Kinetic Study on Nano-ZrO₂ from ZrOCl₂ Solution Modified with Diglycol

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ジグリコール添加した ZrOCl₂ 溶液から合成したナノ ZrO₂ 粒子のキネティックス研究

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Monodispersed yttria stabilized ZrO₂ nanocrystals were synthesized from zirconium oxyhydrate sols chelated with diglycol. The particle growth kinetics as a function of the concentration of ZrOCl₂ solution and molar ratio of ZrOCl₂: diglycol was investigated. It was demonstrated that the rate constant of the particle growth and the final particle size increased with increasing the concentration of ZrOCl₂ solution and decreasing the molar ratio of ZrOCl₂: diglycol. High-resolution transmission electron microscopy (HRTEM) as well as powder X-ray diffraction showed that the as-synthesized nanoparticles were well crystalline.

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1. Introduction

In the past decades, nanoscale ceramic powders have been focused due to the optimum sintering and mechanical properties.¹⁾ However, such particles are so reactive that they tend to agglomerate during synthesis.²⁾ In order to fabricate agglomerate-free nanoscale particles with desired mean size and particle size distribution, control of the kinetics, nucleation and growth is very important. Conventional factors to determine the kinetics include concentration of reactants, character of complexing reagent, and ratio of complexing reagent to the source of nanoparticles.³⁾⁻⁵⁾

Likewise, yttria stabilized tetragonal zirconia is an important structural ceramic with excellent mechanical properties, such as high fracture toughness, strength, and hardness. Extensive researches to produce zirconia powder have been initiated on sol-gel process with the aim of controlling the morphology.^{6),7)} In order to obtain stable sols without precipitation, the additives must be added to restrain both hydrolysis and condensation. Homogenous zirconia sols were prepared from zirconium alkoxides modified with diglycol (HOCH₂CH₂OCH₂OH),⁸⁾ glycol,⁹⁾ acetic acid,¹⁰⁾ acetylacetonate.¹¹⁾ The solubility and reactivity of alkoxides toward hydrolysis and subsequent reactions were modified by exchanging some of the alkoxy groups with carboxylic acid or polyalcohol, whereas the reactivity of the kinetic probe is strongly dependent upon solvent properties.¹²⁾ However, few study about using aqueous solution as the zirconia source has been reported.

In the present study, yttria stabilized ZrO₂ nanocrystals were synthesized by hydrolyzing a ZrOCl₂ solution chelated with diglycol. The kinetics and the rate constant of ZrO₂ nanoparticles growth with different reagent concentrations and the ratio was investigated in detail.

2. Experimental procedure

Zirconium oxychloride octahydrate (ZrCl₂O·8H₂O, 98%) and YCl₃·6H₂O were obtained from Sigma-Aldrich Chemical Company. Diglycol, which was used as a kinetic probe reagent in the present research, was provided from Wako Pure Chemi-

cal Industry, Japan. All the reagents were used as received.

Zirconium oxyhydrate sols at various concentration (0.02 M, 0.05 M), which contained 8 mol% YCl₃·6H₂O (with respect to ZrO₂), were prepared by hydrolysis of ZrCl₂O·8H₂O and YCl₃·6H₂O in distilled water. Then, diglycol were added to the as prepared solutions during vigorous magnetic stirring. 0.02 M ZrOCl₂ solutions were mixed with diglycol at the volume ratio of 5: 1, while 0.05 M ZrOCl₂ solutions were mixed with diglycol at the volume ratio of 1: 1, 3: 2 and 2: 1 respectively. The pH of the mixtures was adjusted to 5 after the mixed source was aged for 8 h.

After ageing from 4 to 240 h, the size of the precipitated ZrO₂ nanoparticles was determined using dynamic light scattering spectrophotometer (DLS-7600, Otsuka Electronics Co., Ltd.). The morphology of the particles was characterized using a transmission electron microscope (TEM, JEM-2010, JEOL).

3. Results and discussion

Figure 1(a) shows the relationship between the reaction time and the particle size as a function of ZrOCl₂ concentration, at which the volume ratio of ZrOCl₂: diglycol is fixed to 5: 1 for 0.02 M ZrOCl₂ solutions and 2: 1 for 0.05 M ZrOCl₂ solutions on purpose of investigate the kinetic of particle growth at same mole ratio of ZrOCl₂: diglycol. The plots show that the particles growth parabolically, with an initial rapid growing with time and an asymptotic approach to a maximum diameter. The growth of the particle size, δ , could be fitted by simple Eq. (1) describing the homogeneous particle growth kinetics,^{13),14)}

$$\delta = \delta_M (1 - e^{-\kappa t}) \quad (1)$$

where δ_M is the final particle diameter, κ is the rate constant dictated by the solution conditions, and t is the reaction time. After fitting to Eq. (1), the δ_M and κ were found and shown in Fig. 1(b). It is seen that the rate constant and the final particle size increase with increasing the ZrOCl₂ concentration. Zukoski et al.¹⁴⁾ studied the kinetics of the growth of uniform

Fig. 1. (a) Particle growth as a function of reaction time at different concentrations of ZrOCl₂ solution: ■ 0.05 M, ▲ 0.02 M, (b) Variation of final particle size (δ_M , ▲) and rate constant (κ , ◆) at different ZrOCl₂ concentration.

Fig. 2. (a) Particle growth as a function of reaction time for 0.05 M ZrOCl₂ solution at different volume ratios of ZrOCl₂: diglycol: ● 1:1, ■ 3:2, ◆ 2:1, (b) Variation of final particle size (δ_M , ▲) and rate constant (κ , ◆) at different volume ratios of ZrOCl₂: diglycol.

silica particles from silica precursor. One important observation was that the silica particles grew by a surface limited mechanism. This observation is likely to hold true for our system as well.

The particle growth kinetic as a function of the ratio of ZrOCl₂: diglycol is shown in Fig. 2(a) for 0.05 M ZrOCl₂ solution. After fitting with Eq. (1), the δ_M and κ were shown in Fig. 2(b). It is shown that the rate constant and the final particle size increase when relatively lower content of diglycol was applied.

It is well known that the sol-gel method is a versatile technique used to obtain ultrafine, homogenous powders of a variety of glass and ceramic materials at low temperature and in short time through the growth of metal oxo-polymers in a solvent. However, the hydrolysis and condensation involved in sol-gel process are generally fast and need to be inhibited to avoid precipitation. Likewise, electrolytes could affect the hydrolysis and condensation kinetics. In the present study, as chelated with diglycol, the precipitation rate was changed. The controlled sol-gel process can be described as follows:

Here, XOH stands for diglycol, while X represents HO(CH₂)₂O(CH₂)₂ functional group. The actual chemical process in the sol is much more complicated than those simplified by Eqs. (2) to (4). Therefore, the hydrolysis, inducing nucleation at the early stage of the sol-gel process, of chelated zirconium

species is reduced due to steric effect. Zhao et al. informed that besides the hydrolysis, diglycol also strongly restrain condensation,⁸⁾ which affects the particle growth rate as well as the final particle size.

When the ratio of ZrOCl₂ to diglycol is constant, lower precursor concentration results in lower condensation rate, which is decided by the distance among nucleates, due to the fewer nucleates per volume. Therefore, the rate constant, κ , decreased with decreasing the concentration of precursor solution. Furthermore, the final particle size would be smaller due to lower collision probability between nucleates and nano-clusters.

When relatively low ratio of ZrOCl₂: diglycol has been used, the hydrolysis of the precursor was relatively slow due to the much more stable chelated structure. Hence, the reaction between nucleates and nanoclusters was slow, which result in slower particles growth. Therefore, the rate constant of the particle growth, κ , decrease with increasing the relative content of diglycol due to the chelating reactions. Hence, highly stable, monodispersed zirconia nanoparticles with controllable particle size were prepared. Besides, lower ratio of ZrOCl₂: diglycol means there are much higher chelated zirconium remained in the mixture after reaction. Therefore, the concentration of nucleates is lower, which results in lower collision probability, and in turn, smaller final particle size.

The TEM micrographs of the as-synthesized zirconia nanoparticles were shown in Fig. 3 after 0.05 M ZrOCl₂ solution chelated with diglycol at a ratio of 3: 2 was reacted for 72 h,. It is seen from Fig. 3(a) that the as-synthesized particles were monodispersed with diameters around 25 nm, which is in good agreement with the results of particle size shown is Fig. 2

Fig. 3. (a) TEM of the as-synthesized particles from 0.05 M ZrOCl₂ mixed with diglycol at a volume ratio of 3: 2 and reacted for 72 h, (b) HRTEM image together with the corresponding power spectrum.

(a). Figure 3(b) shows a HRTEM image together with the corresponding power spectrum. (PS, the square of the Fourier transform of the TEM image). It is shown that the particles are crystalline in the tetragonal structure without the presence of defects that also indicated from powder XRD patterns.

The distance between lattice planes that calculated from power spectrum is about 3×10^{-10} m. Therefore, the faceted particle is parallel to the (111) plane when a crystal lattice with unit cell parameters $a=0.512$ nm and $c=0.525$ nm^{15),16)} was selected.

4. Conclusions

We have demonstrated a simple and effective way to synthesize monodispersed nanocrystalline Y-ZrO₂ particles, using ZrOCl₂ and YCl₃ as the raw material and diglycol as the complexing reagent. The hydrolysis and condensation of ZrOCl₂ was well restrained by using diglycol as complexing reagent. The particle size as a function of reaction time indicated that the rate constant of the particle growth and the final particle size increase with increasing the concentration of ZrOCl₂ solution and the decreasing of the molar ratio of ZrOCl₂: diglycol.

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