

# Remarkable activity enhancement by trimethylsilylation in oxidation of alkenes and alkanes with H<sub>2</sub>O<sub>2</sub> catalyzed by titanium-containing mesoporous molecular sieves

Takashi Tatsumi,\* Keiko A. Koyano and Naoko Igarashi

Engineering Research Institute, School of Engineering, The University of Tokyo, Yayoi, Tokyo 113, Japan

**Titanium-containing mesoporous materials, Ti-MCM-41 and Ti-MCM-48, have been successfully modified by trimethylsilylation to exhibit enhanced catalytic activity in the oxidation of alkenes and alkanes with H<sub>2</sub>O<sub>2</sub>.**

The recent discovery of a new family of mesoporous molecular sieves has received much attention.<sup>1,2</sup> Ti-substituted MCM-41<sup>3</sup> and MCM-48<sup>4</sup> and Ti-substituted hexagonal mesoporous silica (Ti-HMS<sup>5</sup>) have been synthesized, and pioneered the potential to oxidize bulky molecules which cannot enter into the micropores of zeolites such as TS-1, TS-2 and Ti-β. However, it has been reported that Ti-MCM-41 samples show a lower intrinsic activity and lower selectivity toward the use of H<sub>2</sub>O<sub>2</sub> for alkene oxidation than either TS-1 or Ti-β owing to their high hydrophilicity.<sup>6</sup> It has been recently proposed that the hydrophilic/hydrophobic property of Ti zeolites plays an important role in their activity for liquid phase oxidations.<sup>7</sup> We have conducted trimethylsilylation of Ti-MCM-41 and Ti-MCM-48 in order to enhance activity in oxidation with dilute H<sub>2</sub>O<sub>2</sub> through increasing their hydrophobicity. Here, we report that trimethylsilylation of Ti-containing mesoporous molecular sieves, Ti-MCM-41 and Ti-MCM-48, resulted in a remarkable enhancement of catalytic activity in oxidation of alkenes and alkanes with H<sub>2</sub>O<sub>2</sub>.

Ti-MCM-41 was synthesized as previously described.<sup>8</sup> Tetraethylorthosilicate, tetrabutylorthotitanate and cetyltrimethylammonium chloride (CTMACl) were used, and the molar composition of the gels subjected to hydrothermal synthesis was SiO<sub>2</sub>:0.01 TiO<sub>2</sub>:0.6 CTMA:0.3 NMe<sub>4</sub>OH:60 H<sub>2</sub>O. Ti-MCM-48 was similarly synthesized by using CTMACl/OH (Cl/OH = 70/30) as a template.<sup>9</sup> The molar composition of the gels was: SiO<sub>2</sub>:0.02 TiO<sub>2</sub>:CTMA:46.5 H<sub>2</sub>O. Trimethylsilylation was conducted according to literature;<sup>2</sup> 0.5 g Ti-MCM-41 or -48, 10 g Me<sub>3</sub>SiCl and 15 g (Me<sub>3</sub>Si)<sub>2</sub>O were refluxed for 16 h under N<sub>2</sub>. The HCl produced was stripped off and the dry powder obtained was thoroughly washed with dry acetone with centrifuging, and dried at 393 K for 3 h. The samples before and after trimethylsilylation are denoted Ti-MCM-41 or -48 (non-sil) and Ti-MCM-41 or -48 (sil), respectively. A typical oxidation run used 50 mg of a catalyst in 25 mmol of substrate in a round-bottom flask, to which was added 5 mmol of H<sub>2</sub>O<sub>2</sub> (30% aqueous solution). The resulting mixture was stirred at various temperatures.

The X-ray diffraction patterns of Ti-MCM-41 and Ti-MCM-48 materials closely matched those of the pure silica isomorph.<sup>1,2</sup> Although the X-ray diffraction patterns and the *d* spacings were virtually unchanged after trimethylsilylation, the pore diameter determined by the Dolimore-Heal method, the BET surface area, and the pore volume decreased upon trimethylsilylation (Table 1). These observations could be accounted for by assuming that the silanol groups inside the pore were trimethylsilylated.

In the IR spectra of Ti-MCM-41 samples the band at 960 cm<sup>-1</sup>, which is used as evidence for Ti incorporation into the framework in Ti-containing microporous molecular sieves such

as TS-1 and Ti-β,<sup>10,11</sup> has significantly decreased upon trimethylsilylation. Similar phenomena were also observed with Ti-MCM-48. The band was also detected in the spectra of pure silica MCM-41 or -48 (non-sil) and completely disappeared upon trimethylsilylation. Moreover, the intensity of a broad peak in the range 3700–3500 cm<sup>-1</sup> corresponding to silanol groups and adsorbed water in the spectra of both Ti-MCM-41 and Ti-MCM-48 decreased significantly upon trimethylsilylation. To determine the concentration of surface trimethylsilyl groups <sup>29</sup>Si MAS NMR measurements were carried out. Before trimethylsilylation, the <sup>29</sup>Si MAS NMR spectrum of Ti-MCM-41 (non-sil) exhibited two broad resonances, at δ -108.7 (73.7%) for the Q<sup>4</sup> silicate unit and at δ -100.5 (26.3%) for the Q<sup>3</sup> environment. After trimethylsilylation, a new peak ascribed to the silicon atoms of TMS appeared at δ 14.3 and the ratio of Q<sup>3</sup> silicate was significantly decreased. Deconvolution of the spectrum into three peaks (TMS, Q<sup>3</sup>, Q<sup>4</sup>) was made; the molar ratio of TMS:Q<sup>3</sup>:Q<sup>4</sup> was 17.2:11.7:71.1, indicating that the content of silanol groups after trimethylsilylation was 0.208 mol (mol Si)<sup>-1</sup> [mol Si for Ti-MCM-41 (non-sil)], while that of silanol groups before trimethylsilylation was 0.263 mol (mol Si)<sup>-1</sup>. Thus a part of original silanol groups could not be trimethylsilylated and furthermore, the increase in Q<sup>4</sup> species was moderate compared to the expected increase resulting from the substitution of trimethylsilyl groups for silanol H atoms, suggesting that some silanol groups were newly formed during the trimethylsilylation. The incomplete trimethylsilylation is considered to be due to the bulkiness of the trimethylsilyl group (*ca.* 0.6 nm). Despite the incomplete modification of silanol groups, Ti-MCM-41 (sil) was highly hydrophobic; the amount of adsorbed water was measured by TG after exposure to moisture over saturated aqueous solution of NH<sub>4</sub>Cl at room temperature for 24 h; Ti-MCM-41 (sil) adsorbed only 0.29 mass% H<sub>2</sub>O, whereas Ti-MCM-41 (non-sil) adsorbed 55 mass% H<sub>2</sub>O.

We performed oxidation of cyclohexene, hexane and pent-2-en-1-ol with H<sub>2</sub>O<sub>2</sub> on Ti-MCM-41 and Ti-MCM-48 samples. The results are summarized in Table 2. Neither Ti-MCM-41 (non-sil) nor Ti-MCM-48 (non-sil) exhibited significant activity in the oxidation of cyclohexene. However, trimethylsilylation of these Ti-containing mesoporous solids resulted in a *ca.* 20-fold increase in the activity in the oxidation of cyclohexene. Furthermore, non-productive decomposition of H<sub>2</sub>O<sub>2</sub> was inhibited by the trimethylsilylation. The turnover number

**Table 1** Properties of Ti-containing mesoporous molecular sieves before and after trimethylsilylation

Catalyst	Si/Ti	BET surface area/m <sup>2</sup> g <sup>-1</sup>	Pore diameter/nm	Pore volume/ml g <sup>-1</sup>
Ti-MCM-41 (non-sil)	123	1015	2.32	0.88
Ti-MCM-48 (non-sil)	47	1048	2.32	0.91
Ti-MCM-41 (sil)	139	879	1.90	0.82
Ti-MCM-48 (sil)	51	839	1.90	0.71

**Table 2** Effect of trimethylsilylation on catalytic activity of Ti-containing mesoporous molecular sieves

Catalyst	Conversion (mol% of max.)	TON/ mol (mol Ti) <sup>-1</sup>	Selectivity (%)				H <sub>2</sub> O <sub>2</sub> decomposition (%)
			Alcohol	Ketone	Epoxide	Diol	
Cyclohexene oxidation							
Ti-MCM-41 (non-sil) <sup>a</sup>	0.72	5.4	30.0	15.2	0	54.7	57.6
Ti-MCM-48 (non-sil) <sup>b</sup>	2.1	6.1	26.7	32.8	4.7	35.7	61.9
Ti-MCM-41 (sil) <sup>a</sup>	13.3	112.1	14.4	21.0	13.9	50.7	0
Ti-MCM-48 (sil) <sup>a</sup>	38.5	120.9	21.3	17.0	2.2	59.4	0
Hexane oxidation			2-ol	3-ol	2-one	3-one	
Ti-MCM-41 (non-sil) <sup>b</sup>	0	0	—	—	—	—	74.7
Ti-MCM-41 (sil) <sup>b</sup>	0.06	0.50	40.5	59.5	0.0	0.0	0.0
Ti-MCM-41 (sil) <sup>c</sup>	0.20	6.8	22.0	22.9	31.0	24.1	97.3
Ti-MCM-48 (non-sil) <sup>b</sup>	0	0	—	—	—	—	75.0
Ti-MCM-48 (sil) <sup>b</sup>	0.17	0.52	45.4	54.6	0.0	0.0	20.2
Pent-2-en-1-ol oxidation			Pent-2-enal		Epoxide		
Ti-MCM-41 (non-sil) <sup>b</sup>	32.4	242	81.0		19.0		0
Ti-MCM-48 (non-sil) <sup>b</sup>	32.0	92.9	78.9		21.1		3.0
Ti-MCM-41 (sil) <sup>b</sup>	14.7	124	81.6		18.4		0
Ti-MCM-48 (sil) <sup>b</sup>	20.7	59.3	73.4		26.5		0

<sup>a</sup> Catalyst 50 mg, substrate 25 mmol, H<sub>2</sub>O<sub>2</sub> 5 mmol, 323 K, 3 h. <sup>b</sup> Catalyst 50 mg, substrate 25 mmol, H<sub>2</sub>O<sub>2</sub> 5 mmol, 323 K, 2 h. <sup>c</sup> Catalyst 50 mg, substrate 100 mmol, H<sub>2</sub>O<sub>2</sub> 20 mmol, 353 K, 16 h.

(TON) per hour was even higher than that observed with Ti-β at 333 K.<sup>12</sup> The selectivity for epoxide/diol was increased at the expense of allylic oxidation. In the oxidation of hexane, no products were obtained with the non-trimethylsilylated samples, where H<sub>2</sub>O<sub>2</sub> was mostly decomposed. On the other hand, hexane was oxidized on the trimethylsilylated samples with retarded decomposition of H<sub>2</sub>O<sub>2</sub>. The turnover number increased to 6.8 mol (mol Ti)<sup>-1</sup> with increasing reaction temperature, while the rate of H<sub>2</sub>O<sub>2</sub> decomposition increased. The difference in the activity for cyclohexene and hexane oxidation between non-trimethylsilylated and trimethylsilylated samples may be explained in terms of hydrophobicity/hydrophilicity; excess water should prevent non-polar cyclohexene or hexane from adsorbing into the pores of the non-trimethylsilylated catalysts and/or approaching active sites inside the pores. It has been observed that trimethylsilylated catalysts exist in the organic phase because of their hydrophobicity, resulting in mitigation of the inhibition of oxidation caused by water. No leaching of Ti was observed during the oxidation.

As shown in Table 2, pent-2-en-1-ol was oxidized with H<sub>2</sub>O<sub>2</sub> on both Ti-MCM-41 and -48 (non-sil) at a much higher rate than cyclohexene. The enhanced reactivity of this OH-containing alkenes may be due to the possible formation of a ring structure where alcoholic OH is bound to Ti as previously proposed.<sup>13,14</sup> It should be noted that the difference in the reactivity between alkenes and allylic alcohols on TS-1 was not so marked compared to this case.<sup>15</sup> Thus it is conceivable that, because of the presence of a considerable amount of silanol groups, pent-2-en-1-ol containing a polar hydroxyl group more easily migrates into the pores of non-trimethylsilylated catalysts than simple alkenes in competition with water, showing a much higher reactivity than cyclohexene. Trimethylsilylated samples Ti-MCM-41 (sil) and Ti-MCM-48 (sil) exhibited lower activity in the oxidation of pent-2-en-1-ol than the corresponding non-trimethylsilylated samples. Partial removal of silanol groups would reduce the capability to absorb the allylic alcohols through hydrogen bonding. The decreased activity might be also due to the difficulty in access to the active site caused by the introduction of rather bulky trimethylsilyl groups. Studies on the steric environment of the Ti site are in progress using a variety of reactants as probe molecules.

Trimethylsilylation leads to a further advantage: the mesoporous structure of Ti-containing samples is much less resistant

to moisture than that of pure silica samples.<sup>8</sup> For example, the *d*<sub>100</sub> peak height of Ti-MCM-41 (non-sil) decreased by 80% upon exposure to moisture over saturated aqueous solution of NH<sub>4</sub>Cl for 3 days. In contrast the ordered structure of both Ti-MCM-41 (sil) and Ti-MCM-48 (sil) was found to be intact upon exposure to moisture for 30 days.

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## Notes and References

\* E-mail: tatsumi@catal.t.u-tokyo.ac.jp

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