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Catalysis Communications
Volume 10
Number 6
Page range 963-966
Year 2009-02-15
URL http://hdl.handle.net/10228/00006351
Novel hydrothermal preparation of pure brookite-type titanium(IV) oxide nanocrystal under strong acidic conditions

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Abstract

Titanium(IV) oxide (TiO$_2$) nanocrystal with brookite phase was prepared by hydrothermal treatment of titanate nanotubes under strong acidic conditions (perchloric acid, hydrochloric acid and nitric acid). The relative fractions of crystal phases (anatase, rutile and brookite) were strongly dependent on hydrothermal treatment duration and the kind of strong acid used. A high brookite type TiO$_2$ content was obtained by hydrothermal treatment under perchloric acidic solution. Single-phase brookite TiO$_2$ particles were extracted from as-prepared TiO$_2$ by a centrifugal separation procedure, and they exhibited higher photocatalytic activity for acetaldehyde decomposition than TiO$_2$ prepared without the separation procedure.

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1. Introduction

Titanate nanotubes (TNTs) have attracted much attention because of their unique structure and simple preparation method, which was reported by Kasuga et al. [1]. Applications of TNT powders include dye-sensitized solar cells [2], catalyst supports [3,4] and photocatalysts [5]; these applications exploit the chemical and physical properties of TNT powders, such as their large specific surface area and tubular structure. Another very important application of TNTs is as a titanium source for material preparation. Several groups have investigated the structural transformation of TNTs to titanium(IV) oxide (TiO$_2$) by thermal, acid and hydrothermal treatment, and they found that treatment of TNTs under specific conditions results in the formation of characteristic TiO$_2$ nanostructures, e.g., nanorods, nanobelts, nanofibers [6-10]. The main component of their crystal phase is anatase and/or rutile, while a trace amount of brookite is sometimes present [9]. Anatase, rutile and brookite are well known to be the crystal phases of natural TiO$_2$. However, the physical and chemical properties of brookite still remain unclear, in contrast with those of anatase and rutile, which have been extensively investigated. This is due to the low availability of single-phase brookite TiO$_2$ as a result of it being thermodynamically metastable.

Kominami et al. prepared single-phase brookite TiO$_2$ powders for the first time by solvothermal synthesis in which oxobis(2,4-pentanedionato-$O,O'$)titanium was used as the TiO$_2$ precursor and sodium laurate was used as a reagent for controlling the crystal structure [11]. They subsequently investigated the photocatalytic activity of single-phase brookite TiO$_2$ [12,13]. Recently, other groups have also reported single-phase brookite TiO$_2$ having several kinds of characteristic structures, e.g., nanorods and nanotubes [14-18]. However, the photocatalytic properties of these structures were not investigated in these studies.

In the present study, TiO$_2$ powders were prepared by hydrothermal treatment of TNTs under several kinds of strong acidic conditions without using an organic reagent for controlling the crystal structure, such as sodium laurate. Single-phase brookite TiO$_2$ nanocrystals were extracted from as-prepared TiO$_2$, and the photocatalytic properties of these TiO$_2$ powders were investigated.
2. Experimental

2.1 Sample preparation

One gram of TNT powder (TNT-352, Catalysts & Chemicals Ind. Co., Ltd.) was dispersed in 50 cm³ of 2 mol dm⁻³ of an acid solution (perchloric acid (HClO₄), hydrochloric acid (HCl), and nitric acid (HNO₃)) in a Teflon bottle. After stirring the solution, the Teflon bottle was sealed with a stainless steel jacket and heated at 200 °C for 1~50 h in an oven. After this hydrothermal treatment, the supernatant in the bottle was removed. To extract single-phase brookite TiO₂ powders, centrifugal separation was performed by adding Milli-Q water, centrifuging the suspension for 30 min at 5000 rpm, and then filtrating the supernatant (not transparent). The residues obtained both by using and without using the above-mentioned procedure were washed with an aqueous NH₃ solution (1%) and Milli-Q water several times until the ionic conductivity of the supernatant was <10 µS cm⁻².

2.2 Characterization

The crystal structures of the TNT or TiO₂ powders were characterized with an X-ray diffractometer (Rigaku, MiniFlex II) with Cu Kα radiation (λ = 1.5405 Å). The relative surface areas of the powders (S_{BET}) were determined using a surface area analyzer (Quantachrome, Autosorb-1) in conjunction with the Brunauer-Emmett-Teller (BET) equation. The morphologies of the TNT or TiO₂ powders were observed using a transmission electron microscope (TEM; Hitachi, H-9000NAR).

2.3 Photocatalytic decomposition of acetaldehyde

Photocatalytic activities of TNT or TiO₂ samples were evaluated by photocatalytic decomposition of acetaldehyde. One hundred milligrams of TNT or TiO₂ powder, which have a complete extinction of the incident radiation, was spread on a glass dish, and the glass dish was placed in a 125 cm³ Tedlar bag (As one). Five hundred parts per million of gaseous acetaldehyde
was injected into the Tedlar bag, and photoirradiation was performed at room temperature after the
cetaldehyde had reached adsorption equilibrium. The gaseous composition in Tedlar bag were
79 % of N₂, 21 % of O₂, < 0.1 ppm of CO₂ and 500 ppm of acetaldehyde, and relative humidity was
ca. 30 %. A light emitting diode (Nichia, NCCU033), which emitted light at a wavelength of ca.
365 nm and an intensity of 1.0 mW cm⁻², was used as the light source. The concentrations of
acetaldehyde and carbon dioxide (CO₂) were estimated by gas chromatography (Shimadzu, GC-8A,
FID detector) with a PEG-20 M 20% Celite 545 packed glass column and by gas chromatography
(Shimadzu, GC-9A, FID detector) with a TCP 20% Uniport R packed column and a methanizer (GL
Sciences, MT-221), respectively. In the photocatalytic evaluation, P-25 (Japan Aerosil Co., S_BET =
50 m² g⁻¹), which is a well-known commercial TiO₂ photocatalyst with a high photocatalytic
activity, was employed as a standard photocatalyst.

3. Results and discussion

The XRD analysis revealed that the crystal phase of the samples was transformed from TNT
into TiO₂ (anatase, brookite and rutile) after over 1 h of hydrothermal treatment of TNT. Figures
1a and b show XRD patterns of samples before hydrothermal treatment and after 50 h of
hydrothermal treatment under HClO₄ solution, respectively. They indicate that a large fraction of
brookite and small fractions of anatase and rutile were formed. The relative fractions of these
crystal phases exhibited a strong dependence on the duration of the hydrothermal treatment.
Figure 2 shows the relative fractions of the crystal phases (f_A: anatase; f_B: brookite; f_R: rutile) as a
function of the duration of the hydrothermal treatment with HClO₄ as the acid. The relative
fractions of the crystal phases were calculated using the following equation [19]

\[ f_i = k_i S_i / (k_A S_A + k_B S_B + k_R S_R) \]

where \( k_A = 0.886, k_B = 1, \) and \( k_R = 2.721 \) [19]. \( S_A, S_B \) and \( S_R \) are the integrated intensities of peaks
attributed to anatase (101), brookite (121) and rutile (110), respectively. They were estimated by
fitting the XRD patterns in the range of 22~34° with a superposition of five Lorentz functions for
peaks attributed to brookite (120), anatase (101), brookite (111), rutile (110) and brookite (121).
For the calculation, the ratio of integrated intensities of the three peaks attributed to brookite (120), (111), (121) was fixed at 10 : 8 : 9, as determined by JCPDS data.

In Fig. 2, $f_B$ and $f_R$ increase monotonically with an increase in the hydrothermal treatment duration, and $f_A$ has a maximum at about 5 h. This indicates that brookite is relatively stable under HClO$_4$ conditions, while anatase is metastable and is transformed into the other phases. However, phase transformation of fine anatase particles (ST-01, Ishihara Sangyo Co., $S_{BET} = 316$ m$^2$ g$^{-1}$) to brookite was not observed after 5 h of hydrothermal treatment under the same conditions. This result conflicts with the above-mentioned possibility of transforming anatase into brookite. Another plausible reason might be that $f_A$ is underestimated because it is difficult to accurately estimate $S_A$ in the presence of the brookite phase due to the overlapping of the three peaks that occur in the range of 25~26°. The reason for this behavior of the anatase phase is currently under investigation.

TiO$_2$ prepared by 5 h of hydrothermal treatment of TNTs in Milli-Q water or 2 mol dm$^{-3}$ aqueous solution of sodium perchlorate had a smaller $f_B$ than that prepared in HClO$_4$ solution. Some reports have also reported the formation of a large fraction of brookite phase by hydrothermal synthesis from titanium(IV) tetrachloride (TiCl$_4$) under HCl and HNO$_3$ conditions [14,20]. However, 50 h of hydrothermal treatment under HCl and HNO$_3$ conditions induced small $f_B$ ($f_R = 1$ for HCl, $f_R = 0.53, f_B = 0.47$ for HNO$_3$) in the present study, though relatively large $f_B$ was observed for samples prepared by 5 h of hydrothermal treatment ($f_R = 0.72, f_B = 0.28$ for HCl, $f_A = 0.05, f_B = 0.12, f_R = 0.83$ for HNO$_3$). These results indicate that a low pH induce the transformation of TNTs to brookite and the presence of ClO$_4^-$ anions suppress the transformation into rutile, while the presence of Cl$^-$ anions promote the transformation into rutile due to the stabilization of rutile surfaces [21].

Figures 1b and c show XRD patterns of TiO$_2$ powders that were prepared by 50 h of hydrothermal treatment without and with centrifugal separation, respectively. The TiO$_2$ produced without centrifugal separation has an appreciable amount of rutile, whereas the XRD pattern of the TiO$_2$ produced using centrifugal separation contains no peaks that are attributed to rutile. This
indicates that single-phase brookite TiO$_2$ was extracted by the separation procedure of the as-prepared TiO$_2$. Moreover, heat treatment (300 °C, 3 h) of single-phase brookite TiO$_2$ induced no formation of the anatase phase. This result presumably indicates that the single-phase brookite TiO$_2$ contains very little amorphous or TNT phases. The primary particle sizes of rutile ($d_{R(110)}$) and brookite ($d_{B(121)}$) were estimated from peaks attributed to rutile (110) and brookite (121) in XRD patterns using the Scherrer equation ($d = 0.9\lambda/\beta\cos\theta_B$, where $\lambda$ is the wavelength of X-rays, $\beta$ is the full width at half maximum and $\theta_B$ is the Bragg angle) and found to be 35 nm and 23 nm, respectively. However, this difference in particle size is not sufficiently large to explain the reason for the extraction of single-phase brookite TiO$_2$.

Figure 3 shows TEM images of TNT and TiO$_2$ prepared with and without centrifugal separation. The TNTs had tubular structures with inner and outer diameters of ca. 5 nm and ca. 10 nm, respectively (Fig. 3a). TiO$_2$ prepared without centrifugal separation consisted of two kinds of particle shapes (Fig. 3b), namely large rods (ca. 50 nm by ca. 300 nm) and small particles with an aspect ratio of ca. 1 (ca. 30 nm), while only small monodispersed particles with a narrow size distribution were observed in the TiO$_2$ prepared with centrifugal separation (Fig. 3c). TEM observation and XRD analysis indicate that larger rods and smaller particles are attributable to rutile and brookite nanocrystals, respectively. Thus, the effective particle size of the rutile rods was larger than $d_{R(110)}$ due to the rod structure. This large difference in effective particle sizes explains why single-phase brookite TiO$_2$ was extracted by the centrifugal separation. The $S_{BET}$ (61 m$^2$ g$^{-1}$) of TiO$_2$ prepared with the centrifugal separation procedure was slightly larger than that (57 m$^2$ g$^{-1}$) of the TiO$_2$ prepared without centrifugal separation because of the low fraction of the rutile phase with large particle sizes.

The TEM image in Fig. 3c suggests that some brookite particles have specific exposed crystal faces, and lattice fringes were also observed in the TEM images of most of the single-phase brookite TiO$_2$ particles shown in Fig. 3d. The space of lattice fringes (ca. 0.375 nm) indicate that exposed crystal face was attributed to brookite (101) face. This fringe means that the brookite TiO$_2$ particles consisted of a single crystal (i.e., they were not polycrystalline) suggesting that the
brookite TiO₂ particles have high crystallinity, which is important for photocatalytic activity.

Figure 4 shows the time course of CO₂ evolution of acetaldehyde decomposition over TiO₂ samples as a function of the photoirradiation time. The prepared brookite TiO₂ had a higher photocatalytic activity than the other TiO₂ powders. This result is presumably due to the high crystallinity and relatively large surface area of the prepared brookite TiO₂ [22]. Another plausible reason for this may be the specific exposed crystal faces, which induce separation of redox sites that enhances photocatalytic activity [23]. Some reports have revealed that a synergistic effect occurs for some photocatalytic reactions performed over a mixture of small anatase and large rutile particles [24]. However, TiO₂ prepared with centrifugal separation (small brookite particles) exhibited a higher activity than TiO₂ prepared without centrifugal separation (mixture of small brookite particles and large rutile particles), thus a synergistic effect was not observed in the present study for powders consisting of a mixture of brookite and rutile TiO₂. On the contrary, the low activity of rutile rods with specific exposed crystal faces indicates that recombination rate was presumably increased by brookite-rutile contacts. The high photocatalytic activity of the single-phase brookite TiO₂ is attributable to intrinsic photocatalytic properties of brookite TiO₂ that has a high crystallinity and a large surface area.

4. Conclusion

Hydrothermal treatment of TNT under HClO₄ conditions induced formation of brookite phase with trace amounts of the other two phases. The results of hydrothermal treatment of TNT under various conditions indicate that nucleation of brookite phase requires both a suitable pH of the solution in the dissolution process and the presence of the ClO₄⁻ ion to control the formation of crystal structures in the crystallization process. Single-phase brookite TiO₂ was extracted from as-prepared TiO₂ by centrifugal separation. It consisted of a single crystal, and exhibited higher photocatalytic activity, presumably due to its high crystallinity and relatively large surface area.
Acknowledgement

This work was supported by a grant from the Knowledge Cluster Initiative implemented by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the New Energy and Industrial Technology Development Organization (NEDO).

References

Figure Captions

Figure 1  XRD patterns of (a) TNT and TiO$_2$ prepared by 50 h of hydrothermal treatment under HClO$_4$ solution (b) without and (c) with centrifugal separation.
Figure 2  Relative fractions of crystal phases ($f_A$: anatase; $f_B$: brookite; $f_R$: rutile) estimated from XRD patterns as a function of duration of hydrothermal treatment under HClO$_4$ solution.

Figure 3  TEM images of (a) TNT and TiO$_2$ prepared (b) without and (c) with centrifugal separation. (d) High-resolution image of image in (c).

Figure 4  Time course of CO$_2$ evolution of acetaldehyde decomposition over TiO$_2$ prepared (a) without and (b) with centrifugal separation, commercial TiO$_2$ (c) ST-01 and (d) P-25, as a function of photoirradiation time.