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Dynamic phase behavior during sol-gel reaction in supercritical carbon dioxide for morphological design of nanostructured titania

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Dynamic phase behavior during sol-gel reaction in supercritical carbon dioxide is investigated for a morphological design of titania. The sol-gel reactions are conducted using acetic acid (HAc) and titanium tetrabutoxide (TBO) as the precursor of titania at 313–353 K and 20.0 MPa. It is demonstrated the effects of the precursor concentration and temperature on the swelling ratio of the reaction phase and the formation of the homogeneous phase during the reaction in supercritical carbon dioxide. Nano-spherical titania is formed at the condition of lower precursor concentration and temperature 313 K that leads to the larger swelling ratio of the reaction liquid phase. The titania with a hollow urchin-shaped is obtained at 333 K with the higher precursor concentration. It is implied that this unique structured titania is produced by the phase separation between supercritical carbon dioxide and water phases which is the byproduct on the reaction.

1. Introduction

Development of nanostructured titania has been demanded for a lot of the application techniques in a wide range of fields, such as a semiconductor on dye-sensitized solar cell [1–3], catalyst support in fuel cell [4–7] and waste water treatment [8–10]. Controlling morphology and crystal structure of titania can be very important factor to the design of their functional properties for these applications. The titania with anatase crystal phase has been developed actively because of the photocatalytic activity than other crystal phases, rutile and brookite [11]. Some research groups have reported the various morphologies of anatase titania, such as mesoporous sphere [12–14], nano-needle [2,3,5,15], nanotube [7], urchin-shaped [16–18]. Kim and Kwak [14] synthesized the mesoporous spherical titania using hydrothermal treatment and additional washing by water and ethanol. This mesoporous titania resulted in high surface area and high degradation of methylene blue under UV-irradiation. The three-dimensional urchin-shaped titania has been developed using solvothermal method by Zhou et al. [18]. The urchin-shaped titania could be formed by controlling the concentration of titanium tetrachloride and tetrabutyl titanate as the precursors and the reaction temperatures. The urchin-shaped titania was adopted for the anode on dye-sensitized solar cell and led to the photoelectric conversion efficiency higher than those in case of sphere and flow-like titania. Although the hydrothermal and solvothermal techniques have been applied for the nanostructured titania with unique morphologies, there is the problem of the complex process that requires washing or drying operation after the reaction for the fabrication of titania powder.

Supercritical carbon dioxide has been applied as both synthesis and drying solvents for the fabrication of nanostructured titania because of the unique properties, such as low surface tension, high solubility and diffusivity. The technique using supercritical carbon dioxide as both synthesis and drying solvents allows to a simple fabrication process of the titania powder. Some research groups have utilized supercritical carbon dioxide as drying solvents for the porous titania. Iwai et al. [3] has studied the titania fabrication using sol-gel reaction in liquid solvent and the drying in supercritical carbon dioxide and nano-needle titania was produced consequently. The sol-gel reaction in supercritical carbon dioxide has been attracted for controlling the morphology of nanostructured titania [19–22]. The nanostructured titania synthesis by sol-gel reaction and drying in supercritical carbon dioxide been have reported by a research group of Sui et al. [20]. The sol-gel reactions were conducted using titanium tetrabutoxide, titanium isopropoxide and acetic acid. They investigated the effect of the molar ratio of acetic acid to titania precursor on the morphologies of titania. The spherical and needle-like titania were synthesized at the reaction condition of low and high molar ratio of acetic acid to titanium tetrabutoxide, respectively. Supercritical carbon dioxide

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can dissolve into the liquid phase including titania precursor and forms the homogeneous phase during the sol-gel reaction. The concentration of titania precursor in the liquid phase would be reduced dramatically by the swelling of the liquid phase due to the dissolution of carbon dioxide. Also, the phase state in the reaction system would transform to the homogeneous phase. The knowledge of the dynamic phase behavior can be useful and important to understand the mechanism of the formation of nanostructured titania with various morphologies. However, these fundamental studies regarding to the effect of phase behavior dynamics during sol-gel reaction have not been focused on the titania fabrication using supercritical carbon dioxide.

In this work, the dynamic phase behavior during the sol-gel reaction in supercritical carbon dioxide is investigated for the design of the titania morphology. The effect of the precursor concentration and the reaction temperature on the phase behavior is discussed by the swelling ratio of the liquid phase due to the dissolution of carbon dioxide the homogeneous phase formation during the sol-gel reaction. Also, the consequent morphologies and crystal structures of titania by the sol-gel reaction in supercritical carbon dioxide are evaluated. The results of the dynamic phase behavior are applied for the discussion concerning the formation mechanism of the titania with various morphologies.

2. Experimental section

2.1. Chemicals

Titanium tetrabutoxide (TBO) from KANTO CHEMICAL CO., INC and acetic acid (HAc) from Wako Pure Chemical Industries, Ltd was used for the sol-gel reaction. The purities of TBO and HAc were 97.0 and 99.9%, respectively. Carbon dioxide (99.95%) was supplied from Fujii Bussan Co. Ltd.

2.2. Dynamic phase behavior during sol-gel reaction in supercritical carbon dioxide

A dynamic phase behavior during the sol-gel reaction in supercritical carbon dioxide is studied focusing on the swelling of the liquid phase and homogeneous phase formation by the dissolution of carbon dioxide into the liquid phase. The sol-gel reactions were conducted using TBO as titania precursor and HAc. The molar ratio of HAc to TBO was 10. The known amounts of TBO and HAc were loaded into a quartz cell with 4.7 ml in advance. The quartz cell containing the solution of TBO and HAc was capped with a glass fiber and installed to a high-pressure view cell with 72 ml. The concentration of TBO loaded to the high-pressure view cell is listed in Table 1. The concentration is calculated from the loading amount of TBO and the volume of the quartz cell equipped inside the high-pressure view cell. A schematic diagram of the setup for phase behavior observation is given in Fig. S1. Carbon dioxide from the cylinder was passed through the column cell including the silica gel in order to remove the trace amount of water. The purified carbon dioxide was liquefied at a chiller and pressurized by a feed pump. The pressurized carbon dioxide was supplied into the system controlling temperature by air thermostat and achieved to the supercritical fluid. The supercritical carbon dioxide was installed into the high-pressure cell loading TBO and HAc. The pressure was controlled by a back-pressure regulator. The sol-gel reactions using supercritical carbon dioxide were conducted in the high-pressure cell by a batch type operation at 313–353 K and 20.0 MPa. The mixture inside the high-pressure cell was stirred by a magnetic stirrer. The phase behavior during the sol-gel reaction was observed using the high-pressure view cell from the sapphire window as given in Supporting Information, S1. The phase behavior during the sol-gel reaction was captured by using a microscope digital camera with 32 modifications (SPACE Inc.).

The dynamic the phase behavior is evaluated by homogeneous phase formation factor τ and the swelling ratio of the liquid phase α defined as the following equation:

$$\tau = \frac{m_{CO2}}{m_{react}} t \tag{1}$$

$$\alpha = \frac{V_1}{V_0} \tag{2}$$

where m_{CO2} and m_{react} mean the molar amount of carbon dioxide and the solution of TBO and HAc installed to the view cell. The homogeneous phase formation factor means the time required for the system transferring from the vapor–liquid two phases to the homogeneous. This factor is defined that standardized by the loading amount of TBO solution and carbon dioxide as given in Eq. (2). The time required for the homogeneous phase formation t is determined from the phase behavior that the supercritical carbon dioxide–reaction liquid two phase transformed to the homogeneous phase during the sol-gel reaction. V_0 and V_1 are the volume of the liquid phase inside the quartz cell before and after the swelling. These volumes were determined from the height of the liquid phase and the cross-sectional area of the quartz cell. The experiments of the phase behavior are conducted at the precursor concentration that allows to making a significant effect on the phase behavior.

Table 1
Experimental conditions and results of dynamic phase behavior during sol-gel reaction in supercritical carbon dioxide.

Solvent	Temperature (K)	C_{TBO} (mol l^{-1})	$\tau \times 10^{-2}$ (h)	α (−)
TBO + HAc	313	0.062	5.5 ± 0.05	12 ± 0.3
		0.30	3.4 ± 0.01	2.1 ± 0.07
		0.48	0.34 ± 0.01	1.1 ± 0.08
	333	0.062	1.2 ± 0.04	10 ± 0.4
		0.12	1.5 ± 0.02	4.5 ± 0.2
		0.30	0.31 ± 0.01	1.7 ± 0.05
		0.48	0.20 ± 0.005	1.2 ± 0.05
	353	0.25		1.7 ± 0.07
		0.30		1.5 ± 0.07
		0.48		1.1 ± 0.07
HAc	333		0.95 ± 0.01	6.2 ± 0.2
1-butanol			1.0 ± 0.02	5.7 ± 0.2
H_2O				1.1 ± 0.003

C_{TBO}; concentration of titanium tetrabutoxide (TBO), τ; homogeneous phase formation factor defined in Eq. (1) and α; swelling ratio of liquid phase defined in Eq. (2).

2.3. Synthesis of nanostructured titania

A sol-gel reaction for synthesis of nanostructured titania was conducted also using TBO and HAc in supercritical carbon dioxide. A high-pressure cell with 34 ml unlike that for the phase behavior observation at the previous section was used for the synthesis of titania. The known amounts of TBO and HAc were loaded into the high-pressure cell before supplying supercritical carbon dioxide into the system. The molar ratio of HAc to TBO was 10 and the TBO concentrations in the high-pressure cell were 1.47×10^{-2}, 4.41×10^{-2} and 8.36×10^{-2} mol l^{-1}. The sol-gel reaction for the synthesis of the titania was conducted by the experimental procedure as well as those on the phase behavior observation described at the previous section. The reaction times were 3 and 24 h by case of TBO concentration and the mixture was stirred by a magnetic stirrer during the experiments. The experimental conditions of the sol-gel reaction for the titania synthesis are listed in Table 2. The longer reaction time is required for achieving the complete sol-gel reactions in cases of TiO_2-313-b and TiO_2-313-c. The wet titania after the reaction was dried by supercritical carbon dioxide at the