Surface-grafted manganese–oxo species on the walls of MCM-41 channels—a novel oxidation catalyst

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Manganese–oxo species grafted onto the internal walls of MCM-41 channels, showing a high redox catalytic activity for hydrocarbon oxidation, are prepared *via* the reaction of $Mn_2(CO)_{10}$ with Si–OH groups on the surface of mesoporous silica followed by subsequent heat treatment in air.

The recent synthesis of mesoporous silica materials by the cooperative assembly of silica and surfactants has attracted a great deal of research interest. They are characterised by larger pores (1.5–10 nm)[1,2] and larger internal surface areas, and therefore have the potential to be used as size- and shape-selective catalysts for bulky reagents. Attempts to incorporate small amounts of catalytically active transition metals into the framework of the mesoporous silica during synthesis have been reported,[1–6] but success is limited to ions such as Al^{3+}, Ti^{4+} and V^{5+} that can substitute for Si^{4+} without seriously disrupting the mesoporous phase. Moreover, the reported catalytic activity and stability of the synthetic Ti-MCM-41 was not particularly high.[6,7] On the other hand, after calcination, the hexagonal mesoporous phase MCM-41 contains a large number of surface OH groups[2,8] which could provide reaction sites for the entrapment of a wide variety of metal complexes. As a result, encapsulated surface complexes can be used as precursors for the preparation of highly dispersed transition metals. Based on this concept, Thomas and coworkers[7] have recently reported the direct grafting of titanocene in chloroform onto the inner walls of a mesoporous silica. The material, after calcination in air, is claimed to be effective for epoxidation of cyclohexene with tetrabutyl hydroperoxide (TBPH).

The present communication describes the preparation of the first *redox* type of MCM-supported catalyst *via* the surface immobilisation of gaseous $Mn_2(CO)_{10}$. High-resolution TEM shows the Mn-containing particles anchored on the channel walls, leading to a small reduction in pore size and corrugation of the internal walls. A large concentration of manganese–oxygen species, much more active than those of bulk manganese oxides, are available in the Mn-modified MCM-41 for catalytic oxidation.

All manipulations were carried out under an inert atmosphere or under vacuum. The MCM-41 was prepared using $C_{16}H_{33}NMe_3Br$ according to a method previously described.[2] The MCM-41 was then degassed under a stream of flowing nitrogen for 2 h at 300 °C. The MCM-41 (100 mg) and $Mn_2(CO)_{10}$ (50 mg) were placed in an open-ended tubular silica vessel and a quartz-wool plug was used to separate the two materials. The reactor was inserted inside a box furnace. The reactor was then pumped and flushed with nitrogen three times, after which the vacuum was left on. The furnace was heated to 50 °C. When all the $Mn_2(CO)_{10}$ had sublimed through the MCM-41, the material was evacuated for 20 min and taken out under nitrogen for IR studies prior to calcination. Finally, the treated material was heated in air for 2 h at 300 °C to give an intense brown material. High-resolution TEM was carried out using a JEOL 4000EX microscope with an accelerating voltage of 200 kV under optimum defocus conditions.

IR studies revealed that after the sublimation of $Mn_2(CO)_{10}$ onto the MCM-41 intense absorption bands near 2000 cm^{-1} appeared on the treated MCM-41 despite a prolonged period of evacuation. This indicates a strong binding of carbonyl-containing species on the mesoporous silica. However, comparison of the pure dimanganese decacarbonyl complex [2042m, 2034(sh), 2021(sh), 1978s cm^{-1} KBr] with that of the compound in MCM-41 (2047m and 2000s cm^{-1} KBr) shows that there were significant changes in the chemical environment of the carbonyl groups. The colour of the MCM-41 had changed from white to yellowish brown. A direct reaction of the carbonyl complex with the surface Si–OH groups responsible for the immobilisation of the manganese carbonyl species is therefore expected at slightly elevated temperature.

By capping the reactive surface Si–OH terminal groups of the MCM-41 with Me_3SiCl[9] prior to the carbonyl sublimation, we found that no carbonyl species were detected by IR. Chemical analysis of the silanised sample showed that no manganese was present. The reduction in the surface area of the sample was < 10% after silanisation which eliminates the possibility that the manganese carbonyl was excluded because of blocking of the pores during silanisation. This result is consistent with the view that the carbonyl is implanted on the internal silica walls *via* reaction with the surface Si–OH groups. IR spectra showed the absence of any carbonyl stretching bands after calcination of the carbonyl-treated sample. Analysis showed a loading of 8.5% (*m*/*m*) of Mn on the MCM-41, but XRD gave no indication of the presence of crystallised manganese oxides nor any change in the lattice parameters of the mesoporous silica.

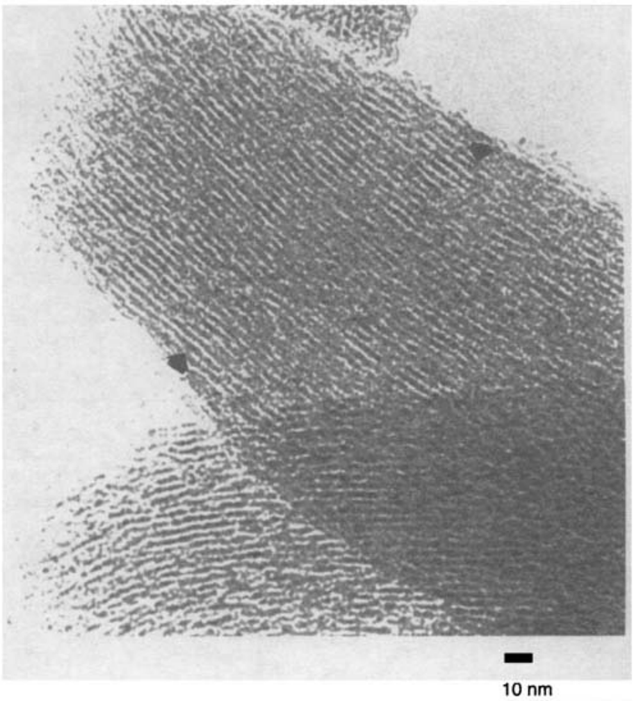

Fig. 1 A high-resolution TEM micrograph showing the walls of the channel grafted with particles. The arrows point to the particles which adopt the same size as the channel.

A comparison of the HRTEM micrographs of the unmodified MCM-41 with the Mn-modified MCM-41 after calcination shows some interesting effects. For the unmodified MCM-41, well defined channels with pore diameters of about 3.0 nm were clearly seen. Good contrast, differentiating the walls and the internal pores, was always obtained. The modified MCM-41, on the other hand, had a very weak contrast. The walls of the channels appeared to be highly corrugated with deposition of tiny particles (weak contrast) on the internal surface. The pore size had been greatly reduced, in some cases, to <2.0 nm. Under high magnification, ultra small particles can be clearly seen grafted onto the channels giving highly irregular channel sizes (Fig. 1). From these electron microscopy studies, we conclude that there is no significant collapse of the porous structure or serious blocking up of the MCM channels, although a few particles of the same diameter as the channels have been found (Fig. 1). BET surface area analysis showed only a small reduction in the apparent surface area of the Mn-modified MCM-41, to 984 $m^2\ g^{-1}$ compared with 1184 $m^2\ g^{-1}$ for the unmodified MCM-41, supporting the TEM observations. Micro-area EDX analysis using a spot diameter of 50 nm also gave very constant Mn:Si ratios (0.35 ± 0.05, no mass absorption coefficents were corrected) when the sample was mapped. It is concluded that Mn species anchored on the walls are very small and are homogeneously distributed. This contrasts to the report in the literature[10] on iron oxide nanoparticles made by incipient impregnation of MCM-41 with a diluted iron nitrate solution followed by calcination at 550 °C. These iron oxide particles adopted the same size as the MCM-41 channel.

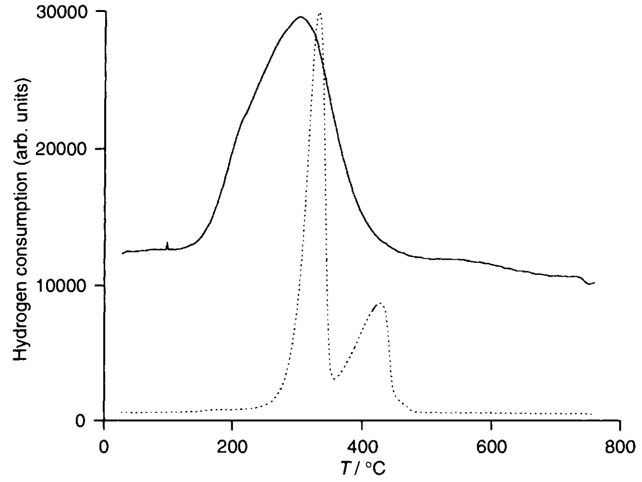

Fig. 2 Temperature programmed reduction (TPR) spectra of: (—) Mn-modified MCM-41; (---) MnO_2 (sample size 10 mg, total flow rate = 10 $cm^3\ min^{-1}$ of 5% H_2 in argon)

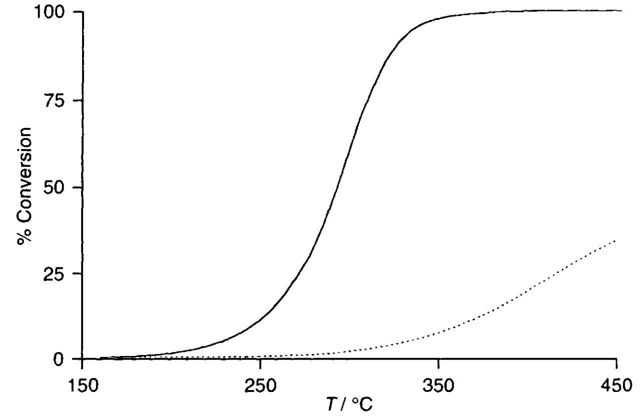

Fig. 3 A plot of propene conversion to carbon dioxide *vs.* reaction temperature. (—) Mn-modified MCM-41; (---) Mn deposited on silica (20 mg of catalyst, total flow rate = 200 $cm^3\ min^{-1}$ with 1000 ppm of propene, 1.25% of oxygen, balanced with helium, using a ramping rate of 7 °C min^{-1} from 25 to 500 °C).

Temperature programmed reduction (TPR) using 5.0% H_2 in argon (10 $cm^3\ min^{-1}$) was conducted for the characterisation of the availability and reactivity of the active oxygen in our Mn-modified MCM-41 (Fig. 2). A TPR spectrum was also acquired using pure MnO_2 for calibration and activity comparison (Fig. 2). It is interesting that the average O/Mn ratio of the Mn-modified MCM-41 was determined to be 2.2. Taking account of the fact that the oxygens of Si–O–Mn surface groups are likely to be irreducible at these low temperatures we conclude that Mn is in a high formal oxidation state. The TPR shows that the reactivity of the oxygen towards hydrogen in the Mn-modified MCM-41 was higher than that of the lattice oxygen in MnO_2. It seems likely that the reactive oxygens in the Mn-modified MCM-41 are readily available because of the highly dispersed nature of the MnO_x species. Because of this difference in reactivity (reduction maximum at *ca.* 290 °C rather than at *ca.* 320 and 420 °C), the nature of the oxygen in the MnO_x/MCM may be different from lattice oxygen, possibly being analogous to a Mn–oxo complex. However, the precise chemical nature of the surface anchored Mn–O species is not yet known.

The Mn-modified MCM-41 catalyses the total oxidation of propene to carbon dioxide very effectively (Fig. 3) as compared with a conventional supported manganese catalyst. As a comparison, $Mn_2(CO)_{10}$ was sublimed over a conventional high surface area silica in an identical manner to that described above. The onset temperature at which this material catalysed the oxidation of propene was approximately 100 °C higher than that for the Mn-modified MCM-41 (see Fig. 3).

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