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課題名：チタニア系ナノチューブの長繊維化に伴う Ti 周辺の局所構造変化
"Local structural change around Ti with the change into long fiber for titania based nanotube"

Introduction

The syntheses of materials with various nanoscale spaces are currently under intensive investigation. Since carbon nanotubes, which have novel properties unlike those of either graphite or fullence, were discovered by Iijima [1], various syntheses of micro- and nanotubes of TiO_2 have been attempted by various method such as template methods[2-4]. Recently, Kasuga et al. treated TiO_2 in the 10 M NaOH aqueous solution for 20 h at 383 K without the need for molds for replication or template and nanotubes with 8 nm in diameter and 100 nm in length[5] were obtained by their experiments. Obtained TiO_2-derived nanotubes by this chemical process are particularly interesting, because of their large specific surface area caused by nanotubular morphology, leading to the development photocatalytic activities. This simple and low-cost synthetic method may be applied in the fabrication of other oxide nanotubes. After this report, many groups have investigated about the structure, formation mechanism, or synthetic condition for the nanotuluar product[6-9]. Recently, the products with various morphologies were obtained by modifying synthetic conditions for this hydrothermal process. Nanowire was obtained by hydrothermal process from anatase and successively post heat-treatment[10]. Yuan and co-workers found that the nanofiber was prepared when anatase was prepared by static hydrothermal treatment at 523 K[11].

In this study, a rotary-hydrothermal (RH) method as a novel synthetic process was used to synthesize a new type of nanotube. Anatase-type TiO_2 were conventional static or rotary-hydrothermally treated in 10 M NaOH aqueous solution at 383 to 473 K. The structural investigation of obtained products by various processes was analyzed by various methods, such as XRD, SEM, TEM, and Ti K-edge XANES.

Experimental Procedure

Synthesis of samples

As a starting material, two grams of anatase-type TiO_2 (Kojundo Chem., Japan) were used. They were added in a NaOH aqueous solution (15 ml) with the concentration of 10 M. Then the specimens were treated under conventional static hydrothermal reaction or rotary hydrothermal reaction at 383 to 423 K for 48 h to 96 h. The speed of rotation was 20 rpm. Obtained products after these treatments were washed with de-ionized water, filtered, and dried at 323 K.

Characterizations

Crystalline phase of samples were determined by X-ray diffraction method (XRD: Rint 2500, Rigaku Co., Ltd, Japan) using CuK α radiation at 40 kV and 50 mA. The XRD profiles were collected between 5-60° of 2 θ angles with a step interval of 0.01° and scanning rate of 4° /min. Various microstructural analyses were performed by scanning electron microscopy (FE-SEM: S-4500, Hitachi, Japan) with accelerating voltage of 15 kV and transmission electron microscopy (TEM: JEM2010/SP, JEOL) with accelerating voltage of 200 kV.

The Ti K-edge X-ray absorption near edge structure (XANES) was recorded at room temperature at BL01B1 in SPring8, Japan synchrotron radiation facility. The operating conditions in the storage ring were at energies of 8.00GeV and intensities of about 100 mV. The Ti K-edge XANES data for the study was corrected by transmission mode using the two-crystal Si (111) monochromator. Ti metallic foil was used to carry out for the energy calibration. The energy was scanned by 0.25 eV steps over the energy range for the Ti-K edge XANES. XANES analyzed by were subtracting a linear background computed by least-square fitting from the pre-edge region and normalized.

Results and discussion

Static hydrothermal process

Figs 1 and 2 show typical TEM images and XRD pattern of the product prepared by a hydrothermal treatment of commercial anatase-type TiO_2 at 383 K at 96 h. As shown in Fig. 1 (a), the obtained product possessed nanotubular structures with about 10 nm in outer diameter and 5 nm in inner diameter and a few hundred nm in length, and they were open-end with several wall layers on both sides. The measured interlayer spacing was about 0.90 nm. Moreover, it was found that the obtained nanotubular product had a scroll structure as shown in Fig. 1 (b). In the XRD pattern of the nanotubular product as shown in Fig. 2, the broad reflection peaks were observed at 2θ of approximately 10°, 24°, 30°, 48°and 62°. The XRD pattern of the synthesized nanotubular product in this study was consistent with nanotubular products prepared in other previous reports. In particular, the peak at 2θ = ca. 10° (d = 0.88 nm) was corresponding to the interlayer spacing value measured by TEM observation, indicating that this product might have layered titanate structures. Thus, TiO_2-derived nanotubes were prepared by the hydrothermal treatment of commercial anatase-type TiO_2 at 383 K for 96 h in 10 M NaOH aqueous solutions.

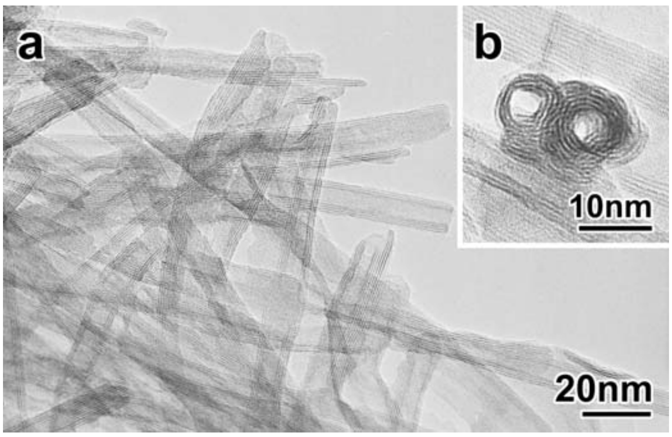

Fig. 1 TEM images of the product prepared by the hydrothermal treatment of commercial anatase-type TiO_2 powder at 383 K for 96 h and the subsequent washing treatment.

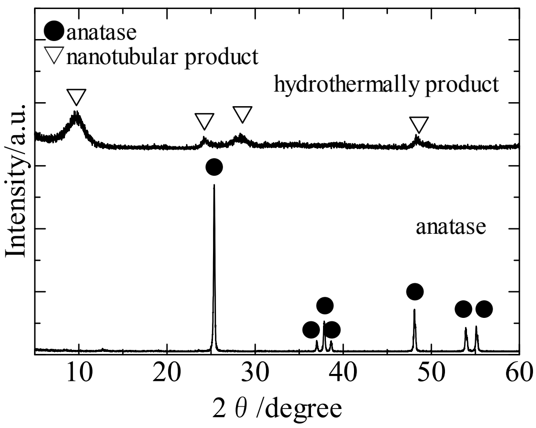

Fig. 2 XRD of the product prepared by the hydrothermal treatment of commercial anatase-type TiO_2 powder at 383 K for 96 h and the subsequent washing treatment.

Background subtracted and normalized Ti K-edge XANES for anatase-type TiO_2 and nanotular product prepared by static hydrothermal process are shown in Fig.3. As shown in Fig.3, the position of the absorption edge for obtained nanotube and anatase were located in the same position. This XANES result imply that Ti in titanate nanotube present as Ti (IV). Pre-edge of Ti K-edge XANES spectra are widely used to derive information on the coordination environment of Ti (IV) in structurally complex oxide materials, such as titanosilicate glasses etc[12-14]. Pre-edge of Ti K-edge XANES for anatase-type TiO_2, nanotubular product prepared by static hydrothermal process, layered $Na_2Ti_3O_7$, and layered $K_2Ti_4O_9$ are shown in Fig. 4. As shown in Fig.4, the pre-edge feature of the nanotube was similar to one of titanates such as $Na_2Ti_3O_7$ and $K_2Ti_4O_9$. Therefore, it was considered that the nanotube could be composed of the titanate compound. Here, although the peak is located at 4963.8eV for the nanotube in pre-edge of Ti-K edge XANES, the peak is not consistent with ones for $Na_2Ti_3O_7$ and $K_2Ti_4O_9$. Since this peak at 4963.8 eV is also observed for anatase-type TiO_2, it was considered that the peak derived from anatase structure. The anatase structure derived from nanotubular structure, not anatase-type TiO_2 as a starting material since XRD result showed nanotubular product had no peaks from anatase-type TiO_2 (Fig. 2). In other words, it was considered that titanate nanotube partly had anatase-like local structure by the formation of the nanotubular structures.

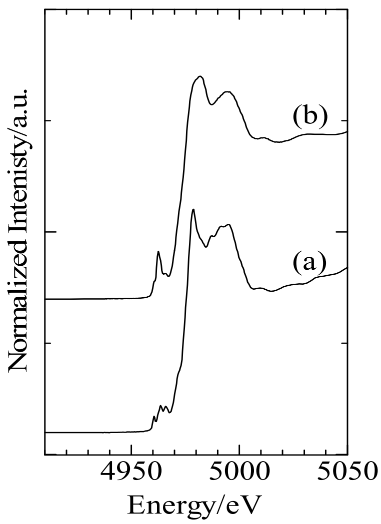

Fig. 3 Ti K-edge XANES of (a) anatase-type TiO_2 and (b) the product prepared by hydrothermal treatment of one for 96 h at 383 K.

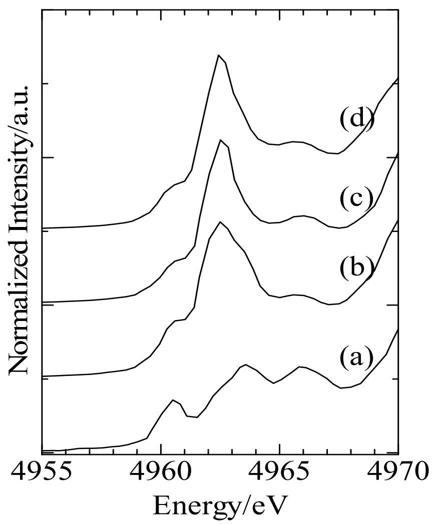

Fig. 4 Pre-edge of Ti K-edge XANES for (a) anatase-type TiO_2, (b) the product prepared by hydrothermal treatment of anatase-type TiO_2 for 96 h at 383 K, (c) $Na_2Ti_3O_7$, and (d) $K_2Ti_4O_9$.

Rotary hydrothermal treatment

Fig. 5 shows SEM and TEM images of the products prepared by rotary hydrothermal treatment of anatase-type TiO_2 with 10 M-NaOH aqueous solution for 48 h at 383 and 423 K. From SEM observation, it was found that the nanowhisker-shaped product and the nanofiber-shaped product were obtained when anatase-type TiO_2 was prepared by rotary hydrothermal treatment at 383 K. In case of rotary hydrothermal treatment at 423 K, the morphologies of obtained products completely were nanofiber-like. According to TEM observation, this fiber-shaped product had tubular structures with 10-50 nm in width and several hundreds micron in length. XRD patterns of products obtained by each treatment at 383 and 423 K indicated the same pattern as the titanate nanotube obtained by the conventional static hydrothermal treatment.

Pre-edge of Ti K-edge XANES for nanotular product prepared by static hydrothermal process and fibrous product prepared by rotary hydrothermal process at 423 K are shown in Fig. 6. As shown in Fig. 6, the pre-edge feature of the fibrous product obtained rotary hydrothermal treatment was similar to one of titanate nanotube by conventional static hydrothermal treatment. In addition, the peak derived from tubular structure was also located at 4963.8 eV for the fibrous H-Ti-O in pre-edge of Ti-K edge XANES. Therefore, it was considered that the fibrous product have the same structure as nanotubes. The fibrous long nanotubular tianate were not able to obtain under conventional static hydrothermal conditions. Therefore, it was considered that morphologies of these nanofibrous products strongly depended on synthetic conditions.

Thus, syntheses of tianate based products with various morphologies were achieved by the rotary-hydrothermal method at low temperatures and for short time, compared to the conventional hydrothermal treatment. Additionally, these results suggested that the diameter and length of nanotubular products and the morphology could be controlled through this process.

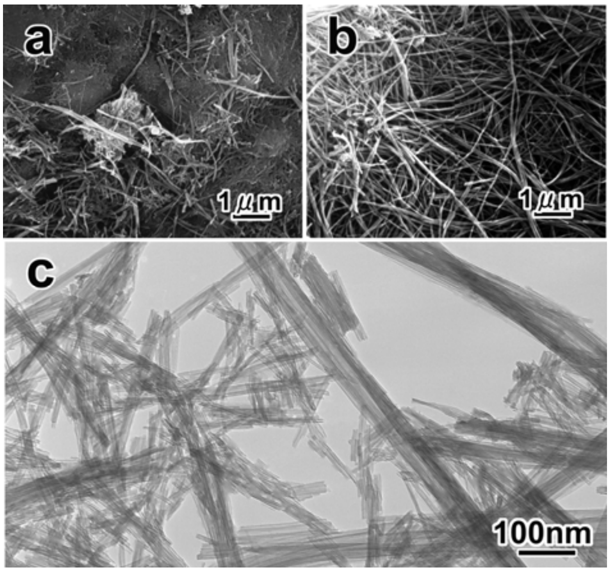

Fig. 5 SEM images of products prepared by rotary hydrothermal treatment of anatase-type TiO_2 for 48 h at (a) 383 and (b) 423 K, and (c) shows TEM image of (b)

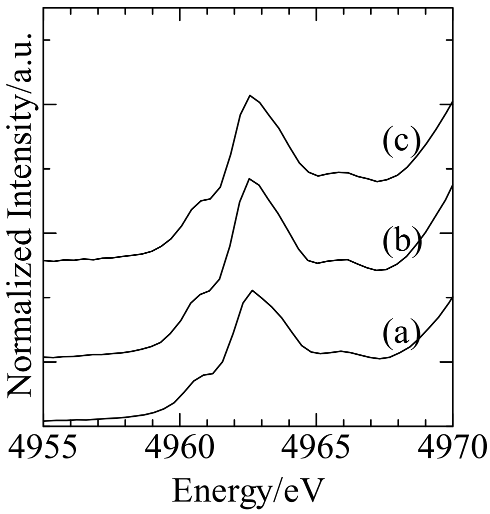

Fig. 6 Pre-edge of Ti K-edge XANES for (a) the product prepared by hydrothermal treatment of anatase-type TiO_2 for 96 h at 383 K, (b) the product prepared by rotary hydrothermal treatment of anatase-type TiO_2 for 48 h at 383, and (c) 423 K

Summary

Titanate based products with various morphologies were synthesized by the hydrothermal method for anatase-type TiO_2 in NaOH aqueous solution systems at low temperatures and for short time in this study. The nanotubular product with approximately 10 nm in outer diameter and approximately 5 nm in inner diameter was obtained by static hydrothermal treatment of anatase-type TiO_2. In case of rotary hydrothermal treatment, the product had fiber-like morphology. From TEM images and pre-edge of Ti K-edge XANES spectra, it was found that the fibrous product had nanotubular structures. Thus, these results suggested that the diameter and length of nanotubes and the morphology could be controlled by this process, leading to development of useful materials for several applications.

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