

# Physiochemical properties of transition metal-grafted MCM-48 prepared using metallocene precursors

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## Abstract

A series of redox mesopore molecular sieves Ti-, V-, Zr- and Mo-MCM-48 were prepared by grafting the respective metallocene onto the MCM-48 host. XRD, TEM, and BET analysis of the transition metal substituted MCM-48 indicated that high crystallinity and pore structure were maintained after grafting. Grafting of the transition metal species to MCM-48 structure was confirmed by IR and UV–vis spectroscopy. The metallocene grafted MCM-48 samples were active for liquid phase oxidation of the bulky 2,6-di-tert-butyl phenol (2,6-DTBP) with aqueous H<sub>2</sub>O<sub>2</sub>. For a given metallocene concentration in grafting solutions, Mo was the least grafted element to MCM-48 surface, but its catalytic activity was superior either to Ti- or Zr-grafted MCM-48. V-MCM-48 showed the highest catalytic activity. Chemical analysis of the mother liquor after reaction, however, showed substantial leaching for Mo and V. Ti and Zr also suffered mild leaching. Further silylation treatment to Ti- and V-MCM-48 could not prevent leaching. Activity for 2,6 DTBP oxidation deteriorated significantly upon silylation for Ti-MCM-48. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* MCM-48; Grafting; Metallocene; 2,6-di-tert-butyl phenol

## 1. Introduction

The mesoporous M41S type materials discovered by Mobil researchers in early 1990s [1] can be made to function as redox catalysts by introducing suitable transition metals to the framework [2,3]. From the structural point of view, MCM-48, due to the two independent three-dimensional channel systems, is expected

to be a better host for liquid phase reactions. Here, we had extended the grafting technique of Maschmeyer et al. [4] to such elements as Ti, V, Zr and Mo in MCM-48. These metal-grafted MCM-48s were characterized and a comparison was made as a catalyst for oxidation of bulky 2,6-di-tert-butyl phenol (2,6-DTBP) using hydrogen peroxide. A particular attention was paid to the integrity of the metallic species grafted to MCM-48 under the liquid phase reaction conditions. The effect of silylation to the metal-grafted samples on catalytic activity and stability was also examined.

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## 2. Experimental

### 2.1. Synthesis of pure silica MCM-48

Pure silica MCM-48 (Si-MCM-48) was prepared using the method of Kim et al [5]. Sodium hydroxide was added to Ludox HS-40 (40 wt.% colloidal silica in water, Dupont) and stirred until clear. It was added to a surfactant solution prepared by dissolving cetyltrimethylammonium bromide (CTMABr) in distilled water and ethanol as co-solvent at 333 K under vigorous stirring. The composition of the resultant gel was 1 SiO<sub>2</sub>:0.7 CTMABr:0.25 Na<sub>2</sub>O:3.5 ethanol:100 H<sub>2</sub>O. After hydrothermal synthesis at 373 K in a teflon-lined autoclave for 4 days, the solid product obtained was filtered and surfactant was extracted from MCM-48 in ethanol–HCl solution at room temperature (1 g solid/ethanol 20 ml + HCl 2 ml). After drying, it was calcined in a muffle furnace at 823 K for 5 h.

### 2.2. Metallocene grafting

Each metallocene (Bis (cyclopentadienyl) titanium dichloride, Bis (cyclopentadienyl) vanadium dichloride, Bis (cyclopentadienyl) zirconium dichloride and Bis (cyclopentadienyl) molybdenum dichloride) was dissolved in chloroform (10 wt.% solution) and allowed to diffuse into MCM-48 for 2 h, and subsequently exposed in situ to triethylamine to activate the silanols of the MCM-48. The grafting reaction was conducted for 3 h under stirring. Metal grafted MCM-48 samples (Ti(G)-MCM-48, V(G)-MCM-48, Zr(G)-MCM-48 and Mo(G)-MCM-48) were obtained by filtration and drying at 353 K. All samples were calcined at 823 K for 5 h.

### 2.3. Silylation treatment

Trimethylsilylation to the metal-grafted samples was conducted according to the procedure by Chen et al. [6]. The transition metal-grafted MCM-48 samples were heated at 573 K to

remove adsorbed water, and then put into a solution of chlorotrimethylsilane in anhydrous *n*-hexane under magnetic stirring at room temperature for 72 h. The solid products obtained after filtration were washed extensively with *n*-hexane and acetone. Silylated samples (Si-MCM-48(S), Ti(G)-MCM-48(S) and V(G)-MCM-48(S)) were dried at 333 K for 24 h and calcined at 823 K for 5 h.

### 2.4. Characterization

The crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered CuK<sub>α</sub> radiation (Philips, PW-1700), and the morphology of the samples were examined by SEM (Hitachi, X-650) and TEM (Philips, CM200). FT-IR spectra were recorded in air at room temperature on a Bomem MB 104 spectrometer using a diffuse reflectance cell. The specific surface areas and average pore diameters were determined by nitrogen physisorption with the BET method at liquid nitrogen temperature using a Micromeritics ASAP 2000. UV–vis diffuse reflectance spectroscopy was performed using dehydrated MgO as a reference in the range of 190–800 nm on a Varian CARY 3E double beam spectrometer. The catalytic activities of all samples were tested for the liquid phase oxidation of 2,6-DTBP to quinone using H<sub>2</sub>O<sub>2</sub> as an oxidant. Reactions were carried out under vigorous stirring in a two-neck glass flask equipped with a condenser and a thermometer using 10 mmol of substrate, 100 mg of catalyst, 10 g acetone as a solvent, and 30 mmol of 35 wt.% H<sub>2</sub>O<sub>2</sub>. The reaction was performed at 333 K for 2 h and the products were analyzed using a GC equipped with a HP-5 capillary column and a FID. After reaction, the mother liquor was examined for dissolved metallic species by ICP (Jobin Yuon, JY-38 VHR).

## 3. Results and discussion

XRD patterns of metallocene grafted MCM-48 s are shown in Fig. 1. The patterns for all

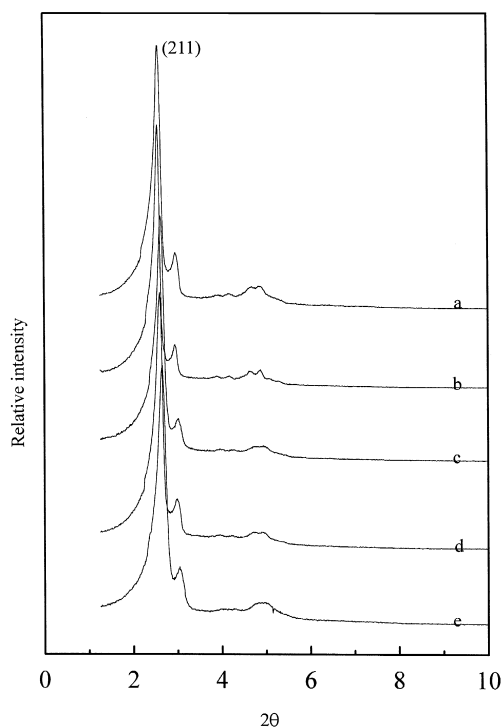


Fig. 1. XRD patterns of transition metal grafted MCM-48 (calcined). (a) Si-MCM-48, (b) Ti(G)-MCM-48, (c) V(G)-MCM-48, (d) Zr(G)-MCM-48, (e) Mo(G)-MCM-48.

MCM-48 samples consist of six to eight distinguishable peaks, which can be indexed to different (*hkl*) reflections of cubic structure [1]. Metallocene grafting did not affect the MCM-48 structural order, whilst transition metal introduced via hydrothermal synthesis routes usually results in a partial loss in long range order of the materials [2]. The *d* values for (211) crystal plane and the unit cell parameters for the samples are summarized in Table 1. The unit cell parameters remained almost constant or de-

creased somewhat for transition metal-grafted MCM-48 samples. Metallic precursors after reaction with surface silanols are expected to remain attached to the surface of MCM-48, and can lead to contraction of cell parameters if the interaction with the silica wall is significant [7]. This feature is in contrast to the hetero-atom inserted to the silica framework by hydrothermal synthesis route [3] in which a transition metal buried inside pore walls can cause the unit cell expansion.

Fig. 2 shows the N<sub>2</sub> adsorption/desorption isotherm and the pore size distribution for the metallocene grafted MCM-48 samples. Metallocene grafting in Si-MCM-48 resulted in total pore volume decrease, and mean pore diameter decreased slightly as was the case for aluminum grafting [8]. Type IV isotherm, typical of mesoporous materials, is maintained and as the relative pressure increases ( $P/P_0 > 0.2$ ), the isotherms exhibit a sharp inflection characteristic of capillary condensation within the mesopores. The sharpness of the steep rise is diminished as a result of transition metal grafting. Fig. 3 are the TEM images of Si-MCM-48 and Ti(G)-MCM-48 samples, which show that uniform mesopore structure of MCM-48 is maintained after metallocene grafting with no detectable metal clusters formed.

Fig. 4 shows the FT-IR spectra of Si-MCM-48, Ti(G)-MCM-48, and V(G)-MCM-48. Spectra after silylation treatment are also shown. The spectrum of pure silica MCM-48 before grafting shows two peaks near 3740 and 3500 cm<sup>-1</sup>. The former is usually assigned to isolated terminal silanols which are more resistant to heat or

Table 1  
Physical properties of transition metal-grafted MCM-48

Catalyst	BET surface area (g/m <sup>2</sup> )	BJH desorption pore size (Å)	BJH cumulative desorption pore volume (cm <sup>3</sup> /g)	Unit cell parameter (Å)
Si-MCM-48	1384	27.4	1.40	83.3
Ti(G)-MCM-48	1376	27.0	1.35	83.8
V(G)-MCM-48	1291	27.0	1.25	82.4
Zr(G)-MCM-48	1369	26.6	1.30	82.4
Mo(G)-MCM-48	1369	26.7	1.30	81.4

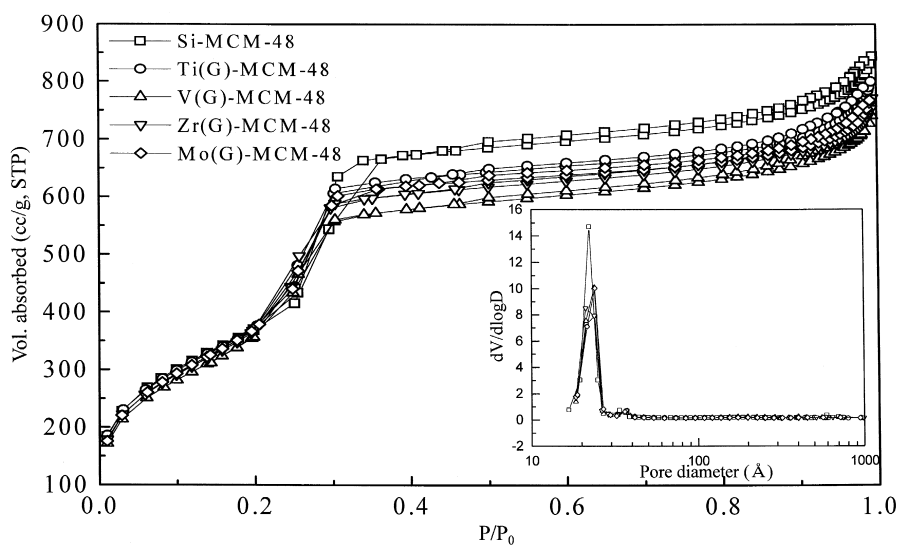


Fig. 2.  $N_2$  adsorption and desorption isotherms and pore size distributions of transition metal grafted MCM-48.

vacuum treatment, while the latter broad peak to hydrogen bonded silanol groups [6,9]. After grafting, significant reduction of  $3740\text{ cm}^{-1}$  peak was observed, which indicates that the metallocene grafting reaction occurred with terminal isolated silanols of Si-MCM-48 [4,8]. Each metallocene can react with three isolated silanols [4], and a fraction of isolated silanol groups remained after grafting resulted in the diminished  $3740\text{ cm}^{-1}$  peak.

Silylation is reported to make the surface hydrophobic and to improve the hydrothermal and mechanical stability of the M41S type materials [10]. Krijnen et al. [11] also reported that silylation could prevent metal leaching from Ti(IV) silsesquioxane immobilized MCM-41. In a spectrum after silylation and drying only (Fig. 4 II), two peaks, one broad near  $3500$  and the other sharp at  $2900\text{--}3000\text{ cm}^{-1}$  were observed. The lower frequency peak corresponds to organic C–H (trimethylsilyl) group of the silylating agent [6] and disappears after calcination.  $3470\text{ cm}^{-1}$  terminal Si–OH peak of metallocene grafted samples disappeared completely after silylation, but a narrow peak at the same position reappeared after calcination.

UV–vis DRS spectra of metallocene grafted MCM-48 samples are shown in Fig. 5. A band

centered at ca. 210 nm is observed in Fig. 5A, and this band is usually assigned to a low-energy charge-transfer transition between tetrahedral oxygen ligands and central  $Ti^{4+}$  ions, indicating framework incorporation of Ti in Si-MCM-48 [12,13]. An anatase-like  $TiO_2$  phase at 330 nm was absent but some polymeric Ti species was suspected to coexist at 240–270 nm. V(G)-MCM-48 sample in Fig. 5B shows three broad absorption bands at ca. 240, 330, and 440 nm; 240 nm peak corresponds to the low-energy charge-transfer bands which can be assigned to O–V electron transfer ( $\pi$ ) $t_2 \rightarrow (d)e$  tetrahedrally coordinated  $V^{5+}$ , 330 nm peak to pseudotetrahedral, and 440 nm peak to octahedral  $V^{5+}$  ions [14,15]. V(G)-MCM-48 sample after calcination was white initially, but upon prolonged exposure to air, its color turns to yellow and subsequently to orange due to water molecules coordinating with vanadium metal centers [8]. Correspondingly, its UV–vis spectrum degenerated to a single broad peak at 440 nm. The spectrum Fig. 5C shows the presence of a characteristic absorption at ca. 210 nm attributable to charge transfer transitions involving the Zr(IV)(tetrahedral configuration) sites [16]. Zr(G)-MCM-48 also shows an absorption at ca. 250 nm, which is observed in  $ZrO_2$  [17].

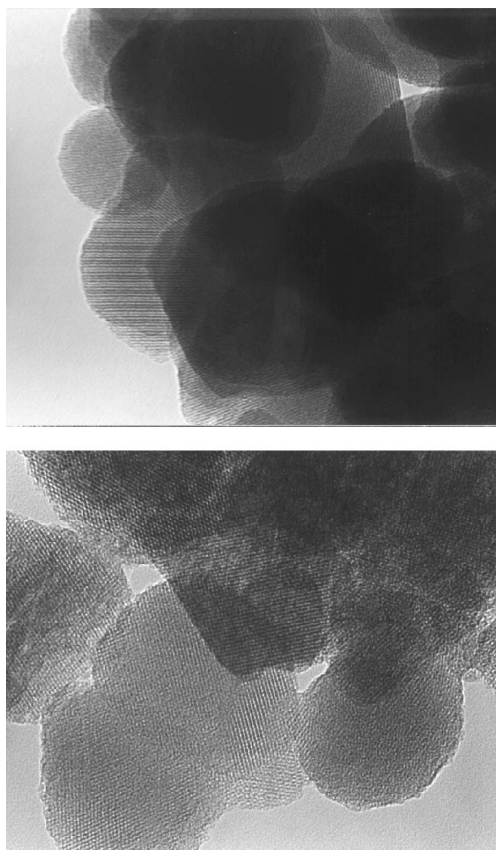


Fig. 3. TEM images (I) Si-MCM-48 and (II) Ti(G)-MCM-48.

Fig. 5D shows UV–vis spectrum of Mo(G)-MCM-48. The absorption bands in 200–280 nm have been assigned to tetrahedral coordination of Mo, and bands in 200–330 nm are usually assigned to octahedral coordination of Mo [18]. Most of Mo is believed to be in tetrahedral coordination.

As shown in Table 2, all of the metallocene grafted MCM-48 samples were active for liquid phase oxidation of 2,6-DTBP with aqueous  $H_2O_2$ . The 2,6-DTBP conversion and hydrogen peroxide selectivity to quinone decreased in the order V(G)-MCM-48 > Ti(G)-MCM-48 > Mo(G)-MCM-48 > Zr(G)-MCM-48. According to EDX analysis, Mo was the least surface grafted element for a given metallocene concentration in a grafting solution, but its turnover frequency was higher than Ti. V(G)-MCM-48 showed the highest catalytic activity with conversion approaching 90%. XRD patterns of the metallocene grafted MCM-48 samples after 2,6-DTBP reaction remained virtually identical to the fresh catalysts, but ICP analysis of mother liquor after reaction indicated substantial leaching for Mo and V. V-HMS was also reported for serious vanadium leaching [19]. Ti and Zr

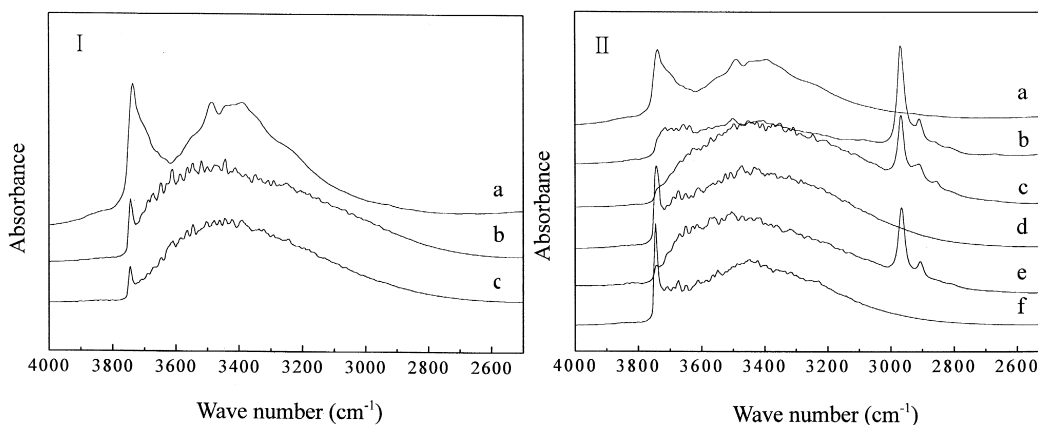


Fig. 4. FT-IR spectra of transition metal grafted MCM-48 samples at room temperature. I: (a) Si-MCM-48<sup>1</sup>, (b) Ti(G)-MCM-48<sup>1</sup>, (c) V(G)-MCM-48<sup>1</sup>. II: (a) Si-MCM-48<sup>1</sup>, (b) Si-MCM-48(S)<sup>2</sup>, (c) Ti(G)-MCM-48(S)<sup>2</sup>, (d) Ti(G)-MCM-48(S)<sup>1</sup>, (e) V(G)-MCM-48(S)<sup>2</sup>, (f) V(G)-MCM-48(S)<sup>1</sup>.

<sup>1</sup> Calcined sample.

<sup>2</sup> After drying only.

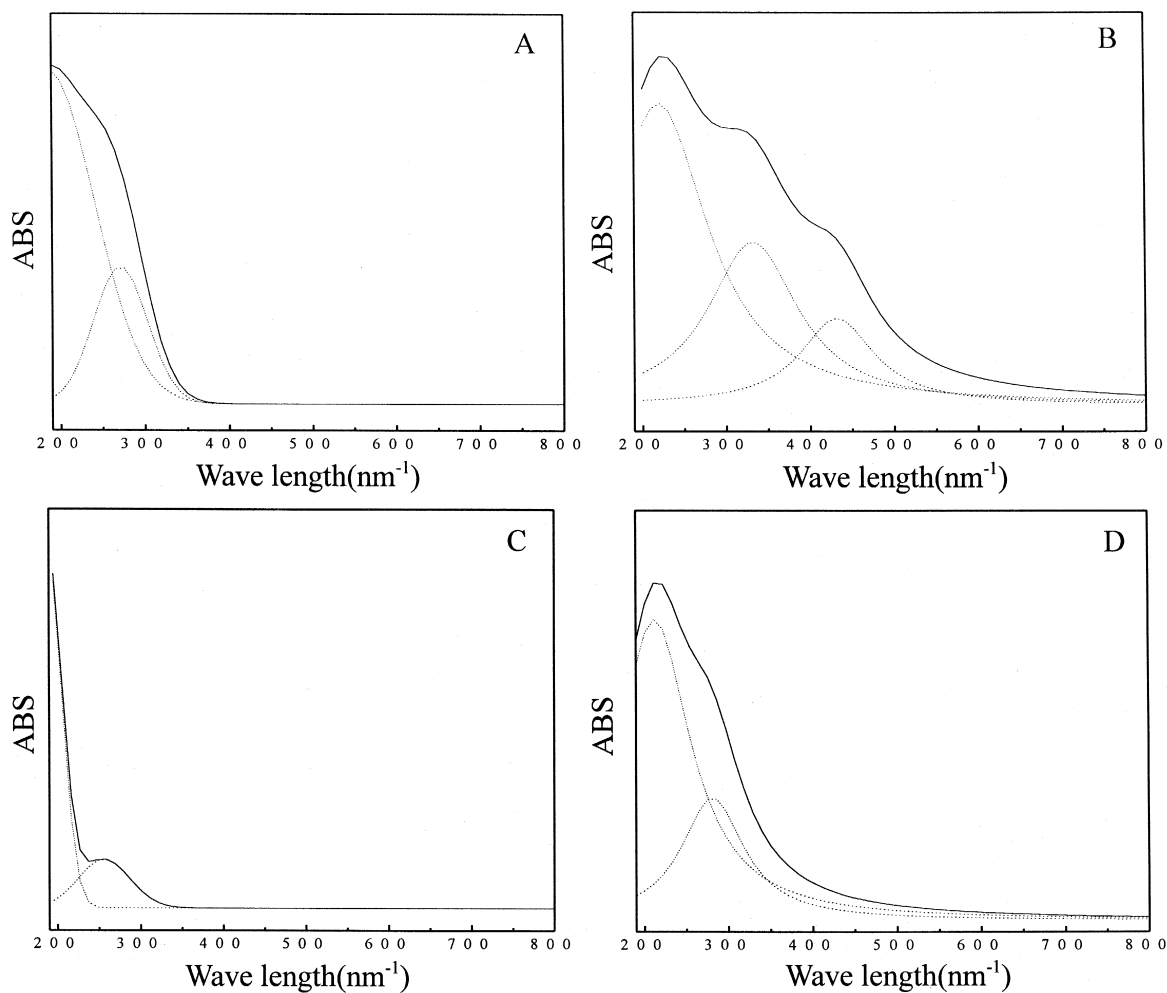


Fig. 5. UV-vis spectra of transition metal grafted MCM-48 samples. (A) Ti(G)-MCM-48, (B) V(G)-MCM-48, (C) Zr(G)-MCM-48, (D) Mo(G)-MCM-48.

Table 2

Catalytic activities of various transition metal grafted MCM-48 for 2,6-DTBP oxidation

Reaction conditions: 10 ml 2,6-DTBP, 30 ml H<sub>2</sub>O<sub>2</sub> (35 wt.% in aqueous solution), 100 mg catalyst, 10 g acetone, 337 K, 2 h.

	EDX (mol%)	Leaching (% of amount of leaching)	2,6-DTBP conversion (%)	Quinone selectivity (%)	H <sub>2</sub> O <sub>2</sub> conversion (%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)
Ti(G)-MCM-48	2.2	1.6	29.4	> 99	66.7	25.2
V(G)-MCM-48	2.8	20.6	89.2	> 99	94.1	63.2
Zr(G)-MCM-48	1.2	1.6	7.4	> 99	67.6	7.3
Mo(G)-MCM-48	0.4	24.0	18.7	> 99	69.3	18.0
Ti(G)-MCM-48(S) <sup>a</sup>	–	0.8	10.6	> 99	–	–
Ti(G)-MCM-48(S) <sup>b</sup>	–	–	10.2	> 99	–	–
V(G)-MCM-48(S) <sup>a</sup>	–	21	92.0	> 99	–	–
V(G)-MCM-48(S) <sup>b</sup>	–	–	87.3	> 99	–	–

<sup>a</sup> Calcined sample.

<sup>b</sup> After drying only.

also suffered mild leaching. Additional, 2 h reaction of the liquid phase after catalyst filtration with addition of extra 30 mmol  $H_2O_2$  resulted in 2,6-DTBP conversions to 28.2%, 99.4%, and 9.3% for Ti, V, and Zr-grafted samples, respectively. Thus, contributions towards reaction by dissolved metallic species for V(G)-, and Zr(G)-MCM-48 are strongly indicated. For Ti(G)-MCM-48, on the other hand, dissolved species do not seem to affect the reaction, since conversion did not increase further in the filtrate. Homogeneous reaction by the dissolved Mo species is also indirectly implicated for Mo(G)-MCM-48, judging by the color change of the catalyst filtered solution from pale to dark brown standing in time. Silylation did not prevent leaching of the metal species from these catalysts. 2,6-DTBP oxidation with  $H_2O_2$  was also tested with the silylated, Ti(G)-MCM-48(S) and V(G)-MCM-48(S). The catalytic activity of V(G)-MCM-48(S) remained almost the same as the unsilylated catalyst, but 2,6-DTBP conversion decreased drastically for Ti(G)-MCM-48(S). Similar decrease in reactivity of silylated Ti-MCM-48 for an OH-containing substrate was also reported by Tatsumi et al. [20], and they explained it as a consequence of reduction in adsorption sites for polar substrate molecule due to reduction in silanol group after silylation. For V(G)-MCM-48, it can be conjectured that most of the reaction is taking place in liquid phase by the V species leached, and in such a case silylation to the solid phase would not have an effect on the mostly homogeneous catalytic activity.

#### 4. Conclusion

Transition metal substituted MCM-48s with redox property were prepared post-synthetically by grafting metallocene precursors to MCM-48. XRD and TEM analysis indicated high structural order of the cubic structure was maintained, and cell parameters changed little after grafting. Pore volume and diameter decreased

somewhat, but Type VI adsorption isotherm exhibiting a characteristic capillary condensation within the mesopores were maintained. FT-IR spectra showed that the metallocene grafting reaction occurred on terminal isolated silanols, and UV-vis spectroscopy exhibited characteristic absorption bands for Ti, V, Zr, and Mo species with various coordination. The transition metal-grafted MCM-48 samples were active for liquid phase oxidation of 2,6-DTBP with vanadium and molybdenum showing high turnover numbers. ICP analysis of mother liquor after reaction, however, revealed substantial leaching for Mo and V. Ti and Zr also suffered mild leaching. Silylation treatment of the metal-grafted samples had no effect on leaching. The catalytic activity of silylated Ti-MCM-48 was adversely affected by silylation.

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