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Synthesis of Rutile-Type TiO₂-SnO₂ Solid Solution Nanoparticles by "Forced Co-Hydrolysis" under Hydrothermal Conditions

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Abstract. Rutile-type TiO₂-SnO₂ solid solution nanoparticles were synthesized via "forced cohydrolysis" of precursor solutions of TiCl₄ and SnCl₄ under hydrothermal conditions at 180~240 °C for 10 h. The lattice parameters a_0 and c_0 of rutile (Ti, Sn)O₂ solid solutions changed according to the Vegard's Law. Rutile-type complete solid solutions in the system TiO₂-SnO₂ were directly formed in all composition ranges at 240 °C. The crystallite size of solid solutions containing more than 20 mol% SnO₂ was maintained in the range of 10 to14 nm by the control of crystallite growth of rutile-type solid solutions owing to the presence of SnO₂. The specific surface area of rutile-type solid solutions corresponded well to the change in crystallite size. The rutile-type solid solutions were metastable and decomposed into Ti and Sn rich phases via heat treatment at 1200 °C.

1. Introduction

Tin dioxide (SnO_2) has attracted attentions as the most common materials used in gas sensing [1], but also as transparent conductor [2], and as heterogeneous oxidation catalyst. Titanium dioxide (TiO_2) has also received considerable attention as photocatalyst [3], white pigment, electrodes in devices including dye-sensitized solar cells [4], and gas sensors. They are wide band gap semiconductors: 3.06 eV for rutile TiO₂ and 3.60 eV for SnO₂ and have several similarities in structural and electronic properties. Mixed oxides of TiO₂ and SnO₂ are attractive in the field of gas sensing. TiO₂ and SnO₂ both adopt the rutile-type tetragonal structure. Therefore, at elevated temperatures, they form substitutional solid solutions which retain the rutile structure of the end members by reaction between TiO₂ and SnO₂ [5], although there exists a miscibility gap. The solid solutions undergo spinodal decomposition into Ti and Sn rich phases due to the existence of the miscibility gap below 1450 °C [6]. Wet chemical route is useful for the synthesis of nanosized particles of inorganic materials in general. The forced hydrolysis is carried out via keeping acidified solutions of metal salts at elevated temperatures for a definite period of time.

In the present study, the synthesis and structure of nanoparticles of solid solutions between TiO_2 and SnO_2 via "forced co-hydrolysis" of precursor solutions of $TiCl_4$ and $SnCl_4$ under hydrothermal conditions were investigated.

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2. Experimental

A mixed aqueous solution of TiCl₄ and SnCl₄ in a total cation concentration (Ti + Sn) of 0.1 mol/dm³ was prepared in a Teflon container. The Teflon container was then placed in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 180-240 °C for 10 h under rotation at 1.5 rpm. After hydrothermal treatment, the precipitate was 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 65 °C. The powder thus prepared was heated in an alumina crucible at heating rate 300 °C /h, held at 1200 °C for 1-168 h in air, and then cooled to room temperature in a furnace.

The as-prepared and heated powders were examined using X-ray diffractometry (XRD) with Cu K α radiation and observed under transmission electron microscopy (TEM). The crystallite size of anatase and rutile was estimated from the line broadening of 101 and 110 diffraction peaks, respectively according to the Scherrer equation. The lattice parameters were measured using silicon as the internal standard. 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). The diffuse reflectance spectra measurements have been made. The optical absorption of these prepared powders was measured using an ultraviolet-visible spectrophotometer.

3. Results and discussion

The XRD patterns of the precipitates formed from the mixed solution of $TiCl_4$ and $SnCl_4$ via hydrolysis at 180 °C are shown in Figure 1. The precipitates were detected as a single-phase rutile-type structure, with the exception of the sample Ti 90 mol% consisting of anatase and rutile, although the precipitate formed at the composition Ti 100 mol% was anatase together with a small amount of brookite and rutile phases.





Figure 1. XRD patterns of precipitates obtained from the mixed solution of $TiCl_4$ and $SnCl_4$ by hydrolysis under hydrothermal condition at 180 °C for 10 h.

Figure 2. Crystallite size of rutile-type solid solutions and anatase obtained under hydrothermal condition at 180 °C for 10 h.

Figure 2 indicates the crystallite size of rutile-type solid solutions and anatase formed by hydrolysis under hydrothermal condition at 180 °C for 10 h. The crystallite size of the rutile-type solid solutions gradually and slightly increased from 7 to 12 nm with increased Ti content in the solid solutions in the range Ti 0 to 80 mol%. The crystallite size of anatase was approximately 8 nm.

The XRD patterns of the precipitates formed from the mixed solution via hydrolysis at 240 °C for 10 h are shown in Figure 3. All the precipitates were detected as a single-phase rutile-type structure, and no trace of diffraction peaks due to another phase were detected with the exception of the sample Ti 90 mol% together with a very slight amount of anatase phase. Slight and gradual shifts of the XRD lines of the rutile phase (cassiterite phase) were observed with changing the ratio of Ti/Sn.

The TEM image of rutile-type precipitate (SnO₂-TiO₂ solid solution) formed from the precursor solution in a ratio of Ti/Sn = 0.50/0.50 under hydrothermal condition at 240 °C for 10 h is shown in Figure 4. The crystallite size of cassiterite SnO₂ that was formed via hydrolysis at 120 °C for 10 h was 2.5 nm, which was estimated on the basis of the line broadening of the XRD pattern. The cassiterite grew to approximately 10 nm in diameter under hydrothermal condition at 240 °C for 10 h. The particle size of rutile-type precipitates slightly increases when the rutile-type solid solution is formed via doping 50 mol% TiO₂. The particle size of the SnO₂-TiO₂ solid solution precipitates was approximately 15 nm in diameter, and relatively high homogeneity in particle size scattering is observed. The change in specific surface areas of the samples was in accordance with the data of the crystallite size of rutile-type precipitates.





Figure 3. XRD patterns of precipitates obtained from the mixed solution of $TiCl_4$ and $SnCl_4$ by hydrolysis under hydrothermal condition at 240 °C for 10 h.

Figure 4. TEM image of precipitate hydrothermally formed at the composition Ti 50 mol% under hydrothermal condition at 240 °C for 10 h.

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The changes in the lattice parameters a_0 and c_0 of the as-prepared tetragonal rutile-type TiO₂-SnO₂ precipitates, as determined via XRD using silicon as the internal standard, relative to the value of Ti content (mol%) showed that the lattice parameters linearly decreased with increased Ti content according to the Vegard's Law. The measured lattice parameters for the end members TiO₂ and SnO₂ showed good coincidence with published JCPDS data. Figure 5 shows the diffuse reflectance spectra of the as-prepared rutile-type solid solutions. The diffuse reflectance spectra continuously varied with changing Ti content in the precipitates.

The time dependence of lattice parameter change of rutile-type solid solution containing 50 mol% TiO_2 via heat treatment at 1200 °C in air showed that the rutile-type solid solutions that were formed via hydrolysis under hydrothermal condition were metastable, and it decomposed into Ti and Sn rich phases via heat treatment at 1200 °C.



Figure 5. Diffuse reflectance spectrum of rutile-type solid solutions.

4. Summary

The solid solutions between TiO_2 and SnO_2 were hydrothermally synthesized as nanoparticles via hydrolysis of acidic precursor solutions of $TiCl_4$ and $SnCl_4$ at 180~240 °C. The change in lattice parameters a_0 and c_0 of rutile (Ti, Sn)O₂ solid solutions followed the Vegard's Law. The crystallite size of solid solutions containing more than 20 mol% SnO_2 was maintained in the range of 10 to 15 nm by the control of crystallite growth of rutile-type solid solutions owing to the presence of SnO_2 . The specific surface area of rutile-type solid solutions corresponded well to the change in crystallite size. The phase separation was observed in $Ti_{0.5}Sn_{0.5}O_2$ by heating at 1200 °C in air.

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