

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231235584>

# Ti–MCM–41 Synthesized from Colloidal Silica and Titanium Trichloride: Synthesis, Characterization, and Catalysis

ARTICLE *in* CHEMISTRY OF MATERIALS · FEBRUARY 2001

Impact Factor: 8.35 · DOI: 10.1021/cm000758h

CITATIONS

61

READS

36

7 AUTHORS, INCLUDING:



Jianqiang Yu

Chinese Academy of Sciences

33 PUBLICATIONS 1,750 CITATIONS

SEE PROFILE



Zhaochi Feng

Chinese Academy of Sciences

151 PUBLICATIONS 4,816 CITATIONS

SEE PROFILE



Zhongmin Liu

Dalian Institute of Chemical Physics

252 PUBLICATIONS 3,358 CITATIONS

SEE PROFILE



Can Li

Guiyang university

503 PUBLICATIONS 15,426 CITATIONS

SEE PROFILE

# Ti–MCM-41 Synthesized from Colloidal Silica and Titanium Trichloride: Synthesis, Characterization, and Catalysis

Jianqiang Yu, Zhaochi Feng, Lei Xu, Meijun Li, Qin Xin, Zhongmin Liu, and Can Li\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,  
Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China

Received September 22, 2000. Revised Manuscript Received January 9, 2001

Titanium-containing mesoporous molecular sieve Ti–MCM-41 has been synthesized using colloidal silica as the silicon source and  $\text{TiCl}_3$  solution as the titanium source and was characterized by X-ray diffraction,  $\text{N}_2$  adsorption, UV–vis, and UV–Raman spectroscopies. The formation of anatase  $\text{TiO}_2$  can be avoided during the synthesis and the crystallization of the molecular sieve because of the relatively low hydrolysis rate of an inorganic  $\text{TiCl}_3$  solution. The characterization results confirm that most  $\text{Ti}^{4+}$  ions are isolated and tetrahedrally coordinated in the framework of MCM-41. Different auxiliary templates, tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), tetrabutylammonium hydroxide, and  $\text{NH}_3\cdot\text{H}_2\text{O}$  were used to synthesize the Ti–MCM-41 molecular sieve. Among them, TMAOH and TEAOH were found to be the most effective auxiliary templates to improve the long-ranged order of the molecular sieves.

## 1. Introduction

Selective oxidation of organic compounds over titanium-substituted zeolites (e.g., TS-1) has received much attention.<sup>1–5</sup> This is mainly because titanium-substituted zeolites show remarkable selective oxidation properties and can be used in environmentally friendly oxidation using  $\text{H}_2\text{O}_2$  as the oxidant. However, because of the small pore size of TS-1 and other microporous zeolites, large organic molecules cannot access the active sites which are located inside the cavities and the channels of the zeolites. This limits the utilization of microporous titanium-containing zeolites to the selective oxidation of bulk organic compounds.

Using a titanium-containing mesoporous molecular sieve can enlarge the opportunity for the selective oxidation of bulk organic compounds.<sup>6</sup> Since the first synthesis of Ti–MCM-41 in 1993,<sup>7</sup> several kinds of titanium-containing mesoporous molecular sieves, such as Ti–HMS,<sup>8–10</sup> Ti–MCM-48,<sup>11–13</sup> and Ti–MSU-1,<sup>14</sup>

have been synthesized and characterized. However, in all instances the syntheses were accomplished using organic precursors, namely, tetraethyl orthosilicate (TEOS) and titanium tetraethoxide (TEOT) or titanium tetrabutoxide (TBOT) as the silicon and titanium sources, respectively. Though it is easy to form a homogeneous gel using organic precursors, one major disadvantage of this method is that the extraframework  $\text{TiO}_2$  is unavoidably formed if the titanium source is not carefully hydrolyzed. In the synthesis of TS-1, for example, it has to be stirred vigorously, cooling the TEOS/TEOT mixture to  $\sim 10^\circ\text{C}$  while adding the TPAOH solution.<sup>15</sup> Another method used to reduce the formation of  $\text{TiO}_2$  deposition is first to dissolve the alkanolates in alcohol, e.g., 2-propanol, and then this solution is consequently added to the synthesis gel. Both methods are complicated and cannot completely avoid the formation of extraframework  $\text{TiO}_2$ .

In this work, we report a novel method to synthesize Ti–MCM-41 using colloidal silica as the silicon source and a  $\text{TiCl}_3$  aqueous solution as the titanium source. Both colloidal silica and a  $\text{TiCl}_3$  solution can dissolve into water, and a homogeneous and stable gel can be easily formed. The inorganic  $\text{TiCl}_3$  solution has a

\* Corresponding author. Tel: 0086-411-4671991 ext. 728. Fax: 0086-411-4694447 or 4685510. E-mail: canli@ms.dicp.ac.cn.

(1) Corma, A.; Navarro, M. T.; Peroz-pariente, J. *J. Chem. Soc., Chem. Commun.* **1994**, 147.

(2) Millini, R.; Perego, G.; Berti, D.; Parker, W. O., Jr.; Carati, A.; Bellussi, G. *Microporous Mesoporous Mater.* **2000**, *387*, 35–36.

(3) Clerici, M. G. *Appl. Catal.* **1991**, *68*, 249.

(4) Ramaswamy, A. V.; Sivasanker, S. *Catal. Lett.* **1993**, *22*, 239.

(5) Arends, I. W. C. E.; Sheldon, R. A.; Wallan, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144.

(6) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(7) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C. U.S. Patent 5,250,282, 1993.

(8) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *368*, 317.

(9) Pinnavaia, T. J.; Tanev, P. T.; Wang, W.; Zhang, W. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 53.

(10) Corma, A.; Cambor, M. A.; Esteve, P.; Martinez, A.; Perez-Pariente, J. *J. Catal.* **1994**, *145*, 151.

(11) Morey, M.; Tuel, A. *Zeolites* **1995**, *15*, 601.

(12) Koyano, K. A.; Tatsumi, T. *J. Chem. Soc., Chem. Commun.* **1996**, 145.

(13) Zhang, W.; Pinnavaia, T. J. *Catal. Lett.* **1996**, *38*, 261.

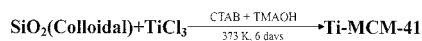
(14) Bagshaw, S. A.; Pouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

(15) Taramasso, M.; Perego, G.; Notari, B. U.S. Patent 4,410,501, 1983.

relatively low hydrolysis rate; thus, the formation of  $\text{TiO}_2$  can be avoided during the preparation of the synthesis gel.

## 2. Experimental Section

The synthesis procedure for Ti-MCM-41 was as follows: the required amount of a  $\text{TiCl}_3$  solution was mixed with 36.3 g of colloidal silica and was stirred for 2 h until a homogeneous gel is formed. Then 20.4 g of a  $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$  (20 wt %) solution with 24 g of 10 wt % tetramethylammonium hydroxide (TMAOH) was added dropwise under vigorous stirring. The pH value of the solution was adjusted to  $\sim 11$  with dilute sulfuric acid. After another 2 h of stirring, the resultant gel was transferred into a Teflon-lined autoclave and heated at 373 K for 6 days. The compositions of the resultant mixture were as follows: 1:x:0.24:y:28  $\text{SiO}_2/\text{TiCl}_3/\text{CTABr}/\text{TRAOH}/\text{H}_2\text{O}$  ( $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9$ , etc.;  $x = 0-40$ ,  $y = 0.18-0.30$ ).



After the crystallization, the solid products were filtered, washed with deionized water, and dried in air at 333 K; finally the as-synthesized Ti-MCM-41 was calcined in  $\text{N}_2$  at 823 K for 24 h and then in air for another 5 h to remove the organic template. A sample of siliceous MCM-41 was also synthesized following the same procedure as described above except for without adding the  $\text{TiCl}_3$  solution.

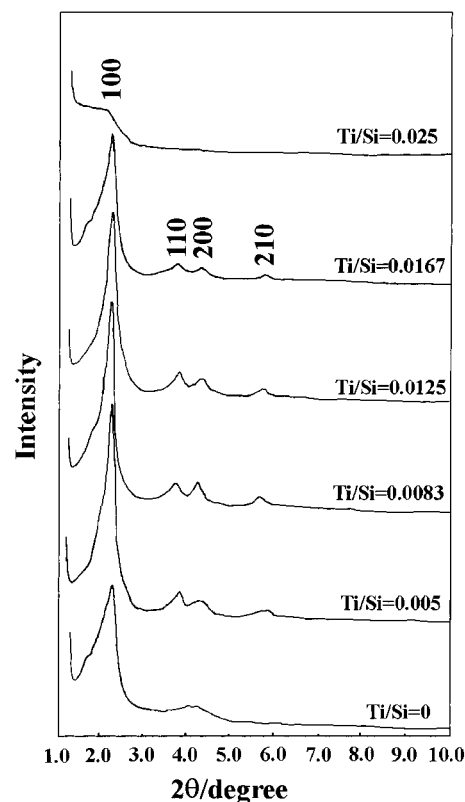
X-ray diffraction (XRD) was recorded on a Rigaku D/MAX-rb diffractometer using  $\text{Cu K}\alpha$  radiation (40 kV and 40 mA).  $\text{N}_2$  adsorption and desorption isotherms were obtained at 77 K on a Coulter Omnisorp 360 CX sorptometer using a continuous adsorption procedure. Diffuse reflectant spectra were recorded in the UV-visible region (UV-240 spectrometer, Shimadzu) using  $\text{MgO}$  as the reference sample. UV-Raman results were recorded on a homemade UV-Raman spectrometer. A 244 nm line from an Innova 300 FRED laser was used as the excitation source.

The epoxidation of cyclohexene was used as the test reaction. Typically, in a glass flask, 0.10 g of catalyst, 5 mmol of reactant, 1 mmol of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and 10 mL of solvent (acetonitrile, 99%) were added and stirred at 343 K. The products were analyzed by gas chromatography-mass spectrometry (GC-MS). The  $\text{H}_2\text{O}_2$  efficiency was estimated by a standard iodometric titration.

## 3. Results and Discussion

**Synthesis.** The XRD patterns of the samples synthesized from colloidal silica and  $\text{TiCl}_3$  are shown in Figure 1. One major peak at about  $2^\circ$  together with three additional small peaks are observed, and the small peaks for the Ti-containing sample are more clearly resolved than those for the Ti-free one. These XRD patterns are the characteristics of MCM-41 and are in good agreement with those reported in the literature.<sup>1,7,16-19</sup> These results suggest that the as-synthesized samples are in the structure of MCM-41. The well-resolved peaks indicate that the samples possess long-range-ordered structures.

The Ti/Si molar ratios of the gel are estimated to be in the range of 0.005–0.025. The Ti-MCM-41 molecular sieve synthesized from a gel with a Ti/Si molar ratio of



**Figure 1.** XRD patterns of MCM-41 and Ti-MCM-41 with different Ti/Si ratios.

**Table 1.** Dependence of the Titanium Content in the Synthesized Ti-MCM-41 on That in the Synthesis Gel

sample <sup>a</sup>	Ti/Si(gel) <sup>b</sup>	Ti/Si(product) <sup>c</sup>	[Ti/Si(product)]/[Ti/Si(gel)]
Ti-MCM-41(200)	0.0050	0.0105	2.1
Ti-MCM-41(120)	0.0083	0.0162	1.95
Ti-MCM-41(80)	0.0125	0.0235	1.88
Ti-MCM-41(40)	0.0250	0.0373	1.49

<sup>a</sup> The number in the parentheses is the Si/Ti molar ratios in the synthesis gel. <sup>b</sup> The Ti/Si molar ratio in the synthesis gel. <sup>c</sup> The Ti/Si molar ratio in Ti-MCM-41 molecular sieves.

0.005 (denoted as Ti-MCM-41(200)) has an intense  $d_{100}$  peak, suggesting that this sample has high crystallinity. Ti-MCM-41(60) has a relative crystallinity of only  $\sim 60\%$  compared to Ti-MCM-41(200). A further increase in the titanium contents resulted in a further loss of the crystallinity; for example, it is only about 20% crystallinity for an as-synthesized Ti-MCM-41(40) with a Ti/Si ratio of 0.025. The content of titanium in the resultant Ti-MCM-41 is found to be dependent on the content of titanium in the synthesis gel (Table 1). The more titanium in the synthesis gel, the more titanium will be incorporated into the framework of the synthesized Ti-MCM-41 molecular sieve.

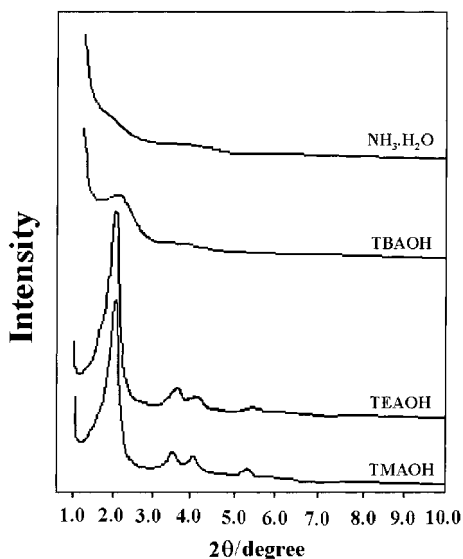
Figure 2 shows the XRD patterns of Ti-MCM-41 synthesized from gel using TMAOH, tetraethylammonium hydroxide (TEAOH), tetrabutylammonium hydroxide (TBAOH), and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  as auxiliary templates, respectively. The intensity of the  $d_{100}$  peak is very high for the two samples prepared with TMAOH and TBAOH as the templates. The intensity of the  $d_{100}$  peak is usually taken as a measure for the crystallinity of the synthesized Ti-MCM-41; thus, the intense  $d_{100}$  peak indicates that the Ti-MCM-41 molecular sieve with

(16) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, 359, 710.

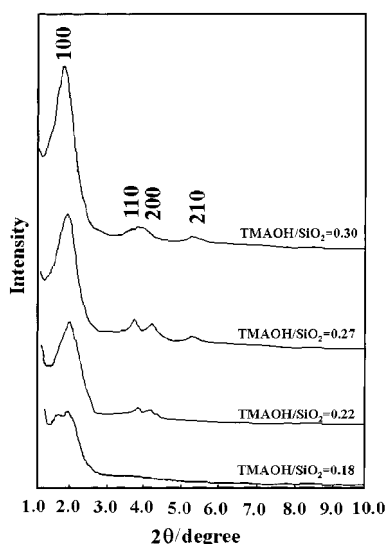
(17) Alba, M. D.; Luan, Z.; Klinowski, J. *J. Phys. Chem.* **1996**, 100, 2178.

(18) Reddy, K. M.; Moudrakovski, I. L.; Sayari, A. *Stud. Surf. Sci. Catal.* **1995**, 98, 18.

(19) Zhang, W.; Fröla, M.; Wang, J.; Tanev, P. T.; Wong, J.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1996**, 118, 9164.



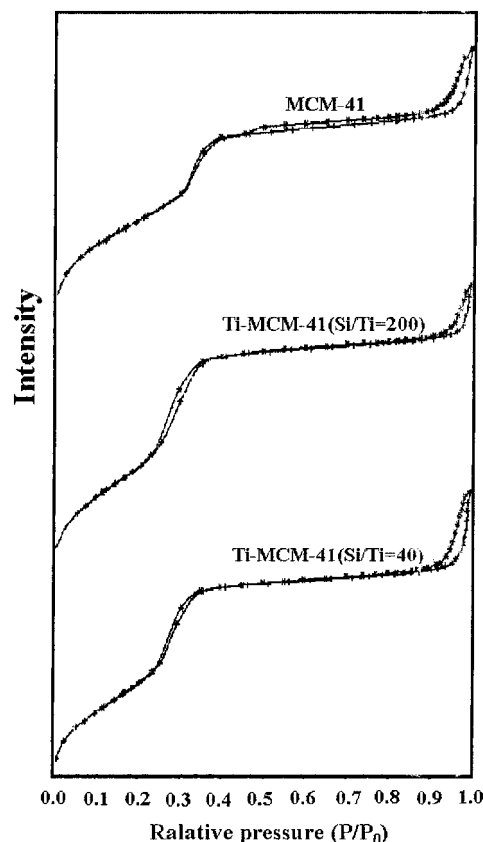
**Figure 2.** XRD patterns of Ti-MCM-41 synthesized with different auxiliary templates.



**Figure 3.** XRD patterns of Ti-MCM-41 synthesized with different TMAOH/SiO<sub>2</sub> ratios.

high crystallinity can be synthesized using TMAOH and TEAOH as auxiliary templates. The intensity of the  $d_{100}$  peak of the material prepared with TBAOH is relative low, suggesting that the crystallinity of the as-synthesized Ti-MCM-41 is not as good as those of the former two samples. Using  $\text{NH}_3 \cdot \text{H}_2\text{O}$  as an auxiliary template, the  $d_{100}$  peak is not observed, suggesting that mainly amorphous material is formed.

Figure 3 shows the effect of TMAOH/SiO<sub>2</sub> ratios on the crystalline and long-ranged order of Ti-MCM-41. The intensity of the  $d_{100}$  peak is enlarged with increasing TMAOH/SiO<sub>2</sub> ratio, suggesting that the crystallinity of Ti-MCM-41 is increased. The  $d_{110}$  and  $d_{200}$  peaks can reflect the long-ranged order of MCM-41-type molecular sieves, and the well-resolved  $d_{110}$  and  $d_{200}$  peaks imply that the hexagonal structure of Ti-MCM-41 is formed. The sample prepared with a TMAOH/SiO<sub>2</sub> ratio of 0.27 has the most well-resolved  $d_{100}$  and  $d_{200}$  peaks. The  $d_{100}$  and  $d_{200}$  peaks for the samples prepared with TMAOH/SiO<sub>2</sub> ratios higher and lower than 0.27 are relatively less resolved. This indicates that the TMAOH/SiO<sub>2</sub> ratio



**Figure 4.** N<sub>2</sub> isotherms of (a) MCM-41, (b) Ti-MCM-41(200), and (c) Ti-MCM-41(40).

has an optimal value; a too high or too low TMAOH/SiO<sub>2</sub> ratio is not of benefit to the formation of the long-range-ordered structure. Furthermore, the planar distance  $d_{100}$  is found to be dependent on the TMAOH/SiO<sub>2</sub> ratio; for example, the value of  $d_{100}$  decreases from 48.8 to 44.3, with the TMAOH/SiO<sub>2</sub> ratio increasing from 0.18 to 0.3.

**N<sub>2</sub> Sorption Isotherms.** Nitrogen adsorption was made to estimate the pore size distributions of Ti-MCM-41.<sup>20,21</sup> The N<sub>2</sub> sorption isotherms of Ti-MCM-41 at liquid nitrogen temperature are presented in Figure 4. N<sub>2</sub> sorption results give the typical type IV isotherms which are defined by Brunauer et al.<sup>22</sup> It indicates that the synthesized Ti-MCM-41 has a mesoporous structure. At a relative pressure  $p/p_0$  between 0.35 and 0.45, the isotherm exhibits a sharp inflection characteristic of capillary condensation within the mesopores. This prominent swing can be used to relate to the structure of the mesopores, and its position determines the characteristic pore size. The fact that the  $p/p_0$  value of Ti-MCM-41 shifts to a lower value compared to that of MCM-41 suggests that the pore size of Ti-MCM-41 decreases with the introduction of titanium species.

The parameters of MCM-41 corresponding to different Ti/Si ratios are compared in Table 2. Obviously, addition

(20) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.

(21) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, 57, 603.

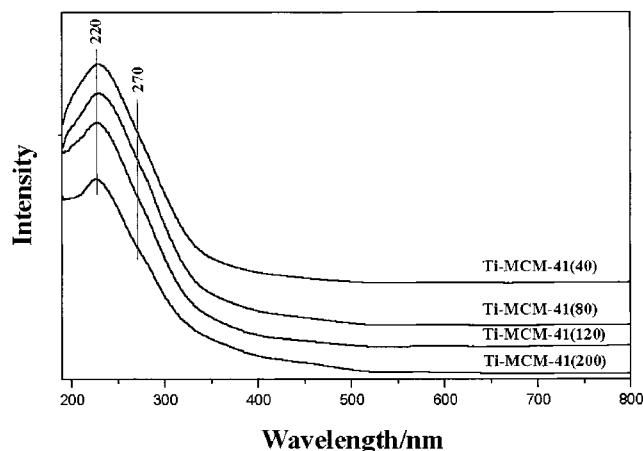
(22) Brunauer, S.; Deming, L. S.; Deming, E.; Teller, E. *J. Am. Chem. Soc.* **1940**, 62, 1723.



**Table 2. Parameters of Ti-MCM-41 Synthesized from Colloidal Silica and  $\text{TiCl}_3$  with Different Ti/Si Ratios**

Ti/Si(gel)	$d_{100}$ (nm)	$a_0^a$ (nm)	BET surface area ( $\text{m}^2/\text{g}$ )	pore vol <sup>b</sup> ( $\text{cm}^3/\text{g}$ )	pore size <sup>b</sup> (nm)	wall thickness (nm)
0	3.74	4.3	789	0.767	3.5	0.79
0.005	3.94	4.6	983	0.942	2.8	1.76
0.017	4.13	4.8	1075	1.177	3.1	1.63
0.025			1036	1.083	3.1	

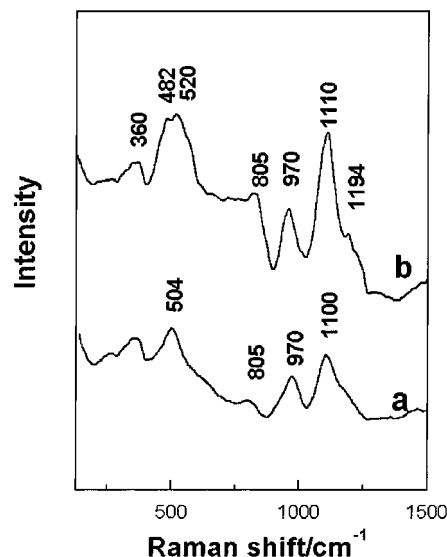
<sup>a</sup> Calculated from  $a_0 = 2d_{100}/\sqrt{3}$ . <sup>b</sup> Determined by using the BJH method from the desorption branch of the  $\text{N}_2$  isotherm.

**Figure 5.** UV-visible diffuse reflection spectra of Ti-MCM-41 with different Ti/Si ratios.

of titanium results in the enlargement of the unit cell size ( $a_0$ ) and the increase of the framework wall thickness, as evidence for the incorporation of titanium into the framework.<sup>19</sup> Furthermore, it is found that the BET surface area increases with the addition of titanium into Ti-MCM-41.

**Diffuse Reflection UV-Vis Spectra.** Diffuse reflection UV-vis spectra of Ti-MCM-41 with different titanium contents are shown in Figure 5. All of the spectra of Ti-MCM-41 show an absorption band centered at 220 nm together with a weak shoulder band at 270 nm, and these bands are different from those of TS-1. The spectrum of TS-1 generally gives a narrow absorption band at 210 nm, which is attributed to the charge-transfer transition associated with an isolated Ti(IV) framework site in tetrahedral coordination.<sup>23</sup> The red shift and the increase in the width of the band at 220 nm for Ti-MCM-41 may be an indication of the Ti in a distorted tetrahedral environment or of the presence of some Ti species in an octahedral coordination sphere.<sup>24,25</sup> However, because the shift of this band toward lower wavelengths is small upon thermal dehydration, most of the Ti sites in Ti-MCM-41 are in the distorted tetrahedral environment.

Because the possibility for some Ti-O-Ti clustering in the framework cannot be unequivocally ruled out for amorphous  $\text{TiO}_2/\text{SiO}_2$  gels, it would exhibit absorption bands in the range of 250–330 nm.<sup>26,27</sup> Partially po-

**Figure 6.** UV resonance Raman spectra of (a) MCM-41 and (b) Ti-MCM-41(200).

lymerized Ti species, which contain Ti-O-Ti bonds and exist in the silicon-rich amorphous phase, would give a broad band at  $\sim 270$  nm.<sup>23</sup> Thus, the weak absorption at 260–270 nm can be attributed to the presence of site-isolated Ti atoms in penta- or octahedral coordination. A similar UV-visible absorbance spectrum, indicative of a high fraction of higher coordinated Ti sites, has also been reported for hydrated TS-1.<sup>28</sup> The lack of the band at 330 nm for the mesoporous Ti-MCM-41 suggests that no bulk titania is formed in Ti-MCM-41 because bulk titania usually gives a broad absorption band at 330 nm. The above results suggest that most of the Ti atoms occupy a site-isolated position in the silica framework of Ti-MCM-41 synthesized from colloidal silica and  $\text{TiCl}_3$ .

**UV-Raman Spectra.** UV-Raman spectroscopy has been demonstrated to be a powerful technique for the identification of isolated titanium atoms in zeolite.<sup>29</sup> The increase in the intensity of the signal-to-noise ratio and the decrease in the fluorescence background greatly enhance the sensitivity of Raman spectra.<sup>29,30</sup> For titanium-containing zeolites, the resonance Raman effect, which comes from the charge-transfer transition from  $\text{O}^{2-}$  to  $\text{Ti}^{4+}$  in the framework, selectively enhances the intensity of the Raman signal by several orders of magnitude. Based on the UV-Raman resonance effect, the framework substitution of titanium atoms can be reliably identified.<sup>31</sup>

Figure 6 shows UV-Raman spectra of Ti-MCM-41 and purely siliceous MCM-41. In the spectrum of MCM-41, Raman bands at 360, 504, 805, 970, and  $1100\text{ cm}^{-1}$  are observed. The bands at 504 and  $1100\text{ cm}^{-1}$  can be assigned respectively to the symmetric and asymmetric

(23) Petrini, G.; Cesana, A.; De Alberti, G.; Genoni, F.; Leofanti, G.; Paclovan, M.; Paparatto, G.; Rofia, P. *Stud. Surf. Sci. Catal.* **1991**, *68*, 761.

(24) Blasco, T.; Corma, A.; Navarro, M. T.; Pariente, J. P. *J. Catal.* **1995**, *156*, 65.

(25) Reddy, J. S.; Dicko, A.; Sayari, A. Third International Symposium on Synthesis of Zeolites and Expanded Layered Compounds, Anaheim, CA, 1995.

(26) Notari, B. *Stud. Surf. Sci. Catal.* **1988**, *37*, 413.

(27) Anpo, M.; Nakaya, H.; Kodama, S.; Kubokawa, Y. *J. Phys. Chem.* **1986**, *90*, 1633.

(28) Geobaldo, C. F.; Bordiga, S.; Zecchina, A.; Giamello, E. *Catal. Lett.* **1992**, *16*, 109.

(29) Stair, P. C.; Li, C. *J. Vac. Sci. Technol., A* **1997**, *15*, 1679.

(30) Xiong, G.; Li, C.; Feng, Z.; Ying, P.; Xin, Q.; Liu, J. *J. Catal.* **1999**, *186*, 234.

(31) Li, C.; Xiong, G.; Xin, Q.; Liu, J.; Ying, P.; Feng, Z.; Li, J.; Yang, W.; Wang, Y.; Wang, G.; Liu, X.; Lin, M.; Wang, X.; Min, E. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2220.

stretching vibrations of the Si–O–Si fragment. The band at 805  $\text{cm}^{-1}$  is the symmetric stretching mode of the  $[\text{SiO}_4]$  tetrahedron,<sup>32–35</sup> which is the unit of the MCM-41 framework. Very interestingly, in the spectrum of Ti–MCM-41, three additional Raman bands at 482, 520, and 1110  $\text{cm}^{-1}$  are observed.

According to our previous study,<sup>31</sup> the Raman bands at 490, 520, and 1125  $\text{cm}^{-1}$  in the UV–Raman spectrum of TS-1 are assigned to the bending, symmetric stretching, and asymmetric stretching vibrations of Si–O–Ti, the framework titanium species. In the UV–Raman spectrum of Ti–MCM-41, the three bands are also significantly enhanced, while these bands are too weak to be detected in the visible Raman spectrum. This is strong evidence for some titanium atoms incorporated into the framework of Ti–MCM-41.

The fact that the frequency of the characteristic band at 1110  $\text{cm}^{-1}$  is lower than that of TS-1 (1125  $\text{cm}^{-1}$ ) possibly indicates that the coordination environment of titanium atoms in Ti–MCM-41 and TS-1 is slightly different. The titanium atoms in TS-1 are strictly fixed in the framework via the tetrahedral coordination; namely, the bond length and the bond angle are rigid. However, the titanium atoms in Ti–MCM-41 are relatively flexible. The highly dispersed Ti– $\text{SiO}_2$  prepared by chemical grafting also results in the shift of Raman bands from 1125 to 1100  $\text{cm}^{-1}$ .<sup>36</sup> It is likely that the coordination situation of titanium atoms in the framework of Ti–MCM-41 is between that for TS-1 and that for Ti– $\text{SiO}_2$ .<sup>37</sup>

**Catalytic Reactions.** The catalytic reactions can be used to investigate the properties of the synthesized Ti–MCM-41 molecular sieve. The epoxidation of cyclohexene using diluted hydrogen peroxide (30 wt %) as the oxidant was selected as an index reaction for Ti–MCM-41. The catalytic results are summarized in Table 3. It shows that four major products, namely, cyclohexene oxide, cyclohexen-1-ol, cyclohexen-1-one, and cyclohexanediol, are formed. This indicates that the reaction is

**Table 3. Selective Oxidation of Cyclohexene on Ti–MCM-41 with Different Contents of Titanium**

sample <sup>a</sup>	Ti/Si ratio	conv	selectivity (%) <sup>b</sup>					$\text{H}_2\text{O}_2$ efficiency
			A	B	C	D	E	
Ti–MCM-41(200)	0.0105	24.7	54.7	18.6	14.5	7.3	4.9	90.2
Ti–MCM-41(120)	0.0162	43.0	53.6	16.5	14.7	12.1	3.1	88.6
Ti–MCM-41(80)	0.0235	45.2	51.9	14.5	14.4	16.0	3.2	89.4
Ti–MCM-41(40)	0.0373	66.8	46.9	11.3	15.9	23.7	2.2	86.7

<sup>a</sup> The numbers in parentheses are the Si/Ti molar ratios in the synthesis gel. <sup>b</sup> A = epoxides; B = cyclohexen-1-ol; C = cyclohexen-1-one; D = cyclohexanediol; E = others.

very complex, but the epoxidation of the C=C double bond is the main reaction on Ti–MCM-41. The conversion of cyclohexene increases with an increase of the titanium content in the samples. This can be explained in terms of the increased active sites with the titanium content. However, the selectivity for epoxide and the efficiency of  $\text{H}_2\text{O}_2$  decreases with the titanium content. This indicates that the number of active sites for epoxidation, possibly the isolated titanium in tetrahedral coordination, is decreased with an increase in the titanium content in the synthesis gel. This is also in accordance with the decreased crystallinity, as shown in Figure 1.

#### 4. Conclusion

Titanium-containing mesoporous molecular sieve Ti–MCM-41 has been synthesized using colloidal silica as the silicon source and a  $\text{TiCl}_3$  solution as the titanium source. The synthesis procedure can be controlled because both colloidal silica and  $\text{TiCl}_3$  can dissolve in water. The relatively low hydrolysis rate of an inorganic  $\text{TiCl}_3$  solution and the slow transformation of  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$  during the course of crystallization avoid the formation of anatase  $\text{TiO}_2$ . Physicochemical characterizations show that the synthesized Ti–MCM-41 molecular sieve is free from extraframework anatase  $\text{TiO}_2$ . Most of the  $\text{Ti}^{4+}$  ions were isolated and tetrahedrally coordinated in the framework of Ti–MCM-41, as confirmed by UV–vis and UV–Raman spectroscopies. The synthesized Ti–MCM-41 are active in the epoxidation of cyclohexene using dilute  $\text{H}_2\text{O}_2$  as the oxidant.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of China for Distinguished Young Scholars (No. 29625305).

CM000758H

(32) Kornatowski, J.; Wichterlova, B.; Jitkovsky, J.; Löffler, E.; Pilz, W. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1067.

(33) Dutta, P. K.; Puri, M. *J. Phys. Chem.* **1987**, *91*, 4329.

(34) Dutta, P. K.; Rao, K. M.; Park, J. Y. *J. Phys. Chem.* **1991**, *95*, 6654.

(35) Kornatowski, J.; Sychev, M.; Kuzenkov, S.; Strnadova, K.; Pilz, W.; Kassner, D.; Preper, G.; Baur, W. H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2217.

(36) Yang, Q.; Wang, S.; Lu, J.; Xiong, G.; Feng, Z.; Xin, Q.; Li, C. *Appl. Catal. A* **2000**, *507*, 194–195.

(37) Tuel, A. *Microporous Mesoporous Mater.* **1999**, *27*, 151.