\delta = -101.1$ (Q^3) and $\delta = -108.8$ (Q^4), and a faint peak at $\delta = -91.2$ (Q^2).

Preparation of MCM-41-$Si(OEt)_nCH_2CH_2CN$ (5): Calcined MCM-41 (0.5 g) was activated at 180 °C under vacuum for 2 h and treated with excess of $NCCH_2CH_2Si(OEt)_3$ in toluene (30 mL). The mixture was stirred under reflux for 66 h. The solution was filtered and the white solid washed several times with 20-mL portions of ether, before drying under vacuum at 100 °C for several hours. − Anal. found C 7.90, H 1.86, N 2.14. − IR (KBr): $\tilde{\nu} = 3441$ cm^{-1} (vs), 3038 (w), 2981 (m), 2932 (m), 2257 (m), 1706 (w), 1638 (s), 1397 (m), 1232 (vs), 1083 (vs), 955 (m), 795 (s), 700 (w), 592 (w), 455 (s). − ^{29}Si MAS NMR spectrum exhibits broad resonances at $\delta = -109.5$, −60.8 and −52.8. − ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at $\delta = -109.0$ (Q^4) and $\delta = -101.6$ (Q^3), a faint peak at $\delta = -92.3$ (Q^2), and two broad overlapping signals at $\delta = -60.3$ and −51.9. − ^{13}C CP MAS NMR spectrum (25 °C): $\delta = 120.2$ ($C{\equiv}N$), 58.6 ($O-CH_2-$), 16.6 ($NC-CH_2-$), 10.2 ($-CH_3$), 7.7 ($-CH_2-Si$).

Preparation of MCM-41-$Si(OEt)_nCH_2CH_2CN/MoO_2Cl_2$ (6): A suspension of activated MCM-41-$Si(OEt)_nCH_2CH_2CN$ (0.46 g) was treated with excess of $MoO_2Cl_2(THF)_2$ in CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for 8 h. The solution was filtered and the pale blue solid washed twice with 15-mL portions of CH_2Cl_2, and one portion of ether (20 mL), before drying under vacuum at room temperature for several hours. − Anal. found C 12.63, H 2.15, Mo 1.0, N 1.86. − IR (KBr): $\tilde{\nu} = 3432$ cm^{-1} (vs), 2987 (m), 2259 (m), 1637 (s), 1429 (m), 1234 (vs), 1082 (vs), 946 (m), 887 (w), 796 (s), 566 (w), 455 (s), 299 (m). − ^{29}Si MAS NMR spectrum exhibits one broad resonance at $\delta = -108.3$, and three broad overlapping signals at $\delta = -52.7$, −60.7 and −70.0. − ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at $\delta = -109.0$ (Q^4) and $\delta = -102.0$ (Q^3), a faint peak at $\delta = -90.8$ (Q^2), and three broad overlapping signals at $\delta = -52.7$, −60.7 and −70.0. − ^{13}C CP MAS NMR spectrum (25 °C): $\delta = 128$ ($C{\equiv}N$), 57.7 ($O-CH_2-$), 16.8 ($NC-CH_2-$), 10.4 ($-CH_3$), 7.8 ($-CH_2-Si$).

Preparation of $MoO_2Cl_2NCCH_2CH_2Si(OEt)_3$ (7): A solution of $MoO_2Cl_2(THF)_2$ (0.83 g, 2.42 mmol) in CH_2Cl_2 (20 mL) was treated with $NCCH_2CH_2Si(OEt)_3$ (1.05 g, 4.84 mmol), and the mixture was vigorously stirred for 30 min. The resulting solution was filtered and concentrated to dryness to give a yellow-brown oil. The very air-sensitive product was washed with hexane and dried in vacuum. Yield: 0.97 g (96%). − $C_9H_{19}Cl_2MoNO_5Si$ (416.18): calcd. C 25.97, H 4.60, N 3.37; found C 26.18, H 4.83, N 3.61. − Selected IR (KBr): $\tilde{\nu} = 2258$ cm^{-1} (s, $N{\equiv}C$), 947 (vs, $Mo{=}O$), 916 (vs, $Mo{=}O$). − ^{13}C NMR spectrum($CDCl_3$, 400 MHz, 20 °C): $\delta = 121.1$ ($C{\equiv}N$), 59.3 ($O-CH_2-$), 18.7 ($NC-CH_2-$), 11.9 ($-CH_3$), 8.8 ($-CH_2-Si$). − ^{29}Si MAS NMR spectrum (25 °C): $\delta = -62.5$.

Preparation of MCM-41/$Si(OEt)_nCH_2CH_2CNMoO_2Cl_2$ (8): Calcined MCM-41 (0.75 g) was activated at 180 °C under vacuum for 2 h and treated with excess of $MoO_2Cl_2NCCH_2CH_2Si(OEt)_3$ (**7**) (0.70 g) in toluene (30 mL). The mixture was stirred at room temperature for 2 h. The solution was filtered and the pale blue solid washed three times with 20-mL portions of ether, before drying under vacuum for several hours. − Anal. found C 9.04, H 1.81, Mo 3.5, N 1.27. − IR (KBr): $\tilde{\nu} = 3441$ cm^{-1} (vs), 2982 (m), 2937 (m), 2912 (w), 2260 (m), 1706 (w), 1638 (s), 1495 (w), 1448 (w), 1429 (m), 1394 (m), 1373 (w), 1322 (w), 1232 (vs), 1083 (vs), 955 (m), 734 (w), 696 (w) 549 (m), 334 (w). − ^{29}Si MAS NMR spectrum exhibits one broad resonance at $\delta = -108.2$. − ^{29}Si CP MAS NMR spectrum exhibits two broad resonances at $\delta = -108.9$ (Q^4) and $\delta = -101.7$ (Q^3), a faint peak at $\delta = -91.2$ (Q^2), one broad resonance at $\delta = -61.9$ and a faint broad resonance at −70.1. − ^{13}C MAS NMR spectrum (25 °C): $\delta = 128.6$, 120.2 ($C{\equiv}N$), 65.8, 59.0 ($O-CH_2-$), 15.9 ($NC-CH_2-$), 9.4 ($-CH_3$, $-CH_2-Si$).

Catalytic Reactions with Modified Mesoporous Materials/Dioxomolybdenum(VI) Complexes as Catalysts: *cis*-Cyclooctene (800 mg, 7.3 mmol), di-*n*-butyl ether (800 mg,) internal standard), **1−8** (175 mg, as catalyst) and 2 mL of 5.5 M *tert*-butyl hydroperoxide in decane were added to a thermostated reaction vessel and stirred for 24 h at 50 °C. − The course of the reaction was monitored by quantitative GC analysis. Samples were taken every 30 min, diluted with dichloromethane, and chilled in an ice bath. For the destruction of hydroperoxide and removal of water, a catalytic amount of manganese dioxide and magnesium sulfate was added. After the gas evolution had ceased, the resulting slurry was filtered through a filter-equipped Pasteur pipette and the filtrate injected into the GC column. − The conversion of cyclooctene and the formation of cyclooctene oxide was calculated from a calibration curve ($r^2 = 0.999$) recorded prior to the reaction course.

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[1] [1a] Halcon (J. Kollar), U.S. Pat. 3,351,635, **1967**; *Chem. Abstr.* **1968**, *68*, 2094. − [1b] Halcon (J. Kollar), U.S. Pat. 3,350,422, **1967**; *Chem. Abstr.* **1968**, *68*, 278.

[2] [2a] R. A. Sheldon, *Aspects of Homogeneous Catalysis* (Ed.: R. Ugo), vol. 4, Reidel, Dordrecht, The Netherlands, **1981**, p. 1. − [2b] R. A. Sheldon, *J. Mol. Catal.* **1980**, *7*, 107−126.

[3] [3a] R. A. Sheldon, I. W. C. E. Arends, H. E. B. Lempers, *Catalysis Today* **1998**, *41*, 387−407. − [3b] R. A. Sheldon, M. Wallau, I. W. C. E. Arends, U. Schuchardt, *Acc. Chem. Res.* **1998**, *31*, 485−493.

[4] R. Murugavel, H. W. Roesky, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 477−479.

[5] [5a] M. Taramasso, G. Perego, B. Notari (Enichem), US Pat. 4 410 501, **1981**; *Chem. Abstr.* **1981**, *95*, 137. − [5b] B. Notari, *Stud. Surf. Sci. Catal.* **1987**, *37*, 413.

[6] [6a] T. Blasco, M. A. Camblor, A. Corma, J. Pérez-Pariente, *J. Am. Chem. Soc.* **1993**, *115*, 11806−11813. − [6b] M. A. Camblor, M. Constantini, A. Corma, L. Gilbert, P. Esteve, A. Martinez, S. Valencia, *Chem. Commun.* **1996**, 1339−1340.

[7] A. Corma, M. T. Navarro, J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.* **1994**, 147−148.

[8] [8a] T. Maschmeyer, F. Rey, G. Sankar, J. M. Thomas, *Nature* **1995**, *378*, 159–162. – [8b] L. Marchese, E. Gianotti, V. Dellarocca, T. Maschmeyer, F. Rey, S. Coluccia, J. M. Thomas, *Phys. Chem. Chem. Phys.* **1999**, *1*, 585–592. – [8c] P. Ferreira, I. S. Gonçalves, F. E. Kühn, M. Pillinger, J. Rocha, A. M. Santos, A. Thursfield, *Eur. J. Inorg. Chem.*, **2000**, 551–557.

[9] [9a] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712. – [9b] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.

[10] [10a] S. O'Brien, J. Tudor, S. Barlow, M. J. Drewit, S. J. Heyes, D. O'Hare, *Chem. Commun.* **1997**, 641–642. – [10b] P. Ferreira, I. S. Gonçalves, F. Mosselmans, M. Pillinger, J. Rocha, A. Thursfield, *Eur. J. Inorg. Chem.* **2000**, 97–102.

[11] V. Alfredsson, M. Anderson, *Chem. Mater.* **1996**, *8*, 1141.

[12] [12a] P. S. Raghavan, V. Ramaswamy, T. T. Upadhya, A. Sudalai, A. V. Ramaswamy, S. Sivasanker, *J. Mol. Catal. A: Chem*. **1997**, *122*, 75–80. – [12b] P. S. Raghavan, M. P. Vinod, *J. Mol. Catal. A: Chem*. **1998**, *135*, 47–53.

[13] I. J. Shannon, T. Maschmeyer, R. D. Oldroyd, G. Sankar, J. M. Thomas, H. Pernot, J. –P. Balikdjian, M. Che, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1495–1499.

[14] A. Corma, A. Fuerte, M. Iglesias, F. Sánchez, *J. Mol. Catal. A: Chem*. **1996**, *107*, 225–234.

[15] [15a] F. E. Kühn, E. Herdtweck, J. J. Haider, W. A. Herrmann, I. S. Gonçalves, A. D. Lopes, C. C. Romão, *J. Organomet. Chem*. **1999**, *583*, 3–10. – [15b] F. E. Kühn, A. D. Lopes, A. M. Santos, E. Herdtweck, J. J. Haider, C. C. Romão, A. G. Santos, *J. Mol. Catal. A: Chem.*, **2000**, *151*, 147–160.

[16] R. Schmidt, M. Stöcker, E. Hansen, D. Akporiaye, O. H. Ellestad, *Microporous Mater.* **1995**, *3*, 443.

[17] S. J. Gregg, K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, London, **1982**.

[18] M. D. Alba, A. Becerro, J. Klinowski, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 849.

[19] A. A. Romero, M. D. Alba, W. Zhou, J. Klinowski, *J. Phys. Chem. B* **1997**, *101*, 5294.

[20] D. Brunel, A. Cauvel, F. Fajula, F. DiRenzo, *Stud. Surf. Sci. Catal.* **1995**, *97*, 173.

[21] R. D. Oldroyd, J. M. Thomas, T. Maschmeyer, P. A. MacFaul, D. W. Snelgrove, K. U. Ingold, D. D. M. Wayner, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2787–2790.

[22] R. A. Sheldon, J. A. Van Doorn, *J. Catal*. **1973**, *31*, 427.

[23] A. Corma, U. Díaz, V. Fornés, J. L. Jordá, M. Domine, F. Rey, *Chem. Commun.* **1999**, 779–780.

[24] [24a] A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouz, M. Janicke, B. F. Chmelka, *Science* **1993**, *261*, 1299. – [24b] J. Xu, Z. Luan, H. He, W. Zhou, L. Kevan, *Chem. Mater.* **1998**, *10*, 3690.

[25] R. Colton, I. B. Tomkins, *Aust. J. Chem.* **1965**, *18*, 447.

[26] [26a] M. Minelli, J. H. Enemark, R. T. C. Brownlee, M. J. O′Connor, A. G. Wedd, *Coord. Chem. Rev.* **1985**, *68*, 169. – [26b] F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Gonçalves, E. Herdtweck, C. C. Romão, *J. Mol. Catal. A: Chem.*, in press.

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