Titania solid solution nanoparticles co-doped with niobium and gallium

Masanori HIRANO† and Takaharu ITO

Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, Yakusa, Toyota, Aichi 470–0392

Anatase-type titania nanoparticles co-doped with niobium and gallium (Ga₃Ti₁₋₂ₓNbₓO₂ solid solutions in the range of X = 0–0.20) were formed from precursor solutions of TiOSO₄, NbCl₅, and Ga(NO₃)₃ under hydrothermal conditions at 180°C for 5 h using the hydrolysis of urea. The effect of dopant materials on the structure, crystallite growth, photocatalytic activity, and phase stability of anatase-type TiO₂ was investigated. The lattice parameters a₀ and c₀ of anatase slightly and gradually increased with increase in niobium and gallium content doped into TiO₂. The anatase solid solutions doped with niobium and gallium (X = 0.10–0.15) showed good photocatalytic activity. Co-doping niobium and gallium into TiO₂ shifted the anatase-to-rutile phase transformation to lower temperature. The temperature range of the anatase-to-rutile phase transformation for the Ga₃Ti₁₋₂ₓNbₓO₂ solid solutions became narrower than that for pure TiO₂. The rutile-type Ga₃Ti₁₋₂ₓNbₓO₂ solid solutions were formed via the phase transformation.

Key-words : Anatase, Rutile, Titania, Solid solution, Photocatalytic activity, Phase stability

1. Introduction

Titania (TiO₂) has been an attractive compound because it can decompose many hazardous organic compounds at room temperature via photooxidizing under near-UV light or sunlight irradiation.1–3 Quite a lot of works on synthesis and characterization of titania photocatalyst have been done.3–5 The investigation on the synthesis routes of nano-sized crystalline particles is one of the approaches for development of photocatalysts with high performances. Intensive attention has been devoted to wet chemical routes to obtain nanometer-sized particles of inorganic materials.6–7 The hydrothermal treatment is well known to be able to synthesize homogeneous nanometer-sized metal-oxide solid solutions from aqueous precursor solutions.8,9 Crystalline metal-oxide nanoparticles have been directly synthesized from aqueous precursor solutions using precipitation and hydrothermal techniques at relatively low temperatures.10 The properties of photocatalyst can be modified by doping various components, and its performance is also influenced by synthesis technique, preparation condition, etc.11 Solid solutions of Ti₁₋ₓZrₓO₂ (0.00 < x ≤ 0.10) and Ti₁₋ₓVₓO₂ (0.00 < x ≤ 0.025) have been shown to have higher photocatalytic activity than pure anatase TiO₂ for the degradation of acetone in air.12,13 On the other hand, it has been shown that direct UV excitation of pure titania is a more efficient photocatalytic process than visible excitation of the doped semiconductor doped with Fe³⁺, Cr³⁺, and Co²⁺.14 Titania solid solution nanoparticles15–17 and titania/silica composite nanoparticles18–20 have been directly synthesized via soft solution routes. The formations of solid solutions doped with niobium oxide and titania/silica composite nanoparticles were effective for the enhancement of photocatalytic activity.19,19 The effect of doping trivalent cations aluminum and gallium into TiO₂ on the morphology and microstructural properties of nanopowders has been reported.20 The investigations on the formation, phase stability, and photoactivity of anatase-type TiO₂ solid solutions doped with niobium21,22 and co-doped with niobium and scandium (Sc₂Ti₁₋₂ₓNbₓO₂) have been done.23,24 The effect of co-doping niobium and aluminum into TiO₂ on the synthesis and properties of nanoparticles has also been investigated.25 In that report, the starting temperature of anatase-to-rutile phase transformation has been delayed by co-doping niobium and aluminum into TiO₂, and anatase-type solid solutions Al₂Ti₁₋₂ₓNbₓO₂ (X = 0–0.2) with improved photocatalytic activity have been formed. On the other hand, with reference to the study on co-doping niobium and gallium into TiO₂ there is a paper on the synthesis and characterization of gallium titanium niobium oxide (Ga₃Ti₁₋₂ₓNbₓO₂) using solid-state reaction via heating mixtures of metal oxide powders.26

In that paper, measurements of unit cell parameters allow two kinds of solid solutions to be considered, one based on the rutile structure when the TiO₂ content is high and the other on the orthorhombic α-PbO₂ structure when the TiO₂ content is low. Exclusive of the rutile-type titania co-doped with niobium and gallium, formation of anatase-type Ga₃Ti₁₋₂ₓNbₓO₂ solid solutions and their properties have not been reported before.

In the present study, direct formation of anatase-type titania nanoparticles co-doped with niobium and gallium (Ga₃Ti₁₋₂ₓNbₓO₂ solid solutions in the range of X = 0–0.20) was performed under mild hydrothermal conditions. The structure, morphology and characteristics such as performance for the photocatalyst and phase stability of their products were investigated.

2. Experimental

2.1 Sample preparation

A mixture of an aqueous solution of reagent-grade Ga(NO₃)₃, TiOSO₄, and ethanol solution of NbCl₅ in different ratios of Ga/Ti/Nb was prepared in a Teflon container. The solution mixture added with aqueous solution of urea was controlled to have a weak basic condition after hydrothermal treatment by the hydrolysis of urea. The suitable amount of the urea solution was
decided as the same amount of H⁺ ion concentration produced by hydrolysis of starting metal salts (Ga(NO₃)₃, TiOSO₄, NbCl₅) as shown in Table 1. This solution mixture in different ratios of Ga/Ti/Nb with total cation concentrations (Ga + Ti + Nb) of 0.1–0.5 mol/dm³ added with suitable amount of the urea solution in the Teflon container was then placed in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 180°C for 5 h under rotation at 1.5 rpm. After hydrothermal treatment, the precipitates were washed with distilled water until the pH value of the rinsed water became 7.0, separated from the solution by centrifugation, and dried in an oven at 60°C. The powders thus prepared were heated in an alumina crucible at heating rate 200°C/h, held at 800–1050°C for 1 h in air, and then cooled to room temperature in a furnace. Commercially available pure TiO₂ powder for photocatalysts (ST-01, anatase-type structure, BET specific surface area: 302 m²/g, crystallite size: 7 nm, Ishihara Sangyo Kaisha Ltd., Osaka, Japan) was used as the reference sample for estimation of the photocatalytic activity.

2.2 Characterization

The phases of the as-prepared and heat-treated powders were examined by X-ray diffractometry (XRD; model RINT-2000, Rigaku, Tokyo, Japan) using Cu-Kα radiation. The morphology of the as-prepared samples was observed by transmission electron microscopy (TEM; model JEM-2010, JEOL, Tokyo, Japan). The crystallite size of anatase was estimated from the line broadening of 101 and 200 diffraction peaks, according to the Scherrer equation, $D_{\text{SR}} = K\lambda/\beta \cos \theta$, where $\theta$ is the Bragg angle of diffraction lines; $K$ is a shape factor ($K = 0.9$ in this work); $\lambda$ is the wavelength of incident X-rays, and $\beta$ is the corrected half-width given by $\beta^2 = \beta_{\text{meas}}^2 - \beta_{\text{str}}^2$, where $\beta_{\text{meas}}$ is the measured half-width and $\beta_{\text{str}}$ is the half-width of a standard sample. The lattice parameters were measured using silicon as the internal standard. The amounts of rutile phase formed in the heated samples were calculated from the equation:

$$F_R = 1/[1 + 0.79(I_K(101)/I_K(110))]$$

where $F_R$ is the mass fraction of rutile in the samples, and $I_K(101)$ and $I_K(110)$ the integrated 101 intensities of anatase and 110 of rutile, respectively. These lines were at $\sim 26^\circ$ in 2θ. The chemical composition of the resultant powders was analyzed using an inductivity-coupled plasma emission spectrometer (ICP; model; ICP575II, Nippon Jarrell-Ash, Japan). The specific surface area of the prepared samples was calculated from the adsorption isotherm of nitrogen at 77 K based on the Brunauer–Emmett–Teller method (BET; model; NOVA 1200, Yussa Ionics, Osaka, Japan). The diffuse reflectance spectra measurements for powder samples have been made. The optical absorption of these prepared powders was measured using an ultraviolet-visible spectrophotometer (V-560, Nihon Bunko, Tokyo, Japan).

The photocatalytic activity and adsorptivity of these prepared powders were separately estimated from the change in the concentration of methylene blue (guaranteed reagent grade, C₁₆H₁₁N₅S, MB) both under ultraviolet ray (UV) irradiation from black light (20 W), and in the dark, respectively. To 250 cm³ of aqueous MB solution (5.0 × 10⁻⁵ mol/dm³), 0.05 g of sample powders were dispersed via ultrasonic stirring for 5 min and maintained in the dark for 24 h with stirring. After the dispersed sample powders in the solution adsorbed MB to the full by holding in the dark for 24 h under stirring, the sample in the solution was maintained for 0–5 h under irradiation of ultraviolet ray with an intensity of 1 mW/cm² under stirring. Thus, the UV-light irradiation time dependence of MB concentration decomposition by the sample powders was estimated by the measurement of the concentration of MB remained in the solution based on the absorbance change using the spectrophotometer.

3. Results and discussion

3.1 Formation of anatase-type solid solutions

The solution mixture that was prepared in different ratios of Ga/Ti/Nb with total metal cation concentration of 0.5 mol/dm³ added with suitable amount of urea solution in the Teflon container was heated under hydrothermal condition at 180°C for 5 h. In the present study, TiOSO₄ and Ga(NO₃)₃ are used due to water-soluble, and NbCl₅ is used because of ethanol-soluble. The TiOSO₄ has a tendency to easily hydrolyze, and nano-sized titania particles are formed by thermal hydrolysis of TiOSO₄.

Figure 1 shows XRD patterns of as-prepared samples at various starting compositions ($X = 0.20$ in Ga₄Ti₃₂₄NbxO₇). The crystalline phase detected in the as-prepared precipitates with composition up to $X = 0.10$ is only a single phase of anatase. A very slight amount of GaOOH phase in addition to anatase phase was detected in the samples with compositions $X = 0.15$ and 0.20. It is observed that the XRD lines become narrow and sharp with increase in the content of dopants niobium and gallium in Fig. 1. This suggests that the addition of these components affects on the crystalline growth and enhancement of crystallinity of anatase in the solution under hydrothermal condition.

The analytical values of the chemical compositions of the as-prepared samples are indicated in Table 1, which were determined by the elemental analysis using an ICP emission spectrometer. The analytical compositions of the as-prepared samples estimated using an ICP emission spectrometer did not so well coincide with the starting compositions of the samples. The content of Ti in the analytical compositions of the as-prepared samples was slightly more than that in the starting compositions of the samples. We should also reconsider the reliability of the chemical quantitative analysis of water of crystallization (n value) associated in the starting material TiOSO₄·nH₂O, although consideration should also be given to the reliability of the ICP analysis. We showed analytical $X$ values in Table 1 based on the analytical contents of Ga and Nb.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting composition (molar fraction)</th>
<th>Urea concentration (mol/dm³)</th>
<th>Analytical value (molar fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ga</td>
<td>Ti</td>
<td>Nb</td>
</tr>
<tr>
<td>0.05</td>
<td>0.050</td>
<td>0.900</td>
<td>0.050</td>
</tr>
<tr>
<td>0.10</td>
<td>0.100</td>
<td>0.800</td>
<td>0.100</td>
</tr>
<tr>
<td>0.15</td>
<td>0.150</td>
<td>0.700</td>
<td>0.150</td>
</tr>
<tr>
<td>0.20</td>
<td>0.200</td>
<td>0.600</td>
<td>0.200</td>
</tr>
</tbody>
</table>
The crystallite sizes of anatase estimated from the XRD line broadening of the 101 and 200 peaks are plotted in Fig. 2 against starting composition $X$. The crystallite size of anatase gradually increased when the contents of doped materials were increased. The crystallite sizes of the samples formed at the compositions $X = 0$–$0.10$ in Ga$_{2}$Ti$_{1-x}$Nb$_{2}$O$_{7}$ were in the range of 12–18 nm. The crystallite sizes grew up to 37–45 nm in the sample with $X = 0.20$. It was confirmed that the co-existence of niobium and gallium component facilitated the crystallite growth of anatase-type titania in the solution mixture under hydrothermal condition.

The TEM images of as-prepared samples are shown in Fig. 3. The crystallite size of anatase estimated from the XRD line broadening in the samples $X = 0$–$0.10$ in Ga$_{2}$Ti$_{1-x}$Nb$_{2}$O$_{7}$ relatively well corresponded to the particle sizes of the samples observed in the TEM images. Although the size of most particles in the samples $X = 0$–$0.10$ was in the range of 15–20 nm, large particles more than 50 nm that are lack of uniformity were observed in the sample $X = 0.20$.

Figure 4 shows the specific surface areas of the as-prepared anatase-type precipitates (Ga$_{2}$Ti$_{1-x}$Nb$_{2}$O$_{7}$) as a function of the value $X$. The specific surface areas of the precipitates decreased slightly and gradually when the value $X$ increased. This result corresponded in some degree to the increase in crystallite size of anatase-type precipitates (Ga$_{2}$Ti$_{1-x}$Nb$_{2}$O$_{7}$).

Small and gradual shifts of the diffraction lines of the as-prepared anatase-type TiO$_{2}$ were observed with increased the value of $X$ in Fig. 1. The corresponding changes in the lattice parameters $a_0$ and $c_0$ of the as-prepared tetragonal anatase-type TiO$_{2}$, as determined via XRD using silicon as the internal standard, relative to the value of analytical $X$, are shown in Fig. 5. The lattice parameters $a_0$ and $c_0$ slightly and gradually increased with increase in the value of analytical $X$ (i.e., increase...
in niobium and gallium content doped into TiO$_2$ although a very slight amount of GaOOH phase was detected in the samples with composition $X = 0.15$ and 0.20. The data in the coexisting area of a very slight amount of GaOOH phase is shown as dotted lines in the figure. The crystalline phase, anatase, which was precipitated directly from the precursor solutions of TiO(SO$_4$), Ga(NO$_3$)$_3$, and NbC$_3$ in the presence of urea, is considered to be solid solutions co-doped with niobium and gallium, because of the corresponding lattice parameter changes and the gradual shifts of the diffraction lines in the XRD patterns with increase in the value of $X$. Replacement of Ti$^{4+}$ by Ga$^{3+}$ and Nb$^{5+}$ can maintain the charge balance of TiO$_2$ solid solutions, which is the key factor for the difference between anatase-type titania doped with niobium$^{(6)(21)(22)}$ and one co-doped with niobium and gallium. In this study, niobium and gallium were co-doped into anatase-type structure under hydrothermal conditions at 180°C in the presence of urea. The diffuse reflectance spectra of the as-prepared anatase-type Ga$_x$Ti$_{1-x}$Nb$_2$O$_5$ solid solutions are shown in Fig. 6. The optical band gap is obtained, using $\alpha h\nu = \text{const}(h\nu - E_g)^n$, where $\alpha$ is the absorption coefficient, $n = 1/2$ for a direct allowed transition, and $n = 2$ for an indirect allowed transition. The band-gap values of the solid solutions were determined from the energy intercept by extrapolating the straight regions of the plot of $(\alpha h\nu)^2$ versus the photon energy $h\nu$ for a direct allowed transition ($E_d$). The band-gap value of anatase solid solutions (Ga$_x$Ti$_{1-x}$Nb$_2$O$_5$, $X = 0$-0.20) was 3.23–3.31 as indicated in Table 2.

3.2 Photocatalytic activity

The adsorptivity and photocatalytic activity of the samples were evaluated separately by the measurement of the concentration of MB remained in the solution after maintenance in the dark and under UV-light irradiation, respectively. After completion of the adsorption of MB by 0.05 g of the sample powders during the maintenance of the solution (5.0 $\times$ 10$^{-2}$ mol/dm$^3$ MB solution of 250 cm$^3$ containing the sample powders) in the dark for 24 h under stirring, UV light was irradiated. Figure 7 shows the effect of the composition of anatase-type Ga$_x$Ti$_{1-x}$Nb$_2$O$_5$ solid solutions on the adsorptivity and photocatalytic activity and the data of the reference pure TiO$_2$ powder ST-01 as changes in the concentration of MB with time in the dark and under UV light irradiation. The MB adsorption increased when the value of $X$ increased to $X = 0.20$. Especially Ga$_{0.1}$Ti$_{0.9}$Nb$_2$O$_5$ solid solution with $X = 0.20$ exhibited high adsorption in the dark, which may be partly due to the presence of the GaOOH phase as shown in the XRD pattern in Fig. 1. The plots of $-\ln(C/C_0)$ versus irradiation time are indicated in Fig. 8. The anatase-type Ga$_x$Ti$_{1-x}$Nb$_2$O$_5$ solid solutions ($X = 0.10$–0.15) showed improved photocatalytic activity in comparison with the sample with pure TiO$_2$ composition ($X = 0$) that was prepared.
under almost the same hydrothermal condition. The decrease in the photocatalytic activity in the sample \( X = 0.20 \) is supposedly due to the decrease in substantial TiO\(_2\) content in the sample and partly because of the presence of the GaOOH phase. This result may suggest that the formation of anatase-type \( \text{Ga}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \) solid solution with higher crystallinity than that in the pure TiO\(_2\), which was due to the enhancement in crystallite growth under the hydrothermal condition, have an effect on the improvement of photocatalytic activity.

3.3 Phase stability and formation of rutile-type solid solutions

The phase stability of the as-prepared anatase-type \( \text{Ga}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \) solid solutions in the course of heating in air was investigated. Figure 9 shows XRD patterns of \( \text{Ga}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \) solid solution after heating at 800–900°C for 1 h. The anatase-to-rutile phase transformation ratios for the present samples (\( \text{Ga}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \)) are plotted as a function of heat treatment temperature in Fig. 10. We have reported on the formation and phase stability of anatase-type TiO\(_2\) solid solutions doped with niobium and gallium by the similar hydrothermal method.\(^{22}\) The anatase phase of niobium-doped solid solutions was fully maintained after heating at 850–1000°C for 1 h by the presence of niobium component. The significant effect of dopant niobium on the improvement of phase stability of metastable anatase was observed. However, a part of added niobium component in titania solid solutions doped with niobium was separated from the anatase-type solid solution phase at >800°C, and it was precipitated as TiNb\(_2\)O\(_7\) and Nb\(_2\)O\(_5\) phase out of the anatase phase before anatase-to-rutile phase transformation. This phenomenon has been borne out by the fact that gradual, continual, and clear decrease in the lattice parameters \( a_0 \) and \( c_0 \) of the as-prepared anatase doped with niobium is observed in the course of heating at 500–800°C with increasing heating temperature before the phase transformation.\(^{22}\) On the other hand, the \( \text{Ga}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \) solid solutions (\( X \leq 0.1 \)) were kept as single phase of anatase before the phase transformation and they transformed into single phase of rutile during further heating. When niobium ions enter substitutionally into TiO\(_2\), the charge of the niobium(V) is kept by the compensation for introductions of structural defects and an appearance of titanium(III) in the niobium-doped TiO\(_2\). The charge balance is kept without structural defects and an appearance of titanium(III) by the entrance of gallium(III) ions substitutionally into TiO\(_2\) as compensation for the introduction of niobium(V) ions in the case of \( \text{Ga}(\text{III})_x\text{Ti}_{1-x}\text{Nb}(\text{V})_2\text{O}_6 \). However, the high phase stability of metastable anatase doped with niobium was significantly decreased by the presence of co-dopant gallium.

The starting temperature of the phase transition was accelerated about 50–100°C by the formation of \( \text{Ga}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \) solid solutions in comparison with pure hydrothermal anatase-type TiO\(_2\) (\( X = 0 \)), although that was delayed in the case of \( \text{Sc}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \), \( \text{Al}_x\text{Ti}_{1-x}\text{Nb}_2\text{O}_6 \) solid solutions.\(^{21,23}\) This may be attributed to the difference in nature of element Ga, Al, and Sc, and related to the properties (e.g., melting temperature...
and diffusivity of mass in heating, etc.) of oxide Ga₂O₃, Al₂O₃, and Sc₂O₃. The completing temperature of anatase-to-rutile phase transition was accelerated by the formation of Ga₄Ti₆₋ₓNbₓO₂ solid solutions as shown in Fig. 10. It was observed that the temperature range of anatase-to-rutile phase transformation for the Ga₄Ti₆₋ₓNbₓO₂ solid solutions became narrower than that for pure TiO₂. The rutile-type Ga₄Ti₆₋ₓNbₓO₂ solid solutions consisting of a single phase were formed through the anatase-to-rutile phase transformation.

4. Summary

The anatase phase of Ga₄Ti₆₋ₓNbₓO₂ solid solutions (X = 0–0.20) was formed as nanosized-particles from the aqueous precursor solutions under mild hydrothermal conditions in the presence of urea. The formation of anatase solid solutions doped with niobium and gallium was effective for the enhancement of crystallite growth of anatase and improvement of photo-decomposition of MB under UV irradiation. The anatase-type Ga₄Ti₆₋ₓNbₓO₂ solid solutions (X = 0.10–0.15) exhibited good photocatalytic activity. The rutile-type Ga₄Ti₆₋ₓNbₓO₂ solid solutions were formed through the anatase-to-rutile phase transformation. The temperature range of anatase-to-rutile phase transformation for the Ga₄Ti₆₋ₓNbₓO₂ solid solutions became narrower than that for pure TiO₂.

References