Structural Studies and Catalytic Activity of MCM-41 and MCM-48 Modified With the Titanocenophane $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$

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Titanium(IV)-grafted mesoporous silicas have been prepared by diffusion of an excess of the *ansa*-bridged titanocene $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ into the channels of hexagonal MCM-41 and cubic MCM-48 in dichloromethane or tetrahydrofuran at room temperature. The choice of solvent determines the course of the reaction and hence the activity of the resulting materials as catalysts in the catalytic epoxidation of cyclooctene with *tert*-butylhydroperoxide. Magic-angle spinning (MAS) NMR (^{13}C, ^{29}Si) spectroscopy was used to characterise the local environment of the surface-bound titanium active sites. When dichloromethane is used, the dominant species anchored to the surface are isolated *ansa*-bridged titanocene fragments. When THF is used, the $[SiMe_2(\eta^5\text{-}C_5H_4)_2]$ unit is lost with the concomitant formation of surface-bound Ti^{IV} species coordinated by THF molecules. These materials showed the best catalytic performance per Ti atom for the conversion of cyclooctene. All materials were further characterised by means of elemental analysis, powder X-ray diffraction (XRD), N_2 adsorption and FTIR spectroscopy.

Introduction

The confinement of redox-active metal centres on the surface of an inorganic oxide support matrix is a recognised route to heterogeneous catalysts for liquid-phase oxidations.[1] In the early Seventies the Shell Ti^{IV}/SiO_2 catalyst was developed for the epoxidation of propylene with ethylbenzene hydroperoxide.[2] An organic peroxide has to be used as the oxygen source in this process because the catalyst is sensitive to deactivation by water. This gives rise to toxic side products. A major step forward came with the discovery of titanium(IV) silicalite-I (TS-1),[3] obtained by the isomorphous substitution of titanium for silicon in the tetrahedral framework sites of silicalite-I, a hydrophobic molecular sieve possessing a three-dimensional system of intersecting elliptical pores with diameters of 5.3 × 5.5 and 5.1 × 5.5 Å. TS-1 is a catalyst for selective oxidations under very mild conditions with aqueous H_2O_2. Its remarkable activity is due to site isolation of Ti^{IV} centres in the hydrophobic pores of silicalite which allows for the simultaneous adsorption of the hydrophobic substrate and the oxidant. Site isolation is important because it prevents the oligomerisation of the Ti^{IV} centres to unreactive μ-oxo species.

TS-1 is a medium pore molecular sieve and its use is restricted to substrate molecules with kinetic diameters 5.5 Å. Thus, new materials with larger pore sizes and different coordination environments have always been sought. Examples include the hydrophilic Ti-doped zeolite β (pore diameter 7 × 7 Å),[4] and the recently discovered ETS-10 (Engelhard Corporation Titanium Silicate) containing tetrahedrally coordinated Si^{4+} and octahedrally coordinated Ti^{4+}.[5] A breakthrough into the mesoporous regime came with the discovery by researchers at the Mobil Corporation of a new generation of surfactant-templated (alumino)silicates (M41S) with 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.[6] The M41S family includes the thermally stable hexagonal MCM-41 and cubic MCM-48 phases. They have properties intermediate between those of SiO_2 and Al_2O_3, and microporous crystalline molecular sieves. Ti-substituted M41S, and related materials, have been prepared directly by either treating Ti alkoxides with silicon compounds, or mixing TiO_2 with silica.[7] One problem with these materials as catalysts is that access by the reactants to the Ti active centres is still somewhat limited as the latter are buried within the inner walls of the mesoporous solid.

An alternative strategy for the incorporation of redox-active metal centres into the internal surface of M41S materials is the covalent attachment of organometallic complexes by reaction with pendant silanol (Si–OH) groups.[1,8] Thomas and co-workers have prepared a heterogeneous titanium(IV) catalyst by diffusing a solution of Cp_2TiCl_2 in chloroform into the mesopores of MCM-41, followed by treatment with Et_3N to activate the Si–OH groups to form Si–O–Ti linkages.[9] The final catalyst is obtained by calcination to remove the organic ligands. An extension of this synthetic methodology comprises the functionalisation of the walls of MCM-41 with ferrocenyl end-groups by a ring-opening reaction of the strained metallocenophane $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]$.[10] We followed up this work to show that

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the organometallic complex reacts in a similar way with the surface silanols of MCM-48 to give a $C_5H_4SiMe_2$–O linkage.[11] We now wish to report studies on the derivatisation of MCM-41 and MCM-48 by direct reaction with the titanocenophane complex $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$. All materials have been characterised by elemental analysis, powder XRD, N_2 adsorption and MAS NMR spectroscopy (^{13}C, ^{29}Si). The derivatised materials are catalysts for the epoxidation of cyclooctene.

Results and Discussion

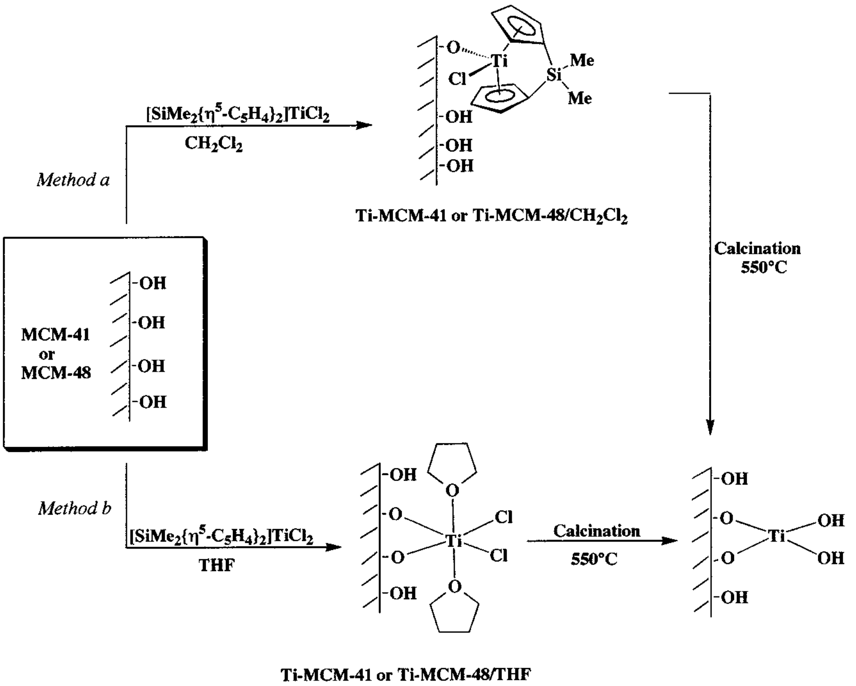
Synthesis and Spectroscopic Characterisation

The introduction of an interannular bridge in titanocene dichloride alters its reactivity considerably, particularly in relation to reduction. A comparison of the redox behaviour of Cp_2TiCl_2 and the dialkylsilyl-bridged derivatives $[SiR_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ showed that the bridged compounds exhibit a single one-electron reversible reduction whereas the unbridged compound exhibits several reduction waves.[12] The stability of the one-electron reduced d^1 Ti^{III} monoanion of the bridged compounds has been rationalised on the basis of the ability of the SiR_2 ligand to restrict the mobility of the Cp rings and to maintain their original canted arrangement. As mentioned above, titanocene dichloride grafted onto mesoporous MCM-41 is a precursor to an active and selective heterogeneous epoxidation catalyst. Detailed spectroscopic and computational studies have confirmed that $(\equiv Si–O)_3TiCp$ is more likely to form than $(\equiv Si–O)_2TiCp_2$.[13] To the best of our knowledge, no studies have yet been made of the effect of the presence of an interannular bridge on the anchoring process, or the catalytic properties, of the grafted product.

The Ti-modified mesoporous materials are designated as Ti-MCM-41/(CH_2Cl_2 or THF) and Ti-MCM-48/(CH_2Cl_2 or THF), and were prepared as depicted in Scheme 1. MCM-41 and MCM-48 were treated with an excess of $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ in either dichloromethane (method a) or THF (method b). The products were isolated by filtration and washed thoroughly with the relevant solvent to remove excess organometallic before drying in vacuo at room temperature.

Method a gave grey/dark-brown, air-sensitive products which transformed to light brown powders after exposure to air for several hours. The products from method b were pale pink/beige powders and not visibly air-sensitive. Elemental analysis indicated that the materials contained approximately 4.2 mass% Ti (method a) or 1.2 mass% Ti (method b). This is consistent with a coverage of titanium atoms of 8.8×10^{-25} mol/nm^2 (0.5 Ti atoms per nm^2) and 2.5×10^{-25} mol/nm^2 (0.15 Ti atoms per nm^2), respectively. The former value is similar to the concentration of surface silanol groups in parent calcined MCM-41, reported to be in the range 1 to 3 per nm^2.[14] Grafted samples were subsequently calcined in air at 550 °C for 10 hours to remove organic components.

After treatment of the mesoporous materials with the titanocenophane complex in CH_2Cl_2 or THF the infrared band of the OH groups at 3742 cm^{-1} was noticeably reduced in intensity. In addition the spectra of MCM-41/CH_2Cl_2 or MCM-48/CH_2Cl_2 show bands at 2962 and 2930 cm^{-1}, representing the asymmetric and symmetric CH_3 stretching vibrations. The IR spectra of these anchored materials and of the starting material show that the C=C stretching modes in the region of 1400 cm^{-1} are similar. The bands assigned to the Cp ring, appearing at 1456 cm^{-1} and



Scheme 1. Modification of MCM-41 and MCM-48 using $[SiMe_2(\eta^5\text{-}C_5H_4)TiCl_2]$

1375 cm^{-1} for the free organometallic, are not shifted to different frequency on anchoring, indicating a similar interaction between the titanium centre and the Cp$_2$SiMe$_2$ group.

The powder X-ray diffraction (XRD) patterns of the parent calcined MCM-41 and MCM-48 can be indexed on a hexagonal unit cell (using the strongest reflection, d$_{100}$, a = 40 Å) and cubic unit cell (using the strongest reflection, d$_{211}$, a = 88.62 Å), respectively. The data for the as-synthesised and calcined Ti-modified MCM materials are consistent with retention of the hexagonal and cubic mesoporous structures throughout the grafting and calcination process (Figure 1 and 2).

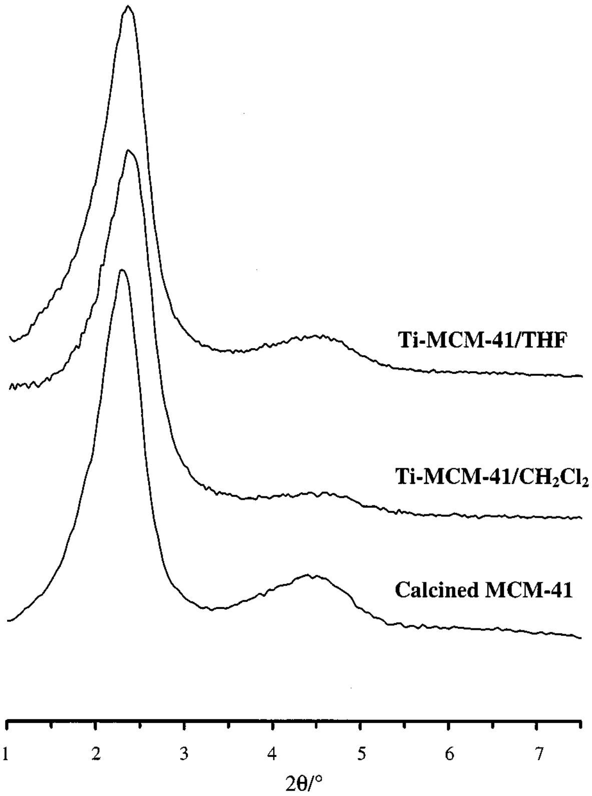


Figure 1. Powder XRD patterns of MCM-41 materials

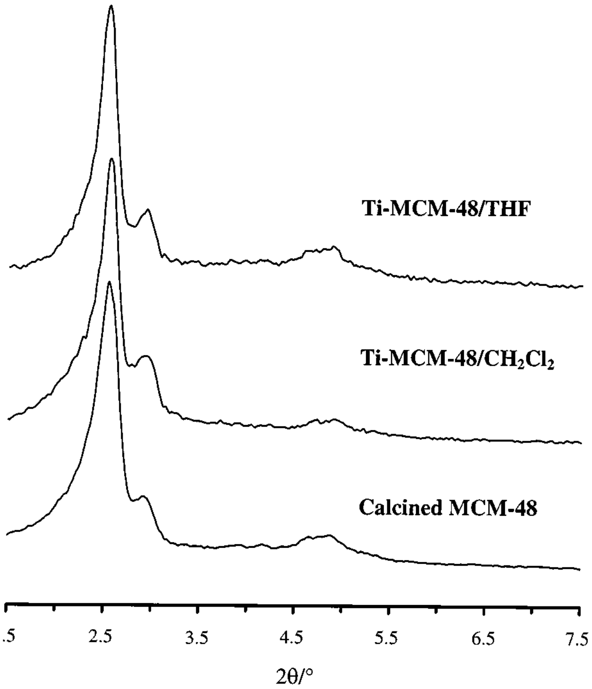


Figure 2. Powder XRD patterns of MCM-48 materials

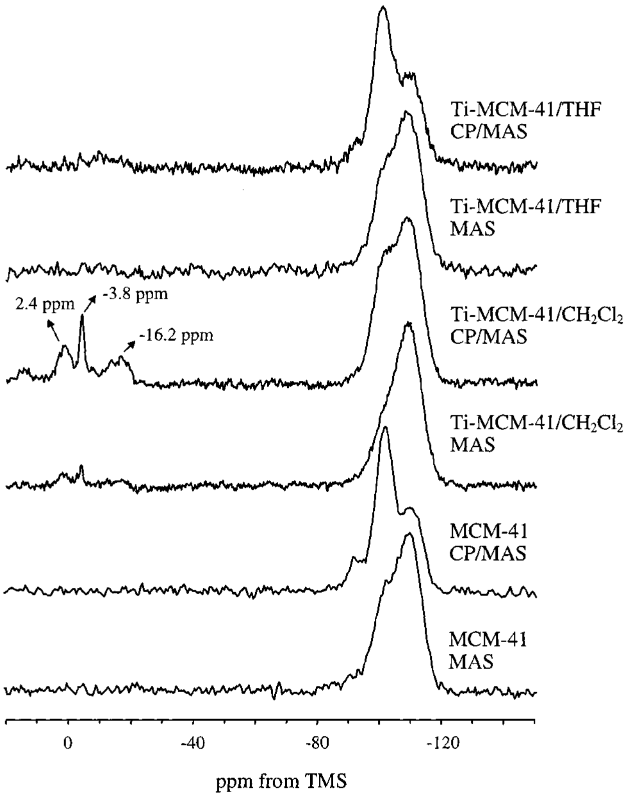


Figure 3. ^{29}Si CP MAS and MAS NMR at room temperature of MCM-41 materials

Figure 3 and 4 show the ^{29}Si CP MAS and MAS NMR spectra for Ti-MCM-41 and Ti-MCM-48 prepared in dichloromethane, respectively. The ^{29}Si CP MAS NMR spectrum of Ti-MCM-41/CH$_2$Cl$_2$ exhibits two broad convoluted resonances, at δ = –108.4 and –100.3 assigned to Q^4 and Q^3 species, respectively [Q^n = Si(OSi)$_n$(OH)$_{4-n}$], together with a shoulder at δ = –92.8 ascribed to Q^2 species. The signal at δ = –3.8 can be assigned to asymmetric [**Si**Me$_2$(η^5-C$_5$H$_4$)$_2$]TiClO–Si in agreement with the ^{29}Si MAS NMR spectrum for [**Si**Me$_2$(η^5-C$_5$H$_4$)$_2$]TiCl$_2$ (δ = –4.0). The other poorly defined broad resonances, at δ = 2.4 and δ = –16.2, are attributed to symmetric [**Si**Me$_2$(η^5-C$_5$H$_4$)$_2$]Ti(O–Si)$_2$ species or to organic decomposition products. A similar result was obtained for Ti-MCM-48/CH$_2$Cl$_2$ (Figure 4). A comparison with the ^{29}Si CP MAS and MAS NMR spectra of the original mesoporous silicate showed that the intensity of the Q^2 and Q^3 species had decreased significantly.

The ^{29}Si CP MAS NMR spectra of Ti-MCM-41/THF and Ti-MCM-48/THF only exhibited two broad, convo-

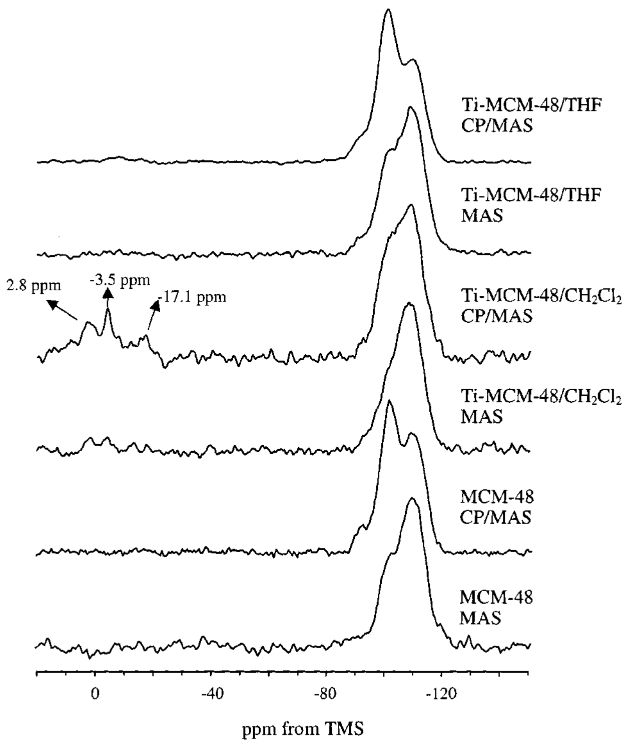


Figure 4. ^{29}Si CP MAS and MAS NMR at room temperature of MCM-48 materials

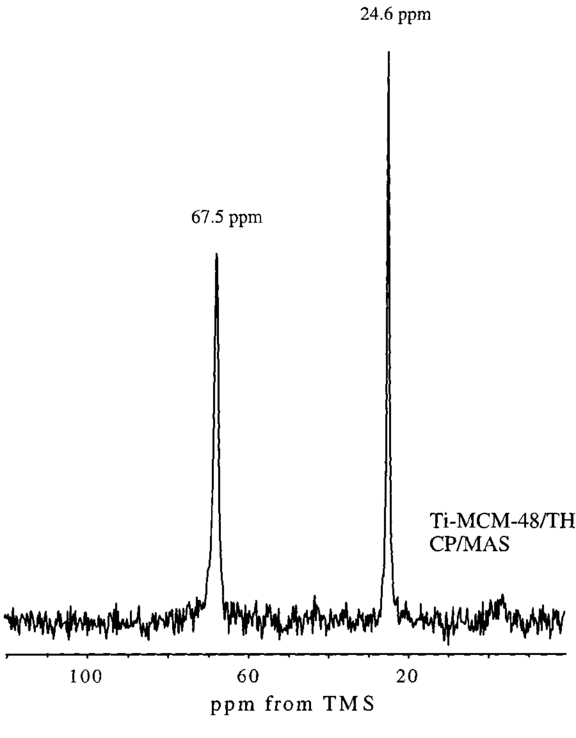


Figure 5. ^{13}C CP MAS NMR at room temperature

luted low-frequency resonances at δ –109.5 (Q^4) and at δ –101.0 (Q^3) together with a shoulder at δ –91 ppm (Q^2) (Figure 3 and 4). These results are consistent with the absence in the IR spectra of bands assignable to the Cp ring. Reaction of the organometallic with MCM-41 and MCM-48 in tetrahydrofuran replaces the Cp_2SiMe_2 group (Scheme 1). Alcohols are known to react with CpTi compounds with the replacement of the cyclopentadienyl group.[15]

Calcination of all these materials (Ti-MCM-41/CH_2Cl_2, Ti-MCM-48/CH_2Cl_2, Ti-MCM-41/THF, and Ti-MCM-48/THF) removes the organic ligand [$SiMe_2(\eta^5\text{-}C_5H_4)_2$ or THF] and these sites are probably occupied by an OH group (Scheme 1). After calcination all these materials give a similar ^{29}Si MAS NMR spectrum. Both the ^{29}Si CP MAS and MAS NMR spectra clearly show the diminished intensity of the Q^2 and Q^3 peaks relative to the Q^4 peak, indicating the esterification of the free hydroxyl groups. The presence of Ti-oxide species anchored to the silica surface is revealed by an IR absorption at around 950 cm^{-1} which has been assigned to the asymmetric stretching mode of Ti–O–Si groups.[7b]

The ^{13}C CP MAS NMR spectra of Ti-MCM-41/CH_2Cl_2 and Ti-MCM-48/CH_2Cl_2 are similar. The signals of the $SiMe_2$ and Cp ligands are slightly affected by immobilisation. Four broad resonances are observed, all of which are broader than those of the related crystalline titanocenophane [$SiMe_2(\eta^5\text{-}C_5H_4)_2$]$TiCl_2$. This broadening is due to the range of chemically different environments in which the molecules are located, giving rise to an envelope of peaks with very similar chemical shifts. The spectrum of Ti-MCM-41/CH_2Cl_2 exhibits four broad resonances at δ = 133.6, 120.6, 115.5 and –1.8 attributed to $(C_5H_4)_2Si$ and $SiMe_2$, respectively. These resonances can be compared with those given by the solid [$SiMe_2(\eta^5\text{-}C_5H_4)_2$]$TiCl_2$ (see Experimental Section). However, immobilisation takes place by elimination of one or more of the original chlorides with the hydrogen atoms from the silanol groups (Si–OH) in the MCM's and the spectrum appears more complicated. The low value of Cl/Ti suggests that the Ti–Cl bonds are involved in the reaction between the metallocene precursor and the MCM-41 or MCM-48 (Scheme 1). Analogous bipodal anchoring of the unbridged Cp_2Ti fragment has also been suggested for the very recently reported titanocene dichloride grafted ITQ-2,[16] a high surface area layered silica.

The ^{13}C MAS NMR spectra of Ti-MCM-41/THF and Ti-MCM-48/THF (Figure 5) only present two peaks at δ = 67.7 and 25.3 attributed to the THF coordinated to the titanium (Scheme 1).

N_2 Adsorption Studies

Figure 6 shows the N_2 isotherms of the parent and modified MCM-41 and -48 materials recorded at 77 K. The parent materials both gave a type IV isotherm with a small hysteresis, the A_{BET} specific surface areas were calculated to be 1035 m^2 g^{-1} for MCM-41 and 950 m^2 g^{-1} for MCM-48. The modified samples exhibit a lower uptake of N_2 than the parent solids as expected for successful incorporation of the organometallic within the pore systems. Adsorption of N_2 on the Ti-MCM-48/CH_2Cl_2 (Figure 6d) and Ti-MCM-41/THF (Figure 6e) samples was found to be very slow re-

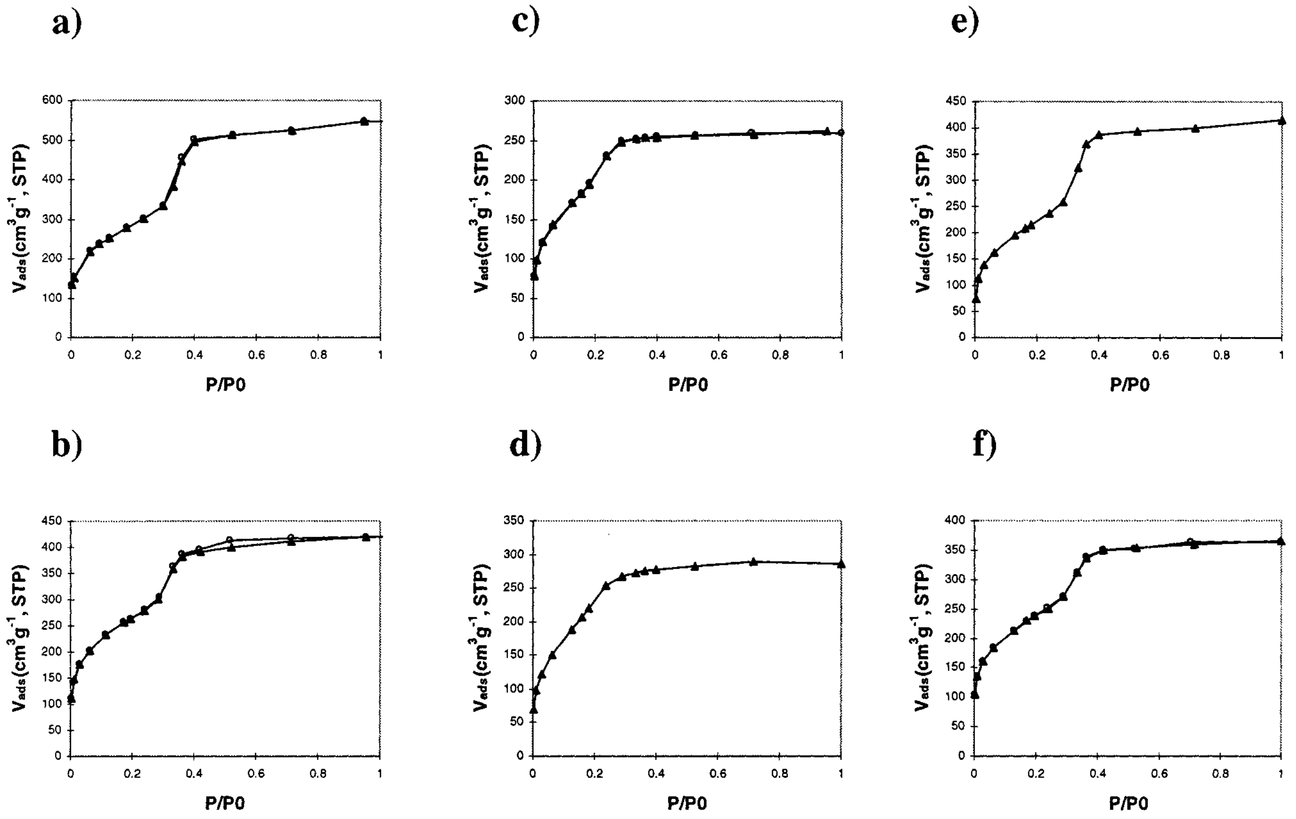


Figure 6. Isotherm of: (a) N_2 adsorption and desorption on MCM-41; (b) N_2 adsorption and desorption on MCM-48; (c) N_2 adsorption and desorption on Ti-MCM-41/CH_2Cl_2; (d) N_2 adsorption on Ti-MCM-48/CH_2Cl_2; (e) adsorption of N_2 on Ti-MCM-41/THF; (f) adsorption and desorption of N_2 on Ti-MCM-48/THF

sulting in nonequilibrium isotherms. The desorption part was not recorded for these two samples.

Inspection of the isotherms reveals that the materials produced using THF as the solvent exhibit a higher uptake of N_2 than those prepared using CH_2Cl_2 indicating that CH_2Cl_2 is superior in the task of promoting incorporation of the organometallic, in agreement with the elemental analysis results. The two samples produced using CH_2Cl_2 also have poorly defined capillary condensation regions as a result of the higher loadings. The incorporation of the organometallic appears to depend on the solvent employed and not on the pore system and pore diameters of the parent solids which are significantly different.

MCM-41 and MCM-48 Derivatives in Oxidation Catalysis

Reports have shown that Ti-MCM-41 materials are active and selective catalysts to perform the epoxidation of olefins by organic hydroperoxides.[7,9] Two distinct kinds of catalysts have been described, as mentioned above. The first accommodates the titanium ions within the walls of the mesoporous silica[7] and the second has the tetracoordinated Ti^{IV} ions grafted onto the inner surface of the mesoporous host.[9] The second catalyst is prepared via a titanocene dichloride-grafted precursor.[9] Surface-grafted Ti-MCM-41 catalysts have been shown to be more active than lattice-embedded Ti-MCM-41 materials in terms of activity per Ti centre, due to a large concentration of accessible, isolated and structurally well-defined active sites.[17]

The Ti-modified mesoporous silicas prepared in this work were screened as catalysts for the epoxidation of cyclooctene at 323 K with TBHP. The experimental details are given in the Experimental Section and results are shown in Figure 7.

It is evident that the materials prepared in CH_2Cl_2 show a higher conversion of cyclooctene after any given period than those prepared in THF. However, the materials prepared in THF are considerably more active in terms of conversion of cyclooctene per mol of titanium atoms. For example, after reacting for four hours, 55% conversion was observed for Ti-MCM-41/CH_2Cl_2 (25 mol cyclooctene per mol of titanium atoms) and 39% for Ti-MCM-41/THF (69 mol cyclooctene per mol of titanium atoms). Conversion was 88% for the former material after 24 h reacting.

As a general observation it can be concluded that [$SiMe_2(\eta^5-C_5H_4)_2$]$TiCl_2$ reacts in a similar way with the internal surfaces of MCM-41 and MCM-48 to give materials with similar titanium loadings, structurally similar monomeric Ti^{IV} species and similar catalytic activities. This is despite the fact that MCM-41 and MCM-48 possess very different mesoporous surfaces.

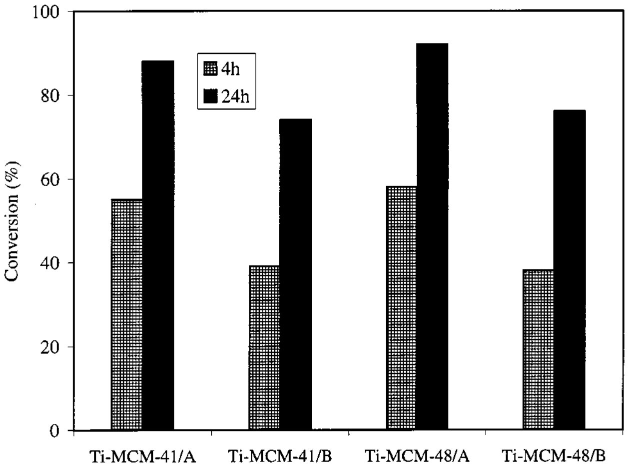


Figure 7. Conversion after 4 h and 24 h reacting in the catalytic oxidation of cyclooctene with TBHP on Ti-MCM materials (A, CH_2Cl_2); (B, THF); see text and Experimental Section for reaction details

Experimental

General: All preparations and manipulations were performed using standard Schlenk techniques under an oxygen- and water-free nitrogen atmosphere. Commercial grade solvents were dried and deoxygenated by refluxing for at least 24 h over appropriate drying agents under a nitrogen atmosphere and freshly distilled prior to use.

Powder X-ray diffraction (XRD) data were collected on a Phillips X'pert diffractometer using Cu-K_α radiation filtered by Ni. Microanalyses were performed at the TU Munich. Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets and/or solutions. ^{29}Si and ^{13}C NMR spectra were recorded at 79.49 and 100.62 MHz, respectively, on 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 μs ^{1}H 90° pulses, 8 ms contact time, a spinning rate of 5.0 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million from 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 ppm from TMS.

Nitrogen adsorption isotherms were recorded using a CI electronics MK2-M5 microbalance connected to a vacuum manifold line. The parent calcined MCM-41 and MCM-48 solids were dehydrated overnight at 723 K to an ultimate pressure of 10^{-4} mbar and then cooled to room temperature prior to adsorption. Extra care with the functionalised materials was necessary due to the possibility of aerial oxidation and therefore transfer to the balance and outgassing of the system was rapid. A lower dehydration temperature of 413 K was used with these samples to further minimise destruction of the functionalities. Nitrogen isotherms were then recorded at 77 K. Equilibration of each data point was monitored using CI electronics' Labweigh software and the pressure monitored using an Edwards Barocel pressure sensor. Specific surface areas, A_{BET}, were determined from the linear part of the BET plot (P/P_o = 0.05–0.3) assuming the average area occupied by a N_2 molecule in the monolayer to be 16.2 Å^2.

$[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ was prepared as described previously.[12] ^{13}C CP MAS NMR (25 °C): δ = 132.6 $[(C_5H_4)_2Si]$, 120.8 $[(C_5H_4)_2Si]$, 116.2 $[(C_5H_4)_2Si]$, –1.2 ($SiMe_2$). – ^{29}Si MAS NMR δ = –4.0 $[SiMe_2(\eta^5\text{-}C_5H_4)_2]$

The hexagonal channel host MCM-41 was synthesised from $[(C_{14}H_{29})NMe_3]Br$ according to published procedures.[18] 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 from $[(C_{16}H_{33})NMe_3]Cl$ according to published procedures.[19] After calcination (540 °C/6 h), the material was characterised by powder XRD, N_2 adsorption and FTIR spectroscopy.

Preparation of Ti-MCM-41. Method A: Calcined MCM-41 (0.5 g) was activated at 180 °C under high vacuum for 2 hours and then treated with an excess of $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 4 days. The solution was filtered off and the grey solid washed three times with 15 mL portions of CH_2Cl_2 before drying under high vacuum at room temperature for several hours. Found: Ti 4.24, Cl 5.38, C 12.37, H 2.60. – IR (KBr): ṽ = 3428 vs, 2962 m, 2930 m, 2858 w, 1637 s, 1456 w, 1402 m, 1380 w, 1236 vs, 1172 w, 1080 vs, 955 m, 807 s, 586w, 453 s cm^{-1}. – ^{29}Si MAS NMR: δ = –108.6 (br.), –3.4 $[SiMe_2(\eta^5\text{-}C_5H_4)_2]$, 3.1 (br.). – ^{29}Si CP MAS NMR: δ = –100.3 (br., Q^3), –108.4 (br., Q^4), –92.8 (weak, Q^2), –3.8 $[SiMe_2(\eta^5\text{-}C_5H_4)_2]$, –16.2 (br.), 2.4 (br.). – ^{13}C CP MAS NMR (25 °C) δ = 133.6 [br., $(C_5H_4)_2Si$], 120.6 [br., $(C_5H_4)_2Si$], 115.5 [br., $(C_5H_4)_2Si$], –1.8 (br., $SiMe_2$).

Method B: Calcined MCM-41 (0.5 g) was activated at 180 °C under vacuum for 2 hours and then treated with an excess of $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ in THF (15 mL). The mixture was stirred at room temperature for 66 hours. The solution was filtered off and the pale pink solid washed three times with 10 mL portions of THF before drying under vacuum at room temperature for several hours. Found: Ti 1.10, Cl 2.00. – IR (KBr): ṽ = 3461 vs, 2976 w, 2932 w, 1637 s, 1383 w, 1235 vs, 1081 vs, 964 m, 801 m, 571 w, 458 s cm^{-1}. – ^{29}Si MAS NMR: δ = –107.9 (br.). – ^{29}Si CP MAS NMR: δ = –100.4 (br., Q^3), δ = –110.2 (br., Q^4), –91.0 (weak, Q^2). – ^{13}C MAS NMR (25 °C) δ = 67.7 (THF), 25.3 (THF).

Preparation of Ti-MCM-48. Method A: Calcined MCM-48 (0.5 g) was activated at 180 °C under vacuum for 3 hours and then treated with an excess of $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 4 days. The solution was filtered off and the grey solid washed three times with 15 mL portions of CH_2Cl_2 before drying under vacuum at room temperature for several hours. Found: Ti 4.10, Cl 5.20, C 11.33, H 2.70. – IR (KBr): ṽ = 3437 vs, 2965 m, 2929 m, 2858 m, 1636 s, 1457 w, 1395 m, 1375 w, 1238 vs, 1076 vs, 956 m, 807 s, 452 s cm^{-1}. – ^{29}Si MAS NMR: δ = –108.2 (br.), –3.6 $[SiMe_2(\eta^5\text{-}C_5H_4)_2]$, 1.9 (br.). – ^{29}Si CP MAS NMR: δ = –101.6 (br., Q^3), –108.5 (br., Q^4), –91.9 (weak, Q^2), –3.5 $[SiMe_2(\eta^5\text{-}C_5H_4)_2]$ –17.1 (br.), 2.8 (br.). – ^{13}C CP MAS NMR (25 °C) δ = 132.0 [br., $(C_5H_4)_2Si$], 124.5 [br., $(C_5H_4)_2Si$], 115.2 [br., $(C_5H_4)_2Si$], –2.0 (br., $SiMe_2$).

Method B: Calcined MCM-48 (0.5 g) was activated at 180 °C under vacuum for 2 hours and then treated with an excess of $[SiMe_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$ in THF (20 mL). The mixture was stirred at room temperature for 66 hours. The solution was filtered off and the pale pink solid washed three times with 20 mL portions of THF before drying under vacuum at room temperature for several hours. Found: Ti 1.30, Cl 2.12. – IR (KBr): ṽ = 3481 vs, 1636 s, 1230 s, 1082 vs, 957 m, 804 m, 564 w, 455 s cm^{-1}. – ^{29}Si MAS NMR: δ = –101.2 (br., Q^3), δ = –108.2 (br., Q^4). – ^{29}Si CP MAS NMR: δ = –100.6 (br., Q^3), δ = –109.2 (br., Q^4). – ^{13}C CP MAS NMR (25 °C) δ = 67.5 (THF), 24.6 (THF).

Preparation of Calcined Samples: As-synthesised Ti-MCM-41 and Ti-MCM-48 were dried in air at 110 °C for 1 h prior to calcination in air at 550 °C for 10 h (heating rate 1 °C/min). The resultant materials have the same textural and structural characteristics as the parent calcined materials.[16]

Catalytic Reactions With Ti-MCM-41 and Ti-MCM-48: *cis*-Cyclooctene (800 mg, 7.3 mmol), *n*-dibutyl ether (800 mg, internal standard), Ti-MCM-41/(CH_2Cl_2 or THF) or Ti-MCM-48/(CH_2Cl_2 or THF) (180 mg) and 5.5 M *t*-butyl hydroperoxide in decane (2 mL) 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 thirty minutes, diluted with dichloromethane, and chilled in an icebath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and magnesium sulfate was added. After the gas evolution ceased the resulting slurry was filtered over a filter-equipped Pasteur pipette and the filtrate injected onto the GC column. The conversion of cyclooctene and formation of cyclooctene oxide was calculated from a calibration curve ($r^2 = 0.999$) recorded prior to the reaction course.

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