Preparation of Wormhole-like Mesoporous TiO_2 with an Extremely Large Surface Area and Stabilization of Its Surface by Chemical Vapor Deposition

Hideaki Yoshitake,[†] Tae Sugihara,[‡] and Takashi Tatsumi*[,‡]

Division of Physical Chemistry, Graduate School of Environment and Information Sciences, and Division of Materials Sciences and Chemical Engineering, Graduate School of Engineering, Yokohama National University

Received June 1, 2001. Revised Manuscript Received August 8, 2001

Mesoporous titania with BET surface area over 1200 m^2/g^{-1} was synthesized by primary amine templating. Dodecyl-, tetradecyl-, and hexadecylamines gave intense XRD patterns with narrow pore-size distributions in which the most probable diameter changed according to the carbon chain length. Thermal treatment was necessary for the formation of a stable structure, which strongly depends on the vapor pressure during the process. No diffraction patterns were observed above $2\theta = 10°$, suggesting the amorphous nature of the mesoporous titania. UV−vis and XANES spectroscopies demonstrated that the local structure of titanium was mainly 5-coordinated and O_h (6-coordinated) Ti. Chemical vapor deposition (CVD) of titanium isopropoxide followed by its decomposition with water vapor was carried out to improve the thermal stability of template-extracted titania. Although this CVD treatment resulted in a decrease in the BET surface area by 20%, the treated TiO_2 showed high thermal stability; surface areas higher than 500 m^2/g^{-1} were retained after calcination at 573 K for 24 h.

Introduction

There has been a great interest in mesoporous silicates with well-defined pore sizes and periodic structure, prepared by templating with surfactant and subsequent calcination. Amphiphilic template-directing methods discovered by Mobile researchers[1] originally employed quaternary ammonium salts. This method was soon adapted to syntheses of oxides of W,[2] V,[3] Mn,[4] and Hf,[5] because mesoporous transition metal oxides with ordered pore structures were expected to be useful for catalytic supports,[6] electronic materials,[7] and optical devices.[8] However, after the calcination to remove the template, these oxides lost their structural order and/or showed lower surface area than expected from that of corresponding mesoporous silica. More general synthetic strategies have been developed using a variety of templates, for example, phosphates,[9−12] sulfates,[11,12] carbonates,[11] primary amines,[13−16] and block copolymer surfactants.[17] Titanium dioxide is a material of interest for its many applications in, for example, photocatalysis and catalyst support. Although mesoporous titania was synthesized by a phosphate templating method, a significant amount of phosphorus remained after the calcination.[10] Antonelli has successfully synthesized phosphorus free mesoporous titania using primary amines.[13]

These surfactant templating syntheses provide, more or less, periodic structures of the mesopore connections with a uniform pore size in addition to large surface area and high surface reactivity. Although each characteristic is probably favorable for most of the applications, the necessary physical properties depend on particular applications. The effect of periodicity of mesostructure, for example, has not been yet investigated well in the applications of these oxides. Pinnavia has stated that

---

* To whom correspondence should be addressed at 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan. FAX: +81-45-339-3941. E-mail: ttatsumi@ynu.ac.jp.

[†] Division of Physical Chemistry, Graduate School of Environment and Information Sciences.

[‡] Division of Materials Sciences and Chemical Engineering, Graduate School of Engineering.

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

(2) Ciesla, U.; Demuth, D.; Leon, R.; Pertoff, P.; Stucky, G.; Unger, K.; Schüth, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1387.

(3) Luca, V.; MacLachlan, D. J.; Hook, J. M.; Withers, R. *Chem. Mater.* **1995**, *7*, 2220.

(4) Tian, Z. R.; Tong, W.; Wang, J. Y.; Duan, N. G.; Krishnan, V. V.; Suib, S. L. *Science* **1997**, *276*, 926.

(5) Liu, P.; Liu, J.; Sayari, A. *Chem. Commun.* **1997**, 577.

(6) Baker, R. T. K.; Tauster, S. J.; Dumesic, J. A. Eds. *Strong Metal-Support Interactions*; ACS Symposium series 298; American Chemical Society, Washington, DC, 1986.

(7) Vichi, F. M.; Tejedor-Tejedor, M. I.; Anderson, M. A. *Chem. Mater.* **2000**, *12*, 1762 and references therein.

(8) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.*, **1995**, *95*, 69 *and references therein.*

(9) Antenolli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2014.

(10) Stone, V. F.; Davis, R. J. *Chem. Mater.* **1998**, *10*, 1468.

(11) Wong, M. S.; Ying, J. Y. *Chem. Mater.* **1998**, *10*, 2067.

(12) Pacheco, G.; Zhao, E.; Farcia, A.; Sklyarov, A.; Fripiat, J. J. *J. Mater. Chem.* **1998**, *8*, 219; Zhao, E.; Hernandez, O.; Pacheco, G.; Hardcastle, S.; Fripiat, J. J. *J. Mater. Chem.*, **1998**, *8*, 1635.

(13) Antenolli, D. M. *Microporous Mesoporous Mater.* **1999**, *30*, 315.

(14) Antenolli, D. M.; Nakahira, A.; Ying, J. Y. *Inorg. Chem.* **1996**, *35*, 3126.

(15) Severin, K. G.; Abdel-Fattah, T. M.; Pinnavaia, T. J. *Chem. Commun.* **1998**, 1471.

(16) Antonelli, D. M.; Ying, J. Y. *Chem. Mater.* **1996**, *8*, 874.

(17) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature*, **1998**, *396*, 152; *Chem. Mater.* **1999**, *11*, 2813.

10.1021/cm010539b CCC: $22.00

silica with wormhole-like framework structures is a more active support than that having ordered hexagonal structure with a comparable uniformity in pore size distributions (e.g., MCM-41, SBA-1 and SBA-15).[18] In the design of the material, it is highly desirable to choose particular structural properties fitting the purpose. In this sense, exploration or optimization of the synthetic route is still necessary for mesoporous titania without incorporation of phosphorus.

In most cases, a large surface area is favorable. However, this is usually accompanied by high surface reactivity, and consequently, such materials lack thermal and chemical stabilities. BET surface area of mesoporous TiO_2 reached 710 m^2/g^{-1}, but its heat treatment in dry air at 623 K led the surface area to be reduced at ca. 50 $m^2\ g^{-1}/h$.[13] This instability in air will restrict its application.

Solid oxides with a large surface area are mostly porous materials. Titania synthesized without expensive templates has great potential for industrial applications. It might lack the structural order of the framework, which does not always mean inferiority to the more ordered ones. There are several reports on mesoporous titania that has comparable surface area and pore size distributions. A semicontinuous extraction of methanolic titania gel with supercritical CO_2 has resulted in titania with BET surface area of 623 m^2/g^{-1} and a narrow pore size distribution centered at 2.6 nm. After calcination at 623 K for 2 h, however, the surface area decreased to 325 m^2/g^{-1}.[19] For other templating synthesis, 1,2-diolates of Ti have been used as a precursor for synthesizing mesoporous titania with a BET surface area of ca. 300 m^2/g^{-1}.[20]

Titania directed with triblock copolymer template is composed of anatase phase. The surface area reaches at most ca. 200 m^2/g^{-1}.[17] When this kind of titania was used as a support of Pt fine particles ($H/Pt = 1.0$), it retained original XRD patterns and surface area, even after the reduction of the catalyst at 673 K brought about a clear suppression of hydrogen adsorption due to SMSI (strong metal−support interactions).[21] This result suggests that the instability at high temperature arises solely from the chemical properties of the wall surface.

It is well-known that pure mesoporous silica from the MCM family is not stable in a moist environment. The structure of MCM-48 and MCM-41 can be collapsed by mechanical compression through a hydrolysis of the Si−O−Si bond in the presence of adsorbed water.[22] Ryoo has also claimed that the structure of MCM-41 was lost upon boiling in water for 2 d due to silicate hydrolysis.[23] These phenomena are likely caused by defects and/or hydroxyl groups on the surface, which initiate the agglomeration of the particles. Trimethylsilylation of MCM-41 improved the stability to moisture and compression.[24] This is partly because the enhancement of hydrophobicity suppresses the concentration of water in the pore and, subsequently, the attachment of water on the surface. The other reason could be that masking of surface active sites by an inactive group ($-CH_3$) is effective to increasing the stability.

When partially oxidized cetyltrimethylammonium glycotitanate complex was treated with Si_2H_6, the enforcement of the mesostructure was achieved so that the template extraction was possible to give mesoporous TiO_2.[25] This method is suggestive of the stabilization of the mesoporous TiO_2 by masking the active site with inert surface species.

We report in this paper the results of the exploration of the synthetic procedures of primary amine-directed mesoporous titania regarding the structural order and surface area. Since the latter property is important in most applications, improvement of the stability by chemical vapor deposition of a Ti compound was carried out without significant loss of the BET surface area.

Experimental Section

Chemicals. Reagent grade decylamine ($C_{10}H_{21}NH_2$), dodecylamine ($C_{12}H_{25}NH_2$), tetradecylamine ($C_{14}H_{29}NH_2$), hexadecylamine ($C_{16}H_{33}NH_2$), and octadecylamine ($C_{18}H_{37}NH_2$) were purchased from Tokyo Kasei Kogyo Co., Ltd. Titanium tetraisopropoxide $Ti(O^iPr)_4$ (Cameleon Reagent, purity > 99%) and *p*-toluenesulfonic acid (Tokyo Kasei Kogyo Co., Ltd. purity > 99%) were also commercially available. These reagents were used as received without further purification.

Synthesis. A typical procedure is as follows. 40 g of water was added slowly to a mixture of titanium tetraisopropoxide (8.0 g) and dodecylamine (2.6 g) at 273 K. After the addition of 0.1 M HCl (1.6 cm^3), the mixture was allowed to stand overnight and transferred to a Teflon container in an oven at 333 K. After 4 d, the solution was filtered and washed with methanol and diethyl ether. The white solid collected was dried in an oven at 373 K for 1 d and transferred into a Pyrex test tube, which was evacuated at 453 K by a vacuum pump. After evacuation for 2 h, the tube was sealed. The powder in the tube was then heated at 453 K for 10 d, with the temperature at the other end being kept between 273 and 373 K. The resulting solid is denoted as **“**thermally treated.**”** This solid was treated with *p*-toluenesulfonic acid, to extract the template. The powder was then dried at 373 K for 2 h. No nitrogen was detected by elemental analysis after extraction.

Chemical Vapor Deposition. Chemical vapor deposition of titanium tetraisopropoxide was carried out in a Pyrex flow reactor. Pure argon passed through liquid $Ti(O^iPr)_4$ at 293 K was introduced to the tube containing the template-extracted powder kept at 353 K. After the deposition for 24 h, the gas was switched to nitrogen, which passed through water at 293 K. The decomposition of deposited titanium alkoxide was completed by water vapor for 12 h. Finally, the powder was treated in a dry air at 393 K for 2 h.

Characterization. X-ray diffraction (XRD) patterns of thermally treated and extracted powders were recorded using an XL Labo diffractometer (MAC Science Co., Ltd.) with Cu Kα radiation (40 kV and 20 mA). Nitrogen adsorption−desorption isotherms were recorded by BELSORP 28SA (BEL Japan Inc.) after the sample was treated at 473 K in vacuo. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to extracted TiO_2. Ultraviolet−visible (UV−vis) spectra were measured in a diffuse reflectance mode on a Varian DMS 300 spectrometer. X-ray absorption

---

(18) Kim, S.-S.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Commun.*, **2000**, 835.

(19) Dutoit, D. C. M.; Schneider, M.; Baiker, A. *J. Porous Mater.* **1995**, *1*, 165.

(20) Saadoun, L.; Ayllón, J. A.; Jiménez-Becerril, J.; Peral, J.; Domènech, X.; Rodríguez-Clemente, *Appl. Catal., B* **1999**, *21*, 269.

(21) Yoshitake, H.; Tatsumi; T. Unpublished data.

(22) Tatsumi, T.; Koyano, K. A.; Tanaka, Y.; Nakata, S. *Chem. Lett.* **1997**, 469.

(23) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.

(24) Koyano, K. A.; Tatsumi, T.; Tanaka, Y.; Nakata, S. *J. Phys. Chem., B* **1997**, *101*, 9436.

(25) Khushalani, D.: Ozin, G. A.; Kuperman, A. *J. Mater. Chem.* **1999**, *9*, 1491.

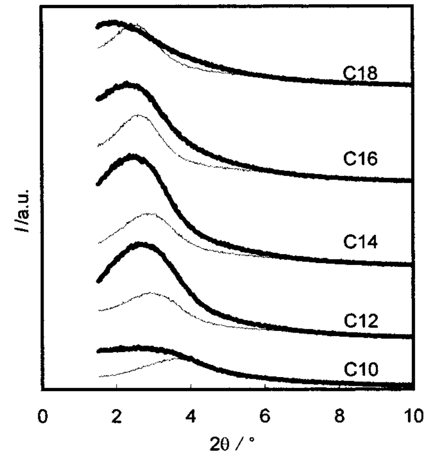

Figure 1. XRD patterns of thermally treated and extracted (bold lines) TiO_2 synthesized with (a) decyl-, (b) dodecyl-, (c) tetradecyl-, (d) hexadecyl-, and (e) octadecylamine in Ti/amine = 2.

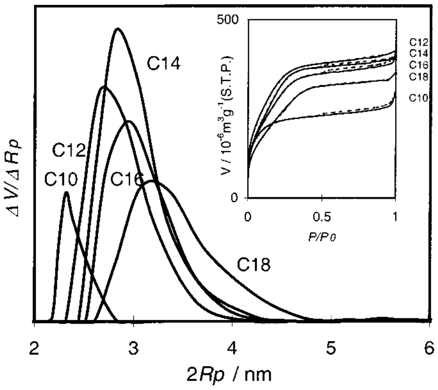

Figure 2. Nitrogen adsorption isotherms and BJH pore size distributions of TiO_2 synthesized with decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecylamine in Ti/amine = 2.

experiments were carried out at BL-9A of the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan (Proposal #2000G269), with a ring energy of 2.5 GeV and a stored current around 300−450 mA. Si(111) double-crystal monochromator was used. The incident X-ray was focused, and the higher harmonics were removed by the total reflection on a Rh−Ni composite mirror. The powder was diluted by boron nitride. A conventional transmission mode with detection by using gas ion chambers was employed. The measurement of each spectrum was completed within 30 min.

Results and Discussion

Optimization of Synthesis. Figures 1 and 2 show the results of X-ray diffraction and nitrogen adsorption/desorption, respectively, for the samples synthesized with various template amines. All C_{10}–C_{18} amines gave the XRD peaks between 2° and 4° for both thermally treated and extracted TiO_2, which are shifted according to the chain length. Dodecyl-, tetradecyl-, and hexadecylamines produced samples showing an intense peak after template extractions. Poorly resolved peaks were observed at $2\theta = 4°-6°$ for some thermally treated powders directed by C_{12}, C_{14}, and C_{16} amines. From these peaks, we could not determine the specific point group to which the structure belongs. The nitrogen adsorption/desorption isotherms (Figure 2, inset) showed virtually no hysteresis and a gradual increase around $P/P_0 = 0.4$, which corresponded to a reversible IV type isotherm in IUPAC nomenclature, indicating uniform mesopores. Pore size distributions were relatively narrow, and the most probable pore diameter slightly increased with the carbon chain length. This shifting tendency is much more clearly correlated with the carbon chain length than that of XRD patterns. The structural parameters deduced from XRD and nitrogen sorption experiments are summarized in Table 1. Assuming an increase of molecular length of 0.26 nm upon adding a $-CH_2CH_2-$ chain unit to an amine, as well as the constant aggregation number, the diameter of the micelle could be enlarged by 0.52 nm, if all the conformations were trans. In the actual hydrated titanium−amine complex micelles in aqueous solution, the addition of an ethylene unit is not reflected by the dynamic length of the chain that determines the diameter of the micelle and, as a result, the size of mesopores. In the series of the same kind of surfactants, an increase in of the carbon number likely results in the linear increase in the dynamic length. It is not true for the series of pore sizes of amine-templated TiO_2. The differences between C_{10} and C_{12} and between C_{16} and C_{18} were large, 0.33 and 0.41 nm, respectively, while those among C_{12}, C_{14}, and C_{16} were small, 0.16 and 0.15 nm. This suggests that the interaction that stabilizes the coordinated complex is effective in a particular range of the size of the micelle. In other words, the primary amine templating method likely stabilizes mesoporous titania of a particular size; their pores are ca. 2.6−3 nm. This is consistent with weak diffraction patterns for C_{10} and C_{18} amines (Figure 1).

Table 1. *d* Spacing, Surface Area, Pore Size, and Pore Volume of Mesoporous Titania

amine	Ti/amine	T, K	$P(H_2O)$, kPa	d, nm	S_{BET}, $m^2\ g^{-1}$	2Rp, nm	Vp, $m^2\ g^{-1}$
C_{10}	2	453	0	2.62	608	2.32	0.348
C_{12}	2	453	0	3.11	1139	2.65	0.527
C_{14}	2	453	0	3.59	1033	2.81	0.559
C_{16}	2	453	0	3.74	942	2.96	0.542
C_{18}	2	453	0	4.02	812	3.37	0.498
C_{16}	1.5	453	0	*a*	881	2.98	0.539
C_{16}	2	453	0	3.56	942	2.96	0.542
C_{16}	3	453	0	2.94	1230	2.78	0.558
C_{16}	4	453	0	2.76	967	2.60	0.475
C_{12}	2	433	0	*a*	185	2.28	0.072
C_{12}	2	453	0	3.11	1139	2.65	0.527
C_{12}	2	473	0	*a*	557	2.82	0.290
C_{12}	2	493	0	*a*	858	2.82	0.446
C_{12}	2	453	0	3.11	1139	2.65	0.527
C_{12}	2	453	0.61	3.11	1256	2.92	0.653
C_{12}	2	453	3.33	3.11	1150	3.06	0.550
C_{12}	2	453	19.9	3.11	1158	2.98	0.572
C_{12}	2	453	101	*a*	154	5.86	0.071

[a] Diffraction peaks were too broad to determine the position.

Whenever the Ti/hexadecylamine ratio in the mixture varied, thermally treated sample had a clear single peak in XRD around $2\theta = 2.75°$. We found no difference in the peak position, intensity, and width in the Ti/amine ratio range between 1.5 and 4. Nevertheless, the intensities were remarkably reduced after the extraction except for Ti/amine = 2. It is to be noted that the Ti/amine ratio is not critical for the formation of the mesostructure but is for the stability of the self-standing wall of titania. A slight surface area variation was observed, as shown in Table 1.

The template extraction of the sample after hydrothermally synthesized for 1 d resulted in no peaks in

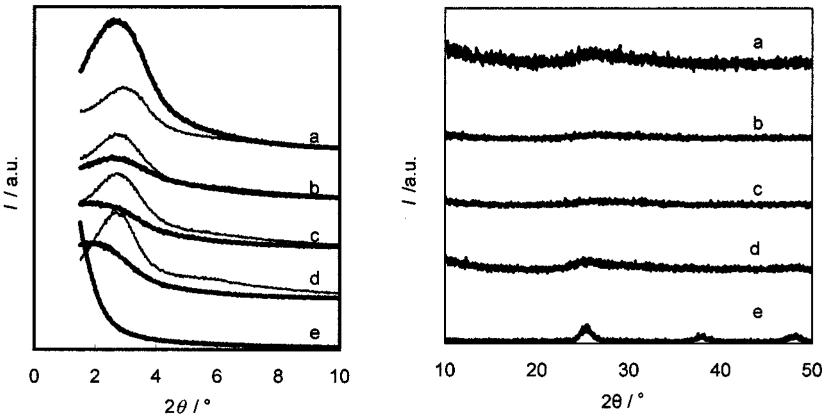

Figure 3. XRD patterns of TiO_2 synthesized by thermal treatment with water at (a) 0, (b) 0.61, (c) 3.33, (d) 19.9, and (e) 101 kPa. Thin lines, after thermal treatment (thermally treated); bold lines, after extraction of dodecylamine template (extracted).

the XRD patterns. This is probably due to the incomplete condensation of TiO_2. A postheat treatment for condensation in the presence of the template was first proposed by Ying and Antonelli.[16] We have investigated the effect of heating temperature and vapor pressure of water. The results are listed in Table 1. Upon varying the temperature from 453 to 493 K, no differences in XRD patterns were found for thermally treated powders, where a single peak appeared around $2\theta = 3^\circ$. On the other hand, except for $T = 453$ K, the peaks almost disappeared after extraction. Despite the destruction of the meso periodicity, BET surface area remained high ($S_{BET} = 557$ or 858 m^2/g^{-1} for $T = 473$ or 493 K, respectively) and the pore size did not change considerably. The treatment at 433 K gave a material with no diffraction peaks and a surface area obviously smaller than that at the other temperatures.

During thermal treatment, water is generated from the TiO_2–template complex, suggesting the dehydration of titanium hydrate. This water vapor could have an effect on the mesoporous structure of the resulting TiO_2. At first, we simply evacuated a test tube containing the hydrothermally synthesized powder at room temperature and then sealed and heated it up to 453 K in an oven. In this procedure, about half of the tubes exploded before the condensation reaction completed. This is certainly because of the rise of vapor pressure in the tubes. To avoid such damage, we heated the powder in a sealed tube while keeping the vapor pressure constant by controlling the temperature of the liquid water generated during this treatment. Only for $P(H_2O) = 0$ kPa was the tube continuously evacuated. The diffraction patterns changed according to the vapor pressure, as shown in Figure 3. At $P(H_2O) = 101$ kPa, no diffraction was obtained below 4°, before and after removal of the template, while peaks attributed to anatase were observed ($2\theta = 25.5^\circ$, 38.1°, and 48.1°). The product obtained at $P(H_2O) = 19.9$ kPa showed a narrower diffraction pattern than any other products, which is comparable to that reported in ref 13, where a hexagonal structure was proposed. The completely dry environment gave the strongest diffraction after extracting amine. Nitrogen adsorption/desorption isotherms in Figure 4 were almost the same except for $P(H_2O) = 101$ kPa, indicating that the surface area and pore size distributions are not sensitive to the vapor pressure below 20 kPa.

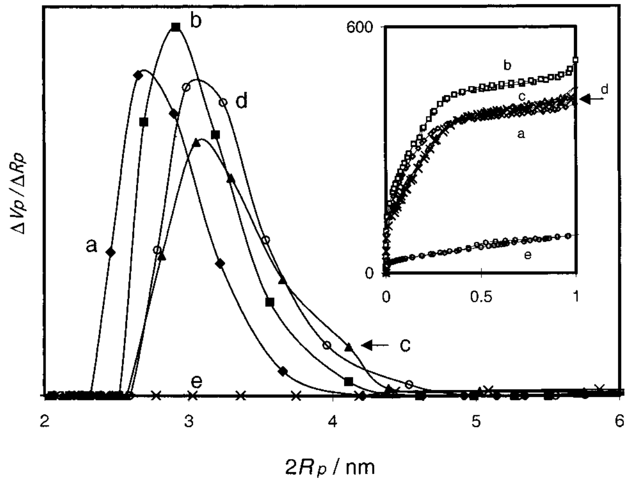

Figure 4. Nitrogen adsorption isotherms and BJH pore size distributions of TiO_2 synthesized by heat treatment with water at (a) 0, (b) 0.61, (c) 3.33, (d) 19.9, and (e) 101 kPa. Broken lines, after thermal treatment (thermally treated); full lines, after extraction of dodecylamine template (extracted).

The composition of the powder treated at $P(H_2O) = 0$ kPa was N/Ti = 0.15. This is lower than those in the literature: 0.36 in ref 13 and 0.4 in ref 26. (In ref 13, dodecylamine was used and there is no information on controlling $P(H_2O)$. In ref 26, decylamine or hexadecylamine was employed, and the authors did not carry out any heat treatment). In sealed tubes, we obtained the material with N/Ti = 0.35. This suggests that the loss of nitrogen was caused by vaporization during the continuous evacuation. Considering that the condition of $P(H_2O) = 0$ kPa is suitable to obtain a high surface area material, coordination stoichiometry at amine/Ti = 0.15 is enough to form the well-structured stable framework.

Despite the extremely high surface area obtained after extraction of the template, to the best of our knowledge, the highest area ever reported, XRD charts could not elucidate a particular point group of the mesostructure; the degree of structural order is lower than those for pure silica MCM-41 (*p*6*m*) and MCM-48 (*Ia*3*d*). This is consistent with TEM and SEM photographs (Figure 5). The distribution of pores in the image is irregular, but each pore retains a certain distance

---

(26) Ulagappan, N.; Rao, C. N. R. *Chem. Commun.* **1996**, 1685.

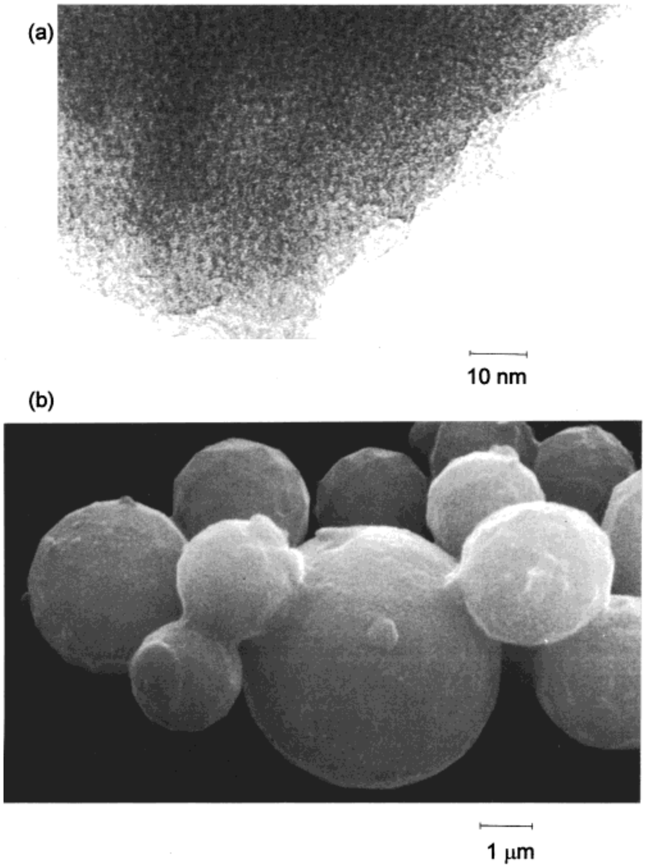

Figure 5. (a) Transmission electron microscopic and (b) scanning electron microscopic images of mesoporous TiO_2 synthesized with dodecylamine template.

from the others. A typical particle in SEM photograph was roughly spherical in shape. With careful observation, it seems composed basically of 54 faces that are obtainable after cutting off all edges of a cube by 24 planes equally inclined to the six planes of the original cube. The crystallite of this shape is hardly generated in the course of the growth of the hexagonal structure. Cubic symmetry is more likely. The same kinds of SEM images were observed in SBA-1 (*pm*3*n*) prepared under various conditions.[27] Since the diffraction patterns were not resolved enough to determine the point group, we conclude that the primary amine templates directed titania into a wormhole-like structure, which is not inconsistent with the XRD patterns in the literature.[13,26]

Recently, mesoporous titanium dioxide has been prepared from a titanatrane derivative compound, using cetyltrimethylammonium bromide as well as a hydrolysis retarding agent.[28] BET surface area reached 606 m^2/g^{-1} and a pore diameter centered at 3.5 nm. It has been also reported that an ultrasound-irradiation-enhanced extraction of amine templates gave a high surface area of 853 m^2/g^{-1} with the pore size of 1.5 nm.[29] But the area decreased 467 m^2/g^{-1} after calcination at 623 K for 8 h. These authors have claimed, from XRD and TEM results, that the mesostructure of titania they obtained was wormhole-like.

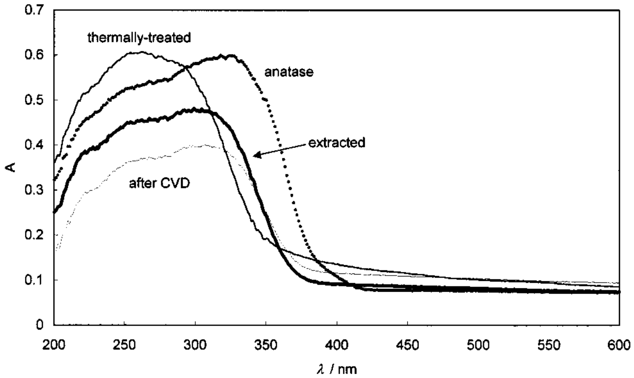

Figure 6. UV–visible spectra of thermally treated and extracted TiO_2. Absorptions of anatase and sample after CVD are shown for comparison.

If the *p*6*m* structure is assumed, wall thickness would be 0.94 nm for a typical sample we synthesized with 2Rp = 2.65 nm and *d* spacing = 3.11 nm. This thickness corresponds to a few atomic layers. On the rutile(110) surface, which is the most frequently studied single-crystal surface of titania, 5-coordinated Ti^{4+} makes lines along with [001] in separating each other by 0.295 nm, and the queues of oxygen atoms on the 6-coordinated Ti^{4+} situate among them.[31] The surface area of rutile-(110), an imaginary solid, is easily calculated with these structural data, i.e., $S = 1440$ m^2/g^{-1}. The BET surface area achieved in Table 1 ranged up to 1256 m^2/g^{-1}, 87% of the theoretical area of “all surface solid”. This is larger than expected from the wall thickness calculated from the *d* spacing and the pore size. This discrepancy can be explained by the nitrogen condensation often observed in the porous materials.

Spectroscopic Characterization. The known bulk structures of titanium oxides, such as rutile, anatase, and brookite, were not detected by XRD except for the extracted TiO_2 thermally treated at $P(H_2O) = 101$ kPa (Figure 3), which had a low BET area as shown in the bottom of Table 1. There are no observable diffraction peaks at $2\theta > 8°$. It is, consequently, concluded that mesoporous titania synthesized in this study has an amorphous nature.

We have carried out UV–vis diffuse reflectance and XANES spectroscopies in order to further investigate the local structure of the TiO_n unit that forms an amorphous solid. UV–vis spectra of thermally treated and extracted titania synthesized with dodecylamine are shown in Figure 6. The absorption occurred at 220, 255, and 305 nm for thermally treated powder, while the extracted samples showed peaks at 220, 255, and 320 nm. After extraction, the last peak shifted to lower energy. In addition to the three absorptions, extracted titania showed an intense band at 335 nm ascribed to anatase. From the spectra of titanosilicates, the bands around 220, 250, and 320 are assigned to a tetrahedral isolated TiO_4 unit, octahedral isolated TiO_6 unit, and octahedral aggregated TiO_2, respectively.[31] While the extracted TiO_2 in Figure 6 composed of all these absorptions, the absence of the band at 335 nm in thermally treated sample suggests that O_h TiO_6 units

---

(27) Che, S.; Tatsumi, T *Chem. Mater.* In press.

(28) Wang, Y.; Tang, X.; Yin, L.; Huang, W.; Hacohen, Y. R.; Gedanken, A. *Adv. Mater.* **2000**, *12*, 1183.

(29) Cabrea, S.; E.Haskouri, J.; Beltrán-Porter, A.; Beltrán-Porter, D.; Marcos, M. D.; Amorós, P. *Solid State Sci.* **2000**, *2*, 513.

(30) Onishi, H.; Iwasawa, Y. *Surf. Sci. Lett.* **1994**, *313*, L783.

(31) Blasco, T.; Camblor, M. A.; Corma, A.; Esteve, P.; Guil, J. M.; Martínez, A.; Perdigón-Melón, J. A.; Vaencia, S. *J. Phys. Chem., B* **1998**, *102*, 75. and references therein.

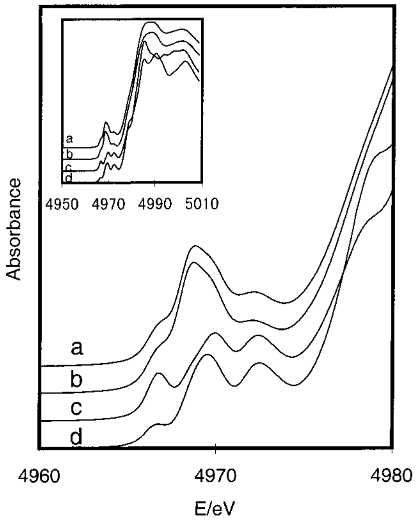

Figure 7. Preedge region of Ti K-edge X-ray absorption spectra: (a) extracted TiO_2, (b) thermally treated TiO_2, (c) anatase, and (d) rutile.

are not as tightly bound as that in anatase, and the size of clusters where the valence orbitals interact one another is small enough to make a clear difference in the O_h species. Before extracting the template, the peak for isolated O_h Ti at 250 nm is more intense than that for O_h Ti of aggregated TiO_2 around 305 nm. On the other hand, the peak at 320 nm is stronger than that at 250 nm after the template extraction. The change in the population of these species upon removing the template suggests that the TiO_6 structure is distorted in TiO_2−template complex and that the acid extraction and successive drying in air relax the structure into a thermodynamically more stable bonding state. This agrees well with the observation in XRD charts (Figures 1 and 3), where the *d* spacing increased after extraction (a shift to lower angle). This is completely different from the removal by calcination, which are accompanied by dehydration and consequent shrinkage of the lattice.

Tetrahedral TiO_4 has been thought to be important to catalytic applications because it is attributed to the active center of many oxidation reactions. We found, however, no evidence in UV−vis spectra that indicated a large population of T_d TiO_4 units in the samples.

Characteristic preedge absorptions were observed in Ti K-edge XANES spectra, as shown in Figure 7. Three small and partially resolved peaks were observed in anatase and rutile, which agreed with the spectra in the literature.[32−34] It is widely known that an s−d transition is forbidden by dipole selection rules but, when the p−d orbital mixing occurs in an absorbing site, the transition becomes allowed. The height and position in the preedge feature depend on the degree of p−d mixing as well as the oxidation state. In the experimental evaluation of the local symmetry of TiO_n, both of the position and intensity of absorption on the chart are important as well as the optics applied for spectral measurements.[33,34] The normalizations of the position and the intensity of the 1s−3d transitions with those of anatase are, therefore, necessary to compare these spectra with the literature. First we calibrated the concentration of Ti by using the height of the inflection points. The intensities (in arbitrary unit) of main preedge peaks of anatase and rutile were 0.0872 at 4968.9 eV and 0.115 at 4968.5 eV, respectively. Thermally treated and extracted powders had a large peak at 4967.9 eV, accompanied by a shoulder peak around 4968.5 eV. Their intensities are 0.232 and 0.185 for thermally treated and extracted samples, respectively. Taken the position (=0 eV) and intensity (=1) for anatase as a standard, the red shift by 1 eV and intensity of 2.66 and 2.12 (for thermally treated and extracted samples, respectively) were deduced, suggesting 5-coordinated Ti, just as in $Na_2Ti_4O_9$, $K_2Ti_4O_9$, and $Rb_2Ti_4O_9$.[33] The shoulder peaks appearing at the same position of the main peak of anatase and rutile demonstrate that the amount of 6-coordinated Ti is not negligible in these amorphous TiO_2.

Since no proper method has been developed for evaluating the population of 4-, 5-, and 6-fold coordinated Ti by using the intensity of the 1s−3d transitions, no conclusion can be drawn on their composition. It is clear, however, that a significant amount of 5-coordinated Ti is included in those bulk titania. Further structural analysis by EXAFS is now underway.

Enhancement of Stability by CVD. It is generally considered that the densities of −OH terminals reach more than 10% in MCM-41. These sites often act as active sites in catalyses but in turn cause a destruction of the surface structure. In addition to the same kind of preparation resulting in an amorphous nature, the wall thickness of mesoporous TiO_2 in this study is extremely low and, consequently, the instability of the framework structure is likely. Curing the defect sites will decrease the chemical activity of the surface and, consequently, the rate of collapse of the structure. If the inactivation process produces only titania, the chemical identity of the mesoporous titania will be retained. For these reasons mesoporous titania, after extraction of the amine template, was exposed to a vapor of titanium tetraisopropoxide followed by hydrolysis and removal of water (CVD treatment). The UV spectrum of thus treated samples was completely the same as that of the extracted one, as shown in Figure 6.

The improvement of the stability is evaluated by the calcination at 573 K in air. Figure 8 shows the change in the pore size upon the calcination of the untreated and treated samples. The distribution did not shift, but the pore volume decreased by CVD. The calcination increased the mean pore diameter, regardless of the CVD treatment; the pore volume decreased, accompanied by the enlargement of the pore size and the half-width. The structural parameters determined by N_2 adsorption experiments are listed in Table 2. BET surface area was also decreased by CVD, from 1139 to 890 m^2/g^{-1}. Part of the area loss is probably due to the reaction of residual −OH and defects during the water vapor treatment. On calcination in air, the rate of decrease of the surface area of CVD-treated TiO_2 is clearly smaller, reduced to ca. 40%, than that without CVD treatment; the loss of the BET surface area by CVD was compensated within 5 h. We measured XRD patterns of all the calcined samples. The growth of peaks

---

(32) Asakura, K.; Inukai, J.; Iwasawa, Y. *J. Phys. Chem.* **1992**, *96*, 829.

(33) Farges, F.; Brown Jr., G. E.; Rehr, J. J. *Geochim. Cosmochim. Acta* **1996**, *60*, 3023.

(34) Farges, F.; Brown Jr., G. E.; Navrotsky, A.; Gan, H.; Rehr, J. J. *Geochim. Cosmochim. Acta* **1996**, *60*, 3039.

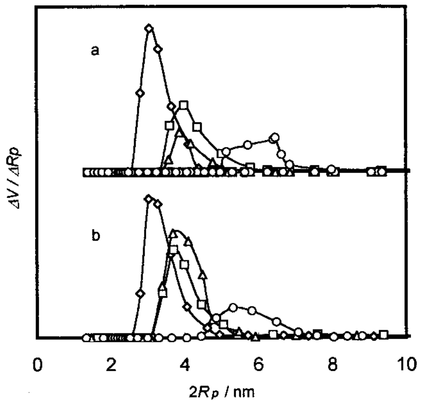

Figure 8. BJH Pore size distributions in the course of calcination at 573 K for (◇) 0 h, (□) 5 h, (△) 12 h, and (○) 24 h, (a) without CVD treatment and (b) with CVD treatment of extracted TiO_2.

Table 2. *d* Spacing, Surface Area, Pore Size, and Pore Volume of Mesoporous Titania in the Course of a Calcination Test at 573 K

	$t_{calcination}$, h	*d*, nm	S_{BET}, $m^2\ g^{-1}$	2Rp, nm	Vp, $m^2\ g^{-1}$
CVD-treated TiO_2	0	3.30	890	3.03	0.452
	5	3.16	725	3.68	0.367
	12	2.97	563	3.70	0.302
	24	2.76	518	5.31	0.301
untreated TiO_2	0	3.11	1150	3.06	0.550
	5	2.97	474	3.99	0.363
	12	2.72	384	3.96	0.306
	24		210	6.46	0.279

was observed at $2\theta = 25.2°$, 38.0°, and 47.9°, which were the marker diffractions of anatase, and the rate of the growth was smaller in the powders with CVD. On the other hand, the decreasing rate of the diffraction intensity around $2\theta = 2.8°$, the peak characteristic of mesostructure, was higher in sample not exposed to CVD. This demonstrates that masking by Ti oxide through CVD was effective in retarding the surface area reduction and mesostructure degradation accompanied by the crystallization of the wall. For both samples, the peak positions curiously shifted to larger angle in the course of the calcination; for example, in the calcination of the CVD sample, the peak at 2.7° at the beginning shifted to 3.0° by 12 h. At 24 h, the peak of the sample without CVD almost disappeared, while that with CVD was still observed. Simultaneous occurrence of pore size enlargement and *d* spacing reduction can be explained by the destruction of the wall and the connection of the neighboring pores. This could bring about the decrease of the surface area.

The above results demonstrate that CVD of titanium tetraisopropoxide stabilizes the order of the mesostructure, surface area, and pore volume, without significantly affecting the mesopore structure and chemical composition at the surface. This method will be applicable to various mesoporous oxides that have an extremely large surface area and lack crystallinity of the wall.

Conclusions

Mesoporous titania was synthesized by templating primary amines. Dodecyl-, tetradecyl-, and hexadecylamines showed intense XRD patterns, and the pore size changes according to the number of carbons in the template molecule. In the thermal treatment after hydrolysis of titanium isopropoxide, the structure of the resulting powder depended on the vapor pressure during the process. XRD, TEM, and SEM results demonstrated that the wall did not crystallize and it was likely that the mesostructure after template extraction was wormhole-like. A BET surface area above 1200 m^2/g^{-1} was achieved. The local structure of titanium was mainly 5-fold and 6-coordinated Ti, which was confirmed by UV−vis and XANES spectroscopies. Deposition and successive decomposition of titanium isopropoxide was carried out on TiO_2 after extraction of the template. Although this CVD treatment reduced 20% of the BET surface area, it clearly improved thermal stability in air without changing the chemical composition.

Acknowledgment. Financial support from Tokuyama Science Foundation is gratefully acknowledged.

CM010539B