Postsynthesis, Characterization, and Catalytic Properties in Alkene Epoxidation of Hydrothermally Stable Mesoporous Ti-SBA-15

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Mesoporous Ti-SBA-15 has been postsynthesized by the titanation of pure silica SBA-15 in glycerol with the assistance of quaternary organic ammonium hydroxides, and has been extensively characterized by various techniques to investigate the mesostructural and catalytic properties, and the chemical nature of the incorporated Ti species, in comparison with those of Ti-MCM-41. To incorporate tetrahedral Ti species into the silica walls of SAB-15, the titanation needs to be carried out at elevated temperature and using an optimum amount of organic ammonium hydroxide. Ti-SBA-15 samples with a Si/Ti ratio ranging from 376 to 16 are successfully prepared with the retention of hexagonal mesostructure by elaborately conducting the titanation. The nature of the Ti species depends greatly on the Ti loading. At Si/Ti ratios higher than 50, the Ti species are mainly tetrahedrally coordinated in isolated states, while poorly dispersed Ti species of octahedral coordination are formed at higher Ti incorporation levels; however, no anatase phase is formed in all cases. The IR band at 948 cm^{-1} due to Si−O−Ti bonds can be used to characterize the tetrahedral Ti species in mesoporous materials, but the techniques of dehydration or trimethylsilylation should be adopted to get rid of the influence of silanol groups. In an actual catalytic reaction, Ti-SBA-15 exhibits not only extremely high thermal stability but also outstanding endurance against Ti leaching not observed for Ti-MCM-41. Ti-SBA-15 is thus presumed to be a promising liquid-phase oxidation catalyst.

Introduction

Mesoporous materials, having uniform mesopores and an extremely high specific surface area, have received extensive attention from researchers in the past decade because of their potential applications as catalysts, adsorbents for large organic molecules, and guest−host chemical supporters.[1−4] From the viewpoint of catalysis, many efforts have been made to introduce metal ions into the most representative mesoporous silica, MCM-41, by direct synthesis or postsynthesis methods.[5−10] Compared to the crystalline microporous materials, the mesoporous catalysts suffer two major disadvantages, that is, low intrinsic catalytic activity due to the amorphous nature of the pore walls and poor hydrothermal and mechanical stability due to the high hydrophilicity derived from abundant surface silanol groups.[11]

To overcome the former weakness, efforts have been made to introduce zeolite-like crystalline orders into the mesoporous materials. For example, with the aid of tetrapropylammonium ions, Al-containing MCM-41 is reported to partially crystallize to form ZSM-5 precursors within the mesopore walls, and then exhibits an enhanced catalytic activity for cumene cracking.[12] Partially dissolving zeolite in carefully controlled basic media and then assembling this zeolite source into mesostructures or pillaring lamellar zeolite with surfactant to construct a micro-mesoporous hybrid structure is an alternative way.[13−15] However, it seems that

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many technical difficulties and limitations still remain in the above approaches.

To increase the stability of mesoporous materials, postmodification and a search for more stable structures have been carried out. Trimethylsilylation effectively removes the surface silanols to greatly enhance the hydrophobicity. This enhances the hydrothermal stability and the catalytic activity especially for Ti-MCM-41-catalyzed liquid-phase oxidation involving water.[16,17] It is easy to consider the improvement of the stability through controlling the synthesis conditions to achieve an extensive condensation of the silica walls or by discovering new materials that are intrinsically stable. In this meaning, SBA-15, synthesized with triblock copolymer, has thicker walls and uniform mesopores ranging from 5 to 30 nm, and then reasonably shows a higher hydrothermal stability than conventional MCM-41.[18,19] Mesoporous pure silica MSU-G thereafter synthesized with novel gemini surfactants is reported to be more hydrothermally stable even than SBA-15 because of a high degree of SiO_4 unit cross-linking.[20] However, to the best of our knowledge, the isomorphous substitution of heteroatoms into MSU-G has not been reported in the open literature so far.

On the other hand, several papers concerning the incorporation of Al, Ti, or V into SBA-15 have been reported.[21−23] In the case of Ti-SBA-15, although it can be synthesized directly under microwave hydrothermal conditions,[24] the postsynthesis method is still overwhelming mainly because SBA-15 needs strongly acidic synthesis conditions. To apply Ti-SBA-15 to a versatile catalyst in the selective oxidation with peroxide oxidants to produce fine chemicals and pharmaceutical substances, Ti should be incorporated essentially as a tetrahedral species but not as a catalytically inactive anatase phase. Unfortunately, the catalytic data are still not available for the Ti-SBA-15 samples either directly synthesized or prepared simply by the incipient-wetness impregnation. Nevertheless, they do not seem to serve as effective epoxidation catalysts because they contain a large amount of anatase especially at high levels of Ti incorporation as evidenced by UV−vis spectra.[22,24] Thus, there is still high potential to prepare Ti-SBA-15 with highly qualitative Ti species applicable to liquid-phase oxidation.

In the present study, we have postsynthesized hydrothermally stable Ti-SBA-15 of various Ti contents with the assistance of quaternary organic ammonium hydroxide. Various techniques have been used to characterize extensively both the pore properties and the Ti states of Ti-SBA-15. The stability against hydrothermal treatment and Ti leaching has been compared between Ti-SBA-15 and Ti-MCM-41 in the actual catalytic epoxidation of alkenes.

Experimental Section

Sample Preparation. Mesoporous silica SBA-15 was hydrothermally synthesized according to the procedures reported previously.[18] Triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEG-PPG-PEG; average molecular weight 5800, Aldrich), was dissolved in deionized water. Tetraethyl orthosilicate (TEOS; Wako) and hydrochloric acid (36 wt %, Wako) were then added to the copolymer solution to obtain a homogeneous solution with a molar composition of SiO_2/0.017 PEG-PPG-PEG/6.55 HCl/169 H_2O. The resultant solution was heated at 308 K with stirring for 20 h and further aged statically at 373 K for 24 h. The white solid product (SBA-15) was filtered, washed with deionized water, dried, and then calcined at 773 K for 10 h.

Ti-incorporated SBA-15, designated Ti-SBA, was prepared by the postsynthesis method using tetrabuthyl orthotitanate (95 wt %, Wako) as a Ti source. In a typical preparation, a certain amount of TBOT was hydrolyzed in 20 mL of glycerol (99 wt %, Wako) containing 0−5 mL of quaternary ammonium hydroxide to obtain a homogeneous solution. To the above solution was added 1 g of SBA-15 without any pretreatment, and the mixture was heated statically to induce titanation at 303−393 K for 20−220 h. The amount of TBOT added was varied to give Si/Ti atomic ratios of 5.7−200. The quaternary ammonium hydroxides used were tetrapropylammonium hydroxide (TPAOH; 25 wt %, TCI), tetraethylammonium hydroxide (TEAOH; 35 wt %, Aldrich), and tetrabutylammonium hydroxide (TBAOH; 45 wt %, TCI). After the titanation, Ti-SBA was filtered and washed with deionized water, and the organic species were burned off at 773 K for 4 h.

For control experiments, Ti-MCM-41 samples, denoted Ti-MCM, with Si/Ti ratios of 37−320 were hydrothermally synthesized.[7]

The trimethylsilylation of mesoporous materials was carried out using hexamethyldisilazane (HMDS).[25] After evacuation at 473 K for 2 h, 1 g of powder was added to 20 mL of anhydrous toluene and 1 g of HMDS in a flask equipped with a cooling condenser, and the mixture was refluxed for 2 h to induce the silylation of surface silanols. The silylated product, Ti-SBA-sil or Ti-MCM-sil, was then filtered, washed with acetone, and dried at 373 K for 5 h.

Characterization Methods. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Rint 2000 diffractometer using Cu Kα radiation, and UV−vis spectra were collected on a Shimadzu UV-2400PC spectrophotometer. The amount of Ti was quantified by inductively coupled plasma emission spectrometry (ICP; Rigaku JY38S). N_2 adsorption measurements at 77 K were carried out on a Coulter SA 3100 volumetric adsorption analyzer after the samples were outgassed for 2 h at 473 K. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer using a KBr pellet technique.[26] Sample diluted in KBr (3 wt %) was pressed into a wafer (31.9 mg cm^{-2} thickness). The wafer was evacuated at 373−773 K in a quartz cell sealed with KBr windows. The spectra were collected in absorbance mode after the cell was cooled to room temperature.

Catalytic Reaction. The epoxidation of cyclohexene was carried out under vigorous stirring in a 50 mL glass flask which was heated with an oil bath. In a typical run, 10 mmol

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Table 1. Effect of Treatment Conditions on Ti Incorporation into SBA-15[a]

		titanation conditions			Si/Ti ratio				
no.	sample	temp (K)	time (h)	TPAOH/SBA-15 (mL g^{-1})	added	incorporated	BET (m^2 g^{-1})	micropore vol[b] (mL g^{-1})	pore size (nm)
1	SBA-15						683	0.152	5.8
2	Ti-SBA1	303	70	3	60	101	653	0.085	5.8
3	Ti-SBA2	373	70	3	60	116	561	0.020	5.8
4	Ti-SBA3	393	70	3	60	110	513	0.014	5.8
5	Ti-SBA4	373	20	3	60	269	613	0.031	5.8
6	Ti-SBA5	373	120	3	60	120	523	0.005	5.8
7	Ti-SBA6	373	220	3	60	114	505	0.001	5.8
8	Ti-SBA7	373	70	0	22	25	654	0.056	5.8
9	Ti-SBA8	373	70	1	22	34			
10	Ti-SBA9	373	70	3	22	72	554	0.015	5.8
11	Ti-SBA10	373	70	5	22	126	484	0.003	5.8
12	Ti-SBA11	373	70	3[c]	60	95	584	0.016	5.8
13	Ti-SBA12	373	70	3[d]	60	105	542	0.013	5.8

[a] Other conditions: parent SBA-15, 1 g; glycerol, 20 mL; 25 wt % TPAOH, 3 mL; time, 70 h. [b] Calculated from *t*-plots. [c] 35 wt % TEAOH. [d] 45 wt % TBAOH.

of cyclohexene (99 wt %, TCI), 10 mL of acetonitrile (99.5 wt %, Wako) solvent, and 0.05 g of catalyst were mixed in the flask and heated to 333 K under agitation. The desirable amount of oxidant, TBHP (70 wt %, Aldrich) or H_2O_2 (30 wt %, Wako), was then added to the mixture to start the reaction. After the catalyst powder was removed from the reaction mixture by centrifugal separation, the products were analyzed on a gas chromatograph (Shimadzu GC-14B) with an FID detector.

Results and Discussion

Postsynthesis of Ti-SBA-15. Glycerol was chosen as the solvent for introducing Ti into pure silica SBA-15 by the postsynthesis method, because it exhibits the advantage of serving as a stabilizing guest molecule due to its high viscosity,[12,27] and is considered to exert a less destructive effect than water solvent on the hydrothermally unstable mesoporous structure.

Table 1 shows the influence of various titanation conditions on the Ti incorporation and the physicochemical properties of SAB-15. The effect of the treatment temperature was investigated at a treatment time of 70 h, TPAOH/SBA-15 liquid-to-solid ratio of 3 mL g^{-1}, and Si/Ti atomic ratio of 60 (Table 1, nos. 1−4). The amount of Ti incorporated into SBA-15 was about half of that initially added, and did not change significantly in the range from 303 to 393 K. On the other hand, the amount of Ti incorporated at 373 K increased with increasing treatment time to 70 h and showed negligible change after 70 h (Table 1, nos. 3 and 5−7), indicating the Ti incorporation took place slowly only to a low level within 20 h. When the treatment temperature and the time were fixed at 373 K and 70 h, respectively, the relative amount of TPAOH aqueous solution to SBA-15 solid was found to significantly influence the absolute amount of Ti incorporated; that is, a lower amount of TPAOH solution resulted in higher Ti incorporation (Table 1, nos. 8−11). The use of TEAOH and TBAOH for the titanation resulted in no obvious difference in the Ti amount from that of TPAOH (Table 1, nos. 3, 12, and 13).

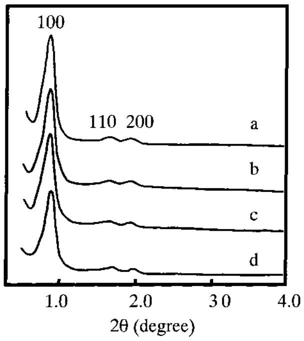

Figure 1. X-ray diffraction patterns of pure silica SBA-15 (a) and Ti-incorporated samples of Ti-SBA2 (b), Ti-SBA4 (c), and Ti-SBA6 (d). For Ti-SBA samples, see Table 1.

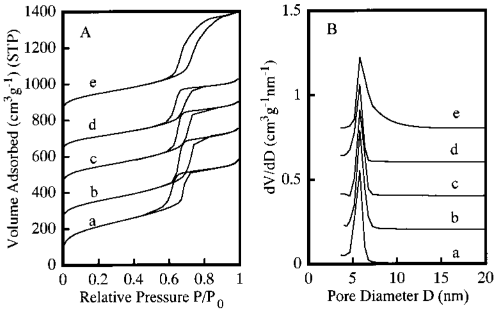

Figure 2. N_2 adsorption/desorption isotherms (A) and pore size distributions (B) for pure silica SBA-15 (a) and Ti-incorporated samples of Ti-SBA2 (b), Ti-SBA3 (c), Ti-SBA4 (d), and Ti-SBA6 (e). For Ti-SBA samples, see Table 1.

Figure 1 shows the XRD patterns of the parent SBA-15 and three representative Ti-SBA-15 samples. All the SBA-15 and Ti-SBA-15 samples exhibited very similar patterns where three well-resolved diffraction peaks due to 100, 110, and 200 reflections were observed. Although a slightly lower intensity of the 100 peak was observed for Ti-SBA-15 prepared under serious conditions (Figure 1d), the well-retained 110 and 200 peaks strongly verified that the characteristic hexagonal features were maintained in Ti-SBA-15.

N_2 adsorption measurements were conducted to further investigate the structural change upon titanation because the XRD patterns may not be so sensitive as to show a slight textural change. Figure 2A shows N_2 adsorption/desorption isotherms for SBA-15 and various Ti-SBA-15 samples. SBA-15 showed a hysteresis loop which typically featured this kind of mesoporous material. The step of increase in the N_2 adsorption amount due to multilayer absorption in the mesopores was observed in a higher pressure region than that of MCM-

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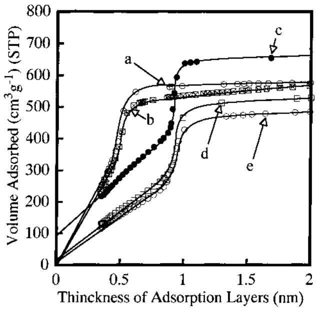

Figure 3. *t*-plots of N_2 adsorption for pure silica MCM-41 (a), Ti-MCM-41 (b), pure silica SBA-15 (c), Ti-SBA2 (d), and Ti-SBA3 (e). For Ti-SBA samples, see Table 1.

41, suggesting SBA-15 has a larger pore size.[24,28] The sharpness of the hysteresis loop was maintained for Ti-SBA-15 samples (Figure 2, curves b−d). Nevertheless, the sample prepared under severe conditions slightly lost the sharpness of the hysteresis loop (Figure 2, curve e), probably due to partial collapse of the mesostructure.

The specific area (BET) and the BJH pore size distribution calculated from the desorption isotherms are summarized in Table 1 and Figure 2B, respectively. The BET surface area of SBA-15 is generally reported to vary in the range of 500−1000 m^2 g^{-1} since the porous properties of this kind of mesoporous material are greatly dependent on the synthesis conditions.[18,19,29] The present SBA-15 fell within the surface area range reported in the literature and was thus considered to be qualitatively good. The specific area was lowered by about 30 m^2 g^{-1} after mild titanation, and further decreased gradually with increasing treatment temperature, treatment time, and relative amount of TPAOH solution (Table 1, nos. 1−11). This can be reasonably explained in terms of a reduced order of the mesostructure, because SBA-15, although consisting of thick silica walls, is still not hydrothermally stable enough to withstand the titanation treatment. Nevertheless, the average pore size was almost the same and the distribution was generally very narrow except for Ti-SBA-15 prepared under severe conditions (Figure 2, curve e).

Different from mesoporous MCM-41, SBA-15 shows both mesoporous and microporous properties which greatly depend on the aging temperature. The presence of micropores has been confirmed either by the carbon replica method or by N_2 adsorption measurement using α_s-plot and *t*-plot methods.[29−33] The *t*-plot analysis was thus used to estimate the micropore volume in the mesoporous materials. The *t*-plots were obtained by using a reference isotherm of a nonporous silica as described previously.[34] As shown in Figure 3a,b, the extrapolation lines of the *t*-plots passed through the origin for MCM-41 and Ti-MCM-41, indicating they lacked micropores. In contrast, SBA-15 gave a straight line not passing through the origin (Figure 3c), which was indicative of distinct microporosity. The micropore volume of SBA-15 obtained from the intercept of the *y*-axis accounted for about 15% of its total volume. Ti-SBA-15 samples showed *t*-plots similar in shape to that of SBA-15, but the intercepts approached the origin (Figure 3d,e), indicating gradual disappearance of the micropores.

The micropore volumes obtained from the *t*-plots are listed in Table 1. Combining these with the above BET analysis, we would propose that the decrease in the surface area during titanation is principally due to the loss of micropores. Since the micropores are probably generated by penetration of hydrophilic poly(ethylene oxide) chains of triblock copolymer into its thick silica walls,[29−33] a hydrothermal heating would shrink the silica walls to mend “holes” therein which are micropores. Incorporation of Ti species into the micropores to remove this wall defect may also partially account for the reduced surface area. Both reasons would make Ti-SBA-15 mesoporous but lack the bimodal porosity of SBA-15. However, very severe titanation at higher temperatures, for a longer time, and by using a larger amount of TAPOH would not only remove the micropores but also destroy the mesopores as evidenced by a broader pore size distribution (Figure 2, curve e) and greatly reduced BET areas (Table 1, nos. 4, 7, 11).

UV−vis spectroscopy was used to characterize the effectiveness of the titanation conditions on the chemical nature and coordination states of the Ti species incorporated. The bands at 200−230, 330, and 260−290 nm are usually taken as clear evidence for the isolated framework Ti, anatase Ti(IV) particles, and octahedrally coordinated Ti species with low dispersion, respectively.[35] The band position is thus indicative of the nature of the Ti species.

Figure 4 depicts the UV spectra of Ti-SBA-15 samples prepared under various conditions. Ti-SBA-15 obtained by titanation at 303 K (Table 1, no. 2) showed a main band at 260 nm besides the 220 nm band, and those prepared at higher temperatures (Table 1, nos. 3 and 4) exhibited essentially the 220 nm band (Figure 4A), although the Ti contents were very similar to those described above. The reaction of the Ti species with the surface silanol groups is suggested to be requisite for Ti incorporation. A certain temperature is presumed to be necessary in crossing the activation energy barrier to cause this reaction to result in isolated Ti species. Titanation at an optimum temperature of 373 K resulted in incorporation of Ti species almost tetrahedrally coordinated, increasing gradually with time (Figure 4B). The addition of TPAOH retarded the Ti introduction (Table 1, nos. 8−11), but effectively controlled the nature of the Ti species as shown by the gradual blue shift of the band from 260 to 220 nm with increasing TPAOH/solid ratio (Figure 4C). The basic aqueous solution of TPAOH would promote the hydrolysis of TBOT, which then prevents the Ti species from aggregating to particles. Nevertheless, too much TPAOH solution added caused structural collapse. Other quaternary organic ammonium hydroxides, TEAOH and

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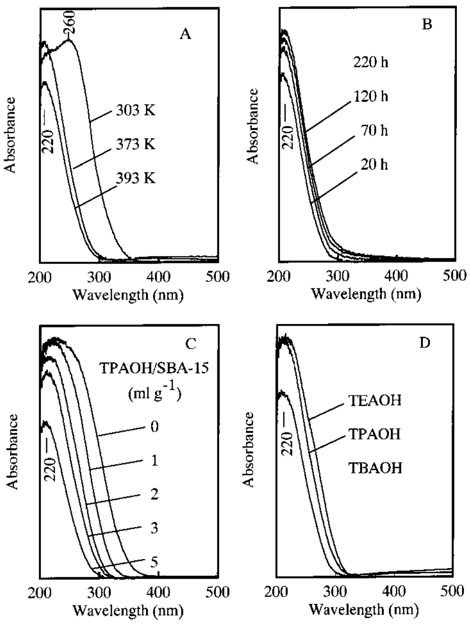

Figure 4. UV−vis spectra for Ti-SBA-15 samples prepared by titanation for 70 h at different temperatures (A), at 373 K for different periods of time (B), with different TPAOH/SBA-15 ratios (C), and in various quaternary ammonium hydroxides (D). For detailed titanation conditions, see Table 1.

Table 2. Postsynthesized Ti-SBA-15[a] and Hydrothermally Synthesized Ti-MCM-41[b] with Various Ti Contents

no.	sample	Si/Ti ratio added	Si/Ti ratio incorporated	BET (m^2 g^{-1})	pore size (nm)
1	Ti-SBA1	200	376		
2	Ti-SBA2	60	116	561	5.8
3	Ti-SBA3	22	80	524	5.8
4	Ti-SBA4	17	57		
5	Ti-SBA5	14	36	542	5.8
6	Ti-SBA6	10	27		
7	Ti-SBA7	7	20	536	5.2
8	Ti-SBA8	5.7	16	515	5.2
9	MCM-41			1158	2.7
10	Ti-MCM1	283	320	1115	3.0
11	Ti-MCM2	110	130		
12	Ti-MCM3	80	76	1115	3.0
13	Ti-MCM4	60	58	1060	2.6
14	Ti-MCM5	35	37	1041	2.6

[a] Postsynthesis conditions: parent SBA-15, 1 g; glycerol, 20 mL; 25 wt % TPAOH, 3 mL; temperature, 373 K; time, 70 h. [b] Hydrothermal synthesis conditions: see ref 7.

TBAOH, showed basically the same effectiveness as TPAOH in forming highly dispersed Ti species (Figure 4D). Therefore, perusal of XRD, ICP, N_2 adsorption, and UV−vis data leads to the conclusion that Ti-SBA-15 containing the tetrahedral Ti species can be optimally postsynthesized by titanation in gycerol at an elevated temperature with organic ammonium hydroxide as a promoting agent for Ti dispersion.

A series of Ti-SBA-15 samples were thus prepared by varying the Ti content in the starting reaction mixture at the optimum conditions as described above. Table 2 shows their physicochemical properties together with those of directly synthesized Ti-MCM-41 samples. The amount of Ti incorporated into SBA-15 silica decreased from about half to one-fourth of the amount initially added when the Si/Ti ratio of the starting mixture decreased, indicating a decreasing efficiency for Ti incorporation.

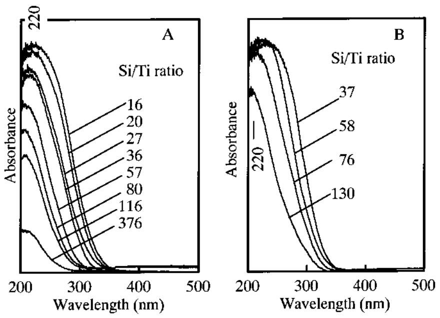

Figure 5. UV−vis spectra for postsynthesized Ti-SBA-15 samples (A) and hydrothermally synthesized Ti-MCM-41 samples (B) both with various Si/Ti ratios. For detailed preparation conditions, see Table 2.

The absorption band maximum was observed at 220 nm in the UV−vis spectra for both Ti-SBA-15 and Ti-MCM-41 (Figure 5). The band gradually red-shifted to the longer wavelength region with increasing Ti content to result in a new shoulder band around 260 nm especially when the Si/Ti ratio was lower than 50. This means octahedral Ti species formed partially within the mesoporous materials at high Ti levels irrespective of the Ti incorporation method (direct or postsynthesis). Nevertheless, no Ti-SBA-15 sample showed the band around 330 nm due to the anatase phase. The present postsynthesis method is presumed to be effective in achieving high Ti dispersion.

IR Spectroscopy Study on Ti-SBA-15 and Ti-MCM-41. IR spectroscopy is a useful technique for characterizing the framework Ti species in microporous crystalline titanosilicates such as TS-1[36] and Ti-MOR.[37] Nevertheless, this method is not so useful for Ti mesoporous materials containing silanols groups or defect sites,[7,26] because those silanol groups or water molecules adsorbed therein also give a similar band. However, we have recently solved this problem by measuring IR spectra after evacuating the samples in situ at elevated temperatures.[26] This new technique was applied here to the characterization of Ti-SBA-15 with IR spectroscopy.

Figure 6 shows the IR spectra of pure silica SBA-15 and Ti-SBA-15 recorded after evacuation at various temperatures. The sample was diluted in KBr pellets (15 wt %) to obtain well-resolved and noncutoff bands in the region lower than 1000 cm^{-1}. SBA-15 showed a band at 968 cm^{-1} before evacuation despite the absence of Ti (Figure 6B). However, the band gradually decreased in intensity with increasing evacuation temperature, and was hardly observed after evacuation at 773 K. This is a result of removal of adsorbed water and dehydroxylation of silanols as evidenced by the disappearance of the broad band at 3200−3600 cm^{-1} (Figure 6A). The same 968 cm^{-1} band was observed for Ti-SBA-15 before evacuation, but the band split into two bands after evacuation at 573 K and turned out to be a new band with a maximum adsorption at 948 cm^{-1} when evacuation was done at 773 K (Figure 6D). These results suggest the 948 cm^{-1} band could be assigned to the tetrahedral Ti species in Ti-SBA-15.

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[36] Bellussi, G.; Rigguto, M. S. *Stud. Surf. Sci. Catal.* **1994**, *85*, 177.

[37] Wu, P.; Komatsu, T.; Yashima, T. *J. Phys. Chem.* **1996**, *100*, 10316.

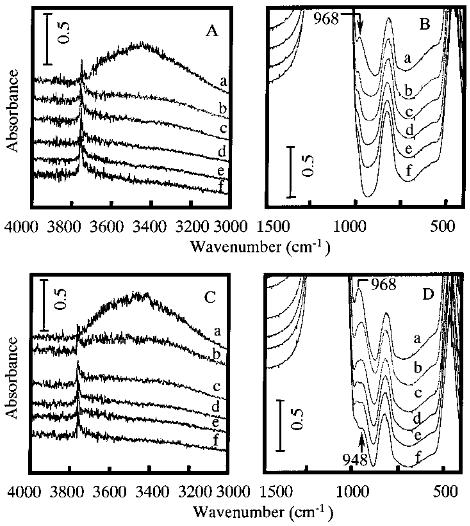

Figure 6. IR spectra for pure silica SBA-15 (A, B) and Ti-SBA-15 (Si/Ti = 36) (C, D) without evacuation (a) and after evacuation at 373 K (b), 473 K (c), 573 K (d), 673 K (e), and 773 K (f) each for 1 h.

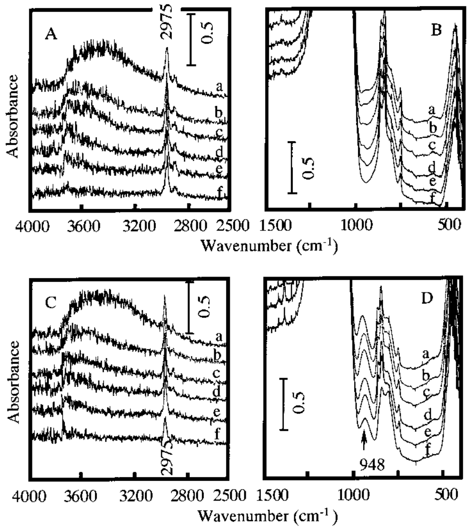

Figure 7. IR spectra for pure silica SBA-15-sil (A, B) and Ti-SBA-15-sil (Si/Ti = 36) (C, D) without evacuation (a) and after evacuation at 373 K (b), 473 K (c), 573 K (d), 673 K (e), and 773 K (f) each for 1 h. Both samples were obtained by trimethylsilylation.

This assignment was further verified by the IR spectra of SBA-15 and Ti-SBA-15 after the trimethylsilylation treatment. The silylation consumes the silanol groups effectively and greatly enhances the hydrophobicity of mesoporous materials.[17] As shown in Figure 7, the silylation developed a band at 2975 cm^{-1} attributed to the C−H stretching vibration of methyl groups,[25] and greatly decreased the intensity of the terminal and hydrogen-bonded silanol bands at 3745 and around 3500 cm^{-1}, respectively. Following the silylation, only a negligible band at 968 cm^{-1} was observed for pure silica SBA-15 even before evacuation (Figure 7B). Silylated Ti-SBA-15, on the other hand, showed the tetrahedral Ti band at 948 cm^{-1}, whose intensity hardly changed with the evacuation temperature (Figure 7D). Combining the results of Figures 6 and 7, we hypothesize that the presence of the tetrahedral Ti species can be confirmed by IR spectroscopy only either after the dehydroxylation at elevated temperatures or after the hydrophobic treatment by silylation. These new techniques would be effectively applicable to the characterization of Ti-containing mesoporous materials.

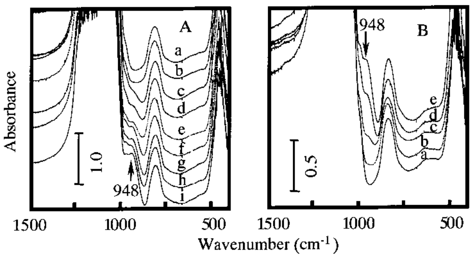

Figure 8. IR spectra for Ti-SBA-15 samples (A) with Si/Ti ratios of ∞ (a), 376 (b), 116 (c), 80 (d), 57 (e), 36 (f), 27 (g), 20 (h), and 16 (i) together with those of Ti-MCM-41 samples (B) with Si/Ti ratios of ∞ (a), 320 (b), 76 (c), 58 (d), and 37 (e). All the spectra were recorded after evacuation at 773 K for 2 h.

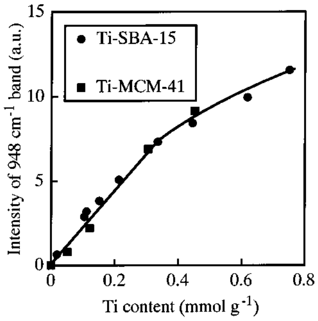

Figure 9. Dependence of the intensity of the 948 cm^{-1} band on the Ti content of Ti-SBA-15 and Ti-MCM-41.

Figure 8 shows the IR spectra of Ti-SBA-15 and Ti-MCM-41 samples with various Ti contents after elimination of the influence of adsorbed water and silanols by evacuation at 773 K. The 948 cm^{-1} band gradually increased in intensity with increasing Ti content. The intensity was proportional to the Ti content in the region lower than 0.35 mmol g^{-1} corresponding to a Si/Ti ratio of ca. 50, and deviated from the linearity in the higher Ti content region (Figure 9). This is consistent with the findings obtained from UV−vis spectra that Ti species are incorporated into the silica framework of SBA-15 to occupy initially the tetrahedral sites and then partially the octahedral sites with a gradual increase in Ti incorporation.

A Comparison of Catalytic Properties and Stability between Ti-SBA-15 and Ti-MCM-41. Ti-MCM-41 and Ti-MCM-48 have been well-known to be promising catalysts for the liquid-phase oxidation of bulky molecules.[7,8,38] Thus, postsynthesized Ti-SBA-15 samples have been tested for the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP). The products obtained were cyclohexene oxide, 1,2-cyclohexanediols formed by a successive solvolysis of the oxide by water on acid sites such as surface silanol groups, and 2-cyclohexen-1-ol and 2-cyclohexen-1-one both due to allylic oxidation. The efficiency of TBHP calculated on the basis of the amount of *tert*-butyl alcohol was at least over 90 mol % in all cases. As shown in Table 3, the main product was cyclohexene oxide, and its selectivity was comparable

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Table 3. Epoxidation of Cyclohexene with TBHP over Ti-SBA-15 and Trimethylsilylated Ti-SBA-15[a]

sample	Si/Ti	convn (mol %)	TON [mol (mol of Ti)$^{-1}$]	product selectivity (mol %) oxide	diols[b]	allylic[c]
Ti-SBA1	80	1.9	76	83.9	6.5	9.7
Ti-SBA2	27	2.8	38	86.9	6.8	6.3
Ti-SBA1-sil[d]	87	21.1	843	97.0	2.0	1.9
Ti-SBA2-sil[d]	28	29.8	437	96.0	2.4	1.6

[a] Epoxidation conditions: catalysis, 0.05 g; cyclohexene, 30 mmol; TBHP, 30 mmol; temperature, 333 K; time, 2 h. [b] 1,2-Cyclohexanediols. [c] Products of allylic oxidation: 2-cyclohexen-1-ol and 2-cyclohexen-1-one. [d] Trimethysilylated by refluxing in hexamethyldisilazane/toluene for 2 h.

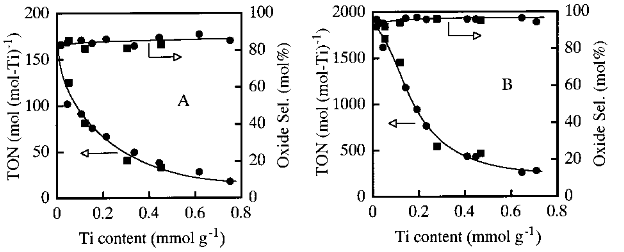

Figure 10. Dependence of the TON and epoxide selectivity on the Ti content for Ti-SBA-15 (●) and Ti-MCM-41 (■) before (A) and after (B) trimethylsilylation. For detailed epoxidation conditions, see Table 3.

between the Ti-SBA-15 catalysts with different Ti contents. Nevertheless, the specific catalytic activity per Ti site, the turnover number (TON), was lower for the catalysts with a higher Ti content. Since the liquid-phase epoxidation is generally believed to be catalyzed by highly dispersed tetrahedral Ti species,[36] the Si/Ti ratio dependence of the TON suggests that a less active Ti species was present in Ti-SBA-15 with a higher Ti content.

Silylation greatly increased the TON and also slightly increased the selectivity for the oxide. The activity enhancement is reasonable because the silylation changes hydrophilic Ti-SBA-15 to a hydrophobic catalyst by removing its silanol groups, which makes both the substrate and oxidant molecules easily accessible to the Ti active sites. The removal of the silanols may block the acidity of Ti-SBA-15 to suppress the solvolysis reaction and then increase the oxide selectivity.

The catalytic properties of Ti-SBA-15 were further compared with those of Ti-MCM-41 in the epoxidation of cyclohexene. The catalytic performance greatly depended on the Ti content as shown in Table 3. To reach reasonable valuations, the reaction was carried out using both the catalysts with various Ti contents. These two Ti-containing catalysts showed very similar behaviors in terms of the catalytic activity and the oxide selectivity, irrespective of the trimethylsilylation (Figure 10). This suggests that Ti-SBA-15 and Ti-MCM-41 are catalytically analogous although they differ in preparation method, surface area, and mesopore size. The silylation enhanced the specific activity of the Ti species about 10 times and increased the oxide selectivity by 10 mol %. The TON sharply declined with increasing Ti content, strongly indicating the presence of less active Ti species as evidenced by UV and IR studies described above especially at a higher level of Ti incorporation. This strongly suggests the importance of obtaining highly dispersed Ti species by paying careful attention in the synthesis.

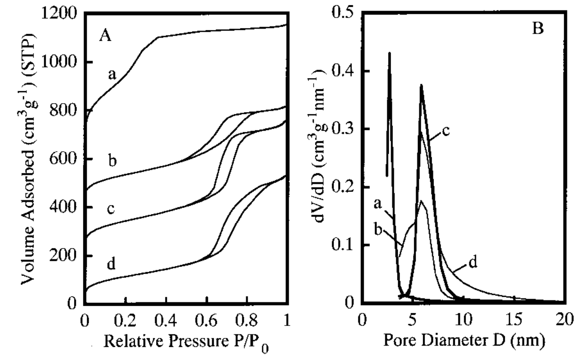

Figure 11. N_2 adsorption/desorption isotherms (A) and pore size distributions (B) of Ti-MCM-41 (a), water-refluxed Ti-MCM-41 (b), Ti-SBA-15 (c), and water-refluxed Ti-SAB-15 (d). The samples were refluxed in water at 373 K for 50 h.

Table 4. Physicochemical Properties of Hydrothermally Treated Ti-SBA-15 and Ti-MCM-41

sample	water treatment temp (K)	water treatment time (h)	wall thickness[b] (nm)	BET (m^2 g^{-1})	pore volume (mL g^{-1})	pore size (nm)
Ti-MCM-41			1.41	1280	0.849	2.65
Ti-MCM-41-H_2O	373	50	*c*	488	0.635	5.79
Ti-SBA-15			6.40	561	0.845	5.79
Ti-SBA-15-H_2O	373	50	6.40	412	0.767	5.79

[a] One gram of solid was refluxed in 50 mL of water. [b] Calculated as $2d_{100}/\sqrt{3}$ − pore size. [c] Not determined because of extensive structural collapse.

Although serving as an effective catalyst for bulky reactions, Ti-MCM-41 is claimed to have the disadvantages of lower thermal stability and easy leaching of Ti species.[17,39] Ti-SBA-15 has been compared with Ti-MCM-41 in thermal stability in boiling water. Figure 11 shows the isotherms of N_2 adsorption and the pore size distributions, and Table 4 summarizes the physicochemical properties before and after thermal treatment. Ti-MCM-41 refluxed in water totally lacked the primary isotherm shape reflecting the typical hexagonal structure, and showed a lower adsorption amount and a hysteresis loop (Figure 11a,b). These results indicate that the wall structure of Ti-MCM-41 collapsed totally to form a disordered pore system. The same treatment also destroyed the structure of Ti-SBA-15 since it showed a less sharp hysteresis loop in the isotherm and a relatively broadened pore size distribution (Figure 11c,d). However, all these changes were very limited and essentially did not alter the porous properties initially possessed by hexagonal SBA-15. Therefore, it is concluded that Ti-SBA-15, as previously declared for pure silica SBA-15,[18] is much superior in thermal stability to Ti-MCM-41. This superiority is presumed to derive from the difference in the wall thickness between Ti-SBA-15 and Ti-MCM-41.

The leaching of Ti has been investigated in the actual epoxidation of cyclohexene with an aqueous solution of hydrogen peroxide. The catalyst was repeatedly used to catalyze the reaction after being washed with acetone and dried at 373 K in air. The amounts of substrate

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(39) Chen, L. Y.; Chuah, G. K.; Jaenicke, S. *Catal. Lett.* **1998**, *50*, 107.

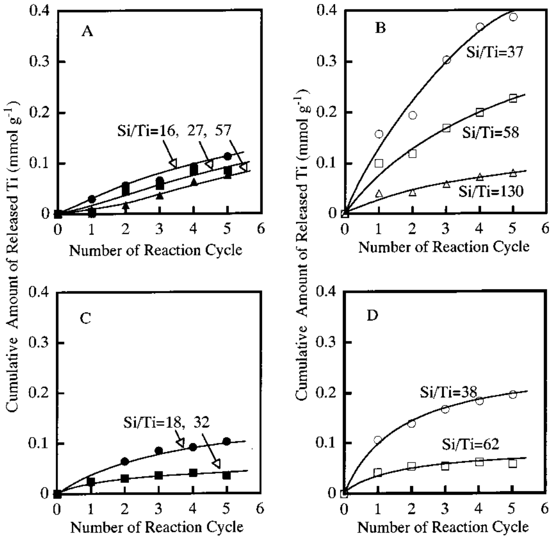

Figure 12. Amount of Ti leached after repeated epoxidation of cyclohexene with H_2O_2 for Ti-SBA-15 (A), Ti-MCM-41 (B), Ti-SBA-15-sil (C), and Ti-MCM-41-sil (D). The Si/Ti ratio shown is that of the starting catalyst. For detailed epoxidation conditions, see Table 3 but with H_2O_2 instead of TBHP.

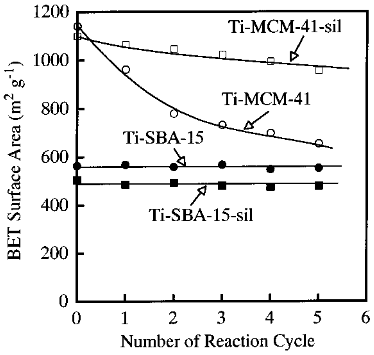

Figure 13. Changes of the surface area with repeated epoxidation of cyclohexene with H_2O_2 for SBA-15, Ti-MCM-41, Ti-SBA-15-sil, and Ti-MCM-41-sil.

oxidant were adjusted to keep the substrate/catalyst ratio constant. The cumulative Ti released by the reaction was calculated from the difference in the Ti content between the starting catalyst and the repeatedly used catalyst. Ti leaching was observed for both Ti-SBA-15 and Ti-MCM-41, and the amount released increased with increasing Ti content (Figure 12A,B), but the absolute amount was extremely lower in the case of Ti-SBA-15. This indicates that Ti-SBA-15 is much more stable than Ti-MCM-41 against the leaching of the Ti species. The silylation hardly influenced the Ti stability of Ti-SBA-15, but greatly enhanced that of Ti-MCM-41 as the amount of Ti released was reduced nearly to half (Figure 12C,D).

To interpret the above phenomena, the change in the surface area following the repeated reaction was investigated (Figure 13). The silylation made both Ti-SBA-15 and Ti-MCM-41 decrease slightly in surface area probably because the organic silane may mend the cavity of defect sites or reduce some adsorption sites for nitrogen molecules. In the case of Ti-SBA-15, the surface area was almost the same after the repeated reaction irrespective of silylation, indicating its high structural stability. However, Ti-MCM-41 decreased gradually in surface area after the repeated reaction unless the silylation was performed to enhance the structural stability. Combining the results of Figures 12 and 13, it is assumed that there are at least two reasons for the Ti leaching in an actual oxidation reaction. First, the hydrogen peroxide molecules interact with the tetrahedral Ti ions to form the catalytically active intermediate species Ti−peroxo complex, which would be easily attacked by water molecules to form octahedral coordination since the water molecules are always present when aqueous oxidant solution is used. In the particular case of mesoporous materials, this interaction would occur more easily due to the highly hydrophilic environment neighboring the Ti species. The cleavage of Si−O−Ti bonds then progresses to result in Ti leaching. This kind of leaching could always occur and is irrespective of whether the wall structure is hydrothermally stable or not. Second, the lack of stability in the wall structure may be a major reason for the Ti leaching. The silica wall, with abundant silanol groups, favors the water adsorption, which promotes the hydrolysis of siloxane bonds to collapse the pore structure especially under hydrothermal conditions (Figures 11 and 13). The structural degradation then significantly disturbs the existing states of the Ti species. These loosened Ti species are then easily pulled out of the silica matrix by water or hydrogen peroxide. The Ti leaching of structurally stable Ti-SBA-15 is thus presumed to be mainly due to the first reason. On the other hand, Ti-MCM-41, having only thin walls and poor stability, is considered to lose its Ti species as a result of the above two reasons acting simultaneously. The Ti leaching of Ti-MCM-41 can only be prevented effectively after the structural stabilization by silylation. The present study suggests that Ti-containing mesoporous catalysts stable against Ti leaching can be prepared by choosing hydrothermally stable silica mesostructures to be adopted for the postsynthesis.

Conclusions

Ti-SBA-15 retaining its textural properties and containing tetrahedrally coordinated Ti species has been successfully prepared by the postsynthesis method using organic ammonium hydroxides as the promoting agent for Ti dispersion. The present method seems to be superior to the previous incipient-wetness impregnation and direct synthesis because of the achievement of anatase-free Ti incorporation. Ti-SBA-15 is verified to serve as an effective liquid-phase oxidation catalyst as is conventional Ti-MCM-41, and exhibits the advantages of enduring both the hydrothermal destruction of mesopores and the Ti leaching whether it is stabilized by trimethylsilylation or not. The present postsynthesis may be applicable to other mesoporous materials if direct incorporation of heteroatoms is impossible for them due to the severity of the synthesis conditions.

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