

# Organically Modified Titanium-Rich Ti-MCM-41, Efficient Catalysts for Epoxidation Reactions

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Highly ordered, titanium-rich organically modified Ti-MCM-41 materials have been synthesized at 413 K using a mixture of organotriethoxysilane and tetraethyl orthosilicate. Various organic substituents on Ti-MCM-41 used in the present study are methyl, vinyl, allyl, 3-chloropropyl, pentyl, and phenyl. The highest amount of Ti incorporated for a given Si/Ti mole ratio of 30 in the synthesis gel was 33.6 in the case of the 3-chloropropyl group. For methyl, vinyl, allyl, pentyl, and phenyl this ratio varied from 42 to 53, which is considerably lower than for unmodified Ti-MCM-41 reported earlier. Whereas incorporation of short chain organic functionality (C<sub>1</sub>–C<sub>3</sub>) causes an increase in the *d* spacing, resulting in wider pore openings, long chain (pentyl) and aromatic (phenyl) substituents cause a decrease in *d* spacing in these mesoporous molecular sieves. An increase in the organic content in the synthesis gel beyond a certain level also causes a decrease in *d* spacing. N<sub>2</sub> and H<sub>2</sub>O adsorption studies revealed that these organically modified well ordered Ti-MCM-41 materials are more hydrophobic than that synthesized in the absence of organic modifiers. These organically modified Ti-MCM-41 materials are efficient catalysts in the epoxidation reaction of unsaturated alcohols followed by cyclization to cyclic ethers using TBHP as oxidant. © 2000 Academic Press

**Key Words:** Ti-MCM-41; organic modification; hydrophobicity; oxidation reactions.

## INTRODUCTION

Titanium-containing mesoporous molecular sieves (1) have attracted much attention in recent times because of their potential for use as selective oxidation catalysts of very bulky organic substrates. However, the activity and selectivity of these Ti-containing mesoporous materials reported so far is not as high as expected in oxidizing relatively less bulky organic substrates (C<sub>3</sub>–C<sub>8</sub>) compared to that exhibited by TS-1 (2). Among various reasons respon-

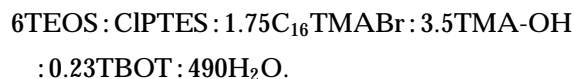
sible for its lower activity, lower hydrophobicity, large particle size, and high Si/Ti mole ratio in the resultant solid are believed to be the main causes. A high temperature synthesis is usually not preferred for these materials because of a dissolution problem with the micelles. The internal silanols present in this mesoporous structure give rise to the hydrophilic nature, thus retarding a liquid phase reaction in the presence of water (being adsorbed more selectively on the catalyst surface rather than the organic reactant) as a diluent or as a product of consumption of H<sub>2</sub>O<sub>2</sub>. Hydrophobicity of this material can be increased by silylating the surface silanols (3) or by organically modifying the silica surface (4). We have reported that a remarkable enhancement of the oxidation activity can be attained by silylation (5). In this regard it is to be noted that hydrophobic titania-silica materials are reported to exhibit outstanding catalytic performance in liquid phase oxidation (6–8).

Continuous efforts are under way to enhance the number of Ti atoms per unit cell in titanosilicate molecular sieves (9). At higher temperature it is well known that the efficiency for the incorporation of Ti in the silicate matrix is higher compared to that at low temperature for a given Si/Ti mole ratio in the gel (10). However, beyond a certain temperature depending upon the composition of the reactant mixture, the concentration of the anatase phase starts growing (10). Here we report the direct synthesis of various organically modified Ti-MCM-41 catalysts which are not only more hydrophobic than the parent one but can be synthesized at a Si/Ti mole ratio of 30 in the synthesis gel at the synthesis temperature 413 K. *Tert*-butyl hydroperoxide (TBHP), a commonly used oxidant, containing less water (70% TBHP, 30% H<sub>2</sub>O) than aqueous H<sub>2</sub>O<sub>2</sub>, is an effective oxidant even for a hydrophilic surface (11). Various organically modified Ti-MCM-41 synthesized here, which contain methyl (12), vinyl, allyl, 3-chloropropyl, pentyl, or phenyl groups, are very efficient in epoxidation and in the following oxidative cyclization (13) of unsaturated alcohols to the corresponding tetrahydrofuran or tetrahydropyran using TBHP as oxidant.

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## EXPERIMENTAL

Various organically modified Ti-MCM-41 materials were synthesized using a mixture of organo-triethoxysilane and tetraethyl orthosilicate (TEOS, TCI) as Si source. Cetyltrimethylammonium bromide (CTMABr, TCI) was used as a template and tetramethylammonium hydroxide (25% aqueous TMAOH, Aldrich) was used to provide alkalinity of the reaction medium. Tetrabutyl orthotitanate (TBOT, Aldrich) was used as Ti source. Isopropyl alcohol (IPA) was used to homogenize the organic and aqueous phases during the gel preparation. The synthesis method employed here is to hydrolyze the silicon alkoxides with the alkaline template solution followed by the addition of titanium alkoxide and subsequent dilution, aging, and autoclaving at an elevated temperature. In a typical synthesis 9.1 g of CTMABr was dissolved in a mixture of 30 g H<sub>2</sub>O and 45 g IPA. To it solution A, consisting of 3.4 g 3-chloropropyltriethoxysilane (CIPTES) and 17.9 g TEOS, and solution B, consisting of 18.2 g TMAOH and 18 g H<sub>2</sub>O, was added together at once and the mixture was stirred vigorously at room temperature for 1 h. After 1 h, 1.15 g TBOT dissolved in 7.5 g IPA was added dropwise to the resultant clear solution and the stirring was continued for 1 h. Then the solution was heated at 353 K for 2 h to remove the added alcohols and those produced during the hydrolysis of the alkoxides (to avoid the dissolution of micelles). Finally 54 g H<sub>2</sub>O was slowly added to the solution during which the clear liquid turns into a turbid gel. This gel was aged overnight (24 h) with continuous stirring. Finally the pH of the resultant gel was measured (usually varying from 11.8 to 12.2 depending on the alkylsilane) and the gel was heated in a closed stainless steel autoclave at an elevated temperature under static or agitating conditions. The molar ratio of various constituents in the synthesis mixture was



Crystallization was carried out in the temperature range 373–443 K for 1 to 5 days. After the hydrothermal treatment the products were filtered, washed thoroughly with water, and dried to get the as-synthesized form of the organically modified Ti-MCM-41. Surfactant was removed from this as-synthesized form by treatment with HCl/EtOH to get the template free pure Cl-propyl-Ti-MCM-41. Me-Ti-MCM-41 was synthesized following an identical procedure except for the addition of methyltriethoxysilane instead of 3-chloropropyltriethoxysilane. Similarly vinyltriethoxysilane, allyltriethoxysilane, pentyltriethoxysilane, and phenyltriethoxysilane were used for the synthesis of vinyl-, allyl-, pentyl-, and phenyl-modified Ti-MCM-41.

As-synthesized as well as the template-free samples were characterized by XRD, TG, and CHN analysis. Acid-

extracted samples were characterized through FT-IR (both at ambient atmosphere in KBr pellets and under vacuum using self-supported wafers), UV-visible spectroscopy, field emission SEM, and N<sub>2</sub> and H<sub>2</sub>O adsorption measurements. Elemental analysis of the solid samples was carried out by ICP measurement. All the samples used in the present study for the catalysis were activated at 473 K for 2 h before reaction. Liquid phase batch reactions were conducted in a two-necked flask at the desired temperature maintained in an oil bath. TBHP (70% solution in water, Wako Chemicals) was used as an oxidant. At various time intervals products were analyzed by capillary gas chromatography (using FID detectors) and finally products were identified through GC-MS. H<sub>2</sub>O<sub>2</sub> efficiency in the reaction was evaluated by titrating the final reaction mixture with a standard ceric solution.

## RESULTS AND DISCUSSION

## Synthesis

Synthesis conditions and physico-chemical properties of the various organically modified and unmodified Ti-MCM-41 samples are shown in Table 1. From the table it is clear

TABLE 1  
Synthesis of Organically Modified Ti-MCM-41

Sample Nos.	TEOS/ <i>R</i> -TES	Si/Ti in		Synthesis temp. (K) <sup>a</sup>	Time (days)	<i>I</i> <sub>100</sub> <sup>b</sup>	Carbon content <sup>c</sup>
		Gel	Product				
1	6 <sup>d</sup>	30	45.2	373, s	5	96	8.10
2	6 <sup>d</sup>	∞	—	373, t	4	99	8.23
3	6 <sup>d</sup>	30	41.3	413, s	2	98	8.16
4	6 <sup>d</sup>	30	38.9	413, t	1	95	8.11
5	6 <sup>d</sup>	15	—	443, s	2	0	—
6	6 <sup>d</sup>	15	—	443, t	1	0	—
7	6 <sup>d</sup>	60	59.7	413, s	0.8	100	8.21
8	3 <sup>d</sup>	30	33.6	413, s	2	77	13.29
9	∞	∞	—	413, t	1	83	—
10	∞	60	73.2	413, s	1	80	—
11	∞	60	79.8	413, t	1	76	—
12	∞	30	69.0	413, s	2	15	—
13	∞	30	56.8	413, t	2	LMP <sup>e</sup>	—
14	4 <sup>d</sup>	∞	—	373, s	4	100	11.34
15	6 <sup>f</sup>	∞	—	373, t	6	52	4.14
16	6 <sup>f</sup>	30	48.7	413, s	2	65	4.09

<sup>a</sup> Temperature of hydrothermal treatment, s, static; t, tumbling conditions.

<sup>b</sup> Intensity (%) of (100) XRD reflection of the sample with respect to that of most ordered materials (samples 7 and 14) obtained in the present study.

<sup>c</sup> % from the CHN analysis of the repeatedly HCl/EtOH-treated sample.

<sup>d</sup> *R*, 3-chloropropyl.

<sup>e</sup> Lamellar mesophase (LMP).

<sup>f</sup> *R*, methyl.

that only in the presence of organic modification, Ti-MCM-41 can be synthesized with a Si/Ti ratio as low as 30. However, pure Ti-MCM-41 cannot be synthesized without organic modification below a Si/Ti molar ratio of 60 in the synthesis gel. With a Si/Ti input molar ratio of 60, the resultant solid shows an output Si/Ti molar ratio of 73.2 (sample 10) under static conditions, whereas under tumbling the Si/Ti ratio turns out to be 79.8 (sample 11). With a decrease in this ratio, ordering of the mesophase decreases drastically. Under static conditions, the Ti-MCM-41 synthesized (with Si/Ti = 30, sample 12) without any organic modifier thus shows relatively poor ordering. On the other hand, an attempted synthesis of organic free Ti-MCM-41 with Si/Ti = 30 under tumbling conditions leads to the lamellar mesophase (LMP, Fig. 1d; Table 1, Sample 13) at 413 K, as shown below.

### Characterization

Figure 1 shows the XRD patterns of various samples listed in Table 1. Figures 1a, 1b, 1c, and 1d correspond to sample numbers 1, 4, 12, and 13, respectively. In Figs. 1a and 1b all distinct peaks of MCM-41, the 100, 110, 200, and 210 reflections, are present and their intensities are quite pronounced. Sample 12, synthesized at 413 K from the same Si/Ti ratio in the gel under organic-free condition is also very poorly ordered and with low intensities for the 210 and 211 reflections and devoid of the 211 one. Thus it is a rather disordered mesoporous material. The limit of incorporation is, however, restricted up to Si/Ti = 30 in the synthesis gel; below this input Si/Ti mole ratio amorphous material results (Table 1, samples 5 and 6).

CHN analysis reveals the presence of silanol OH and absorbed water protons in the acid exchanged sample as the H : C mole ratio shifts to higher values from its hypothetical value of 2 (for  $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Cl}$ ) or 3 (for  $-\text{CH}_3$ ).

In Table 2 various physico-chemical properties of Ti-MCM-41 samples with various organic substituents are reported. It is seen that with increase in chain length from methyl to 3-chloropropyl, the  $d_{100}$  values gradually increase. The size of pore openings increases simultaneously with increasing length of the alkyl chain. However, for pentyl (sample 19) and phenyl (sample 20) modification this value is quite low. This may be due to the fact that these organic functionalities ( $\text{C}_5$  or more) are too big to be accommodated in a regular order inside the channels. This causes strain, less stability, and thus formation of less ordered materials with relatively low surface areas and pore openings. It is noteworthy that the pore diameter estimated by the D-H method from the  $\text{N}_2$  adsorption data is several angstroms smaller than the actual one. Therefore the wall thickness listed in Table 2 may be considerably larger than the actual wall thickness.

In Fig. 2 the adsorption-desorption isotherms of  $\text{N}_2$  for samples 1, 4, 12, and 13 (corresponding to those of Fig. 1)

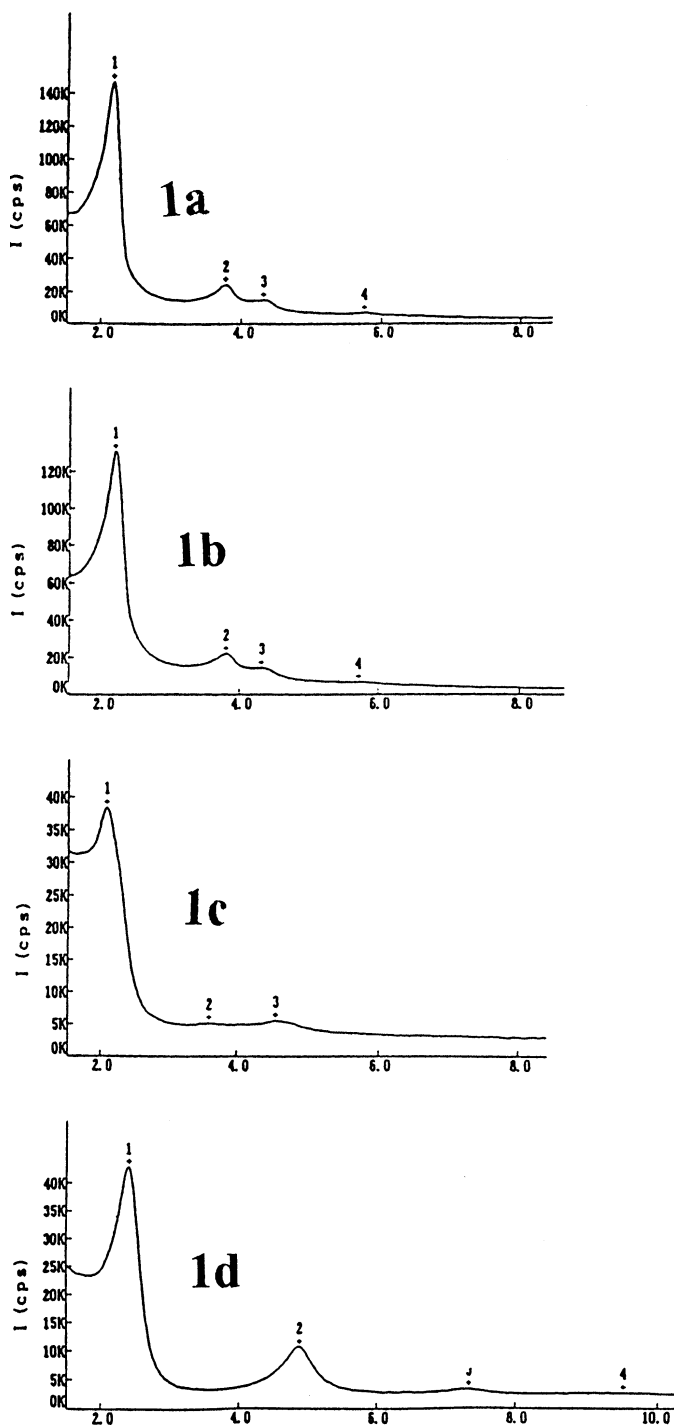


FIG. 1. XRD patterns of various Ti-MCM-41 (a-d) correspond to calcined samples 1, and 4, 12, and 13, respectively.

are shown. Except for sample 13, which shows an XRD pattern characteristic of a lamellar structure before calcination, the isotherms are of type IV in nature and show distinct capillary condensation steps as observed for well ordered mesoporous materials (14).  $\text{N}_2$  adsorption results for Cl-propyl-Ti-MCM-41 materials (represented by samples 1

TABLE 2  
Physico-chemical Properties of Various Ti-MCM-41<sup>a</sup>

Sample No.	Organic group	ST <sup>b</sup>	Si/Ti <sup>c</sup>	<i>I</i> <sub>100</sub> <sup>d</sup>	BET (m <sup>2</sup> g <sup>-1</sup> )	<i>d</i> <sub>100</sub> (Å)	PD <sup>e</sup> (Å)	WT <sup>f</sup> (Å)	<i>V</i> <sub>m</sub> <sup>g</sup> (molecules nm <sup>-2</sup> )
12	None	48	69.0	15	1072	37.1	22.4	20.3	2.73
16	Methyl	24	48.7	65	1447	36.8	23.2	19.3	1.38
17	Vinyl	22	47.6	74	1346	41.6	25.2	22.9	2.16
18	Allyl	20	44.5	61	1097	40.9	27.4	19.8	2.78
4	Cl-propyl	22	38.9	95	1218	42.4	27.4	21.6	1.16
19	Pentyl	40	53.0	37	923	32.9	20.8	17.2	2.91
20	Phenyl	48	42.1	32	846	34.5	21.2	18.6	4.12

<sup>a</sup> Synthesis conditions: Si/Ti = 30 in gel, synthesis temperature 413 K under tumbling conditions, TEOS/organosilane mole ratio = 6.

<sup>b</sup> Hydrothermal synthesis time in hours.

<sup>c</sup> Si/Ti mole ratio in the product after the acid extraction.

<sup>d</sup> Intensity (%) of the (100) XRD reflection with respect to that of the most ordered material obtained in the present study.

<sup>e</sup> Pore diameter measured by N<sub>2</sub> adsorption (D-H method).

<sup>f</sup> Wall thickness = (2*d*<sub>100</sub>/√3) - PD.

<sup>g</sup> Water adsorption capacity in number of H<sub>2</sub>O molecules nm<sup>-2</sup>.

and 4) indicate regular ordered phases with BET surface areas higher than 1100 m<sup>2</sup> g<sup>-1</sup>. Sample 8 shows a BET surface area of 1425 m<sup>2</sup> g<sup>-1</sup>. The pore size distribution also shows a very narrow and strong band. In Tables 2 and 3 pore diameters of various organically modified Ti-MCM-41 samples are reported. From the tables it is seen that in a series of Cl-propyl-Ti-MCM-41 samples the largest pore diameter of 27.4 Å was observed for sample 4. Allyl-Ti-MCM-41 (sample 18) also shows the same pore opening. Pore volumes observed for these samples (Cl-propyl-Ti-MCM-41 with different organic loading, shown in Table 3) are also very high. For the methyl, vinyl, and allyl modifications pore volumes were 1325, 1274, and 1282 mm<sup>3</sup> g<sup>-1</sup>, respectively. However, for the rather bulky pentyl- and phenyl-modified Ti-MCM-41 samples these volumes were low (632.8 and 453.2 mm<sup>3</sup> g<sup>-1</sup>, respectively).

In Table 2, *V*<sub>m</sub> (H<sub>2</sub>O monolayer adsorption density) of various organically modified Ti-MCM-41 samples are shown. BET surface areas (from N<sub>2</sub> adsorption measurements) and the volume of water adsorption per gram of the corresponding samples (from the BET plot of the H<sub>2</sub>O adsorption isotherm) are used to calculate the *V*<sub>m</sub> (H<sub>2</sub>O molecules nm<sup>-2</sup>). The water adsorption capacities for Cl-propyl-Ti-MCM-41 (samples 4, 8, 21, and 22) are consid-

erably low (0.83–1.38 molecules nm<sup>-2</sup>), decreasing with increasing organic loading (see below), vis-à-vis 4.0 molecules nm<sup>-2</sup> in the case of amorphous silica and 2.73 in the case of Ti-MCM-41 without any organic modification. The relatively high value of *V*<sub>m</sub> for the pentyl- and phenyl-modified samples can be attributed to the decrease in ordering for the corresponding samples.

UV-vis spectra for various Ti-MCM-41 samples are shown in Fig. 3. It is clear that sample 14, which is devoid of Ti, does not have any absorption in the 200- to 260-nm range (curve a). Sample 12, which is very poorly ordered Ti-MCM-41 (without any organic modification) shows a band at 220–230 nm (curve b), attributed to incorporated tetrahedral Ti in the mesoporous structure; however, its intensity is considerable lower than that of Cl-propyl-MCM-41 (sample 4, Si/Ti = 38.9, curve c).

FT-IR spectra of dry KBr-pelletized samples at room temperature are shown in Fig. 4. A strong band at 960 cm<sup>-1</sup> known to be responsible for the Si–O–Ti stretching frequency (2) is quite pronounced for both samples 4 (curve b) and 8 (curve c). Even in the case of sample 14 (curve a) which does not possess any Ti, this band around 960 cm<sup>-1</sup> was observed. This band at 960 cm<sup>-1</sup> can be attributed to the presence of silanols in this mesoporous structure.

TABLE 3  
Effect of Organic Loading on Physico-chemical Properties of Ti-MCM-41

Sample No.	TEOS/CIPTES	Si/Ti product	<i>I</i> <sub>100</sub> <sup>a</sup>	N <sub>2</sub> adsorption			H <sub>2</sub> O adsorption ( <i>V</i> <sub>m</sub> molecules nm <sup>-2</sup> )
				PV (mm <sup>3</sup> g <sup>-1</sup> )	BET (m <sup>2</sup> g <sup>-1</sup> )	<i>d</i> <sub>100</sub> (Å)	
21	8	45.3	74	1118	1047	41.6	1.38
4	6	38.9	95	1148	1218	42.4	1.16
22	4	37.4	80	1370	1235	40.0	1.04
8	3	33.6	77	1536	1425	37.7	0.83

<sup>a</sup> Intensity (%) of the (100) XRD reflection with respect to that of the most ordered material obtained in the present study.

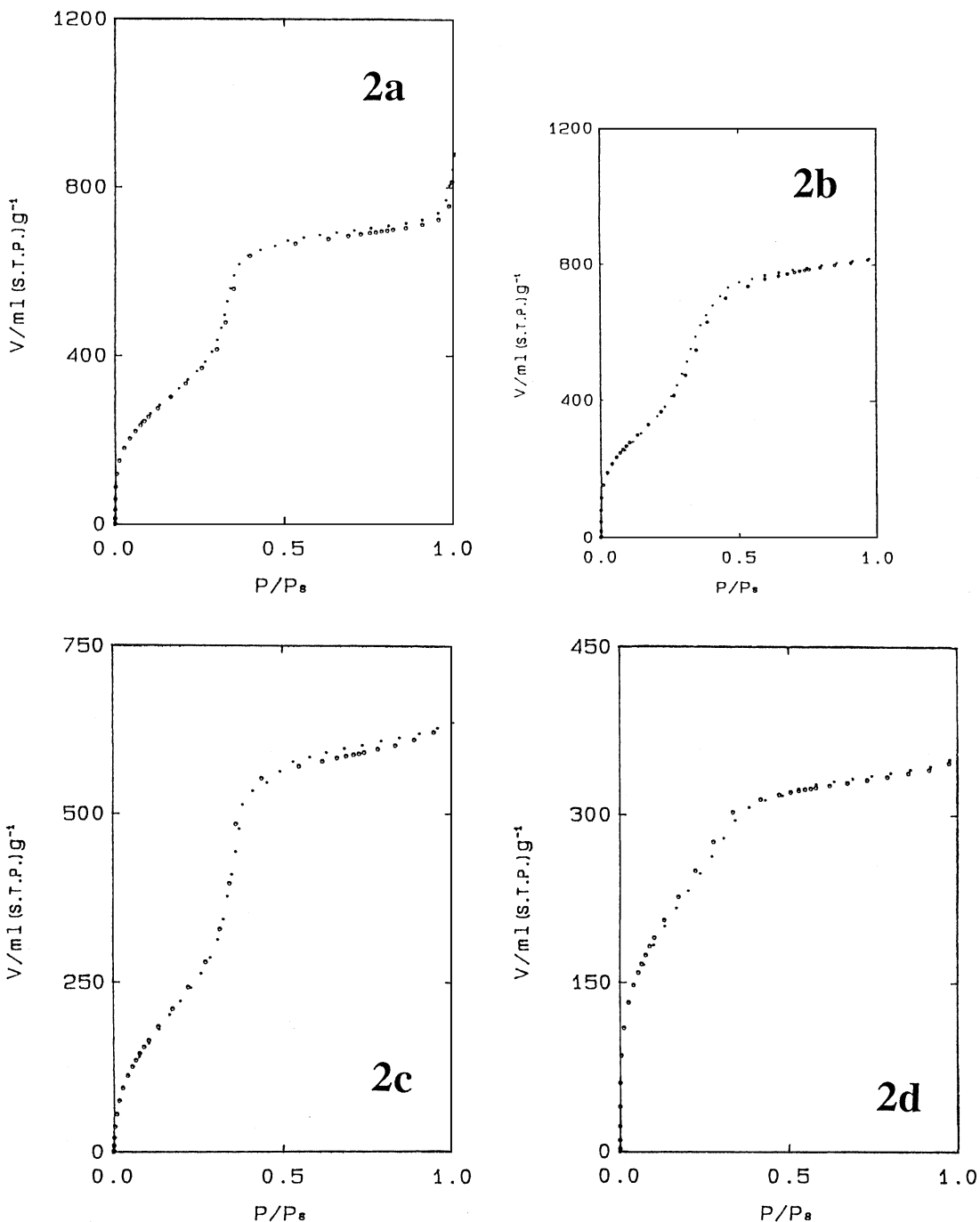


FIG. 2. Adsorption isotherm of samples 1 (a), 4 (b), 12 (c), and 13 (d), at 77 K.

FT-IR spectra of the self-supported sample 4 are taken under vacuum at 373, 573, and 773 K (not shown). A medium C-H stretching band that appeared at  $2920\text{ cm}^{-1}$  in Fig. 4 becomes very strong in the self-supported vacuum FT-IR spectra. With increase in temperature from 573 to 773 K this band intensity decreases as expected because of the removal of organic moiety due to Si-C cleavage at this high temperature. Simultaneously, the O-H stretching band

(which appeared at  $3300\text{--}3750\text{ cm}^{-1}$ ) becomes more pronounced and at 773 K a sharp silanol band at  $3717\text{ cm}^{-1}$  was observed.

The ratio of TEOS/organosilane in the mother gel is another important factor in determining the Ti incorporation and hydrophobicity of the resultant mesoporous materials. Table 3 illustrates the result using CIPTES as organic modifier. Among the four different TEOS/CIPTES ratios

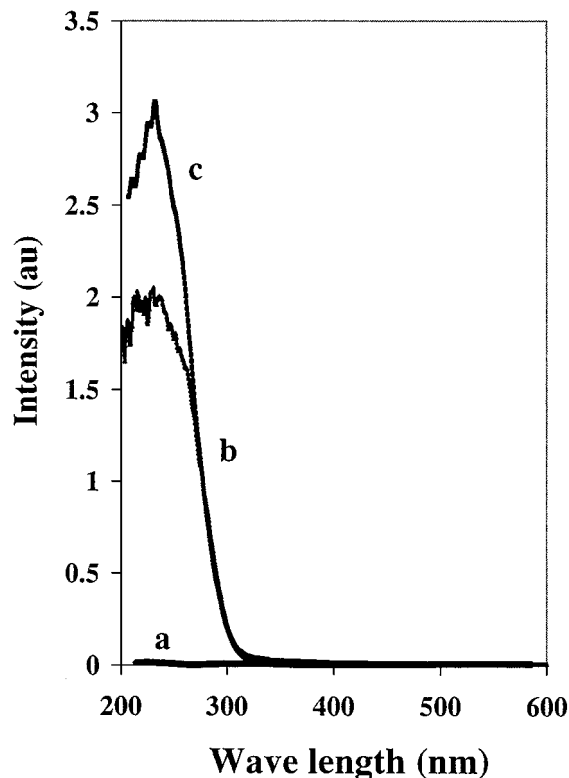


FIG. 3. UV-vis spectra for various MCM-41 materials: (a) sample 14, (b) sample 12, (c) sample 4.

of 3, 4, 6, and 8, the ratio 6 gives the best result in terms of structure ordering. A decrease in this ratio below 6 resulted in a progressive decrease in pore opening as well as a drop in the (100) XRD peak intensity of the resultant solid. However, the Ti loading, surface area, and internal void volume (i.e., inverse of density), as well as hydrophobicity, increase with the increase in organic content in the starting gel. This may be due to the fact that beyond an optimum fitting in the organic functionality in the mesopore, there is a decrease in ordering. In attempted syntheses with a TEOS to CIPTES ratio of 1 : 1 and using only CIPTES as silica source, no mesoporous materials were obtained.

### Catalysis

In Table 4 results of the catalytic activity of various organically modified Ti-MCM-41 are shown. TS-1 and Ti-beta have recently been employed in the oxidative cyclization of unsaturated alcohols (13). Contrary to TS-1 where TBHP is not effective in either of the hydrophilic and hydrophobic solvents, in the case of Cl-propyl-Ti-MCM-41 the catalytic activity drastically increases with changing the oxidant from H<sub>2</sub>O<sub>2</sub> to TBHP as observed for Ti-Al-Beta (11). Moreover, using H<sub>2</sub>O as dispersion medium (15) for the Cl-propyl-Ti-MCM-41/TBHP system the activity increases further. Thus, Cl-propyl-Ti-MCM-41 synthesized here is effective for such oxidative cyclization reactions under liquid phase reaction conditions using TBHP as oxidant. The major product in the oxidative cyclization of 4-penten-1-ol (1) is tetrahydrofuran-2-methanol (3) (formed by exo attack)

TABLE 4

### Catalytic Activity of Cl-C<sub>3</sub>H<sub>6</sub>-Ti-MCM-41 in the Oxidative Cyclization of Various Substrates Using TBHP as Oxidant

Entry	Substrate	Solvent/phase	Conv. %	Time (h)	Product selectivity (%)
1	1	CH <sub>2</sub> Cl <sub>2</sub>	42.4	12	3, 78.2 4, 16.7 —One, 5.1
2 <sup>a</sup>	1	Acetone	3.6	12	3, 7.2 2, 23.0 —One, 69.8
3	5	Acetone,	63.5	4	7, 89.8 8, 4.9 —One + diol 5.3
4 <sup>b</sup>	5	Acetone	92.0	4	7, 99.0 — Cis-4-hexenal, 1
5 <sup>c</sup>	5	Acetone	78.2	3	7, 25.4 — 6, 74.6
6 <sup>d</sup>	5	Acetone	15.1	24	7, 11.7 6, 32.2 —One + diol 56.1
7	5	H <sub>2</sub> O, triphase	92.7	12	7, 92.4 8, 1.2 6, 5.7
8 <sup>e</sup>	5	H <sub>2</sub> O, triphase	92.0	12	7, 100 — —
9 <sup>c,f</sup>	5	Acetone	77.0	3	7, 23.1 — 6, 76.9
10 <sup>g</sup>	5	Acetone	35.5	6	7, 86.3 — —One, 13.7
11	9	Acetone	84.4	6	11, 14.5 12, 42.2 13, 43.3

Note. Reaction condition: substrate : TBHP = 1 : 1, solvent or dispersion medium = 10 g for 10 mmol of substrate, temp. 333 K, catalyst 20% with respect to the substrate, for entries 1, 2, 3, 5, and 9; sample 4 (Cl-propyl-Ti-MCM-41, Si/Ti = 38.9) was used as catalyst.

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> used as oxidant with substrate : H<sub>2</sub>O<sub>2</sub> = 1 : 1.

<sup>b</sup> TS-1 (Si/Ti = 29.0) was used as catalyst.

<sup>c</sup> Chloropropyl-Ti-MCM-41 (Si/Ti = 33.6, sample 8, Table 1) was used as catalyst.

<sup>d</sup> Sample 12 was used as catalyst.

<sup>e</sup> Me-Ti-MCM-41 (Si/Ti = 41.7, sample 16, Table 1) was used as catalyst.

<sup>f</sup> After the experiment number 5, the catalyst was washed thoroughly with acetone and then treated with 0.1 M HCl solution in EtOH for 8 h at 333 K and finally dried at 373 K for 2 h and then used as catalyst for this experiment.

<sup>g</sup> Sample 20 (phenyl-Ti-MCM-41, Si/Ti = 42.1) was used as catalyst.

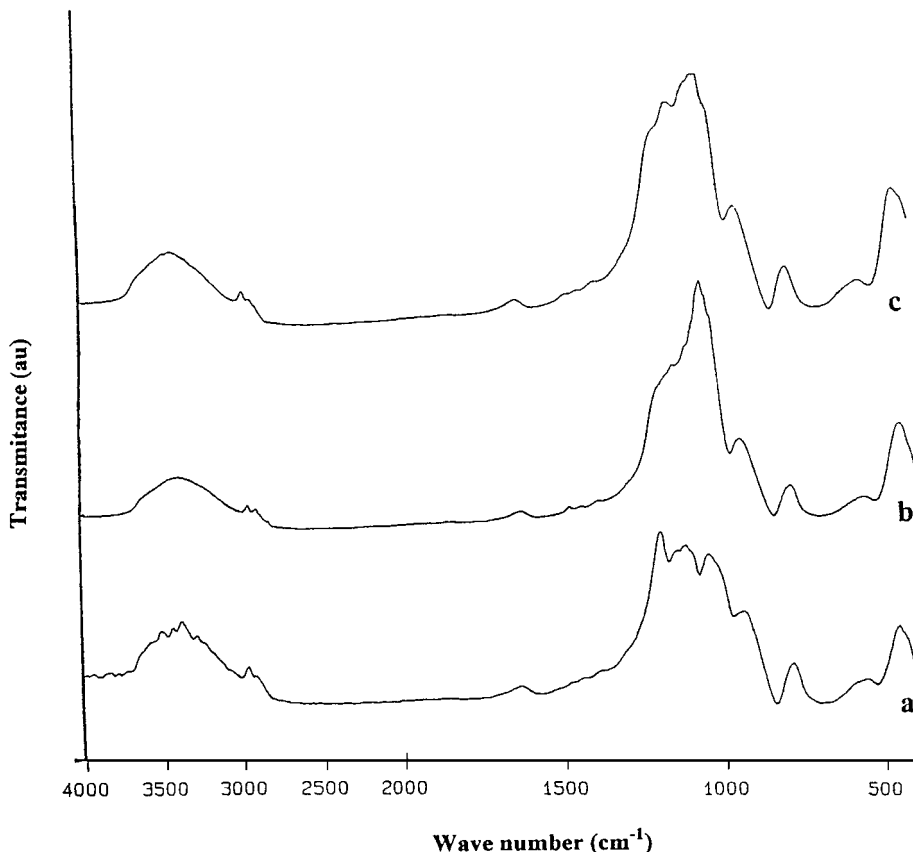


FIG. 4. FT-IR spectra at RT for samples 14 (a), 4 (b), and 8 (c).

whose concentration increases drastically by shifting the oxidant from dilute  $\text{H}_2\text{O}_2$  to TBHP (Table 4, entries 1 and 2). Intermediate epoxide (**2**) and 3-hydroxytetrahydropyran (**4**, endo product) are the other products of this reaction. Oxidation of the alcohol functionality to the corresponding aldehyde occurs to a large extent using dilute  $\text{H}_2\text{O}_2$  as oxidant.

Whereas the five-membered oxacycle (**7**), the product of oxidative cyclization, forms exclusively from *cis*-4-hexene-1-ol (**5**) over Cl-propyl-Ti-MCM-41 (sample 4, Table 4, entry 3) and TS-1 (entry 4, control experiment), organic rich Cl-propyl-Ti-MCM-41 (sample 8, entry 5) yields a very high concentration of intermediate epoxide 4,5-epoxyhexanol (**6**) even after longer reaction time along with tetrahydrofuran derivative (**7**). Ti-MCM-41 without any organic modification (sample 12, purely inorganic) shows poor activity under identical reaction conditions (Table 4, entry 6). It is pertinent to mention that although Me-Ti-MCM-41 (sample 16) is less ordered than Cl-propyl-Ti-MCM-41 (sample 4) the catalytic activity in cyclization of *cis*-4-hexene-1-ol is almost identical (Table 4, entries 7 and 8) under triphase conditions (15). In spite of the low ordering and moderately good UV-vis spectra, the high surface area and hydrophobicity (Table 2) may be responsible for the high catalytic activity of sample 16.

When sample 8 (Table 1) with high organic content (TEOS/CIPTES = 3, hydrophobic) and highest Ti containing Ti-MCM-41 was used as catalyst in the oxidation of *cis*-4-hexene-1-ol, the reaction rate increases and 78.2% conversion of the unsaturated alcohol was obtained in a relatively short reaction time. However, interestingly the concentration of the unconverted intermediate epoxide was quite high (Table 4). Initially a very high concentration (85% selectivity after 1 h reaction time at 70.0% conversion level) of 4,5-epoxy-hexanol **6** was observed which gradually converted to **7** (Fig. 5) as the reaction continued for longer time. In contrast, for other catalysts used in the present study (including TS-1 for comparison, Table 4) cyclized products are observed even at the initial stages of the reaction (13). A polar acidic surface usually facilitates the oxirane ring opening by intramolecular attack of the -OH functionality. This indicates that the highly hydrophobic nature of the catalyst protects the intermediate epoxide toward cyclization to the corresponding tetrahydrofuran derivative. The presence of these bulky chloropropyl groups in large numbers in the close vicinity of the active Ti sites may hinder the formation of the aquated titanium hydroperoxo species (14), which is believed to be the origin of acidity in titanium silicates in the presence of water and thus acid promoted cyclization is restricted to a large extent. Very recently it

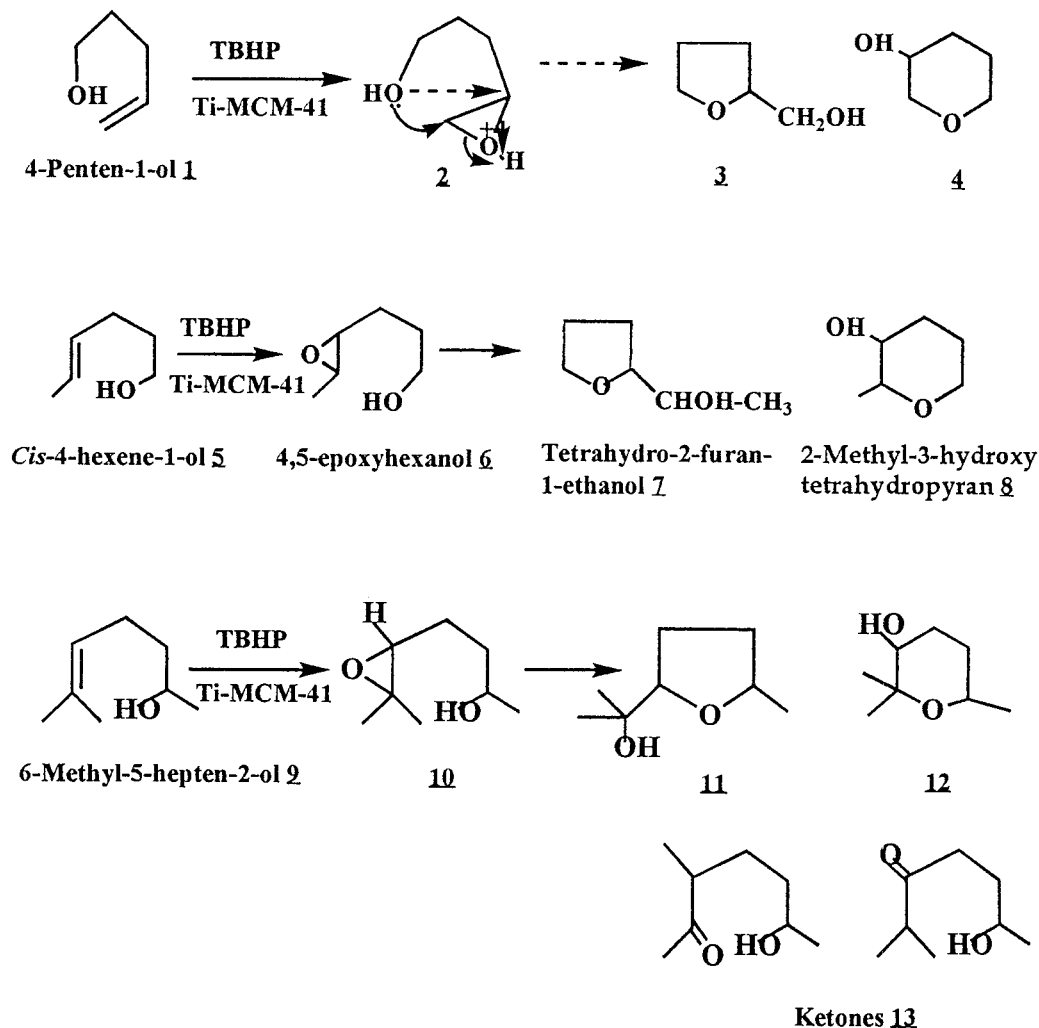


FIG. 5. Reaction pathways for the oxidative cyclization of 4-penten-1-ol, *cis*-4-hexene-1-ol, and 6-methyl-5-hepten-2-ol over a Ti-MCM-41/TBHP system.

has been reported that dry TBHP is a better oxidant than commercial TBHP (which contains 30% water as diluent) for the epoxidation of cyclohexene over Ti-MCM-41 (17). Experiments are under way to improve the selectivity of epoxides using such conditions.

In order to check the catalytic efficiency for repeated cycles and the possibility of leaching of Ti from these organo-Ti-MCM-41 one controlled experiment using sample 8 (taken as representative, Cl-propyl-Ti-MCM-41 with Si/Ti = 33.6) was carried out. After the experiment of entry 7, the catalyst was washed thoroughly with acetone and then treated with 0.1 M HCl solution in EtOH for 8 h at 353 K and finally dried at 373 K for 2 h and then used as catalyst for this experiment. Results are given in Table 4 (entry 9). In the second cycle using the catalyst and after HCl/EtOH treatment, the catalytic activity remained practically the same with very little enhancement in the selectivity for epoxide. Thus, it can be concluded that al-

most no Ti leached out during the liquid phase reaction from these organo-Ti-MCM-41 materials. A catalytic run for phenyl-Ti-MCM-41 (sample 20) was carried out in the oxidative cyclization of *cis*-4-hexene-1-ol using TBHP (entry 10, Table 4). The activity was not high compared to the Cl-propyl-Ti-MCM-41 samples; probably this low activity is due to the low hydrophobicity and low surface area of sample 20. Oxidative cyclization product **7** was the major product along with a considerable amount of the oxidation of alcohol functionality.

In the oxidation of 6-methyl-5-hepten-2-ol (**9**), the intermediate epoxide (**10**) has the possibility of either rearrangement or cyclization either via exo or endo attack (to lead to five- and six-membered oxacycles) over TS-1 and Ti-beta (18). However, in the present case over TBHP/Cl-propyl-Ti-MCM-41 the ratio of tetrahydropyran (**12**) to tetrahydrofuran (**11**) increases drastically although the concentration of rearranged ketones (**13**) remains almost the same.



This may be due to wider pore in this mesoporous Ti-MCM-41 that can accommodate the larger oxacycles (18). In our earlier work using water as dispersion medium (triphasic conditions) we had shown that the TS-1/H<sub>2</sub>O<sub>2</sub> system favors selective dihydroxylation (19). However, in the present case over organo-Ti-MCM-41/TBHP using water as dispersion medium dihydroxylation products are negligible (Table 4, entry 11).

### Mechanistic Aspects

The role of the organic modifier in the synthesis gel during the formation of the mesophase is to orient the organic head group of the surfactant micelles closer to the organic functionality of the organosilane and thus help to bring more order. However, the nature of the organic moiety influences the orientation of the surfactant micelles to a different extent. From methyl to vinyl, allyl, and chloropropyl, increasing the chain length progressively yields wider pore materials, probably due to the long range repulsion between the organic moieties. In the case of Cl-propyl-Ti-MCM-41, due to the halogen present in the organic group, organo-inorganic surfactant micelles could fit more suitably in the corresponding mesoporous structure. More homogeneity in the reaction medium (i.e., the ratio of Si/Ti in the gel and that incorporated in the mesoporous solid comes closer) and this slightly polar organic environment may facilitate the condensation between Ti and Q<sub>3</sub>/Q<sub>4</sub> silicate species. This may cause more Ti incorporation in the chloropropyl modified Ti-MCM-41 samples.

From Table 4 it is clear that there is not much difference in the catalytic activities of 3-chloropropyl and methyl modified Ti-MCM-41 (entries 7 and 8) in the oxidative cyclization of *cis*-4-hexene-1-ol (**5**). Thus, although the nature of the alkyl group influences the synthesis and the texture (size of the pore opening, surface area, Ti-incorporation) of the mesoporous organo-Ti-MCM-41 materials to various extent, from a catalytic point of view not much difference in the activity was observed due to the introduction of different alkyl groups used in the present study. The change in the selectivity, mainly the enhanced selectivity for the epoxide, can be attributed to the hydrophobicity of the corresponding organo-Ti-MCM-41 samples.

### CONCLUSIONS

Methyl-, vinyl-, allyl-, chloropropyl-, pentyl-, and phenyl-modified Ti-MCM-41 can be synthesized with a relatively high titanium-containing mother gel at 413 K in 1–2 days. The efficiency of the incorporation of Ti is higher when organosilane is used as a Si source along with TEOS than when TEOS was used alone. Among the organic modifications used in the present study, the 3-chloropropyl group shows the highest Ti incorporation in the resultant solid with wider pores, high surface area, and large pore vol-

ume. With the increase in Ti loading and increase in chain length of the alkyl group (from C<sub>1</sub>–C<sub>3</sub>), the *d* spacing increases. However, for longer chain organosilane and for an organosilane containing an aromatic group, the reverse trend was observed. Chemical analyses revealed that high Ti loading in this organically modified Ti-MCM-41 was observed when the TEOS to 3-chloropropyltriethoxysilane molar ratio progressively decreased from 8 to 3. There is an optimum ratio for TEOS to organotriethoxysilane where wider pore Ti-rich Ti-MCM-41 with considerable high surface area and hydrophobicity could be obtained. Moreover, Ti-MCM-41 cannot be obtained with a Si/Ti mole ratio below 60 in the synthesis gel in the absence of organotriethoxysilane. These organically modified Ti-MCM-41 samples are more hydrophobic than those synthesized in the absence of organic modifier, being efficient catalysts in the epoxidation and oxidative cyclization using TBHP as oxidant under mild liquid phase reaction conditions. The oxidation activity increases four- to fivefold by using TBHP as oxidant over that seen when using aqueous H<sub>2</sub>O<sub>2</sub>.

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