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Kinetics study to identify reaction-controlled conditions for supercritical hydrothermal nanoparticle synthesis with flow-type reactors

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ABSTRACT

Flow-type reactors are effective for the precise control of reaction conditions and high throughput production. To enhance the effectiveness of this process, the establishment of a design method is required. For this purpose, the effects of operating parameters on supercritical hydrothermal nanoparticle synthesis in a flow-type reactor were examined. Ceria nanoparticles were formed from 2.0 mM cerium nitrate at reaction temperatures ranging from 200 to 380 °C and with a flow rate of 11.6–37.5 mL/min. In addition, channel sizes of 0.3, 1.3, and 2.3 mm were used for the mixing point. Rapid mixing and higher temperatures were found to enable the formation of smaller nanoparticles. Furthermore, all experimental results were summarized using dimensionless numbers. Though the Reynolds number was related to the effect of mixing on particle formation, this number is independent of the reaction rate. Results were correlated using the Damköhler number, the ratio of reaction rate to mixing rate. From the threshold value of the Damköhler number, reaction-controlled conditions where the particle size was independent of the flow/mixing rate could be predicted.

1. Introduction

Metal oxide nanoparticles have unique mechanical, chemical, and physical properties, which differ from bulk materials. These properties enable a wide range of applications in novel functional materials, such as high-refractive index materials [1,2], magnetic materials [3–5], and catalysts [6–10].

In the synthesis of metal oxide nanoparticles, supercritical hydrothermal processing has advantages such as increased nucleation rate, higher dispersion, higher rate of reaction, and better shape control over other conventional processes [11]. Under supercritical conditions (e.g., above 374 °C and 22.1 MPa for water), the fluid exhibits some advantageous properties for nanoparticle syntheses in continuous processes, such as low viscosity and high diffusivity [12]. This process is also environmentally benign, since supercritical water can dissolve organic compounds because of a low dielectric constant and replace an organic solvent to "green" water in reactions and separations. Therefore, the implementation of supercritical conditions is useful in an industrial scale production of nanoparticles.

Numerous supercritical hydrothermal syntheses of nanoparticles have been demonstrated using a batch-type reactor [5,13–17]. Conventional batch reactors are easy to operate and are suitable for use in lab-scale production. However, the precise and rapid control of reaction conditions and the implementation of large-scale production are problematic. Reactions for the supercritical hydrothermal synthesis of metal oxide nanoparticles are usually rapid because of the low density and dielectric constant of supercritical water [18,19]. Thus, to achieve control of the reaction conditions, instantaneous mixing is required. In addition, to achieve a large degree of supersaturation, a sudden temperature rise is essential. Therefore, rapid heat transfer is also important for producing small and homogeneous nanoparticles.

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Considering the above issues, a continuous flow-type system is suitable for use in nanoparticle synthesis. Furthermore, for large-scale production, nanoparticles were synthesized using flow-type reactors under subcritical and supercritical conditions [6,20–25]. Use of a flow-type reactor containing submillimeter- to millimeter-scale channels (called microreactors) has been reported to enhance both mass and heat transfers and mixing rate [26–30]. The enhanced performance is due to increased surface and interface area in a miniaturized channel. Several microreactors for supercritical hydrothermal syntheses have been developed [29–31].

Systematical development of a high throughput process for industrial production is one of the main goals of basic research of chemical engineering. In this context, to implement flow-type reactors in industrial applications, the establishment of design methodology is essential. However, to date, flow-type reactors have been developed by trial and error based on each reaction system. Therefore, to enhance the effectiveness and accelerate the development of continuous processes, establishing a design method to determine the optimal operating conditions and sizes of flow-type reactors is required.

Therefore, we examined the effects of operating parameters on supercritical hydrothermal nanoparticle synthesis in a flow-type reactor. From the thorough optimization of operating parameters for the flow-type reactor, in particular, parameters related to mixing rate (i.e., flow rate and mixer channel size), a design guideline using dimensionless numbers was established.

2. Experimental

2.1. Materials

CeO_2 nanoparticles were synthesized as a model system for establishing a design methodology for the flow-type reactor. All the reagents were analytically pure and used without further purification. $Ce(NO_3)_3{\cdot}6H_2O$ (Wako Pure Chemical Industries, Ltd., >98.0%) was used as the cerium ion source for the preparation of CeO_2. The cerium nitrate was first hydrolyzed by mixing with supercritical water and subsequently dehydrated. The precursor was prepared by dissolving $Ce(NO_3)_3{\cdot}6H_2O$ in distilled water (Daiwa Pharmaceutical Co., Ltd.). A $Ce(NO_3)_3$ concentration of 2.0 mM was used for all operating conditions described in the following section to prevent clogging in the flow type reactor. With low flow rate and slow mixing, the formation of large particles caused clogging of the reactor.

2.2. Experimental setup

The continuous hydrothermal synthesis of CeO_2 nanoparticles was carried out with a lab-scale flow-type reactor, as shown in Fig. 1. The precursor and distilled water were fed into the reactor using high-pressure pumps (JASCO Co., PU-2086 Plus, and Nihon Seimitsu Kagaku Co., Ltd., NP-KX-500-40, respectively). The water was heated and mixed with the precursor in a T-mixer. The flow rates of the precursor and preheated water were 3.1–10.0 mL/min and 8.5–27.5 mL/min, respectively. The flow rate was calculated by measuring the weight of fluid from the reactor outlet (flow rate accuracy: ±5%). The flow ratio of the precursor to preheated water was kept constant (2.75). Three types of T-mixers were used to change the inner diameter of the system (a union tee for a 1/8 in tube (i.d. 2.3 mm, Swagelok), a union tee for a 1/16 in tube (i.d. 1.3 mm, Swagelok), a low dead volume union tee for a 1/16 in tube (i.d. 0.3 mm, Swagelok). In addition, a 1/16 in tube (i.d. 0.8 mm, 0.05 m length) was used to connect the mixer to the 1/16 in tube, and a 1/8 in tube (i.d. 1.8 mm, 0.05 m length) was used to connect the mixer to the 1/8 in tube. Furthermore, a 1/8 in tube (i.d. 1.8 mm, 0.1–1.8 m length) was connected as a reactor. The total reaction channel length was 0.15–1.85 m. All tubes and the mixers were made of SUS316 stainless steel. Cartridge heaters (Hakko Electric Co., Ltd., HLT3141) were used to preheat the water and maintain a constant reaction temperature, through wrapping of each channel around one cartridge heater. The temperatures of the heaters were controlled by temperature regulators (OMRON Corporation, G32A-E-VR). The mixer and reactor channel were covered by heat insulator (Rock Wool, MG Mighty Cover ALGC, NM-8602, NICHIAS Corporation) as shown by the dashed line in Fig. 1. Temperatures were measured using K-type thermocouples (Sukegawa Electric Co., Ltd., T35-SK2-B-1.6-U-200-EXD). The reaction temperature was determined as the temperature immediately after the mixer (denoted by T1 in Fig. 1). The reaction temperature ranged from 200 to 380 °C, and the temperature control accuracy was within ±5 K. The reactant concentration was low, and thus the effect of reaction heat was negligible. To cool the solution following the reaction, a shell-type cooler was connected to the end of the reactor. Cooling water (17 °C) was supplied to the cooler using a small piece of cooling water circulation apparatus (Sibata Scientific Technology Ltd., Cool Man C580). The reaction pressure was maintained at 30 MPa using a backpressure regulator (TESCOM Corporation, 27-1764-24).

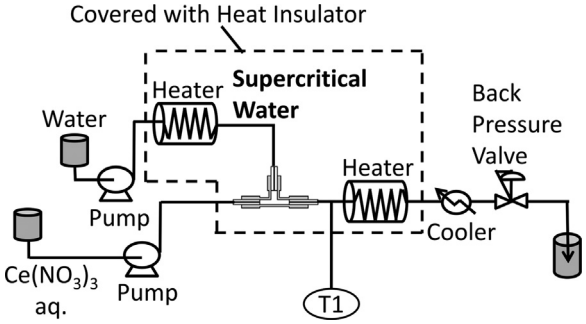

Fig. 1. Schematic representation of the flow-type reactor for the hydrothermal synthesis of CeO_2 nanoparticles. The symbol T1 denotes a thermocouple to set reaction temperatures.

2.3. Analysis

Transmission electron microscopy (TEM, Hitachi Ltd., H-7650) was used to observe the size and the shape of the particles. A TEM grid (JEOL Ltd., Cu150) was prepared by placing a drop of the collected solution on the plate. The resulting grid was dried at room temperature (20–25 °C) for 12 h. The mean particle size and the standard deviation were obtained by measuring 300 particles in the TEM images using a caliper. Particle size was taken as the diagonal length of the particle. The produced particles were separated by centrifugation at 10100 rpm for 20 min. The particles were then freeze-dried for 48 h and analyzed by X-ray diffraction (XRD, RIGAKU, SmartLab 9MTP). The concentration of Ce^{3+} ions in the fluid from the reactor outlet was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPECTRO, SPECTORO ARCOS). From this evaluation, the conversion of reactant X can be calculated using the following equation:

$$X = 1 - \frac{\text{Concentration of } Ce^{3+} \text{ in the fluid from the reactor outlet}}{\text{Concentration of reactant based on whole reactant fluid}} \quad (1)$$