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Synthesis, characterization, and catalytic properties of Ti-containing mesoporous molecular sieves prepared using a fluorosilicon compound

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Abstract

Titanium substituted mesoporous molecular sieves were prepared using H_2SiF_6 as a silicon source with the mole ratio of SiO_2:TiO_2:HF:NH_4OH:CTMABr:H_2O = 1:0.011–0.043:5.40:6.48:0.49:246. Titanium substituted silica-based mesoporous molecular sieves (Ti-MMS) with good crystallinity and narrow pore size distribution could be prepared at atmospheric pressure in several hours. The material obtained was characterized by using XRD, N_2 physisorption, TEM, and UV–VIS spectroscopy. Its structural property is very much like MCM 41 with one-dimensional hexagonal lattice geometry. Titanium environment in Ti-MMS is believed to be very uniform relative to other types of titanium substituted M41S type materials, and titanium seems to exist mostly in isolated tetrahedral sites. Catalytic conversions for 2,6-DTBP (di-*tert*-butyl phenol) oxidation and cyclohexene epoxidation with H_2O_2 increased linearly with titanium contents in Ti-MMS within Si/Ti = 89–22 range. Ti-MMS showed catalytic activity close to that of Ti-MCM 41 of the same metal loading, but less active than Ti-HMS or Ti-MCM 48, because of the one-dimensional channel system of the Ti-MMS. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mesoporous materials; Titanium; UV–VIS spectroscopy; 2,6-di-*tert*-Butyl phenol; Cyclohexene epoxidation

1. Introduction

Redox molecular sieves effective in large organic molecule transformations in liquid phase reactions had emerged by incorporating various transition metal species such as Ti, V, Zr, Mn, or Sn into the mesoporous silica hosts of M41S type materials [1]. Bulk of such studies investigated titanium as a redox metal, and they were usually prepared by introducing a suitable titanium precursor during hydrothermal synthesis steps in which surfactant templating mechanism of $S^+I^-/S^+X^-I^+$, or S^0I^0 type operates in basic or neutral media [2]. Alternatively, post-synthetic incorporation of titanium using titanocene [3] or titanium alkoxide [4] grafting was also reported. Whilst the latter were claimed to be more catalytically active due to less likelihood of titanium being buried inside the wall, they are more prone to leaching in reaction media. These studies have established that improvements in hydrothermal stability and enhanced hydrophobicity are two desirable properties for titanium containing mesoporous materials for large organic molecule oxidation reactions using H_2O_2 as oxidant. In this work, we report an alternative synthesis method for titanium containing mesoporous molecular sieves (Ti-MMS) prepared in the presence of fluoride ion. Fluoride has been successfully used to extend the pH range over which anionic silica

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precursors can be utilized to create organized periodic structures [5,6]. Acid environment provided by HF can be useful for titanium incorporation into the silica mesopore structure by minimizing the chances for titanium species precipitated as hydroxide, and can also lead to enhanced hydrothermal stability [7]. Supporting characterization work and probe catalytic reaction of 2,6-DTBP (di-*tert*-butyl phenol) oxidation and cyclohexene epoxidation were carried out to investigate its physico-chemical properties as a redox molecular sieve.

2. Experimental

The substrate mixtures with the mole ratio of $SiO_2:TiO_2:HF:NH_4OH:CTMABr:H_2O = 1:0.011–0.043:5.40:6.48:0.49:246$ were used to prepare a series of Ti-MMS with different titanium contents. 20 g of H_2SiF_6 solution (10 wt.% SiO_2) was prepared by gradually dissolving 2 g of SiO_2 (grade 62, 60–200 mesh, Aldrich) to 18 g of 25% HF (48%, Merck). Various amounts of $Ti(OC_3H_7)_4$ (97%, Aldrich) were added to the H_2SiF_6 solution. Upon complete dissolution, pH of the solution becomes between 1.5 and 2.1. These solutions were added at once to 130 g of the ammonia-surfactant mixed solution which was prepared by adding 30 g of NH_4OH to 100 g of 4 wt.% CTMABr (cetyltrimethyl ammonium bromide; 99%, BDH) in distilled water. After stirring vigorously at 60°C for 5 min, pH of the solution becomes 7.3–8.0, depending on the amount of $Ti(OC_3H_7)_4$. A white gel was formed within 10 s, which was aged at 60°C for 5 h. The resulting solid product was recovered by filtration, washed five times with distilled water, and dried at 60°C. The dried sample was calcined at 600°C for 4 h to remove the surfactant. These samples are designated as Ti-MMS-*X*, where *X* is the Si/Ti ratio of the substrate mixture.

The crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered Cu Kα radiation (Philips, PW-1700), and the morphology of the samples was examined by TEM (Philips, CM 200). The specific surface area and average pore diameters were determined by N_2 physisorption with the BET method at liquid nitrogen temperature using a Micromeretics ASAP 2000 automatic analyzer. UV–VIS diffuse reflectance spectroscopy was performed on a Varian CARY3E double-beam spectrometer using MgO as a reference in the range of 190–750 nm in ambient conditions. Titanium content of the Ti-MMS was analyzed using XRF (Siemens SRS 303). The catalytic properties of the samples were tested for the liquid phase oxidation of 2,6-DTBP (di-*tert*-butyl phenol) to quinone and cyclohexene epoxidation using H_2O_2 as an oxidant. Reactions were carried out under vigorous stirring in a two-neck pyrex round bottom reactor equipped with a condenser and a thermometer. The oxidation of 2,6-DTBP was conducted at 337 K for 2 h using 10 mmol of substrate, 100 mg of catalyst, 10 g acetone as a solvent, and 30 mmol of 35 wt.% H_2O_2. Cyclohexene epoxidation reaction was carried out at 333 K for 3 h using 33 mmol substrate, 10 mmol H_2O_2, 20 ml methanol (solvent), and 200 mg catalyst. The products were analyzed by using a HP

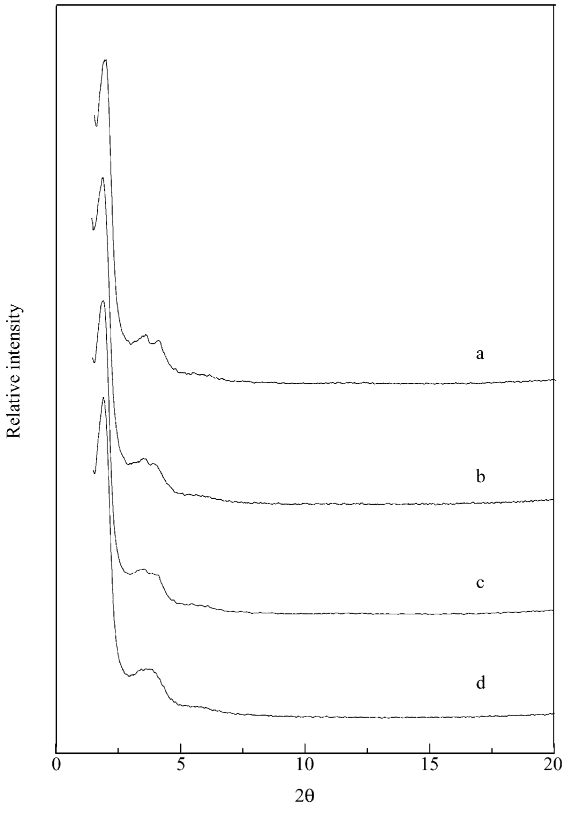

Fig. 1. XRD patterns: (a) Si-MMS, (b) Ti-MMS 93, (c) Ti-MMS 46, (d) Ti-MMS 23.

Table 1
Physical properties of Ti-MMS

Samples[a]	Si/Ti mole ratio by XRF	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	Basal spacing (Å)
Ti-MMS 93	89.3	888	1.10	31.4	41.2
Ti-MMS 46	44.6	911	0.98	31.0	41.5
Ti-MMS 23	22.4	882	1.13	31.3	42.2
Si-MMS	∞	1040	1.20	31.2	40.7

[a] Last digit denotes Si/Ti mole ratio in the substrate mixture.

5890 series II GC equipped with a HP-5 capillary (for 2,6-DTBP reaction) or Supelco Nukol^{TM} fused silica capillary column (for cyclohexene reaction) with a FID.

3. Results and discussion

Table 1 summarizes the structural properties of the Ti-substituted mesoporous molecular sieves prepared

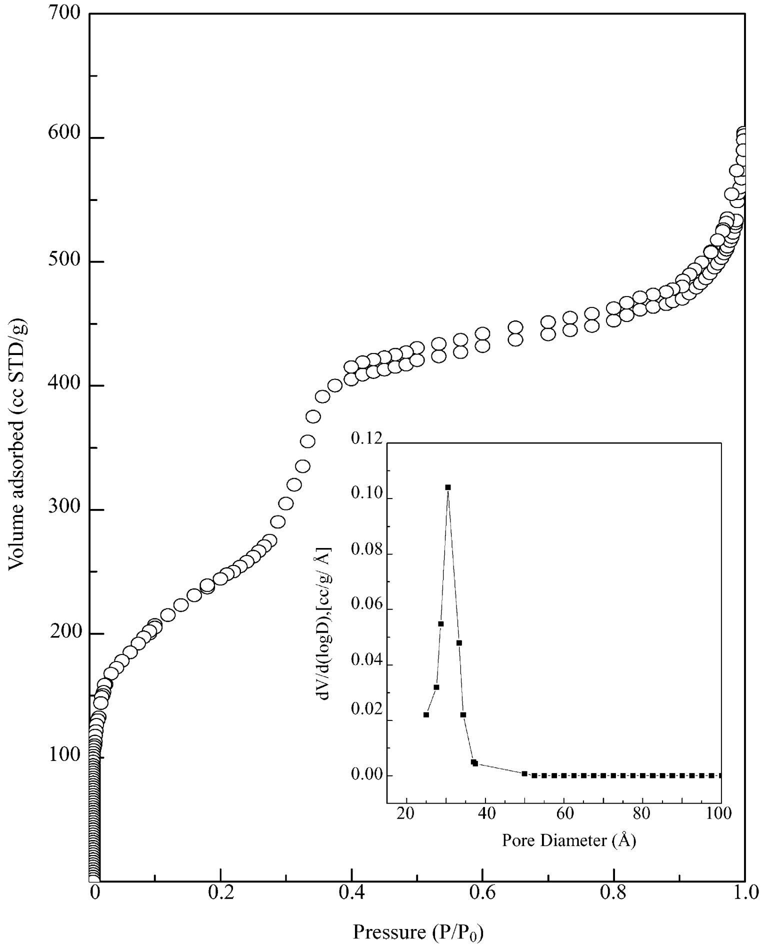

Fig. 2. N_2 adsorption and desorption isotherm and pore size distribution of Ti-MMS 93.

hydrothermally with fluoride ion. The surface area of Ti-MMS samples prepared varies from ca. 880 to 910 m^2/g, and the incorporation of titanium decreases the specific surface area and pore volume compared with a pure silica analog. The change in basal spacing as titanium increases suggests Ti incorporation in the walls of the mesoporous silicate framework. No clear influence of Ti content on the pore diameter was observed within the Ti range examined. The Si/Ti ratio of the calcined products and those of the initial gel mixtures were very close, indicating that virtually all the titanium in the initial gel mixture was incorporated to the final product. Fig. 1 shows the XRD patterns of calcined Ti-MMS together with pure silica analog. All the samples exhibit well-defined (1 0 0) reflections in the XRD patterns. These (1 0 0) reflections moved slightly to the left and concurrently long range order of MCM 41 diminished as Ti is incorporated. (1 1 0), (2 0 0), and (2 1 0) peaks which are indicative of the long range order of the hexagonal MCM 41 structure were somewhat smeared and this phenomenon becomes more pronounced as the titanium content increases. This is in agreement with the earlier findings that the introduction of hetero-atoms such as titanium usually resulted in less well resolved X-ray diffractograms with diminished long range order [8,9]. As shown in Fig. 2, the hexagonal pore structure of the one of the samples, Ti-MMS 93, is confirmed by TEM. Fig. 3 presents the N_2 adsorption isotherms and the corresponding BJH pore size distribution curves for Ti-MMS 93. The abrupt increases in the $P/P_0 = 0.2$–0.35 region and the corresponding maxima in the pore size distribution curves indicate the uniform mesopores of ca 3.1 nm diameter.

UV–VIS spectra of the calcined Ti-MMS taken in ambient conditions are given in Fig. 4. The spectra of Ti-MCM 41, Ti-HMS, and Ti-MCM 48 are also given for comparison. UV–VIS spectra of Ti-containing mesoporous materials are usually characterized by broad absorption bands centered at 220 and 260–270 nm as reported by Zhang et al. [2]. For TS-1 [10] and Ti-beta [11], an intense band at ca. 220 nm has been assigned to the ligand-to-metal charge transfer involving isolated Ti atoms in tetrahedral coordination, on which two water molecules may form part of the metal coordination sphere, increasing the coordination close to 6. According to this assignment, the band at ca.220 nm in Ti-substituted mesoporous materials may be associated with isolated Ti(IV) framework sites fundamentally similar in character to those in TS-1. The shoulder at 270 nm probably corresponds to partially polymerized hexa-coordinated Ti species [10], and some Ti–O–Ti clusters can co-exist with the isolated Ti sites in all the mesoporous samples to some extent. A broad absorption band occurring at 325 nm is typical for ligand to metal charge transfer in bulk titania. Absence of a shoulder at ~330 nm indicates that Ti-MMS are free of anatase phase. Compared with other titanium containing mesoporous materials such as Ti-MCM 41, Ti-HMS, and Ti-MCM 48,

Fig. 3. TEM image of Ti-MMS 93.

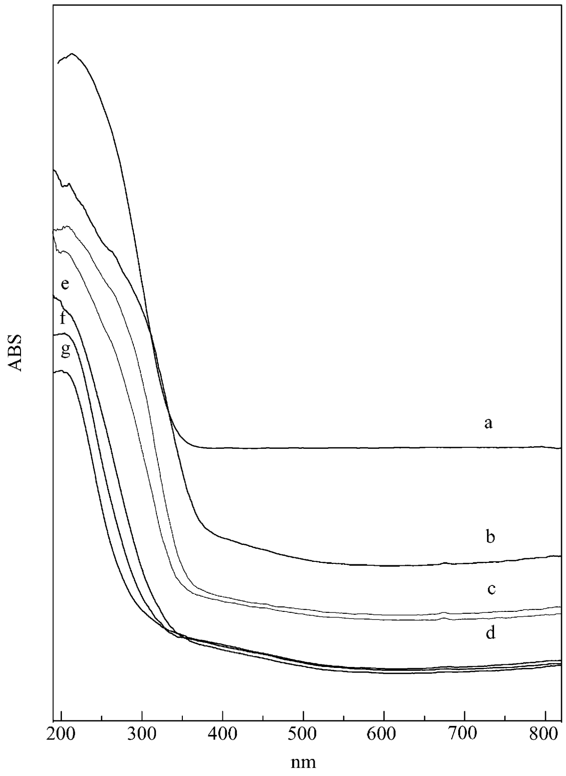

Fig. 4. UV–VIS spectra of titanium containing mesoporous materials: (a) Ti-MCM 48, (b) Ti-MCM 41, (c) Ti-HMS, (d) Ti-HMS, (e) Ti-MMS 23, (f) Ti-MMS 46, (g) Ti-MMS 93.

Ti-MMS displays negligible shoulder peak in 270 nm, and such features were maintained as the titanium content increases from Si/Ti = 95 to 35. It is believed that most of the titanium exist in isolated position with little polymeric Ti formation, and this may be a consequence of mixing $Ti(OC_3H_7)_4$ with a silicon source in acidic condition in Ti-MMS preparation.

Catalytic performances of Ti-MMS were tested for the oxidation of relatively bulky aromatic compound, 2,6-DTBP and smaller cyclohexene epoxidation. The catalytic results are summarized in Table 2 for the oxidation of 2,6-DTBP. The catalytic activity of Ti-MMS for 2,6-DTBP oxidation was found to be similar to that of Ti-MCM 41, and its activity increases proportional to the amounts of titanium incorporated in the structure. Despite the better Ti dispersion of Ti-MMS implicated in the UV–VIS spectra than Ti-MCM 41, catalytic activity of Ti-MMS was not superior to Ti-MCM 41. It is believed to be a consequence of substantially thicker pore walls for MMS material [6], which can lead to higher portion of titanium being buried inside the wall for Ti-MMS. As reported [4,12], Ti-MCM 48 with three-dimensional pore structure and Ti-HMS with small particle size and textual mesoporosity proved to be advantageous in liquid phase reactions, and resulted in higher conversions. Further 2 h reaction of the liquid phase after catalyst filtering with addition of little extra H_2O_2 to make up for the spent oxidant, resulted in no further increases in conversion, and contributions towards reaction by dissolved metallic species for Ti-MMS can be regarded negligible. It seems that presence of titanium in isolated tetrahedral sites is not a prerequisite for 2,6-DTBP oxidation using mesoporous molecular sieve catalysts [13]. We have also prepared a series of Ti-HMS with Si/Ti = 0.5–50 and applied to 2,6-DTBP reaction under the identical reaction conditions, and found that conversion increases smoothly to Si/Ti = 1.0 with the maximum conversion

Table 2
Catalytic reaction data for 2,6-DTBP oxidation using various Ti-containing mesoporous materials[a]

Samples	Si/Ti ratio of the substrate	2,6-DTBP oxidation		
		Conversion (%)	H_2O_2 efficiency (%)	Conversion after hot catalyst filtering (%)
Ti-MMS 23	23	17.4	16.2	16.2
Ti-MMS 46	46	13.6	12.7	12.7
Ti-MMS 93	93	11.5	10.9	10.5
Ti-MCM 41	48	14.8	15.3	–
Ti-MCM 48[b]	46	29.4	30.5	–
Ti-HMS	50	19.3	22.3	–

[a] Reaction conditions: 10 mmol 2,6-DTBP, 30 mmol H_2O_2 (35 wt.% in aqueous solution), 100 mg catalyst, 10 g acetone, 337 K for 2 h.

[b] Titanium introduction by post-synthetic grafting of titanocene.

Table 3
Catalytic reaction data for cyclohexene epoxidation[a]

Samples	Si/Ti ratio of the substrate	Cyclohexene conversion (%)	Selectivity (%)				
			Cyclohexene oxide	1-ol	1-one	Mono-ethers	Diol, di-ethers
Ti-MMS 23	23	20.6	2.3	5.8	15.3	38.3	38.3
Ti-MMS 46	46	13	1.5	4.8	13	34.3	46.4
Ti-MMS 93	93	7.5	2	6.4	17	31.4	43.2

[a] Reaction conditions: 0.2 g catalyst, 20 ml methanol, 33 mmol cyclohexene, 10 mmol H_2O_2 (35 wt.% in aqueous solution), 60°C for 3 h.

of ca. 32.5%; obviously, substantial portion of titanium at this high loading is expected to exist in polymeric forms. No detrimental reduction in H_2O_2 selectivity was accompanied by increases in titanium. Ti-MMS was also tested for cyclohexene expoxidation reaction, and the catalytic performance data are reported in Table 3. Again, conversion when plotted against titanium loading showed a linear relationship, and selectivity to various products remained almost constant. The major products were cyclohexene diol and its methyl ethers as reported by Chen et al. [14] for Ti-MCM 41. Lewis acid sites of titanium containing mesoporous materials are believed to convert the initially formed cyclohexene oxide to diols and mono- and di-alkyl ethers via further reaction with water and methanol [15].

4. Conclusions

In summary, following conclusions have been emerged from this study:

1. Titanium substituted derivatives of the silica-based mesoporous molecular sieves (Ti-MMS) could be prepared with good crystallinity at atmospheric pressure in just several hours using H_2SiF_6 as a silica source. Its structural and catalytic properties are very much like Ti-MCM 41 with hexagonal lattice and one-dimensional pores.
2. Titanium environment in Ti-MMS was very uniform relative to other types of titanium substituted M41S type materials, and believed to exist mostly in isolated tetrahedral sites.
3. Catalytic conversions for 2,6-DTBP oxidation and cyclohexene epoxidation increased linearly with titanium contents in Ti-MMS within 1–4 mol% range. Ti-MMS showed catalytic activity close to that of Ti-MCM 41 of the same metal loading, but less active than Ti-HMS or Ti-MCM 48, which is believed to be due to one-dimensional channel system of the Ti-MMS. Thicker pore walls of MMS material may lead to higher portion of titanium being buried inside the wall for Ti-MMS despite the enhanced dispersion of titanium at surface.

Acknowledgements

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