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Preparation of Monodispersed Crystalline Germanium (IV) Oxide Particles

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Abstract

Monodispersed crystalline hexagonal germanium (IV) oxide particles with an average size of $2.0\ \mu\text{m}$ were prepared by cooling from 50 to 10°C an ethanolic mixed solution (30% by volume) of $8.4 \times 10^{-2}\ \text{mol dm}^{-3}$ germanium (IV) and $1.7\ \text{mol dm}^{-3}$ hydrochloric acid, for example. A fraction of soluble germanium (IV) species in a supernatant solution finally reached 0.36 at 10°C after 325h. A rate-determining step of the particle growth was revealed to be a polynuclear layers mechanism as judged from the fractional change of the germanium (IV) species. Uniform cuboidal particles of crystalline germanium (IV) oxide were also prepared by oxidizing at 100°C a mixed solution of $0.11\ \text{mol dm}^{-3}$ tris(oxalato)germanate (IV) complex, $4.0\ \text{mol dm}^{-3}$ sulfuric acid, and ethanol of 13% by volume with $2.2\ \text{mol dm}^{-3}$ hydrogen peroxide.

Additionally, uniform tetrahedral particles of $\text{Na}_2\text{Ge}_3\text{O}_7 \cdot 7\text{H}_2\text{O}$ were obtained at 100°C and pH 8.5 from an ethanolic solution (50% by volume) of $3.5 \times 10^{-2}\ \text{mol dm}^{-3}$ 8-quinolinolato-germanium (IV) complex in the presence of sodium ions.

Key-Words : *Uniform Oxide Particles, Monodispersed Germanium (IV) Oxide Particles, Particle Preparation*

1. Introduction

Uniform colloid particles are very useful and important in the field of material science and technology, not only in that of academic studies of colloid science. Thus, many kinds of well-defined monodispersed particles of metal (hydrous) oxides^{1,2)}, such as aluminium(III)^{3,4)}, chromium(III)⁵⁾, gallium(III)^{6,7)}, etc., have been prepared by forced hydrolysis of corresponding metal ions at elevated temperatures. However,

uniform germanium (IV) oxide particles have not been prepared from a homogeneous solution, although monodispersed spherical particles of silica and titania were prepared as quadrivalent compounds by several methods^{8–12)}.

In the present work, preparation of monodispersed germanium(IV) oxide particles were studied through a simple process based on a difference in the solubility^{13–16)} of germanium (IV) oxide in a hydrochloric acid/ethanol/water mixed solution. In addition, uniform particles of germanium(IV) oxide and corresponding composite oxide were also obtained from tris(oxalato)germanate(IV) and 8-quinolinolato-germanium(IV) solutions, respectively, by an aging method including a redox reaction.

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2. Experimental

2.1 Materials

Germanium(IV) oxide of 99.99% purity (Kanto Chemical Co.) was molten with ten times quantity of sodium carbonate in a platinum crucible. The solid thus obtained was dissolved in doubly distilled water together with hydrochloric acid to yield a germanium(IV) solution acidified at pH 2. Then, sodium ions were removed from the solution by passing through an H-type cation exchange resin (Amberlite IR120B) column. The solution ($\sim 0.13 \text{ mol dm}^{-3}$) was filtered through a membrane filter, $0.2 \mu\text{m}$ in pore size, before use as a stock solution of germanium(IV). A total concentration of germanium(IV) in the stock solution was determined spectrophotometrically using molybdenum blue method¹⁷⁻¹⁹.

Potassium tris(oxalato)germanate(IV)²⁰⁻²² was prepared as follows: a mixture of 0.064 mol germanium(IV) oxide, 0.064 mol potassium oxalate monohydrate, and 0.128 mol oxalic acid dihydrate in 300 cm^3 of water was refluxed for about 3 h until the solids were completely dissolved. Then, 320 cm^3 of 95 % ethanol was added at 40°C with stirring to yield crystals of potassium tris(oxalato)germanate(IV) upon further cooling at $\sim 0^\circ\text{C}$.

8-Quinolinolatermanium(IV) solution was prepared by adding a $3.5 \times 10^{-2} \text{ mol dm}^{-3}$ 8-quinolinol solution to germanium(IV) solution obtained from alkali fusion of germanium(IV) oxide, as described above, at specified concentrations and pH, but without elimination of sodium ions. The solution thus prepared was filtered through a membrane filter, $0.2 \mu\text{m}$ in pore size, before use as a stock solution.

2.2 Procedures

In order to obtain uniform germanium(IV) oxide particles through a simple process by a temperature dependence of their solubility, an ethanolic mixed solution (30% by volume) of germanium (IV) was prepared at a concentration range from 7.1×10^{-2} to $9.0 \times 10^{-2} \text{ mol dm}^{-3}$ [Ge

(IV)] with stirring at 50°C . An aliquot of the mixed solution (40 cm^3) thus prepared was charged in a screw-capped Pyrex glass tube at 50°C and quickly cooled to 10 or 25°C in a thermostated bath and kept for a desired period of time (1–10h). Resulting particles were centrifuged at 3000 rpm and repeatedly washed with a distilled water/ethanol mixture at room temperature using an ultrasonic bath.

A supernatant solution was further filtered through a membrane filter, $0.1 \mu\text{m}$ in pore size, in order to determine spectrophotometrically a concentration of soluble germanium(IV) species using molybdenum blue method¹⁷⁻¹⁹.

Monodispersed crystalline germanium(IV) oxide particles were also prepared by oxidizing at 100°C for 15 h a tris(oxalato)germanate(IV) solution at an initial pH range between 7.9 and 8.9 with hydrogen peroxide or ammonium peroxodisulfate. In addition, uniform crystalline sodium germanate(IV) particles were prepared by aging at 100°C for 35 min an 8-quinolinolatermanium(IV) solution at an initial pH 9.5 in the presence of sodium ions. The pH values in this work are defined as apparent ones, because those obtained empirically are slightly shifted from real values in the alcohol/water mixed media²³.

Morphology and size of the particles were observed with a scanning electron microscope (Japan Electron Optics Laboratory, model JSM 5200). The particles were identified with an X-ray powder diffractometer (Rigakudenki, Geigerflex model RAD IIIA). Diffraction angles were calibrated using a standard silicon. Differential thermal analysis (DTA) and thermogravimetry (TG) of the particles were carried out using a DTA analyzer (Seiko Instrument, model SSC-5200).

3. Results and Discussion

3.1 Formation of Monodispersed Germanium(IV) Oxide Particles from Germanium(IV)/Hydrochloric acid/Ethanol/

Fig. 1 Scanning electron micrograph of polyhedral GeO_2 particles obtained by cooling at 10°C for 3 h an ethanolic solution (30% by volume) of $8.4 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Ge(IV)}]_t$ and 1.7 mol dm^{-3} HCl .

Water Mixed Solutions.

Figure 1 shows uniform particles obtained by cooling quickly from 50 to 10°C a mixed solution of $8.4 \times 10^{-2} \text{ mol dm}^{-3}$ germanium(IV), 1.7 mol dm^{-3} HCl , and ethanol of 30% by volume and keeping for 3 h at the same temperature. An average size of the polyhedral particles thus obtained was estimated to be $2.0 \mu\text{m}$ with a relative standard deviation of 0.08. Such uniform particles could be also prepared even at 25°C . Any particles did not appear at an initial concentration of germanium (IV) less than $7.0 \times 10^{-2} \text{ mol dm}^{-3}$ at 10°C . Thus, an enough supersaturation of germanium (IV) species should be achieved for producing uniform germanium(IV) oxide particles. Solubility¹³⁻¹⁶⁾ of germanium(IV) oxide is much greater than those of common trivalent metal oxides, so that an optimum concentration range for preparing uniform germanium(IV) oxide particles would be greater as much as about two orders than those for the corresponding uniform trivalent metal oxide particles.

Figure 2 displays the X-ray powder diffraction pattern of the same particles. The particles were identified as well-crystallized hexagonal

Fig. 2 X-ray powder diffraction pattern of uniform GeO_2 particles obtained under the same conditions shown in Fig. 1.

Fig. 3 DTA and TG patterns of the same GeO_2 particles taken at heating rate of $20^\circ\text{C min}^{-1}$.

germanium(IV) oxide, the spacings and relative intensities of which were agreed well with those in a literature²⁴⁾.

Figure 3 shows results of differential thermal analysis (DTA) and thermogravimetry (TG) of the monodispersed particles taken at a heating rate of $20^\circ\text{C min}^{-1}$. The sample was previously dried in a desiccator for more than one week before DTA-TG measurement. Two endothermic peaks around 330 and 740°C accompanied

Fig. 4 Growth of uniform GeO_2 particles at 10 and 25°C during reaction at the same concentrations shown in Fig. 1.

Fig. 6 Dependence of kind of alcohol on particle size of GeO_2 under the conditions shown in Fig. 1.

Fig. 5 Effect of acid concentration on particle growth of GeO_2 at an early stage of reaction under the same conditions shown in Fig. 1 except for acid content. Conditions: $[\text{Ge}(\text{IV})]_t = 8.4 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{HCl}]_t = 1.7 \text{ mol dm}^{-3}$ (a) and 3.4 mol dm^{-3} (b), and ethanol 30% by volume.

about 3% of weight loss in contrast to few weight change below 300°C. These two broad endothermic peaks suggest an existence of two kinds of structural water in the particles, although a sharp endothermic peak at 1125°C was due to fusion of germanium (IV) oxide.

3.2 Particle Growth of Germanium(IV) Oxide.

Figure 4 shows changes in size of the monodispersed germanium (IV) oxide particles during the reaction at 10 and 25°C under the conditions given in **Fig. 1**. The particles grew linearly with an almost identical growth rate at 10 and 25°C, except for an early stage of the reaction. An average size of the particles obtained at 10°C was somewhat larger than that produced at 25°C, depending on degree of supersaturation.

Figure 5 shows an effect of acidity of the solution on particle growth at an initial stage of the reaction under the same conditions shown in **Fig. 1** except for the acid concentration. The particle growth was significantly enhanced with increasing the acid concentration from 1.7 to 3.4 mol dm^{-3} . Such pronounced effect of acid content on the particle growth would arise from an apparent solubility of germanium (IV) oxide¹⁴⁾ dependent on acidity, as usually observed in the case of silica²⁵⁾. **Figure 6** also shows an effect of a kind of alcohol in a mixed solvent on growth of uniform germanium (IV) oxide particles under the same concentrations. Higher alcohols such as 2-propanol and *t*-butanol clearly enhanced growth rate of the germanium (IV) oxide particles than ethanol, whereas morphology of the

Fig. 7 Change in concentration of soluble Ge(IV) species during reaction at 10°C under the same conditions shown in Fig. 1.

particles did not depend on the kind of the alcohol.

3.3 Growth Mechanism of Germanium(IV) Oxide Particles

Figure 7 shows a concentration change of soluble germanium (IV) species as a function of reaction time at 10°C, for example, under the same conditions shown in **Fig. 1**. The concentration finally reached $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ (a fraction of 0.36) at 10°C after 325 h. Almost the same feature of the fractional change was also observed at 25°C with a final fraction of 0.49 ($4.0 \times 10^{-2} \text{ mol dm}^{-3} [\text{Ge(IV)}]_t$) after 260 h.

The reaction degree, α , is defined as:

$$\alpha = (C_0 - C) / (C_0 - C_s), \quad (1)$$

where C_0 , C_s and C are the initial and final concentrations of germanium(IV) species, and that at reaction time t , respectively. Thus, the modal size, r , of monodispersed particles at t can be expressed as :

$$r = r_t \alpha^{1/3}, \quad (2)$$

where r_t is the final size of the particle.

According to Nielsen²⁶⁾, the change in the reaction degree, $d\alpha/dt$, is given by the following equation (3) for the growth of particles through

Fig. 8 Plots of reaction degrees of GeO_2 particles at 10°C obtained from results in Fig. 7. Reaction time, t' , in the figure is normalized in terms of induction period.

a polynuclear layers mechanism as :

$$\frac{d\alpha}{dt} = K_p \alpha^{2/3} (1 - \alpha)^{(m+2)/3} \quad (3)$$

$$K_p = 1.8 r_t^{-1} k_m^{1/3} C_0^{(m+2)/3} d^{7/3} D^{2/3}, \quad (4)$$

where k_m and m stand for the apparent rate constant of the two-dimensional surface nucleation and its exponential concentration dependence, d is the height of the surface nuclei, and D is the diffusion coefficient of the species. The parameters K_p and m can be calculated by a least-squares method using logarithmic values of $d\alpha/dt$, α , and $(1 - \alpha)$ obtained from the results shown in **Fig. 7**, because K_p is constant under given conditions. Changes in the observed reaction degree were previously smoothened by a polynomial equation. The values of K_p and m were estimated as 13.8 and 3.81 at 10°C, respectively.

The solid curve in **Fig. 8** shows the reaction degrees obtained from numerical integration of Eq. (3) by the Runge-Kutta method using the parameters obtained above, which agreed well with the empirical ones over a wide range of reaction time. Similar numerical treatment was also made assuming the diffusion mechanism²⁶⁾.

Fig. 9 Scanning electron micrograph of cuboidal GeO_2 particles precipitated from tris(oxalato)germanate (IV) solution by aging at 100°C for 15 h. Conditions : $[\text{Ge(IV)}]_t = 1.1 \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{H}_2\text{O}_2]_t = 2.2 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 4.0 \text{ mol dm}^{-3}$, and ethanol 13% by volume.

Calculated values, however, did not fit the experimental data. Thus, it would appear that the polyhedral particles of germanium (IV) oxide grow through the polynuclear layer mechanism including desolvation and dehydration process even at low temperatures.

3.4 Formation of Germanium(IV) Oxide Particles from Tris(oxalato)germanate(IV) Solutions.

The formation of tris (oxalato) germanate (IV) complex is exothermic¹⁷⁻¹⁹. Therefore, in order to prepare uniform particles, this complex solution was aged at 100°C over a concentration range from 4.3×10^{-2} to $5.4 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Ge(IV)}]_t$ and initial pHi from 7.9 to 8.9. However, any particle did not appear, because the oxalato complex is so stable to release free germanium (IV) species even at higher temperatures. Thus, oxalate anions as the ligand were oxidized to degrade the complex with hydrogen peroxide or ammonium peroxodisulfate, leading to germanium(IV) hydroxocomplexes. **Figure 9** shows cuboidal particles, with an average size of $3.4 \mu\text{m}$ and a relative standard deviation of 0.12, obtained by aging at 100°C for 15 h a mixed

Fig. 10 Scanning electron micrograph of $\text{Na}_2\text{Ge}_3\text{O}_7 \cdot 7\text{H}_2\text{O}$ particles prepared from 8-quinolinolato-germanium(IV) solution in the presence of sodium ions by aging at 100°C and pHi 8.5 for 35min. Conditions: $[\text{Ge(IV)}]_t = 3.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{C}_9\text{H}_7\text{NO}]_t / [\text{Ge(IV)}]_t = 2.0$, and ethanol 50% by volume.

solution of 0.11 mol dm^{-3} tris(oxalato)germanate (IV), 4.0 mol dm^{-3} sulfuric acid, 2.2 mol dm^{-3} hydrogen peroxide, and ethanol 13% by volume. The particles thus obtained were identified as well-crystallized hexagonal germanium (IV) oxides²⁴) by X-ray powder diffractometry. However, this procedure was somewhat disadvantageous due to disturbance of homogeneous reaction by carbon dioxide bubbles generated at the oxidation of oxalate anions.

3.5 Formation of Germanium(IV) Compound Particles from 8-Quinolinolato-germanium(IV) Solutions.

Preparation of germanium(IV) compound particles was attempted using 8-quinolinolato-germanium(IV) complex. The enthalpy change of the formation of 8-quinolinolato-germanium(IV) complex²⁷) has been reported to be $-76.0 \text{ kJ mol}^{-1}$. Thus, free metal ions should be released from the complex at elevated temperatures. **Figure 10** displays tetrahedral particles obtained by aging a solution of $3.5 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{Ge(IV)}]_t$, a concentration ratio, $[\text{C}_9\text{H}_7\text{NO}]_t / [\text{Ge(IV)}]_t$, of 2.0, and ethanol of 30% by volume at the pHi of 8.5 and 100°C for 35 min

in an oil bath. An average size of the particles thus obtained was estimated to be $2.6\ \mu\text{m}$ with a relative standard deviation of 0.17. The particles thus obtained were identified as $\text{Na}_2\text{Ge}_3\text{O}_7 \cdot \text{H}_2\text{O}$ by X-ray powder diffractometry²⁸⁾. However, morphology and uniformity of the particles were strongly dependent on the preparing conditions such as germanium(IV) concentration, initial pH, and alcohol content.

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