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Structural and oxidative properties of Mn-MCM41 catalysts synthesised by MOCVD method

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Abstract

Molecular organic chemical vapour deposition (MOCVD) is employed to implant various gaseous manganese precursors onto mesoporous MCM-41 silica. After heat treatment in air these samples show significantly higher catalytic activity than Mn/MCM-41 samples prepared by a conventional impregnation method for *trans*-stilbene epoxidation to *trans*-stilbene oxide using *tert*-butylhydroperoxide (TBHP) as an oxidant. In contrast, the same MOCVD samples gave much poorer activity than the impregnation samples in diphenylmethane oxidation reaction using air as the oxidant. Catalyst characterisation (infrared, temperature programmed reduction, EXAFS, etc.) indicates that discrete entities of Mn species (Mn-oxo and/or bridging Mn-oxygen structures, etc.) are formed on the surface of the MCM-41 by the MOCVD technique. This is attributed to initial reactions of gaseous organo-manganese complexes with surface silanol groups, followed by their oxidation in air during the heat treatment. On the other hand, in the wet impregnation samples, bulk Mn oxide phases are deposited onto the MCM-41 structure. It is thus believed that the discrete supported manganese-oxygen species of high electrophilicity are the active sites for the oxygen transfer reaction in the *trans*-stilbene oxidation. However, the nucleophilic lattice oxygen of the bulk Mn oxide phases prepared by the wet impregnation is responsible for the effective hydrogen abstraction in the diphenylmethane oxidation. It is also evident that the catalytic activity of the MOCVD samples depends crucially on the type of precursors used. Thus, the result clearly suggests that active and ultraselective Mn-oxygen catalytic sites for a particular oxidation reaction may be tailored through the use of different chemical precursors using the MOCVD technique.

Keywords: Mn-MCM41; MOCVD; Stoichiometry

1. Introduction

Many traditional organic reactions use stoichiometric reagents because they provide excellent activity, selectivity and specificity at low temperatures. However, the necessity to regenerate these materials after reaction leads to the production of large quantities of waste. Due to growing environmental concerns, the laws and regulations governing the disposal of industrial effluents are becoming increasingly tighter. The foremost challenge for the fine chemical manufacturing industries is therefore to seek cleaner processes in order to minimise the production of waste [1]. One way is by replacing stoichiometric reagents with catalytic materials [2–6].

Selective oxidation of organic molecules in fine chemical industry is a very important reaction. However, the progress in replacing stoichiometric oxidants has been very slow. There have been some recent advancements, using *structurally well-defined*

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catalysts together with *peroxides* (H_2O_2 or organic peroxides) as oxidants for the selective oxidation reactions. Microporous materials such as zeolites [7], aluminophosphates (ALPO), silicoaluminophosphates (SAPO) with regular arrays of internal channels and uniform pores have been extensively studied [8–13]. These materials have a large internal surface and specific sites available for active metal substitution, allowing one to prepare materials with a homogeneous distribution of active sites required for an ultra-selective process. Some new industrial processes based on this approach have thus been developed. A typical example is TS-1, a titanium-modified silicate that catalyses olefin epoxidation, alcohol oxidation, ketone ammoximation and phenol hydroxylation in the presence of 30% hydrogen peroxide. One major problem of these microporous supported catalysts is their small pore size (<14 Å), which limit their use to reactions in which small molecules are involved [14]. These materials thus make very little impact in fine chemical manufacturing where the organic substrates are considerably bigger than the pore sizes.

During the past few years, we [15–17] and other researchers [18,19] have been working on the immobilisation of various Mn species onto the mesoporous MCM-41 silica material with the aim of developing new selective oxidation catalysts for fine chemical catalysis. The MCM-41 as a support (with plenty of silanol groups) can provide a large internal surface area and uniform surface for subsequent modification and the larger pore dimensions would allow tackling of bulky chemicals of interest. The method in which metal ion source (Mn) is introduced as a reactant into the reaction gel for hydrothermal synthesis [20] and the ion-exchange method applying to the Al-MCM-41 [21–25] have been widely reported. These two methods, however, have several problems, e.g., a loosely ordered mesoporous structure or low metal loadings on the surface. In contrast, we reported the first redox Mn-MCM-41 prepared by MOCVD technique [26,27] where well-defined Mn-oxo species are anchored on the silica surface at a very high coverage [15,16]. This catalyst showed high activity for propene oxidation. Iwamoto and co-workers [18] have also recently reported a template ion-exchange (TIE) method for implantation of Mn ions onto MCM-41 at a high loading. In this paper, we present our work on the preparation of various Mn-oxygen species on MCM-41 by the MOCVD technique using different Mn chemical precursors and the study of their catalytic oxidative activities for *trans*-stilbene epoxidation using *tert*-butylhydroperoxide (oxygen transfer reaction) and diphenylmethane oxidation in air (oxidative hydrogen abstraction), respectively.

2. Experimental

2.1. Catalyst preparation

2.1.1. Chemical vapour deposition (CVD)

The mesoporous silica support MCM-41 was prepared according to the published method [28] using $C_{16}H_{33}N(CH_3)_3Br$ as the template. The sample was dried at 300°C in a flow of nitrogen for 2 h in the post-synthesis treatment prior to use. All manipulations were carried out in an inert atmosphere or in vacuum. The four manganese precursors, dimanganese decacarbonyl, bromopentacarbonylmanganese, cyclopentadienylmanganese and manganocene were purchased from Aldrich (purity$\geq$98%) and used without further purification.

Each precursor was placed in a Schlenk tube in a given amount together with 200 mg MCM-41. The four tubes were then evacuated, sealed and left in an oven at the appropriate reaction temperature for 48 h. After cooling at room temperature; the mixtures were heated under dynamic vacuum in order to remove any unreacted precursor. We estimated that there was about 1×10^{22} Si–OH groups per gram of MCM-41 hence the theoretical monolayer of Mn species carried by the MCM-41 material is expected to be around 9 wt.%. The Mn contents of all our samples were below this theoretical maximum (Table 5). Therefore, there will be no more than a monolayer of anchored precursors attached on the mesoporous silica. After cooling to room temperature under dynamic vacuum, the materials were finally calcined in flowing air at 300°C for 2 h. The conditions of preparation depending on the precursor used are given in Table 1.

2.1.2. Wet impregnation

Two solutions with 0.25 wt.% Mn were prepared: $KMnO_4$ (> 99%, BDH) in acetone and $Mn(acac)_3$ (Aldrich) in cyclohexene. The $KMnO_4$ solution in acetone was added to MCM-41 that had been dried in

Table 1
Conditions for the preparation of Mn-modified MCM-41 catalysts using CVD

Precursor	Mass used (mg)	Reaction temperature (°C)	Evacuation temperature (°C)
$Mn_2(CO)_{10}$	73	120	90
$BrMn(CO)_5$	100	120	90
$CpMn(CO)_3$	71	150	90
$Mn(Cp)_2$	69	150	170

static air at 250°C for 3 h. The mixture was stirred in a sealed flask at room temperature for 16 h, then dried in an oven at 110°C for 4 h. The $Mn(acac)_3$ solution in cyclohexene was added in the same way to dry MCM-41. This mixture was stirred in a sealed vessel for 24 h, then dried at 110°C for 19 h, the resulting powders were then calcined in static air at 300°C for 2 h.

2.2. Catalyst testing

Trans-stilbene (96%, *t*-S), *tert*-butylhydroperoxide (5–6 M solution in decane, TBHP) and diphenylmethane (>99%, DPM), were purchased from Aldrich and used without further purification. Oxidation reactions were carried out using the following methodology: given amounts of substrate, catalyst, oxidant were introduced into the round-bottom flask and stirred under optimised conditions of solvent, pressure (P), temperature (T) and reaction time (Table 2).

In the case of *trans*-stilbene oxidation a fixed amount of oxidant (TBHP) was added into the reaction mixture. In the DPM oxidation a continuous supply of air was used as the oxidant, which was purged into the reaction mixture via a sintered glass frit at a flow rate of 400 $cm^3 min^{-1}$.

The reaction mixture was analysed by HPLC, a Perkin Elmer Series 200 lc pump equipped with a reverse phase C-18 column (Brownlee, ValueLine Spheri-5 C18, 220×4.6 mm) and a diode array detector 235C. A mixture of acetonitrile and water was used as the eluent with a total flow rate of 1.5 $cm^3 min^{-1}$.

2.3. Catalyst characterisation

Infra-red spectra were obtained from potassium bromide pressed discs, using a Perkin Elmer 1720 FTIR spectrometer.

X-ray diffraction patterns were obtained using a Spectrolab series 3000, CPS 120 X-ray diffractometer (Cu Kα radiation, λ=0.154098 nm).

BET surface areas were measured via nitrogen physisorption at liquid nitrogen temperature over the relative pressure range P/P_0=0–0.3 using an apparatus built in-house.

Temperature programmed reduction (TPR) analysis were carried out using an apparatus built in-house. The samples were heated at a rate of 10°C min^{-1} from room temperature to 750°C in a flow of 5% H_2 in Ar (10 $cm^3 min^{-1}$). A thermal conductivity detector enabled to measure the hydrogen consumption of each sample. Its response was sampled every second via a PE NELSON 900 Series Interface and the data were treated using PE NELSON software.

3. Results and discussion

3.1. Structural properties of these materials

3.1.1. XRD studies

The obtained MCM-41 XRD patterns agreed very well with the patterns published in the literature [28]. Before calcination, it exhibits at low angle (2°) the four typical peaks corresponding to the d_{100}, d_{110}, d_{200}, d_{210} reflections of a regular hexagonal array of pores with a lattice parameter a_0=47.3 Å. After calcination, it exhibits one sharp peak a $2\theta=2°$ correspon-

Table 2
Reaction conditions

Reactant	Oxidant	Catalyst	Solvent	P (atm)	T (°C)	Reaction time (h)
t-S, 1 mmol	TBHP, 0.5 mmol	18 mg (∼33 μmol Mn)	CH_3CN:DMF (18:2 cm^3)	1, dry N_2	55	24–72
DPM, 300 mmol	Air, 400 $cm^3 min^{-1}$	60 mg (∼100 μmol Mn)	–	1, air	150	12

ding to the d_{100} reflection and some very broad peaks at high angles giving a calculated lattice parameter of a=43.3 Å.

The XRD patterns of the calcined samples prepared by MOCVD all exhibit one sharp peak at low angle, also corresponding well to the d_{100} reflection of an hexagonal array and giving the calculated lattice parameters of a=41.0, 41.4, 42.3 and 40.4 Å for MCM-41 treated with $Mn_2(CO)_{10}$, $BrMn(CO)_5$, $CpMn(CO)_3$ and $Mn(Cp)_2$, respectively. There was no extra peak observed in all the MOCVD samples. Thus, our results clearly show that the modification of MCM-41 by MOCVD with manganese precursors does not significantly affect the MCM-41 structure. On the other hand, the XRD patterns of the conventional impregnation $KMnO_4$/MCM-41 and $Mn(acac)_3$/MCM-41 samples also exhibit one sharp peak at $2\theta=2^\circ$ corresponding to the d_{100} reflection. However, the calculated lattice parameters of a=38.8 and 39.4 Å, respectively, indicate a small but significant reduction in the hexagonal channel width for these two samples. Apart from the common broad peaks observed in both unmodified and modified MCM-41 there were clearly other extra broad peaks at higher angles in those samples prepared by the wet impregnation method. They were attributed to some crystalline Mn oxide or potassium manganese oxide phases deposited onto MCM-41 structure. Unfortunately, accurate phase identifications were not achieved successfully.

3.1.2. Surface area measurements

The BET surface area measurements (Table 3) show that the wet impregnation of manganese precursor salts induces a dramatic reduction in the total surface area of the material. This reduction is particularly significant in the case of potassium permanganate, which accounts for a loss in surface area of more than 50% with regard to the unmodified MCM-41.

With the information provided by the XRD it is evident that wet impregnation generates considerably large Mn-containing particles, which deposit heavily on the MCM-41 structure and block the pore entry from both external and internal sides. The $Mn(acac)_3$ seems to give a better dispersion than the $KMnO_4$ sample.

In contrast, the CVD method gives no major reduction in BET surface areas where the surface areas of all the samples are of above 1000 $m^2\,g^{-1}$. With comparable Mn loadings as the wet impregnation samples (Table 5), we believe that the CVD method generates very small Mn cluster-like species that anchor onto the channel walls, hence no blockage of the pores is encountered.

3.1.3. Mn species anchored onto the surface

The characteristic peaks in the FTIR spectra of the MOCVD samples are listed in Table 4. For $Mn_2(CO)_{10}$ and $BrMn(CO)_5$, the number of CO stretching bands decreases and their frequencies shift after they reacted with MCM-41. We previously used EXAFS to study the surface immobilised $Mn_2(CO)_{10}$ on MCM-41. We identified four Mn–C distances at 1.876 Å, four Mn–O distances at 3.013 Å, a Mn–Si distance at 3.529 Å (new interaction) and a Mn–Mn distance at 3.112 Å, hence implying that the $Mn_2(CO)_{10}$ lost two CO groups upon immobilisation to the internal walls of the MCM-41 via forming two Si–O–Mn bonds. In this FTIR study, it clearly indicates that the chemical environments of the manganese species for both compounds have been

Table 3
BET surface areas of the calcined materials prepared by wet impregnation and by MOCVD method

	Materials	Surface area of the calcined sample ($m^2\,g^{-1}$)
Support	MCM-41	1236
Wet impregnation samples	$KMnO_4$/MCM-41	550
	$Mn(acac)_3$/MCM-41	950
MOCVD samples	$Mn_2(CO)_{10}$-modified MCM-41	1214
	$BrMn(CO)_5$-modified MCM-41	1207
	$CpMn(CO)_3$-modified MCM-41	1216
	$Mn(Cp)_2$-modified MCM-41	1052

Table 4
FTIR CO-stretching band frequencies (cm^{-1}) for the manganese precursors (from the literature), the as-synthesised and calcined samples

Precursors	$\nu_{\text{CO-stretching}}$ (cm^{-1})		
	Precursor	Mn-modified MCM-41: as-synthesised	Mn-modified MCM-41: after calcination
$Mn_2(CO)_{10}$ [29]	2042	2048	None
	2034	2005	
	2021		
	1978		
$BrMn(CO)_5$ [30]	2134	2020	None
	2079	2007	
	2050		
	2001		
	1959		
$CpMn(CO)_3$ [31,32]	2029	2018	
	1946	1959	None
		1942	
		1925	
		1914	

altered, after their immobilisation on the MCM-41 material. It is therefore conceivable that Mn can directly bind to the surface of MCM-41 through, possibly, the nucleophilic substitution reaction of Si–OH groups with the carbonyl species.

For $CpMn(CO)_3$, the CO-stretching band frequencies are shifted but their number is actually increased after reaction with MCM-41. The increase in number of bands is thought to relate to some new surface Mn species formed and the relative strong peak intensities support at least some partial retention of carbonyl groups. However, it is interesting to find that the CH stretching bands of 3125 and 3096 cm^{-1} attributed to the Cp group [33] totally disappear from the spectrum. This would indicate that the Cp group is preferentially detached from Mn upon its immobilisation onto the MCM-41 surface.

For $Mn(Cp)_2$, CH stretching bands (between 3000 and 2800 cm^{-1}) can still be observed in the spectrum of the as-synthesised Mn-modified MCM-41 indicating no complete detachment of Cp group from the immobilised Mn species.

The total absence of CO stretching bands and the CH stretching bands particularly in the spectrum of the calcined $Mn(Cp)_2$/MCM-41 suggest that the immobilised Mn species are transformed into Mn-oxygen groups during the air calcination.

3.1.4. Oxidising properties of the surface species

Temperature programmed reduction (TPR) was studied in order to characterise the availability and reactivity of active oxygen in these materials. The TPR profiles of the calcined Mn samples prepared by MOCVD all exhibit a major reduction peak: 320°C for MCM-41 treated with $Mn_2(CO)_{10}$, 330°C for MCM-41 treated with $BrMn(CO)_5$ and $Mn(Cp)_2$ and 350°C for MCM-41 treated with $CpMn(CO)_3$.

This is very similar to the TPR profiles of the calcined materials prepared by wet impregnation such as $Mn(acac)_3$/MCM-41 and $KMnO_4$/MCM-41 which exhibit a similar reduction peak at 330 and 350°C, respectively (Fig. 1).

However, by careful inspection of the MOCVD samples reduction profiles with those of the wet impregnation samples we note that the general shape of the TPR peaks are different: all samples prepared by MOCVD technique exhibit *a shoulder* in the major reduction peak (all the shoulders appear at about 250°C, the $Mn(Cp)_2$ sample giving significantly the lowest temperature shoulder), which is absent from all the TPR profiles of the calcined samples prepared by wet impregnation. The lower reduction peak associated with the MOCVD samples suggests that this method produces a more reactive Mn-oxygen species than the wet impregnation method. Another main difference is

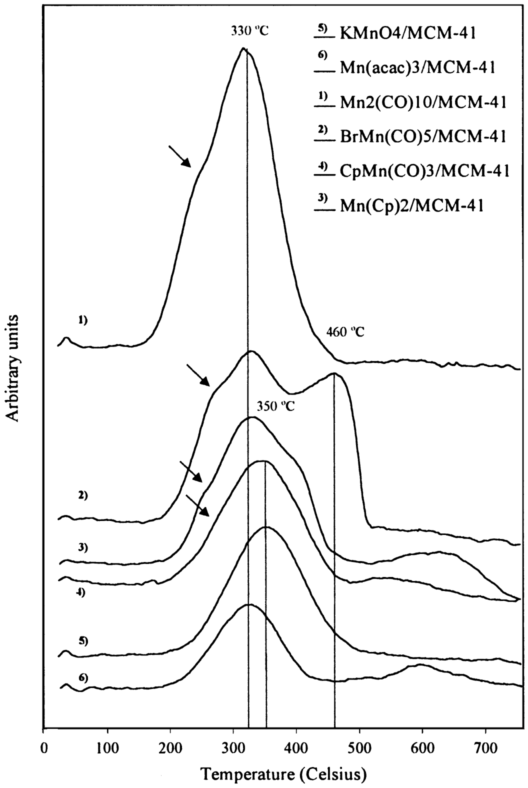
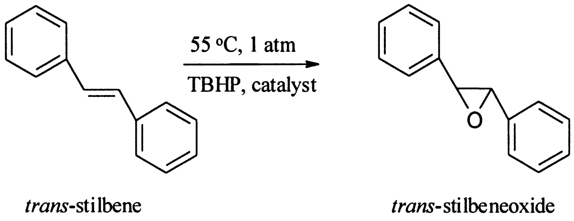


Fig. 1. Temperature programmed reduction of various calcined Mn containing MCM-41 samples.



Scheme 1.

in the TPR profile of BrMn$(CO)_5$-modified MCM-41, which contains a second reduction peak at 460°C.

3.2. Catalytic properties of these materials

3.2.1. Oxidation of trans-stilbene using TBHP

All the air-calcined materials were tested as catalysts for the *trans*-stilbene oxidation using TBHP as an oxidant; the results are compiled in Table 5. Catalytic stilbene oxidation has been extensively studied [18,34,35] and was chosen as a model to evaluate our materials for the efficiency of catalysing oxygen transfer reaction (Scheme 1).

The main product (>95%) of this reaction is the alkene epoxide, *trans*-stilbeneoxide. Without catalyst, this reaction gives a very poor yield of 0.3% in 24 h. The support alone, MCM-41, seems to have a very limited catalytic activity, converting only 2.7% of the reactant in 24 h. The selectivity obtained over all of our samples is generally higher than 95% but was found to vary from one catalyst to another. There is a

Table 5
Catalytic properties of Mn-modified MCM-41 materials in the oxidation of *trans*-stilbene to *trans*-stilbeneoxide

Catalyst	Mass (mg)	Mn (wt.%)	T (°C)	Yield of *trans*-stilbeneoxide (%)			TOF (mmol mol Mn^{-1} h^{-1})[a]
				t=24 h	t=48 h	t=72 h	
None	–	–	55	0.26	0.87	–	–
MCM-41	19.2	0	55	2.7	3.6	–	–
MnO_2 (99.999%)	1.9	63.2	55	1.7	2.2	–	33
$KMnO_4$/MCM-41	20.6	6.8	55	7.2	–	–	121
Mn$(acac)_3$/MCM-41	18.6	8.6	55	9.6	–	–	138
$Mn_2(CO)_{10}$/MCM-41	18.8	8.2	55	12.7	–	–	190
BrMn$(CO)_5$/MCM-41	19.5	5.5	55	12.9	–	–	272
CpMn$(CO)_3$/MCM-41	17.5	5.7	55	10.6	12.7	–	247
Mn$(Cp)_2$/MCM-41	19.6	3.2	55	9.9	14.9	18.3	365

[a] TOF stands for turnover frequency.

minor degree of carbon–carbon bond cleavage leading to by-products such as benzaldehyde, benzoic acid, and acetophenone, etc.

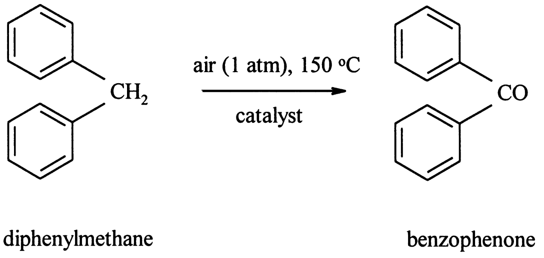
The main feature of this catalytic study is that all the catalysts prepared by our MOCVD technique exhibit greater activities than the catalysts prepared by the wet impregnation giving higher turnover frequencies for *trans*-stilbeneoxide production. The order of catalytic activities for the air-calcined samples for stilbene oxidation reaction is as follows:

$$\begin{aligned} &\mathrm{Mn(Cp)_2/MCM\text{-}41} > \mathrm{BrMn(CO)_5/MCM\text{-}41} \\ &\quad > \mathrm{CpMn(CO)_3/MCM\text{-}41} > \mathrm{Mn_2(CO)_{10}/MCM\text{-}41} \\ &\quad > \mathrm{Mn(acac)_3/MCM\text{-}41} > \mathrm{KMnO_4/MCM\text{-}41} \end{aligned}$$

For the catalysts prepared by CVD, the turnover frequencies apparently depend on the nature of the precursor at a given surface coverage.

3.2.2. Oxidation of diphenylmethane using air

All the air-calcined materials were also tested for the diphenylmethane oxidation using oxygen in air as an oxidant. Under the reaction conditions used, the reaction can occur in both the absence and presence of catalyst giving exclusively benzophenone. We obtain more than 25% benzophenone yield by heating diphenylmethane in air without catalyst under our reaction conditions. This clearly reveals that this particular substrate can initiate radical chain reactions under gaseous oxygen at elevated temperatures (Scheme 2). It is conceivable that such oxidation reaction is initiated via hydrogen abstraction by the oxygen, giving diphenylmethyl radicals which can undergo subsequent reactions to form benzophenone. Please note that similar reaction pathways have been elucidated in the partial oxidation of methane to formaldehyde [36].



Scheme 2.

As seen from Table 6, different catalytic productivities (vary from −30 to 33) are obtained implying that some catalysts give higher benzophenone yields and some catalysts inhibit the oxidation as compared to the result obtained without using catalyst. It is interesting to note that the samples prepared by wet impregnation give a good catalytic activity for this type of oxidation reaction. On the other hand, the MOCVD samples, in particular the air-calcined $\mathrm{Mn(Cp)_2/MCM\text{-}41}$ and $\mathrm{BrMn(CO)_5/MCM\text{-}41}$ samples giving amongst the highest activities for *trans*-stilbene oxidation, apparently inhibit this type of oxidation reaction.

4. Discussion

We showed that MOCVD is a valuable synthetic method for the modification of the mesoporous silica MCM-41 with manganese precursors. The resulting modified materials not only retain the high surface area and the regular mesoporosity associated with the MCM-41 structure but also disperse the

Table 6
Catalytic properties of Mn-modified MCM-41 materials in the oxidation of diphenylmethane to benzophenone

Catalyst	Mass (mg)	Mn (wt.%)	T (°C)	Yield of benzophenone (%) at t=12 h	Catalytic productivity (mol mol Mn^{-1} h^{-1})[a]
No catalyst	–	–	150	25.3	–
$\mathrm{KMnO_4/MCM\text{-}41}$	60	6.8	150	35.1	32.99
$\mathrm{Mn(acac)_3/MCM\text{-}41}$	60	8.6	150	36.1	28.74
$\mathrm{Mn_2(CO)_{10}/MCM\text{-}41}$	60	8.2	150	35.6	28.75
$\mathrm{BrMn(CO)_5/MCM\text{-}41}$	60	5.5	150	24.5	−3.32
$\mathrm{Mn(Cp)_2/MCM\text{-}41}$	60	3.2	150	21.2	−29.33

[a] Catalytic productivity is defined as: (total mole of benzophenone formed in the catalyst system minus the mole of benzophenone formed by pure substrate reactions without catalyst) per mole of Mn per hour.

active Mn atoms on the surface of MCM-41 very well. Our material characterisation suggests that this MOCVD method can generate solid supported molecular 'akin' species, which were highly dispersed with maximum conformity of the support morphology. It is generally accepted that epoxidation reaction using organic peroxide involves formation and transfer of electrophilic oxygen over active metal species such as in soluble complex environment [37] or as isolated sites in a solid matrix [1]. It is therefore not surprising to find that our MOCVD samples gave a much higher activity in *trans*-stilbene oxidation than those of wet impregnation samples. Since the conventional impregnation method generates considerably large Mn oxide crystallites which likely cover only a part of the surface (blocking pores), as a result, it leads to a poor activity. It is worthwhile to note that another technique, the template ion-exchange technique claimed to generate well-dispersed Mn ions into MCM-41 structure by Iwamoto and co-workers [18], also showed a higher activity for *trans*-stilbene oxidation than their wet impregnation sample. This agrees well with the present conclusion that dispersion towards site isolation is very important for this oxygen transfer reaction. It is interesting to note that our MOCVD catalysts gave about 200–300 turnover frequency (TOF) which was significantly higher than their Mn-MCM-41 samples of about 100 under comparable reaction conditions. It is, however, stressed that comparison of the two types of catalysts should be conducted under identical experimental conditions before a solid conclusion can be drawn.

An important point from this work is that a Mn catalyst having a discrete molecular nature or existing as an isolated site could be in marked contrast to the three-dimensional repetitive units observed in many manganese oxide lattices where most of the Mn-oxygen ions are buried deep inside the bulk. In many cases, the oxidation rates over the solid materials are limited by the mass transfer of the reactive species. In addition, the nature of oxygen (degree of electrophilicity and nucleophilicity) attached to the Mn atoms can also be markedly different. It is very interesting to point out that the molecular 'akin' Mn species prepared by MOCVD method (such as air calcined $Mn(Cp)_2$/MCM-41 and $BrMn(CO)_5$/MCM-41) show a very good activity for *trans*-stilbene oxidation but inhibits diphenylmethane oxidation. The superior catalytic activity of these MOCVD catalysts toward *trans*-stilbene oxidation is attributed to their active oxygen with a high electron affinity (electrophilic) for the attack of electron-rich double bond of the stilbene molecule. However, the oxidation of saturated hydrocarbons of the typical example diphenylmethane would require an initial hydrogen abstraction by active oxygen species (nucleophilic) leading to radical oxidation reactions. Thus, it is argued that the electrophilic oxygen in MOCVD samples may somehow interact with electron rich radicals and act as radical quenchers for the inhibition of diphenylmethane oxidation. On the other hand, nucleophilic oxygen associated with oxygen atoms in the bulk oxygen lattice in the wet impregnation samples is active for such a particular radical oxidation reaction. Notice that Clark et al. [38] also reported a substantial increase in the benzophenone yields from the air-oxidation of diphenylmethane by simply adding $KMnO_4$/silica as a catalyst.

From our MOCVD study, we also found a significant difference in catalytic activity by using different precursors even at a comparable concentration. Our EXAFS studies revealed that different forms of manganese-oxygen species are formed depending on the type of precursors used [16,39]. This suggests that the method could allow one to tailor a particular surface active species for a particular catalytic reaction hence ultraselective reactions can be achieved.

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References

[1] R.A. Sheldon, J. Mol. Catal. A 107 (1996) 75.

[2] J.H. Clark, D.G. Cork, H.W. Gibbs, J. Chem. Soc., Perkin Trans. 1 (1983) 2253.

[3] J.H. Clark, D.G. Cork, J. Chem. Soc., Chem. Commun. (1982) 635.

[4] J.T.B. Ferreira, W.O. Cruz, P.C. Vieira, M. Yonashiro, J. Org. Chem. 52 (1987) 3698.

[5] N.A. Noureldin, Tetrahedron Lett. 22 (1981) 4889.

[6] J. Chisem, I.C. Chisem, J.S. Rafelt, D.J. Macquarrie, J.H. Clark, J. Chem. Soc., Chem. Commun. (1997) 2203.

[7] J.H. Clark, S.R. Cullen, S.J. Barlow, T.W. Bastock, J. Chem. Soc., Perkin Trans. 2 (1994) 1117.
[8] J.D. Chen, J. Dakka, E. Neeleman, R.A. Sheldon, J. Chem. Soc., Chem. Commun. (1993) 1379.
[9] A. Corma, Chem. Rev. 97 (1997) 2373.
[10] B. Jayachandran, M. Sasidharan, A. Sudalai, T. Ravindranathan, J. Chem. Soc., Chem. Commun. (1995) 1523.
[11] J.H. Clark, K. Martin, A.J. Teasdale, S.J. Barlow, J. Chem. Soc., Chem. Commun. (1995) 2037.
[12] S.L. Regen, C.J. Koteel, J. Am. Chem. Soc. 99 (1977) 3837.
[13] Z. Liu, G.M. Crumbaugh, R.J. Davis, J. Catal. 159 (1996) 83.
[14] J.M. Thomas, Nature 368 (1994) 289.
[15] R. Burch, N.A. Cruise, D. Gleeson, S.C. Tsang, J. Chem. Soc., Chem. Commun. (1996) 951.
[16] R. Burch, N.A. Cruise, D. Gleeson, S.C. Tsang, J. Mater. Chem. 8 (1998) 227.
[17] S.H. Lau, V. Caps, K.W. Yeung, K.Y. Wong, S.C. Tsang, Micropor. Mespor. Mater. 32 (1999) 279.
[18] M. Yonemitsu, Y. Tanaka, M. Iwamoto, J. Catal. 178 (1998) 207.
[19] P. Sutra, D. Brunel, J. Chem. Soc., Chem. Commun. (1996) 2485.
[20] D. Zhao, D. Goldfarb, Stud. Surf. Sci. Catal. 97 (1995) 181.
[21] E.A. Gunnewegh, S.S. Gopie, H. van Bekkum, J. Mol. Catal. A 106 (1996) 151.
[22] K.R. Kloetstra, H. van Bekkum, J. Chem. Soc., Chem. Commun. (1995) 1005.
[23] M. Hartmann, A. Pöppl, L. Kevan, J. Phys. Chem. 99 (1995) 17 494.
[24] A. Pöppl, M. Newhouse, L. Kevan, J. Phys. Chem. 99 (1995) 10 019.
[25] S.-S. Kim, W. Zhang, T.J. Pinnavaia, Catal. Lett. 43 (1997) 149.
[26] M. Okumura, S. Tsubota, M. Iwamoto, M. Haruta, Chem. Lett. (1998) 315.
[27] G. Grubert, J. Rathousky, G. SchulzEkloff, M. Wark, A. Zukal, Micropor. Mesopor. Mater. 22 (1998) 225.
[28] 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. 114 (1992) 10 834.
[29] H. Haas, J. Chem. Phys. 47 (1967) 2996.
[30] H.D. Kaesz, J. Am. Chem. Soc. 89 (1967) 2844.
[31] T.S. Piper, J. Inorg. Nucl. Chem. 1 (1955) 165.
[32] B.V. Lokshin, J. Organomet. Chem. 77 (1974) 69.
[33] D.J. Parker, J. Chem. Soc. A (1970) 480.
[34] A.M.J. Jorna, A.E.M. Boelrijk, H.J. Hoorn, J. Reedijk, React. Funct. Polym. 29 (1996) 101.
[35] C.J. Liu, W.Y. Yu, S.G. Li, C.M. Che, J. Org. Chem. 63 (1998) 7364.
[36] T.R. Baldwin, R. Burch, G.D. Squire, S.C. Tsang, Appl. Catal. 74 (1991) 137.
[37] K.A. Jørgensen, Chem. Rev. 89 (1989) 431.
[38] J.H. Clark, A.P. Kybett, P. Landon, D.J. Macquarrie, K. Martin, J. Chem. Soc., Chem. Commun. (1989) 1355.
[39] V. Caps, S.C. Tsang, in preparation.