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Preparation and Formation Mechanism of Mesoporous Titania Particles Having Crystalline Wall

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Mesoporous titania particles having anatase-type crystalline wall were prepared using a low-temperature crystallization technique. Crystalline mesoporous titania was obtained through the sol−gel process of titanium oxysulfate sulfuric acid hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) at 333 K in the presence of cetyltrimethylammonium bromide (C16TAB), a cationic surfactant. The mesoporous titania with hexagonal structure was formed according to the following mechanism. Nuclei of ultrafine titanium hydroxide oxide ($TiO(OH)_2$) were formed from $TiOSO_4$ on the periphery of the surface of cationic C16TAB micelles at the primary stage of sol−gel reaction. Then, heat treatment at 333 K induced the transformation of the particle wall from $TiO(OH)_2$ to anatase nanocrystal, which resulted in the formation of mesoporous titania with a crystalline wall. Moreover, the presence of bromide ion (Br^-), the counterion of C16TAB, was shown to suppress the collapse of mesostructure by retarding the transition from anatase to rutile.

Introduction

Mesoporous materials[1−6] prepared using molecular assemblies of surfactant as template have a highly ordered pore structure with a high specific surface area and have gathered increasing attention because of their possible application as adsorbent, catalyst, and separatory material. Although the wall of mesoporous materials is desired to have a crystalline structure when these materials are used as catalyst, it is generally amorphous and the crystallization by calcination results in the collapse of the uniform mesopore structure. Then, various methods have been prepared to provide mesoporous materials with a crystalline wall. Inagaki et al. reported the preparation of mesoporous organic−silica hybrid particles with a crystalline wall using organic−inorganic hybrid molecules as silica precursor.[7,8] Domen et al. showed that the calcination after coating the inner wall of amorphous mesoporous materials with carbon could cause crystallization without collapse of the mesopore structure.[9] However, the methods mentioned so far need a very complicated process in comparison with the synthesis of amorphous mesoporous materials. Ozin et al. indicated that the mesoporous titania thin *film* having anatase wall was prepared using triblock co polymer as template materials.[10−12] However, there is no report that describes the preparation of mesoporous titania "*particles*" having crystalline wall using cationic surfactant as template material.

Meanwhile, we have recently succeeded in the direct synthesis of mesoporous titania particles having an anatase-type nanocrystalline wall by applying a low-temperature crystallization technique.[13] Crystalline mesoporous titania was obtained through the sol−gel process of titanium oxysulfate sulfuric acid at 333 K in the presence of cetyltrimethylammonium bromide, a cationic surfactant. No detailed work has been done, however, on the effect of reaction conditions, the molecular structure of titania precursor, and surfactant upon the formation of mesoporous crystalline titania. The present work aims at preparing of mesoporous titania particles having a crystalline wall using various titania precursors and cationic surfactants and elucidating their formation mechanism.

Experimental Section

Materials. Cethyltrimethylammonium bromide (C16TAB) (Aldrich) was used as template material for mesopore formation. Alkyltrimethylammonium bromides ($C_nH_{2n+1}N(CH_3)_3Br$; C*n*TAB,

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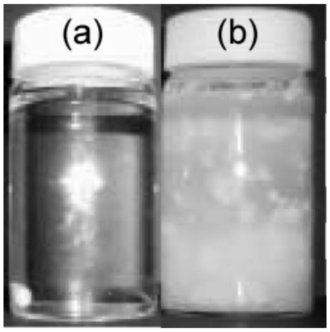

Figure 1. Photographs of the aqueous solutions just after mixing C16TAB and titania precursors, (a) $TiCl_4$ and (b) $TiOSO_4$, at room temperature.

where *n* denotes the number of carbon atoms in the alkyl chain; Tokyo Kasei Kogyo Co. Ltd.) were also used as template material to examine the effect of alkyl chain length on titania particle formation. Titanium oxysulfate sulfuric acid hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) (Aldrich) and titanium(IV) chloride ($TiCl_4$) (Wako Pure Chemical Industries) were used as titania precursor. Potassium bromide (KBr) (Wako) was used as salt to examine the effect of halogen ion concentration and ionic strength on the pore and crystalline structure of titania obtained.

Preparation of Titania Particles. Titania particles were prepared in the following way. A 3 M amount of $TiOSO_4$ aqueous solution and 60 mM alkyltrimethylammonium bromide solution were mixed at room temperature, and the mixture was stirred at 333 K for various length of time. Then, the particles obtained were filtered, washed with ultrapure water, and dried at 393 K for 10 h. The same procedures were performed to prepare titania particles using 3 M $TiCl_4$ aqueous solution, instead of $TiOSO_4$ solution.

Evaluation of Characteristics of Mesoporous Titania. The pore and crystal structure of the titania−surfactant composite particles obtained were respectively evaluated through low- and wide-angle X-ray diffraction (XRD) measurements (Philips, X′pert-MPD Cu Kα radiation). The effect of the chain length of alkyltrimethylammonium bromide on titania particle formation was investigated by turbidimetry on the mixture of $TiOSO_4$ and tetramethylammonium bromide (C1TAB) or *n*-hexyltrimethylammonium bromide (C6TAB) after being stirred for various hours at room temperature.

Results and Discussion

Effect of Titania Precursor on the Structural Properties of Particles Obtained. Figure 1 shows photographs of the mixtures just after 3 M titania precursors and 60 mM C16TAB aqueous solution were mixed at room temperature. While the solution prepared using $TiCl_4$ was colorless and transparent (Figure 1a), titania particles were rapidly formed when $TiOSO_4$ was used (Figure 1b). Figure 2 shows the XRD patterns of titania particles formed. The low-angle XRD pattern (Figure 2a) had three diffraction peaks ($2\theta = 2.2$, 3.8, and 4.2°) assigned to the hexagonal structure of mesoporous materials. The distance between pores estimated using Bragg's equation was 4 nm. This distance almost coincided with that for mesoporous silica and titania having a hexagonal structure reported so far.[13−15]

Figure 2b shows the wide-angle diffraction pattern of these titania particles. The pattern exhibited none of the peaks assigned to the titania crystalline structure, which suggest that the wall of mesoporous titania obtained was amorphous. Titanium hydroxide oxide ($TiO(OH)_2$) that is insoluble in water was formed by the hydrolysis of $TiOSO_4$. The presence of a quaternary ammonium group, the hydrophilic group of C16TAB, was suggested to promote this reaction. Thus, $TiO(OH)_2$ was formed on the surface of C16TAB molecular assemblies in the position-selective $TiOSO_4$ hydrolysis. Hexagonal-type mesoporous particles composed of aggregated fine $TiO(OH)_2$ particles were formed because C16TAB formed hexagonal liquid crystals through the interaction between $TiOSO_4$ and C16TAB. A milky solution was observed when $TiOSO_4$ and C16TAB solutions were mixed, whereas a transparent solution was obtained when $TiCl_4$ and C16TAB solutions were mixed because the presence of C16TAB was unable to promote hydrolysis of $TiCl_4$.

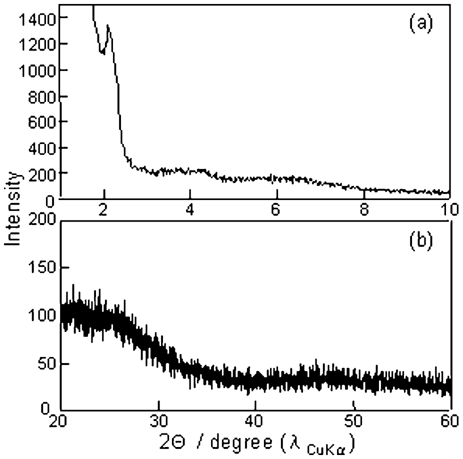

Figure 2. (a) Low- and (b) wide-angle X-ray diffraction (XRD) patterns of titania particles just after mixing C16TAB and $TiOSO_4$ solutions at room temperature.

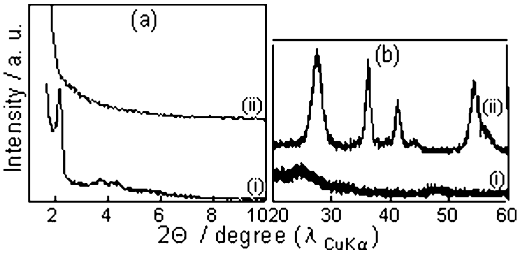

Figure 3. (a) Low- and (b) wide-angle XRD patterns of titania particles prepared using various titania precursors at 333 K, (i) $TiOSO_4$ and (ii) $TiCl_4$.

Figure 3 shows the XRD patterns of titania particles after the system was stirred at 333 K for 24 h. The low-angle XRD pattern of the particles prepared using $TiOSO_4$ as titania precursor (Figure 3a(i)) had three sharp diffraction peaks assigned to the regularity of hexagonal pore structure, while the particles synthesized using $TiCl_4$ showed no diffraction peaks which are characteristic of mesoporous structure (Figure 3a(ii)). Figure 3b shows the wide-angle diffraction patterns of titania particles. The XRD pattern of the particles synthesized using $TiOSO_4$ exhibited three peaks around $2\theta = 25$, 48, and 55°, which are characteristic of anatase-type titania, while that of those synthesized using $TiCl_4$ had peaks assigned to rutile-type titnia. These findings strongly suggest that mesoporous titania particles having an anatase crystalline

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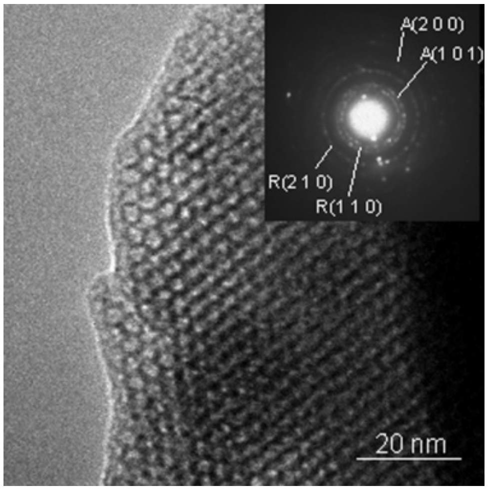

Figure 4. Typical transmission electron microscope (TEM) image and electron diffraction (ED) pattern (inset) of crystalline mesoporous titania after calcination at 723 K for 2 h. A and R in the ED pattern represent anatase and rutile, respectively.

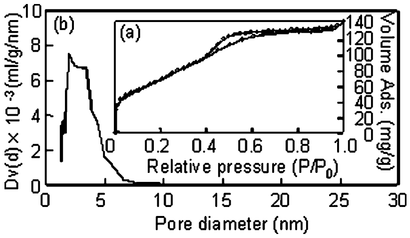

Figure 5. (a) N_2 adsorption and desorption isotherms and (b) pore size distribution of the obtained titania particles after calcination 723 K for 2 h.

wall are obtained at 333 K only when $TiOSO_4$ is used as titania precursor.

Figure 4 shows a typical transmission electron microscopic (TEM) image and the electron diffraction pattern (Figure 4 inset) of mesoporous titania particles prepared using $TiOSO_4$ and calcined at 723 K for 2 h. This sample kept a uniform honeycomb structure even after calcination, and the ED pattern shows that the wall of the honeycomb structure is made of a mixture of anatase- and rutile-type crystal structures. Although mesoporous titania particles with amorphous wall lost their regular honeycomb structure after crystallization by calcination at 723 K for 2 h, the crystalline particles synthesized at 333 K maintained their hexagonal structure even after calcination for removal of surfactant. These results confirmed that the wall of the mesoporous powders synthesized at 333 K has an anatase crystalline wall. Nitrogen adsorption measurements for the particles revealed that the adsorption and desorption isotherms exhibit a behavior which are characteristic of solids with mesopores (type IV, S-shaped isotherm) (Figure 5a) and show a hysteresis phenomenon that suggests the presence of cylindrical pores.[16] Estimation of specific surface area and pore size distribution showed that particles have a large specific surface area of 262.25 m^2/g and pores with sizes around 3 nm (Figure 5b), a value identical with the interpore distance calculated using Bragg's equation for the uncalcined titania particles. These results mentioned so far confirmed the successful preparation of "crystalline" mesoporous titania particles with regularly hexagonal pore structure when the sol−gel reaction of $TiOSO_4$ was performed at 333 K for an appropriate time length. The following experiments for investigating the formation mechanism of crystalline mesoporous titania were carried out using $TiOSO_4$ as titania precursor.

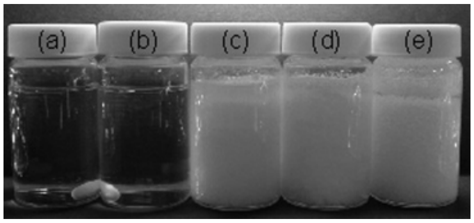

Figure 6. Photographs of aqueous solutions just after mixing aqueous solution of 3 M $TiOSO_4$ with solutions of quaternary ammonium bromides having different alkyl chain lengths. Panels a−e are for C1TAB, C6TAB, C12TAB, C14TAB, and C16TAB, respectively.

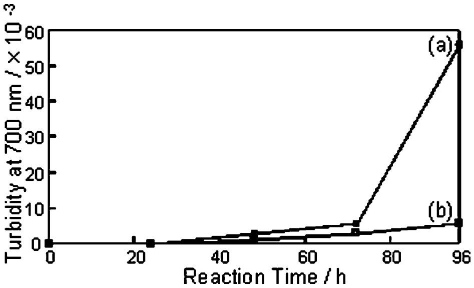

Figure 7. Changes in the turbidity of aqueous mixed solutions of $TiOSO_4$ with (a) C6TAB or (b) C1TAB.

Effect of Alkyl Chain Length of Alkyltrimethylammonium Bromide on the Formation of Titania Particles. The effect of the alkyl chain length of alkyltrimethylammonium bromides on the formation of titania particles was studied using mixtures of aqueous solutions of 3 M $TiOSO_4$ and alkyltrimethylammonium bromides having different alkyl chain lengths. Figure 6 shows photographs of the mixtures right after 3 M titania precursor and 60 mM alkyltrimethylammonium bromide aqueous solutions were mixed at room temperature. Solutions prepared using C1TAB (Figure 6a) and C6TAB (Figure 6b) were colorless and transparent, while particles were rapidly formed when C*n*TAB ($n \geq 12$) were used (Figure 6c−e). The turbidity of the mixture of $TiOSO_4$ and C16TAB decreased with decreasing C16TAB concentration. These findings suggest that the amount of surfactant affects particle formation and titania particle formation needs the presence of surfactant molecular assemblies.

In addition, the rate of particle formation was turbidimetrically investigated when C6TAB and C1TAB were used (Figure 7). The increasing rate in turbidity was faster for C6TAB (Figure 7a) than for C1TAB (Figure 7b). Micelle catalyst usually has a high catalytic activity that increases with increasing alkyl chain length because an increase in the chain length leads to increasing the surface charge density of micelles. Since micelles were formed and their surface charge density was high for alkyltrimethylammonium bromides having longer alkyl chain length (CnTAB; $n \geq 12$) in the present work, the surface of micelles was suggested to work as catalyst and this function promoted $TiO(OH)_2$ formation.

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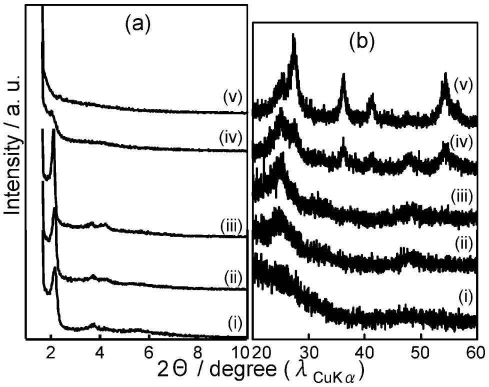

Figure 8. Effect of heating time on the meso structure and crystallinity of titania. Heating time ranged from (i) 12 to (v) 120 h. (ii), (iii), and (iv) are for 24, 48, and 72 h, respectively.

Effect of Reaction Time on Meso Structure and Crystal Structure of Titania Particles. The effect of reaction time at 333 K on meso structure and crystal structure of titania particles was investigated. Titania particles were prepared from aqueous solutions of 3 M $TiOSO_4$ and 60 mM C16TAB. Figure 8 shows the (a) low- and (b) wide-angle XRD patterns of the particles. Because the particles prepared under stirring at 333 K for 12 h had no peak characteristic of crystal structure (Figure 8b(i)), the particles formed at the primary stage of the sol−gel reaction were amorphous. In contrast, titania particles prepared by heating the system for 24 h were of anatase structure. The crystal structure of titania changed from anatase to a mixture of anatase and rutile after stirring over 48 h.

Titania particles having an anatase structure (Figure 8a(ii), (iii)) kept their hexagonal pore structure though the regularity of the pore structure deteriorated. The change from anatase to a mixture of anatase and rutile occurred while exhibiting no peaks assigned to hexagonal structure on the low-angle XRD pattern (Figure 8a(iv), (v)). These results suggested the collapse of hexagonal structure in the crystal structure transformation.

Effect of the Counterion (Bromide Ion) of the Surfactant on the Structural Properties of Titania Particles. Halogen ions affect the crystal structure of titania obtained through sol−gel process. Hence, the effect of bromide ions (Br^- ions), the counterion of the surfactant, used was examined on the structural properties of titania. Figure 9 shows the XRD patterns of titania prepared using (a) ultrapure water (without Br^- ion), (b) 60 mM KBr aqueous solution, and (c) 60 mM C16TAB aqueous solution. Temperature and time of reaction were 333 K and 24 h, respectively. While titania particles prepared using ultrapure water consisted of a mixture of anatase and rutile crystals, the peaks assigned to anatase crystal were detected in the XRD patterns of titania particles prepared in the presence of Br^- ions (Figure 9b,c). However, particles obtained in the presence of KBr (b) also had a broad peak assigned to rutile crystal. This result indicated that the crystal structure began to transform from anatase to rutile. KBr (b) and C16TAB (c) affected differently the crystallinity of titania even at the same Br^- ion concentration. This finding suggests that while the KBr added system had a free growth process of seed crystal, nanoclusters composed of $TiO(OH)_2$ were formed on the periphery of surfactant micelles at the primary stage in the surfactant-added system and they transformed into anatase crystals, keeping their particles size unchanged. These findings indicate that the preparation of mesoporous titania having a crystalline wall requires the presence of the counterion of the surfactant (Br^- ion) so that the crystal of titania can keep an anatase structure and molecular assemblies of the surfactant can keep the nanoordered crystal size unchanged.

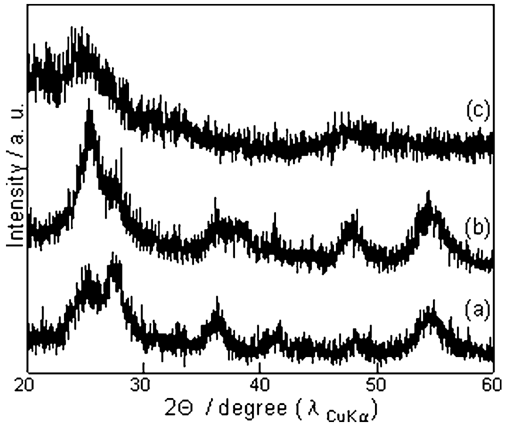

Figure 9. XRD patterns of titania particles prepared by heating $TiOSO_4$ aqueous solution (a) without and (b) with KBr and (c) with C16TAB.

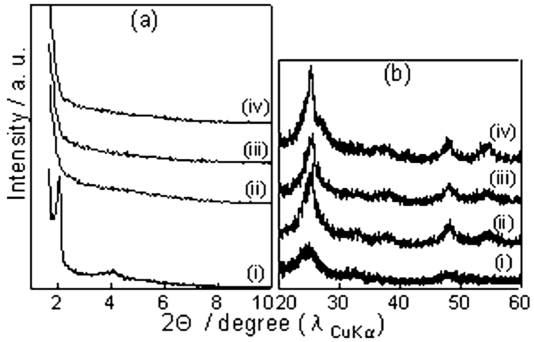

Figure 10. Effect of heating time on meso structure and crystallinity in the presence of 780 mM KBr. Heating time ranged from (i) 24 to (iv) 120 h. (ii) and (iii) are for 48 and 72 h, respectively.

Effect of Salt Addition on the Structural Properties of Titania. To suppress the transformation from anatase to rutile structure, mesoporous titania was prepared in the presence of 780 mM KBr. Figure 10 shows the XRD patterns of titania particles prepared under stirring at 333 K for various time lengths. The regular pore structure was almost disrupted while the system was heated over 48 h, because the peaks assigned to hexagonal structure disappeared in the low-angle XRD pattern of titania (Figure 10a) prepared by stirring over 48 h. In contrast, all wide-angle XRD patterns (Figure 10b) had peaks assigned to anatase structure.

The growth of anatase crystals seemed to cause the collapse of hexagonal structure because the half-bandwidth of the peak became narrower with increasing reaction time. These findings suggest that the collapse of regular hexagonal pore structure occurred by both the increasing anatase crystallinity and the transformation from anatase to rutile structure. Compositions of CTAB and $TiOSO_4$, reaction temperature, reaction time, and the presence of counterion affected the formation of anatase crystal around the hydrophilic moiety of the surfactant (CTAB) molecular assemblies.

The crystalline mesoporous titania particles can be obtained only in the condition for the formation of very small anatase crystal (ca. 1 nm).

Conclusions

In this study, the preparation and formation mechanism of mesoporous titania particles having a crystalline wall using various titania precursors and cationic surfactants were investigated. Crystalline mesoporous titania with a hexagonal structure was formed according to the formation mechanism mentioned below. The intermediary compound obtained from titanium oxysulfate sulfuric acid hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) was bound to the hydrophilic group of cetyltrimethylammonium bromide (C16TAB) by the strong interaction, and titanium hydroxide oxide ($TiO(OH)_2$) was quickly formed. The crystallization of titania from amorphous to anatase form was caused by heating at 333 K, and the wall of mesoporous titania was formed. In this process, bromide ions (Br^- ions) played the role of keeping the crystal structure at anatase and surfactant molecular assemblies keeping its crystal size small. However, the collapse of hexagonal structure occurred due to the distortion of the wall of mesoporous titania brought about by the increased crystallinity because excessively prolonged heat treatment failed to suppress the crystal growth of tittania. Preparation of mesoporous titania particles with crystalline wall needed suitable reaction condition (reaction time, reaction temperature, and molar ratio of surfactant and $TiOSO_4$). This suggests that the complex interaction between surfactants and titania precursors would yield mesoporous titania having a crystalline wall.

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