SYNTHESIS AND PROPERTIES OF TITANIA NANOPARTICLES AND NANOTUBES /SILICA COMPOSITE GELS

Masanori Hirano and Shunsuke Oya

Dept. of Applied Chemistry, Aichi Institute of Technology
1247,Yakusa, Toyota, Aichi, Japan
hirano@aitech.ac.jp

ABSTRACT

Titania/silica composite gels were synthesized through sol-gel process using sodium metasilicate (Na_2SiO_3) and titania nanotubes or titania nanoparticles with anatase, rutile, and brookite-type structures. The titania nanotubes and the brookite-type nanoparticles were formed under basic hydrothermal conditions in the presence of NaOH. The rutile- and the anatase-type titania nanoparticles were hydrothermally synthesized by the hydrolysis of acidic $TiCl_4$ and $TiOSO_4$ solutions, respectively. Their photocatalytic activity and adsorptivity were evaluated by the measurement of the concentration of methylene blue remained in the solution after maintained with stirring in the dark or under UV-light irradiation. The titania/silica composite gels containing 20% anatase-type titania showed good photocatalytic activity.

1. INTRODUCTION

Titanium(IV) oxide (titania, TiO_2) is attractive as an effective catalyst for photooxidizing a variety of hazardous organic chemicals in air and in water at room temperature [1]. Among main three polymorphs: anatase (metastable), rutile (stable), and brookite (metastable), the anatase-type TiO_2 has been known to exhibit good photocatalytic activities. The properties of titania photocatalyst can be modified by doping various components [2-5]. The addition of SiO_2 (amorphous silica) to titania has been reported to be effective for the enhancement of the phase stability [6] and photocatalytic activity [7] of anatase-type titania. We have applied thermal hydrolysis of acidic aqueous $TiOSO_4$ solution in order to directly load nanometer-sized anatase-type titania on the silica gel particles [8] under mild hydrothermal conditions.

The present study was concerned with the investigation of the synthesis of various kinds of titania/silica composite gels consisting of amorphous silica and titania nano-sized crystals with single phase and various polymorphs. Titania nanotubes (TNT) and brookite-type nanoparticles were formed under basic hydrothermal conditions in the presence of NaOH. Rutile- and anatase-type titania nanoparticles were hydrothermally synthesized by the hydrolysis of acidic $TiCl_4$ and $TiOSO_4$ solutions, respectively. Using sodium metasilicate (Na_2SiO_3) and the titania nanotubes or the titania nanoparticles with anatase, rutile, and brookite-type structures, titania/silica composite gels were synthesized through sol-gel process. The structure, morphology, and properties as performance for the photocatalyst of their products were investigated.

2. EXPERIMENTAL

Aqueous solutions of reagent-grade $TiOSO_4$ or $TiCl_4$, and solution mixtures of $TiOSO_4$ and NaOH prepared in Teflon containers were placed in stainless-steel vessels, respectively. After the vessels were tightly sealed, they were heated at 180°C or 120°C for 24 h. After hydrothermal treatment, thus obtained titania nanoparticles and nanotubes were mixed with sodium metasilicate (Na_2SiO_3) in the presence of HCl under controlled pH conditions with stirring. The composite gels obtained were washed with distilled water, separated, and dried. The phases of the as-prepared samples were examined by X-ray diffractometry (XRD). The morphology of the as-prepared samples was observed under transmission electron microscopy (TEM). The crystallite size of titania was estimated from the line broadening of diffraction peaks, according to the Scherrer equation. The specific surface area of the prepared samples was calculated based on the BET method. The photocatalytic activity and adsorptivity of these prepared samples were estimated from the change in the concentration of methylene blue ($C_{16}H_{18}N_3S$, MB) both under ultraviolet ray (UV) irradiation from black light and in the dark, respectively. The UV-light irradiation time dependence of MB decomposition was estimated from the absorbance change with the spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Formation of titania/silica composite gels

Hydrothermal treatment was conducted in order to prepare single phase of titania nano-sized crystals with various polymorphs and titania nanotubes. XRD patterns of as-prepared titania samples that were precipitated under various controlled hydrothermal conditions are shown in Fig. 1. Three types of titania nanoparticles with anatase-, rutile-, and brookite-type structures and titania nanotubes were directly synthesized as single phase, respectively. Since rutile-type titania coexisting with anatase-type titania was synthesized under hydrothermal condition at 180°C by the hydrolysis of acidic $TiCl_4$ solution, hydrothermal treatment was carried out at high temperature of 240°C to prepare single phase rutile-type titania (R 240). Anatase-type titania (A 180) was hydrothermally synthesized by the hydrolysis of acidic $TiOSO_4$ solution at 180°C. Brookite-type titania (B 180) was formed under basic hydrothermal conditions at 180°C in the presence of NaOH. Titania nanotubes (TNT 120) were obtained from $TiOSO_4$ solution under basic hydrothermal condition at 120°C using NaOH.

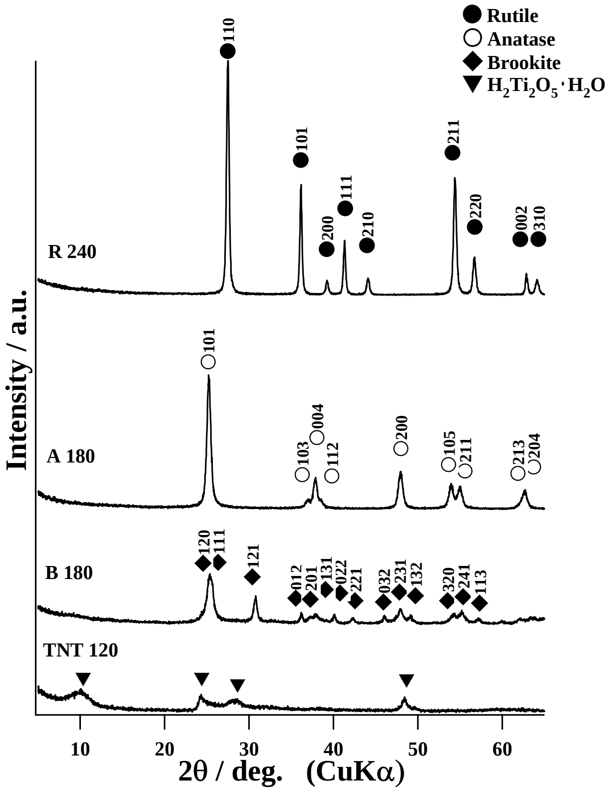

Figure 1: XRD patterns of precipitates obtained at various hydrothermal conditions.

Figure 2 shows TEM images of the as-prepared titania samples that were formed under various hydrothermal conditions. The anatase-type titania particles were of relatively even size. Since the rutile-type titania was prepared at higher temperature of 240°C than the cases of titania with other polymorphs, the morphology of rutile particles was rod-like with good crystallinity. The brookite-type titania and TNT were spindle-like and fibrous, respectively. The crystallite sizes of anatase-, rutile-, and brookite-type titania estimated from the XRD line broadening in the samples were 16, 29, and 19 nm, respectively. The crystallite sizes of anatase, rutile, and brookite relatively well corresponded to the particle sizes of the samples observed in the TEM images.

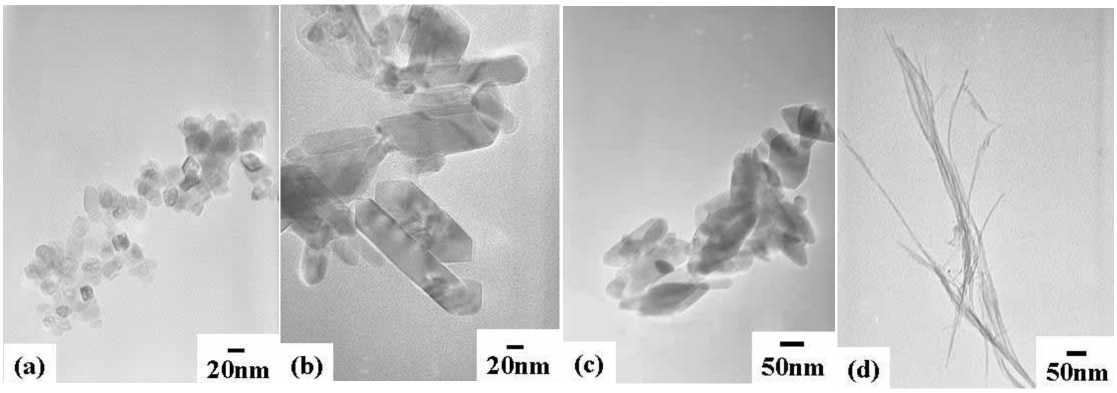

Figure 2: TEM images of precipitates obtained under various hydrothermal conditions. (a) A 180, (b) R 240, (c) B 180, (d) TNT 120.

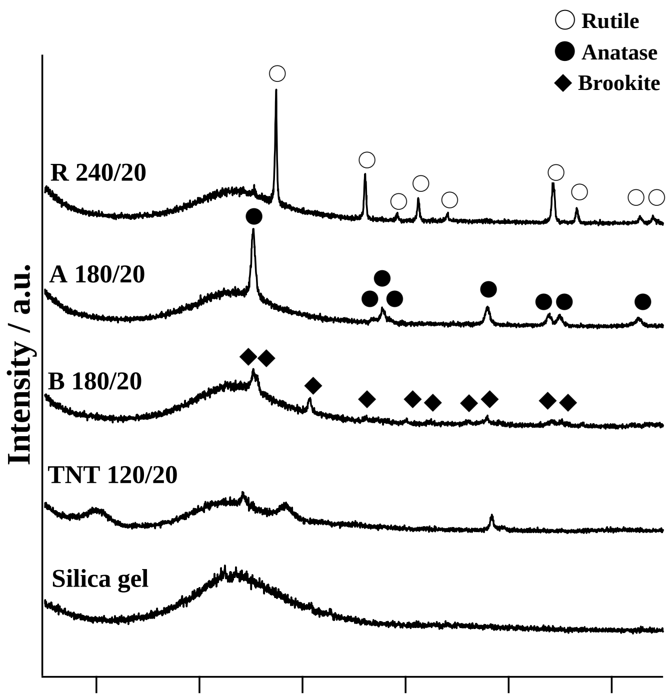

Figure 3: XRD patterns of titania/silica composite gels and silica gel.

Titania/silica composite gels were synthesized through sol-gel process using sodium metasilicate (Na_2SiO_3) and hydrothermally prepared titania. XRD patterns of titania/silica composite gel samples containing 20% anatase-, rutile-, and brookite-type titania nanoparticles and titania nanotubes in comparison with silica gel are shown in Fig. 3. They correspond to sample names: A 180/20, R 240/20, B 180/20, and TNT 120/20, respectively. The XRD patterns show that the composite gels are composed of amorphous silica having a broad peak and titania crystals with various polymorphs. The BET surface area of the titania/silica composite gels containing 20% anatase-, rutile-, and brookite-type titania were 602, 680, 411 m^2/g, respectively. In this study, titania/silica composite gels were successfully synthesized through sol-gel process using sodium metasilicate (Na_2SiO_3) and hydrothermally prepared titania nanotubes or titania nanoparticles with anatase, rutile, and brookite-type structures.

3.2 Photocatalytic activity

The decrease in the MB concentration of the solution containing anatase-type titania (A 180) after maintenance in the dark and under UV irradiation is shown in Fig. 4 as an example. The decrease in the concentration of MB in the dark corresponds to the adsorptivity of MB by the sample. The difference between the decrease amount in the concentration of MB in the dark and that under UV irradiation corresponds to the photocatalytic decomposition amount of MB by the sample, that is to say photocatalytic activity. The photocatalytic decomposition amount of MB was observed to gradually increase with increase of maintenance time although the anatase-type titania did not show much adsorption amount of MB.

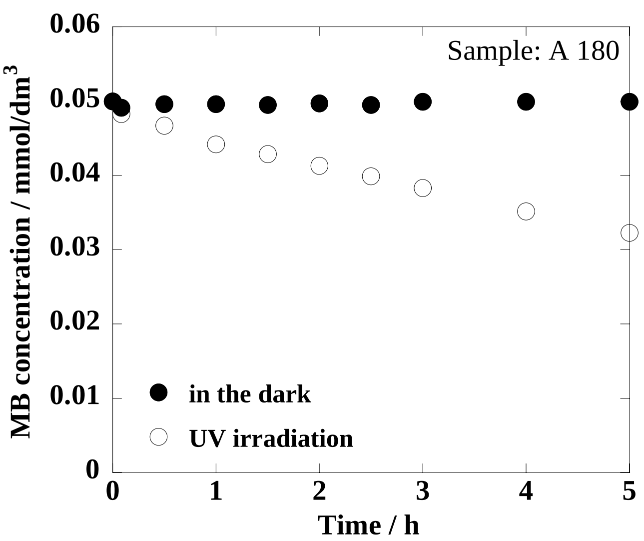

Figure 4: Change in MB concentration of the solution in the presence of anatase-type titania (A 180) with stirring time in the dark and ultraviolet irradiation time.

The photocatalytic activity of titania/silica composite gels that were prepared through sol-gel method using titania synthesized under hydrothermal conditions, were estimated in the same manner as those of pure titania. Figure 5 shows the decrease in the MB concentration of the solution containing titania/silica composite gel containing 20% anatase-type titania (A 180/20) after maintenance in the dark and under UV irradiation. The MB concentration of the solution containing titania/silica composite gel decreased at the beginning of the stirring time in the dark in comparison with the case of pure titania (Fig. 4). This decrease amount in the concentration of MB in the dark which corresponds to the adsorptivity of MB by the sample may be ascribed to the formation of composite gel consisting of 20 mol% titania and 80mol% silica. The composite gel showed relatively large amount of photocatalytic decomposition of MB notwithstanding low content (20 mol%) of photoactive titania in the samples as compared with the case of pure titania.

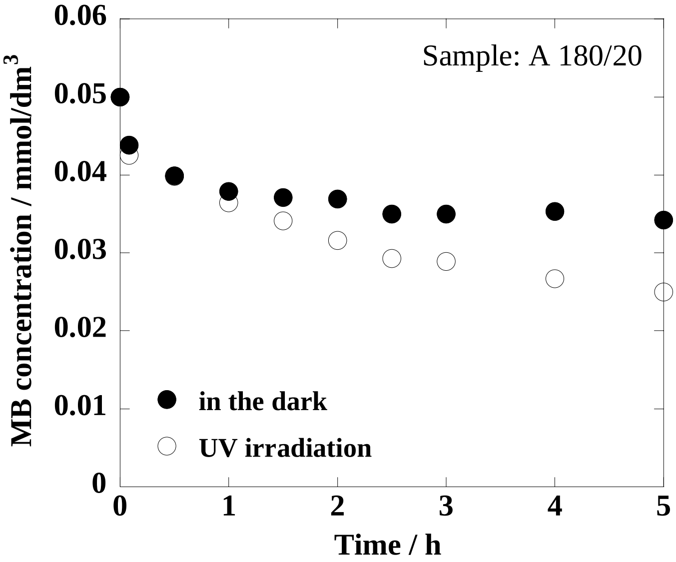

Figure 5: Change in MB concentration of the solution in the presence of titania/silica composite gel containing 20% anatase-type titania (A 240/20) with stirring time in the dark and ultraviolet irradiation time.

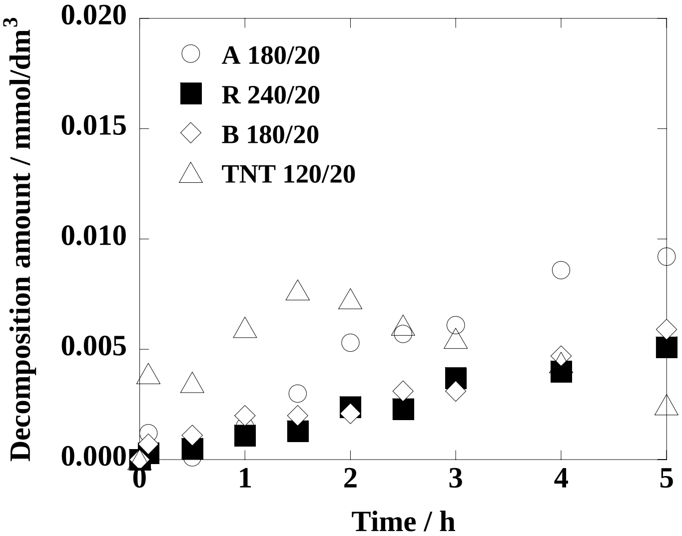

Figure 6: Change in photocatalytic decomposition amount of MB for the solution in the presence of titania/silica composite gels containing 20% titania having various structures with maintenance time.

In Fig. 6 is shown the photocatalytic activity of titania/silica composite gels containing 20% titania with different structures prepared under various hydrothermal conditions, which is plotted as changes in the photocatalytic decomposition amount of MB against maintenance time in the dark and under UV irradiation. Although the content of photoactive titania is 20 mol% in the composite gel samples as compared with the case of pure titania, it can be seen from the figure that the composite gel containing anatase-type titania (sample: A 180/20) has relatively good photocatalytic activity. As a result, it was shown that the titania/silica composite gels containing 20% anatase-type titania showed good photocatalytic activity.

4. CONCLUSIONS

Titania/silica composite gels were formed by sol-gel method from sodium metasilicate and titania prepared under hydrothermal conditions. To investigate the effect of the structures of titania on the photocatalytic activity of titania/silica composite gels, titania with various structures as anatase, rutile, brookite, and nanotubes were synthesized under hydrothermal conditions. Rutile- and anatase-type titania nanoparticles were hydrothermally synthesized by the hydrolysis of acidic $TiCl_4$ and $TiOSO_4$ solutions, respectively. Brookite-type titania nanoparticles and titania nanotubes were formed under basic hydrothermal conditions in the presence of NaOH.

The adsorptivity which was evaluated by the measurement of the concentration of methylene blue remained in the solution in the dark markedly increased by the formation of composite gels consisting of amorphous silica and photoactive titania, as compared with the case of pure titania. The composite gels showed good photocatalytic activity under UV-light irradiation notwithstanding low content (20 mol%) of photoactive titania in the samples in comparison with the case of pure titania.

REFERENCES

1- Fox, M. A. and Dulay M. T., “Heterogeneous Photocatalysis,” *Chem. Rev*., 1993;93:341-357.

2- Hirano, M. and Date, K., “Scandium-Doped Anatase (TiO_2) Nanoparticles Directly Formed by Hydrothermal Crystallization”, *J. Am. Ceram. Soc*., 2005;88:2604-2607.

3- Hirano, M., Ota K. and Ito T., “Anatase-Type (TiO_2 and ZrO_2-Doped TiO_2 Directly Formed from Titanium(III) Sulfate Solution by Thermal Hydrolysis: Effect of the Presence of Ammonium Peroxodisulfate on their Formation and Properties”, *J. Am. Ceram. Soc*., 2005;88:3303-3310.

4- Hirano, M. and Matsushima K., “Effect of Niobium on the Structure and Photoactivity of Anatase (TiO_2) Nanoparticles”, *J. Nanosci. Nanotechnol*., 2006;6:762-770.

5- Hirano, M. and Ito T., “New Anatase-Type $Ti_{1-2X}Nb_XAl_XO_2$ Solid Solution Nanoparticles: Direct Formation, Phase Stability, and Photocatalytic Performance”, *J. Nanosci. Nanotechnol*., 2006;6:3820-3827.

6- Hirano, M., Ota K. and Iwata H., “Direct Formation of Anatase (TiO_2) / Silica (SiO_2) Composite Nanoparticles with High Phase Stability of 1300°C from Acidic Solution by Hydrolysis under Hydrothermal Condition”, *Chem. Mater.*,2004;16:3725-3732.

7- Hirano, M., Ota K., Inagaki, M. and Iwata H., “Hydrothermal Synthesis of TiO_2/SiO_2 Composite Nanoparticles and Their Photocatalytic Activities”, *J. Ceram. Soc. Jpn.*, 2004;112:143-148.

8- Hirano, M. and Ota K., “Preparation of Photoactive Anatase-Type TiO_2/Silica Gel by Direct Loading Anatase-Type TiO_2 Nanoparticles in Acidic Aqueous Solutions by Thermal Hydrolysis”, *J. Mater. Sci.*, 2004;39:1841-1844.