Ti-containing MCM-41 catalysts for liquid phase oxidation of cyclohexene with aqueous H_2O_2 and tert-butyl hydroperoxide

L.Y. Chen, G.K. Chuah and S. Jaenicke*

Department of Chemistry, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Republic of Singapore

Framework Ti-substituted and Ti-grafted MCM-41 mesoporous material has been prepared by direct hydrothermal synthesis and a post-synthesis grafting method. The materials have been tested as catalysts for cyclohexene oxidation with aqueous H_2O_2 and tert-butyl hydroperoxide (TBHP). With aqueous H_2O_2 in methanol, the major products were cyclohexene diol and its methyl ethers. No cyclohexene oxide was produced. Titanium leaching was a serious problem, and the catalyst lost its activity irreversibly after only one cycle of reaction. With TBHP, the selectivity for cyclohexene oxide was near 100%, titanium leaching was negligible, and the catalyst could be repeatedly used after regeneration without suffering significant activity loss. However, the reaction rate was lower than when H_2O_2 was used. Framework substituted material and catalysts prepared by Ti-grafting onto a MCM-41 support behaved similar, but the Ti-grafted MCM-41 is somewhat more active. The turnover frequency (TOF) per mole of Ti decreases with an increase of Ti content in the catalyst. This is caused by a reduced Ti dispersion within the silica matrix.

Keywords: Ti-containing MCM-41, selective oxidation, aqueous H_2O_2, tert-butyl hydroperoxide (TBHP), Ti leaching

1. Introduction

The discovery of the crystalline titanium silicalites TS-1 and TS-2 by researchers at Enichem [1] initiated an intense effort to study catalytic oxidations by redox titanosilicate molecular sieves. This resulted in the commercialization of two processes: the oxidation of phenol to cathechol and hydroquinone, and the ammoximation of cyclohexanone. The advantages of the TS zeolites are the high selectivity to the desired products and the possibility to use dilute aqueous H_2O_2 as oxidant. However, the microporous nature of the material hinders its use for reactions involving bigger molecules, like those of interest to the fine-chemical and pharmaceutical industries. Therefore, it is necessary to develop new catalysts with larger pores. Ti-Beta was reported to be effective for the oxidation of bulky reactants [2]. Baiker et al. [3] reported that a titania–silica aerogel prepared by supercritical drying was an efficient catalyst. Mesoporous titanium-containing M41S and HMS materials have recently been prepared and tested as catalysts. Ti-MCM-41, in which the titanium is incorporated into the framework of siliceous MCM-41, is an effective catalyst for epoxidations of bulky reactants [4,5]. Ti-HMS prepared via templating with a neutral surfactant is also very active towards such reactions [6,7]. The activity of another member of the M41S family, cubic MCM-48 with framework titanium, has been reported to surpass that of hexagonal Ti-MCM-41 [8]. Recently, the grafting of metallocene complexes onto mesoporous silica has been reported as another route to active epoxidation catalysts [9]. A con-

version as high as 3 mmol cyclohexene per gram of catalyst per minute was achieved when tert-butylhydroperoxide (TBHP) was used as oxidant.

In this study, we have prepared Ti-containing MCM-41 catalysts both of the framework Ti-substituted and the Ti-grafted type. A Ti-grafted amorphous silica and a TS-1 zeolite were prepared as reference materials. The structures of these catalysts have been characterized by FT-IR, XRD and UV absorption. Their catalytic properties have been investigated with the oxidation of cyclohexene with H_2O_2 and tert-butyl hydroperoxide (TBHP) as test reaction. The influence of the catalyst structure and the type of oxidant on the title reaction was studied.

2. Experimental

2.1. Synthesis of framework Ti-substituted mesoporous MCM-41

Framework substituted MCM-41 with different titanium content was synthesized hydrothermally from tetrapropylorthotitanate (TPOT, Merck) and tetraethylorthosilicate (TEOS, Merck). A typical preparation procedure is as follows. 14.4 g of TEOS was mixed with 0.27 g of TPOT at 0°C for half an hour, then 62 ml cetyltrimethylammonium hydroxide (CTMAOH) in 25 wt% aqueous solution was added dropwise while stirring. The mixture was heated to 80°C and stirred at this temperature for 1 h to bring the hydrolysis of TEOS and TPOT to completion. It was then transferred into a Teflon-lined stainless steel autoclave, and kept at 120°C for two days

---

* To whom correspondence should be addressed.

under autogenous pressure. After it had cooled down to room temperature, the resulting mixture was filtered, the filtrate was washed with plenty of deionized water, dried at ambient temperature overnight and finally calcined in air at 550°C for 8 h. The heating rate was 1°C/min in the calcination step. The titanium content was varied by using different amounts of TPOT while keeping the other conditions the same. Purely siliceous MCM-41 was prepared in the same way but without adding TPOT in the synthesis mixture.

2.2. Grafting of Ti onto mesoporous MCM-41

The grafting of titanium onto MCM-41 was carried out according to Maschmeyer et al. [9]. TPOT dissolved in isopropanol or dichlorotitanocene in chloroform were used for the grafting reaction. A reference material was prepared by the same method, using a non-porous fumed silica (Degussa Aerosil 300) as support.

2.3. Catalyst characterization

The titanium content in the materials was determined by X-ray fluorescence (XRF). The BET surface area, pore volume and pore size distribution were obtained from nitrogen adsorption–desorption isotherms measured at 77 K with a NOVA 2000 (Quantachrome) porosimeter, using the BJH method [10]. IR spectra were recorded with a resolution of 4 cm^{-1} using a Bio-Rad FTS 165 FT-IR spectrometer. The UV absorption of solids was measured as described before [11]. A Siemens 5005 X-ray instrument was used to analyze the XRD patterns of the solid samples.

2.4. Oxidation of cyclohexene

Cyclohexene (99%, Merck), methanol, acetone, dichloromethane, acetonitrile (HPLC grade, Fisher)

and H_2O_2 (35 wt% in water, Merck) were used as received. TBHP (70 wt% in water, Fluka) was dried with anhydrous $MgSO_4$. The catalysts were dried at 350°C for 1 h before being transferred into the reactor. Typically, the reaction mixture consisted of 0.1 g of catalyst, 10 mmol cyclohexene, 11 mmol oxidant (TBHP or H_2O_2) and 10 ml of solvent. The reaction was carried out at 40°C under N_2 in a Pyrex flask with reflux condenser. The products were identified by GC/MS (HP MS-5988). Samples were withdrawn at different reaction times and analysed by GC (SPB-5 capillary column, FID detector). The turnover frequency (TOF) is defined as moles cyclohexene converted per mole of titanium per hour (h^{-1}). Catalyst stability was tested by separating the used catalyst from the reaction solution. It was then dried at 120°C overnight and calcined in air at 550°C for 4 h before it was used again.

3. Results and discussion

3.1. Structural characteristics of the Ti-containing MCM-41 materials

The properties of the materials prepared for this study are given in table 1. The catalysts are divided into three groups. The first group (samples 1–3) was prepared by direct hydrothermal synthesis. XRD patterns for these samples are shown in figure 1. It can be seen that samples with Ti content < 2 wt% retain the MCM-41 structure. The diffraction peak at 2–3° corresponds to a d_{100} spacing of about 41–47 Å which is in agreement with the literature [12]. The appearance of a second diffraction peak at around 4° indicates a highly ordered MCM-41 structure for these two samples. N_2 adsorption–desorption measurements confirmed that these materials were mesoporous with an average pore diameter of about 31 Å. Both surface area and pore diameter decreased with

Table 1
Characteristics of the Ti-containing catalysts (fresh samples)

No.	Catalyst	Preparation method	Ti (wt%)	BET surface area (m^2/g)	Average pore diameter (Å)
1	Ti-MCM-41	D.H.	0.99	985	31
2	Ti-MCM-41	D.H.	1.82	921	31
3	Ti-MCM-41	D.H.	3.76	741	–
4	Ti/MCM-41	P.S.	1.53	846	31
5	Ti/MCM-41	P.S.	4.67	788	29
6	Ti/MCM-41	P.S.	4.27	801	31
7	Ti/SiO$_2$ [b]	P.S.	3.45	349	–
8	sample 2	850°C cal.	1.82	667	24
9	sample 2	950°C cal.	1.82	106	–
10	TiO$_2$–SiO$_2$	sol–gel	5.18	397	–
11	TS-1	D.H.	1.93	463	–

[a] D.H.: direct hydrothermal synthesis; P.S.: post-synthesis modification.
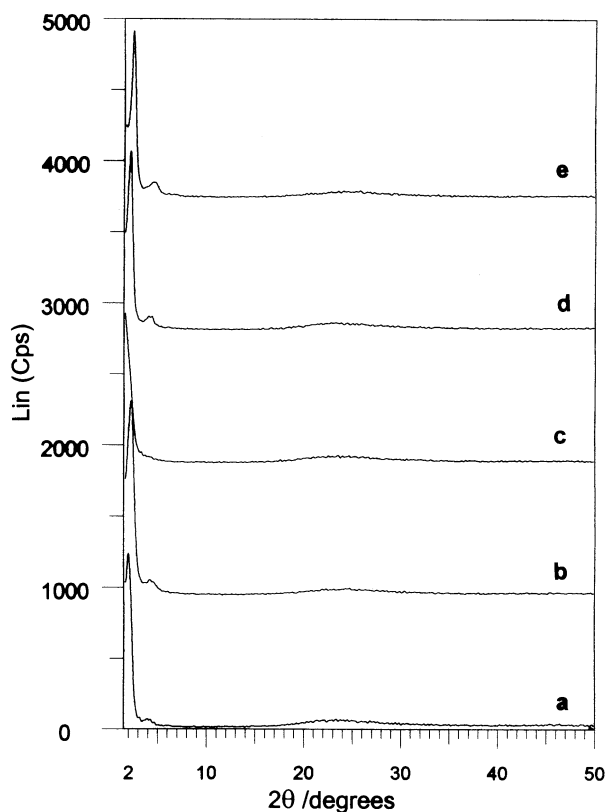[b] SiO$_2$ is Aerosil 300 (Degussa), a non-porous fumed silica with ca. 300 m^2/g.

Figure 1. XRD patterns of Ti-MCM-41 with various Ti-content. (a)–(c) Hydrothermally synthesized: (a) sample 1 with 0.99 wt%, (b) sampel 2 with 1.82 wt% and (c) sample 3 with 3.76 wt%; (d), (e) prepared by post-synthesis modification: (d) sample 4 with 1.53 wt% and (e) sample 5 with 4.67 wt%.

increasing titanium content. When the titanium content reached 3.7 wt%, the MCM-41 structure was lost. Although the surface area was still high, the pore size distribution showed no mesopores in this sample. The second group of catalysts (samples 4–7) were obtained by post-synthesis modification [9], i.e., by grafting dichlorotitanocene (samples 4 and 5) or TPOT (sample 6) onto MCM-41. The sharp diffraction peak at low angle in the XRD confirms that the material remained mesoporous even when the Ti content was as high as 4.67 wt%. However, the surface area and pore diameter decreased with increasing Ti loading. Thus, post-synthesis modification is superior to the direct hydrothermal synthesis for preparing MCM-41 mesoporous materials with high Ti content. Sample 7 is prepared by grafting TPOT onto a non-porous silica, while samples 8 and 9 are Ti-MCM-41 (sample 2) which was calcined in air at 850 and 950°C, respectively. Sample 8 was still mesoporous, but the average pore diameter had shrunk to 24 Å and the BET surface area decreased to 667 m^2/g. After heating to 950°C, the mesoporous structure collapsed completely. Sample 10 is a mixed TiO_2–SiO_2 oxide prepared by the sol–gel process. Sample 11 is a TS-1 zeolite prepared according to ref. [1].

When a titanium compound is grafted onto dehydroxylated MCM-41, there are two kinds of sites that can accommodate the Ti atom. One is the defect site formed during dehydroxylation, and the other is the silanol group. The former accounts for the insertion of Ti into the framework, whereas the latter is the binding site for the grafting of titanium onto the wall of the mesopore. The IR-band of the silanol group at 3744 cm^{-1} is considerably attenuated after the introduction of Ti, indicating that the grafting reaction is dominant. Some insertion of titanium into the MCM-41 framework may also take place. The IR absorption at 964 cm^{-1} which is generally attributed to the presence of Ti–O–Si connectivities [13,14] is found in all the Ti-containing samples (figure 2). XRD (figure 1) confirmed the absence of any separate TiO_2 (anatase) phase in either the grafted or the hydrothermally synthesized samples. This is also corroborated by the absence of an UV absorption band above 300 nm. At low titanium content, the UV spectra were similar to those of TS-1. However, the charge transfer band in the UV absorption shifted to a longer wavelength range when the titanium content increased (figure 3). This is possibly caused by an increase of the amount of the extra-framework Ti species or Ti–O–Ti bonds [3].

3.2. Catalytic performance of framework Ti-substituted MCM-41

The results for the reaction of cyclohexene with H_2O_2 catalysed by Ti-MCM-41 are shown in table 2. No cyclohexene oxide was found in the products, instead, the major products were cyclohexadiol and its mono- and
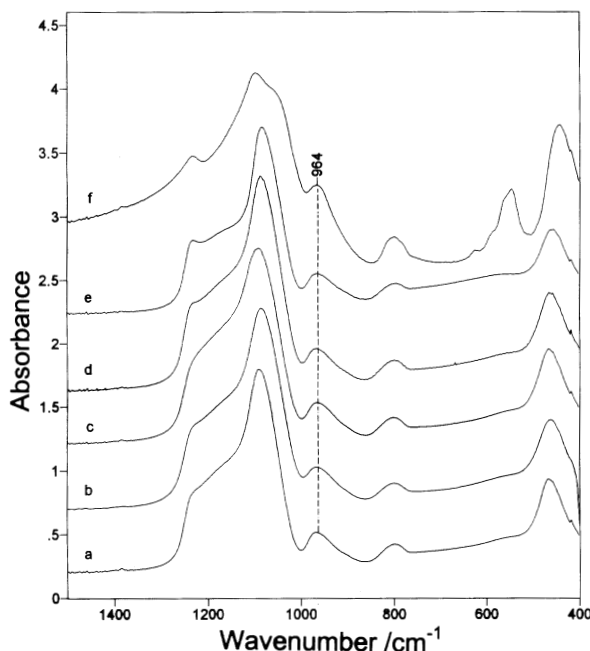

Figure 2. FT-IR spectra of Ti-MCM-41. (a)–(c) Hydrothermally synthesized: samples 1, 2 and 3; (d), (e) prepared by post-synthesis modification: samples 4 and 5; (f) TS-1.
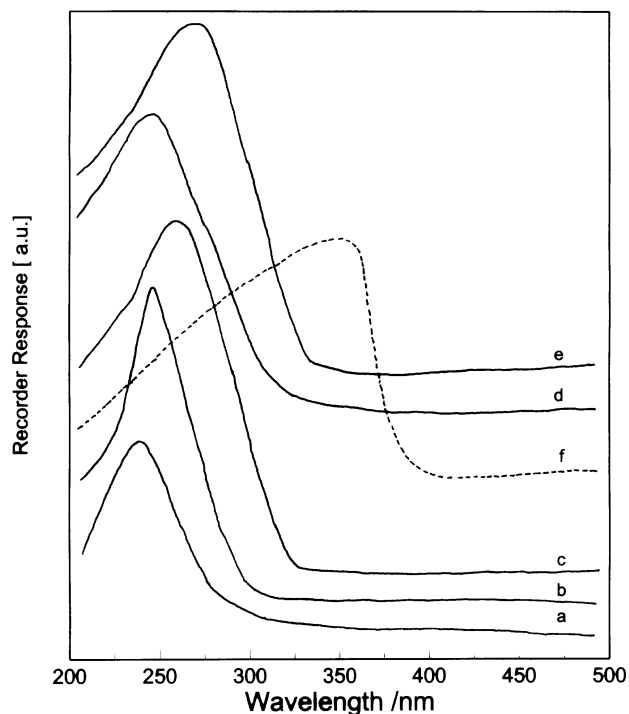
Figure 3. UV spectra of Ti-containing silicates. (a) TS-1 zeolite; (b), (c) hydrothermally synthesized (samples 2 and 3); (d), (e) prepared by post-synthesis modification (samples 4 and 5); (f) TiO_2.

dimethyl ethers. Small amounts of cyclohex-2-ene-1-ol and cyclohex-2-ene-1-one were also detected. The initially formed cyclohexene oxide undergoes further reactions with H_2O and methanol, catalyzed by the acidic sites of the catalyst [15]. With the relatively small cyclohexene, the transition state for the solvolysis reactions can form inside the mesopores. However, if a bigger molecule, e.g., α-pinene, was oxidized with aqueous H_2O_2 under similar reaction conditions, the epoxide was formed with high selectivity.

The results shown in table 2 indicate that the cyclohexene conversion increases with an increase of the titanium content in the catalyst. However, the turnover frequency (TOF) per titanium site decreased when the

titanium content was increased. At higher titanium content, the dispersion of titanium in silica is lower, as indicated by the shift of UV absorption band to the longer wavelengths. At a high Ti content, more Ti–O–Ti entities connectivities are formed, which are much less active towards oxidation reactions [3]. The catalytic activities of all the catalysts dropped significantly when the catalysts were re-used. The cyclohexene conversion decreased by a factor of 2–3 compared to that of the fresh catalyst. As we will see later, this is the result of titanium leaching from the catalyst.

With TBHP as oxidant, the presence of water is detrimental to the reaction. Therefore, most of the water was removed from TBHP by drying with anhydrous $MgSO_4$. Since even the water adsorbed on the Ti-containing MCM-41 inhibited the reaction, the catalysts had to be dried at $350°C$ for 1 h before use. In such an anhydrous system, the selectivity to cyclohexene oxide was close to 100%. The catalysts exhibit good stability in TBHP and can be regenerated repeatedly without suffering much loss in activity. Full catalytic activity is restored by calcining the used catalyst in air at $550°C$ for 4 h. It can be seen from table 3 that there is only a slight decrease of cyclohexene conversion or TOF even when the catalyst was used for the third recycle. The reaction rate of cyclohexene with TBHP is lower than with H_2O_2. This can be attributed to the higher steric constraint for the transition state inside MCM-41 pores and the less electrophilic character of the active species $Ti–OOC(CH_3)_3$ as compared to $Ti–OOH$ in the case of oxidations with H_2O_2 [16].

3.3. Catalytic performance of Ti-grafted MCM-41

The catalytic performance of the Ti-grafted MCM-41 was similar to that of the framework Ti-substituted samples (tables 4 and 5). The turnover frequency of cyclohexene with H_2O_2 was higher than with TBHP. A higher Ti content resulted in a lower turnover frequency, irrespective of the oxidant used. The product distribution was also similar. The major products were cyclohexene diol and its methyl ethers with H_2O_2 whereas with

Table 2

Results of cyclohexene oxidation with aqueous H_2O_2 (35 wt%) over Ti-MCM-41 prepared by direct hydrothermal synthesis [a]

No. of catalyst	Run [b]	Cyclohexene conversion (%) (TOF (h^{-1}))	Selectivity (%)			
			-1-ol	-1-one	mono-ethers	diol and di-ethers
1	1st	24.7　(19.9)	6.6	4.2	45.5	43.7
	2nd	7.2　(15.5)	1.8	7.2	22.6	68.5
2	1st	41.8　(18.3)	3.0	10.7	23.1	63.2
	2nd	14.9　(13.3)	1.8	8.8	9.7	79.7
3	1st	52.9　(11.2)	3.6	14.3	23.0	59.1
	2nd	21.7　　(9.4)	2.0	9.9	16.2	71.9

[a] Reaction conditions: 0.1 g catalyst, 10 ml methanol, 10 mmol cyclohexene, 11 mmol H_2O_2, $40°C$, 6 h.

[b] Turnover frequencies for the second run have been calculated based on the Ti-content of the used catalyst (data in table 6).

Table 3
Cyclohexene oxidation with TBHP catalysed by Ti-MCM-41 prepared by direct hydrothermal synthesis [a]

No. of catalyst	Cyclohexene conversion (%) (TOF (h^{-1}))		
	1st run	2nd run	3rd run
1	4.7 (3.8)	4.6 (3.7)	4.3 (3.5)
2	8.4 (3.6)	7.9 (3.5)	7.9 (3.5)
3	8.9 (1.9)	8.0 (1.7)	6.6 (1.4)

[a] Reaction conditions: 0.1 g catalyst, 10 ml CH$_2$Cl$_2$, 10 mmol cyclohexene, 11 mmol TBHP, 40°C, 6 h.

TBHP, the only product was cyclohexene oxide. However, the cyclohexene TOF was much higher for the Ti-grafted catalyst than that of the framework Ti-substituted one with a similar Ti content with either H$_2$O$_2$ or TBHP. Samples 2 and 4 have a similar Ti content, but the TOF with H$_2$O$_2$ was 25.4 h^{-1} for the Ti-grafted sample 4 while it was only 18.3 h^{-1} for the framework substituted sample 2. Oldroyd et al. [17] also found that the grafted catalyst was more active than the framework substituted one. The simplest explanation for this difference is the location of the active titanium species as we cannot identify much structural difference between these two types of catalyst. In the framework substituted samples, the titanium species are buried inside the wall of the catalyst pore. Therefore, the accessibility of these titanium species for the bulky reactants is greatly restricted. In the grafted samples, however, most of the titanium species are grafted on the wall of the pore, where they are readily accessible to the reactants.

The influence of the oxidant on the catalyst stability is the same for framework Ti-substituted and grafted samples. The activity was considerably lower when the catalyst was re-used if aqueous H$_2$O$_2$ was used as oxi-

dant. However, when TBHP was used, the regenerated catalyst was almost as active as the fresh one even after several recycles of reaction (table 5).

Sample 6 was also prepared by the grafting method, but using TPOT instead of dichlorotitanocene as the Ti precursor. The activity of this catalyst was not as high as that of the catalyst prepared from dichlorotitanocene. Possibly this was caused by the oligomerization of TPOT during catalyst preparation, which resulted in a lower dispersion of the titanium species [9].

The pore structure of the catalyst plays an important role in the oxidation of cyclohexene, especially when the bulky oxidant TBHP is used. When the framework Ti-substituted MCM-41 (sample 2) was heated at 850°C, there remained some mesopores, but the mesoporous structure was completely destroyed at 950°C (table 1). However, the catalyst composition did not change. It can be seen from tables 4 and 5 that the catalytic activity of this sample decreased significantly when it had been heated at a high temperature. After the destruction of the mesoporous structure, its activity was as low as that of TiO$_2$–SiO$_2$ oxide and TS-1 zeolite. Catalyst 7, which was prepared by grafting TPOT on a non-porous fumed silica, had a much lower activity than when a mesoporous MCM-41 was used as support. The effect of mesopore on the reaction rate was more conspicuous with the bulky TBHP as oxidant. No reaction was observed when TS-1 was used as catalyst for the oxidation of cyclohexene with TBHP, because the pores of TS-1 (about 6 Å) are too narrow to accommodate both the bulky cyclohexene and TBHP simultaneously.

3.4. Titanium leaching with aqueous H$_2$O$_2$ as oxidant

We have already seen that there are significant differ-

Table 4
Results of cyclohexene oxidation with H$_2$O$_2$ over Ti/MCM-41 prepared by the post-synthesis method and other Ti-containing silica catalysts [a]

Code	Type	Run	Cyclohexene conversion (%) TOF (h^{-1}))	Selectivity (%)			
				-1-ol	-1-one	mono-ethers	diol and di-ethers
			MCM-41 structure				
4		1	48.6 25.4	4.3	14.4	22.3	59.0
		2	10.9	1.2	6.3	10.1	82.4
5		1	75.8 12.9	7.6	26.4	22.2	43.7
		2	56.4	5.5	20.2	18.6	55.7
6		1	38.5 7.2	5.2	22.5	27.2	45.1
		2	5.9	2.0	9.7	22.0	66.3
			other Ti-containing silicates				
7	non-	1	18.6 4.3	5.5	22.2	27.3	45.0
	porous	2	6.1	5.0	14.2	21.3	59.5
8		1	5.2 2.3	2.6	20.4	12.9	64.1
9		1	3.7 1.6	3.2	22.3	0	74.5
10	xerogel	1	9.6 1.5	1.5	7.2	23.5	67.8
11	TS-1	1	2.7 1.1	86.8	0	0	13.2

[a] Reaction conditions: 0.1 g catalyst, 10 ml methanol, 10 mmol cyclohexene, 11 mmol H$_2$O$_2$ (35% aqueous solution), 40°C, 6 h.

Table 5
Stability of the Ti-containing catalysts during oxidation of cyclohexene with TBHP[a]

Catalyst[b]	Cyclohexene conversion (%) (TOF (h^{-1}))		
	1st run	2nd run	3rd run
4	15.5 (8.1)	15.3 (8.0)	15.3 (8.0)
5	9.9 (1.7)	9.4 (1.6)	8.8 (1.5)
6	8.6 (1.6)	7.0 (1.3)	6.4 (1.2)
7	2.2 (0.5)	1.7 (0.4)	1.7 (0.4)
8	3.0 (1.3)	2.7 (1.2)	2.7 (1.2)
9	1.4 (0.6)	1.3 (0.6)	1.1 (0.5)
10	2.6 (0.4)	1.9 (0.3)	1.9 (0.3)
11	no reaction	no reaction	no reaction

[a] Reaction conditions: 0.1 g catalyst, 10 ml CH_2Cl_2, 10 mmol cyclohexene, 11 mmol TBHP, 40°C, 6 h.
[b] Catalyst codes as in table 1.

ences when using H_2O_2 or TBHP as oxidant. With H_2O_2, the catalyst lost its activity irreversibly after only one cycle of reaction, while the catalyst used with TBHP could be used repeatedly after regeneration without significant loss of activity. Lee et al. [18] have reported that the catalyst structure was destroyed when aqueous H_2O_2 was used as oxidant. We, however, find that the Ti-MCM-41 structure is preserved under our reaction conditions. This is substantiated by XRD and N_2 physisorption results. The significant loss of activity with aqueous H_2O_2 may be attributed to titanium leaching from the catalyst. The most obvious evidence for the titanium leaching is the yellow colour of the reaction solution. FT-IR and analysis of the titanium content by XRF allow one to quantify the permanent loss of titanium from the catalysts (figure 4 and table 6). About 50% of the titanium leached out after the first two cycles of reaction under our reaction conditions. The IR spectra clearly show a reduced intensity of the 964 cm^{-1} peak after the first recycle of reaction. This is an indication of the decrease of the amount of Ti–O–Si bonds. With TBHP, the titanium leaching was negligible. The intensity of the 964 cm^{-1} band did not change. However, the BET surface area became smaller and the average pore size decreased by about 1–2 Å after three recycles of reaction. These changes may account for the slight decrease of the catalyst activity.

To test whether a homogeneous reaction occurred when H_2O_2 was used as oxidant, the catalyst was pretreated with an H_2O_2 aqueous solution as in the normal reaction procedure, but without adding the reactant. After 2 h under reaction conditions, the mixture was separated by centrifugation. The reaction with cyclohexene was then carried out using the solid and the clear yellow solution, respectively. The solution showed immediately some activity, while the solid was much less active during the first 2 h of reaction. However, it
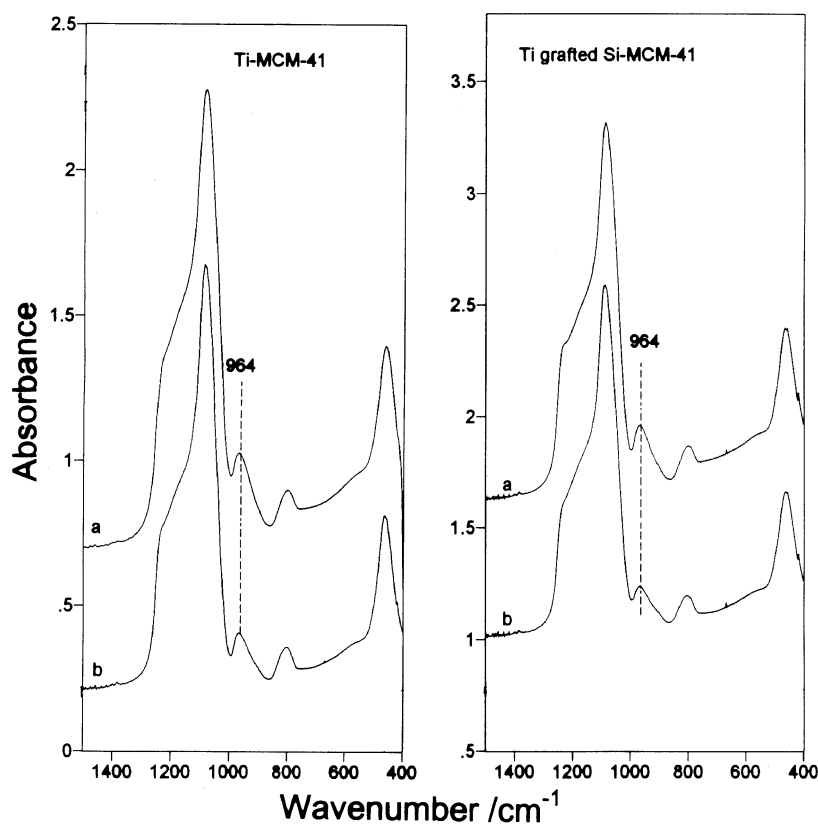

Figure 4. FT-IR spectra of a hydrothermally synthesized Ti-MCM-41 (sample 2, left) and a post-synthesis modified MCM-41 (sample 4, right) before (a) and after use with H_2O_2 as oxidant (b).

Table 6
Changes in some catalyst properties after reaction using H_2O_2 or TBHP as oxidant (determined after the second run for H_2O_2, after the third run for TBHP)

No. of catalyst	Oxidant	Ti (wt%)	BET surface area (m^2/g)	Average pore diameter (Å)
1	(fresh)	0.99	985	31
	TBHP	0.91	902	28
	H_2O_2	0.37	943	29
2	(fresh)	1.82	921	31
	TBHP	1.78	763	29
	H_2O_2	0.89	915	30
3	(fresh)	3.76	741	–
	TBHP	3.65	521	–
	H_2O_2	1.83	698	–
4	(fresh)	1.53	846	31
	TBHP	1.52	753	31
	H_2O_2	0.60	831	31
5	(fresh)	4.67	788	29
	TBHP	4.52	685	28
	H_2O_2	2.34	772	28

became active again if it was left for a longer time. These results suggest that the leached titanium species in solution could catalyze the oxidation reaction. Polar molecules like H_2O_2, H_2O and CH_3OH are responsible for titanium leaching. The mechanism is suggested in scheme 1.

In the presence of polar ligands L, the tetrahedral Ti species changes to octahedral co-ordination. If the interaction with the polar molecules is sufficiently strong, one or more Ti–O–Si bonds may break. When all these bonds break, the Ti species will no longer be restricted by the framework and can move freely into the solution [19]. The influence of the polarity of the solvent on Ti leaching is substantiated by experiments with different solvents. When a less polar solvent like acetone or dichloromethane was used with aqueous H_2O_2, the Ti leaching was less serious, but the TOF was lower too.

With TBHP as oxidant, only the heterogeneous reaction plays a role. In this case, it is suggested that the tetrahedral Ti species do not turn into octahedral form when they interact with TBHP to form the active Ti-peroxide species because of a steric effect and the absence of small polar molecules. Therefore, no Ti species will leave its original location, and no titanium leaches out.
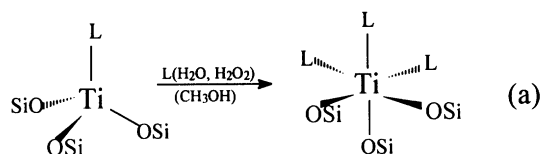
Scheme 1.

4. Conclusions

MCM-41 mesoporous material with high Ti content cannot be prepared by direct synthesis but is accessible by the post-synthesis method. Under similar reaction conditions, the Ti-grafted MCM-41 was more active than the framework substituted one for the oxidation of cyclohexene with either aqueous H_2O_2 or TBHP. Other trends showed not much difference for both types of catalyst. Oxidations with H_2O_2 proceed at a higher rate than with TBHP, and the reaction can be carried out in the presence of water whereas the presence of water is detrimental with TBHP. However, the selectivity to cyclohexene oxide is almost 100% with TBHP while the predominant products are cyclohexene diol and its methyl ethers with H_2O_2. Titanium leaching was a serious problem with aqueous H_2O_2 irrespective of the catalyst preparation method. The catalysts lost significant activity even after only one cycle of reaction. With TBHP, titanium leaching was negligible and the catalyst could be repeatedly used after regeneration without suffering much activity loss. The mesoporous structure of the catalyst plays an important role in the oxidation of cyclohexene, especially when bulky TBHP was used.

References

[1] M. Taramasso, G. Perego and B. Notari, US Patent 4410501 (1983).
[2] M.A. Camblor, A. Corma, A. Martinez and J. Pérez Pariente, J. Chem. Soc. Chem. Commun. (1994) 1491.
[3] R. Hutter, T. Mallat and A. Baiker, J. Catal. 153 (1995) 177; 157 (1995) 665.
[4] T. Blasco, A. Corma, M.T. Navarro and J. Pérez Pariente, J. Catal. 156 (1995) 65.
[5] A. Sayari, Chem. Mater. 8 (1996) 1840.
[6] P.T. Tanev, M. Chibwe and T. Pinnavaia, Nature 368 (1994) 321.
[7] W. Zhang, M. Froba, J. Wang, P.T. Tanev, J. Wong and T.J. Pinnavaia, J. Am. Chem. Soc. 118 (1996) 9164.
[8] K.A. Koyano and T. Tatsumi, J. Chem. Soc. Chem. Commun. (1996) 145.
[9] T. Maschmeyer, F. Rey, G. Sankar and J.M. Thomas, Nature 378 (1995) 159.
[10] E.P. Barrett, L.G. Joyner and P.P. Halenda. J. Am. Chem. Soc. 73 (1951) 373.
[11] L.Y. Chen, S. Jaenicke, G.K. Chuah and H.G. Ang, J. Electron. Spectrosc. Rel. Phen. 82 (1996) 203.
[12] 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 and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[13] M. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti and G. Petrini, Stud. Surf. Sci. Catal. 48 (1989) 133.

[14] R.C. Huybrechts, I. Vaesen, H.X. Li and P.A. Jacobs, Catal. Lett. 8 (1991) 237.

[15] D.T. On, M.P. Kapoor, P.N. Joshi, L. Bonneviot and S. Kaliaguine, Catal. Lett. 44 (1997) 171.

[16] A. Corma, P. Esteve, A. Martinez and S. Valencia, J. Catal. 152 (1995) 18.

[17] R.D. Oldroyd, J.M. Thomas, T. Maschmeyer, P.A. MacFaul, D.W. Snelgrove, K.U. Ingold and D.D.M. Wayner, Angew. Chem. Int. Ed. Engl. 35 (1996) 2787.

[18] C.H. Rhee and J.S. Lee, Catal. Lett. 40 (1996) 261.

[19] A. Zecchina, S. Bordiga, C. Lamberti, G. Ricchiardi, C. Lamberti, D. Scarano, G. Petrini, G. Leofanti and M. Mantegazza, Catal. Today 32 (1996) 97.