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Relationship between size distribution of synthesized nanoparticles and flow and thermal fields in a flow-type reactor for supercritical hydrothermal synthesis

Ken-ichi Sugioka [a], Kyohei Ozawa [b], Masaki Kubo [b], Takao Tsukada [b,*], Seiichi Takami [c], Tadafumi Adschiri [d], Katsumi Sugimoto [e], Nobuyuki Takenaka [e], Yasushi Saito [f]

[a] *Department of Mechanical Systems Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu-shi, Toyama 939-0398, Japan*
[b] *Department of Chemical Engineering, Tohoku University, 6-6-07 Aramaki, Aoba-ku, Sendai 980-8579, Japan*
[c] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
[d] *WPI Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
[e] *Department of Mechanical Engineering, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan*
[f] *Research Reactor Institute, Kyoto University, 2, Asashiro-Nishi, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan*

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ABSTRACT

In this work, CeO_2 nanoparticles were synthesized hydrothermally with supercritical water using a tubular flow reactor with three different configurations and various flow rates of the feed solution and supercritical water, and the effects of the reactor configuration and the flow rates of the two streams on the size distributions of the synthesized nanoparticles were investigated. In addition, the flow and thermal fields in the reactors were calculated numerically under the experimental conditions using FLUENT software, where the numerical results for the flow and thermal fields were also verified by neutron radiography. Comparing the experimental results of nanoparticle synthesis with the numerical results, it was revealed that the size distributions of the synthesized nanoparticles could be explained well on the basis of the flow patterns and temperature distributions in the reactor, which depended on the reactor configuration and process conditions.

1. Introduction

Various experimental and numerical works have been reported concerning the mixing behaviors of the reactant feed solution and supercritical water streams in continuous flow reactors for supercritical hydrothermal synthesis of nanoparticles [1–6], because the mixing in the reactor strongly influences the size distribution and morphology of synthesized nanoparticles [7–9]. Kawasaki et al. [5] have performed continuous supercritical hydrothermal synthesis of NiO nanoparticles, comparing with the CFD simulation results for three types of reactors, and revealed the correlation between the heating rate of feed solution and average size of synthesized nanoparticles. Sierra-Pallares et al. [6] have also carried out the CFD simulations of supercritical hydrothermal reactors, and investigated the effects of the reactor configuration and dominant convection type on the mixing efficiency in the reactor. However, there have been few works which visualized the flow in an actual reactor under the practical process conditions for synthesizing nanoparticles or which verified the numerical results of the flow patterns in the reactor under supercritical conditions, although the supercritical "on chip" microfluidics set-up recently developed allowed direct visualization of flow in the microreactor at high pressure and temperature [10,11]. Recently, we have performed neutron radiography to visualize the mixing behavior of supercritical water and room-temperature water corresponding to the metal salt feed solutions in a T-junction connected with 1/8-in. tubes, that were actually used for supercritical hydrothermal synthesis of metal oxide nanoparticles [12–15], and then clarified the effects of the reactor configuration and the flow rates of the two streams on the distributions of water density and temperature in the reactor [16,17]. We also carried out numerical simulations of the three-dimensional unsteady flow and thermal fields in the tubular flow reactor using FLUENT software, and verified the calculated temperature distributions by comparing them with the distributions obtained by neutron radiography [17]. Moreover, we performed tomography measurements to obtain the three-dimensional

* Corresponding author.
E-mail address: tsukada@pcel.che.tohoku.ac.jp (T. Tsukada).

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distributions of the neutron attenuation in the tubular flow reactor, rotating the pieces to supply and mix supercritical water and room-temperature water [18]. In our previous works [16–18], it was demonstrated that neutron radiography is an effective tool for clarifying the mixing behavior and temperature distributions in an actual reactor for supercritical hydrothermal synthesis in addition to a numerical simulation. Therefore, our next step is to clarify the relationship between the mixing behaviors of the two streams, i.e., the metal salt aqueous solution and supercritical water, in the reactor and the characteristics of synthesized nanoparticles to propose design strategies for the production of nanoparticles with desired characteristics using a tubular flow reactor.

In this work, supercritical hydrothermal syntheses of CeO_2 nanoparticles were performed while varying the configuration of the reactor and the flow rates of the aqueous feed solution and supercritical water, and the size distribution and average size of the synthesized nanoparticles were measured using a scanning electron microscope (SEM). Here, the ranges of Reynolds number evaluated on the basis of the flow rates of the feed, the supercritical water and their mixture were 10–60, 1700–2550 and 1350–2430, respectively. In addition, the flow and thermal fields in the reactor were obtained by numerical simulation and verified by neutron radiography. Then, on the basis of the experimental and numerical results, the relationship between the size distribution of the synthesized nanoparticles and the mixing behaviors of the metal salt aqueous solution and supercritical water in the reactor was discussed.

2. Experimental methods

Ceria (CeO_2) nanoparticles were synthesized hydrothermally in supercritical water following the reactions below.

$$Ce(NO_3)_3 + 4H_2O \rightarrow Ce(OH)_4 + 3HNO_3 + H^+ + e^- \quad (1)$$

$$Ce(OH)_4 \rightarrow CeO_2 + 2H_2O \quad (2)$$

Here, H^+ and e^- represent a proton and an electron, respectively. The starting material, cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$), was purchased from Wako Pure Chemical Industries, Ltd.

Fig. 1(a) shows a schematic diagram of the tubular flow reactor used to synthesize various nanoparticles in previous works [13,19] and the CeO_2 nanoparticles in this work. This reactor is also the same as that used for neutron radiography in a previous work [17] to visualize the mixing behavior of supercritical water and room-temperature water in the reactor, except for the presence of the filter in the figure. The filter, whose pore size is approximately 500 nm, was installed slightly before the back-pressure regulator to prevent large aggregates of synthesized nanoparticles occluding the regulator. The T-junction in the reactor, at which the two streams of 10 mM $Ce(NO_3)_3$ aqueous solution and supercritical water are mixed and reacted, comprised a Swagelok union tee and SUS316 tubes whose outer diameter and wall thickness were 1/8 in. and 0.71 mm, respectively. The T-junction was covered with a thermal insulator. The mixed stream was heat-exchanged at a jacket cooler, in which a coolant at 288 K was allowed to flow, to terminate the hydrothermal reaction. The cooled suspension with synthesized nanoparticles was collected from the outlet using a polypropylene conical tube. The pressure in the reactor was maintained at approximately 25 MPa using a back-pressure regulator (TESCOM, 26-1700 Series). The size distribution and average size of the synthesized nanoparticles were evaluated using a SEM (S-4800, Hitachi High-Technologies Co., Japan).

In this work, the T-junctions with three different configurations (Cases 1–3) shown in Fig. 1(b) were used to investigate the effect of the reactor configuration on the size distributions of the synthesized nanoparticles, similarly to that in our previous work [17]. The flow rate of supercritical water Q_{SCW} was 8.0 or 12.0 g/min, and the flow rate of the metal salt aqueous solution Q_F was varied from 1.0 to 6.0 g/min. Here, the minimum and maximum values of Reynolds number for the streams of the supercritical water, metal aqueous feed solution and their mixture after mixing at the T-junction, i.e., (Re_{min}, Re_{max}), are (1700, 2550), (10, 60) and (1350, 2430), respectively. The temperatures of the streams of supercritical water and aqueous solution were 660 K and room temperature, respectively.

3. Numerical model

The three-dimensional unsteady numerical simulations of the flow and thermal fields in the tubular flow reactor for supercritical hydrothermal synthesis of nanoparticles shown in Fig. 1 were conducted using ANSYS FLUENT 12.1 software. The numerical models of the flow and temperature fields in the reactor including the

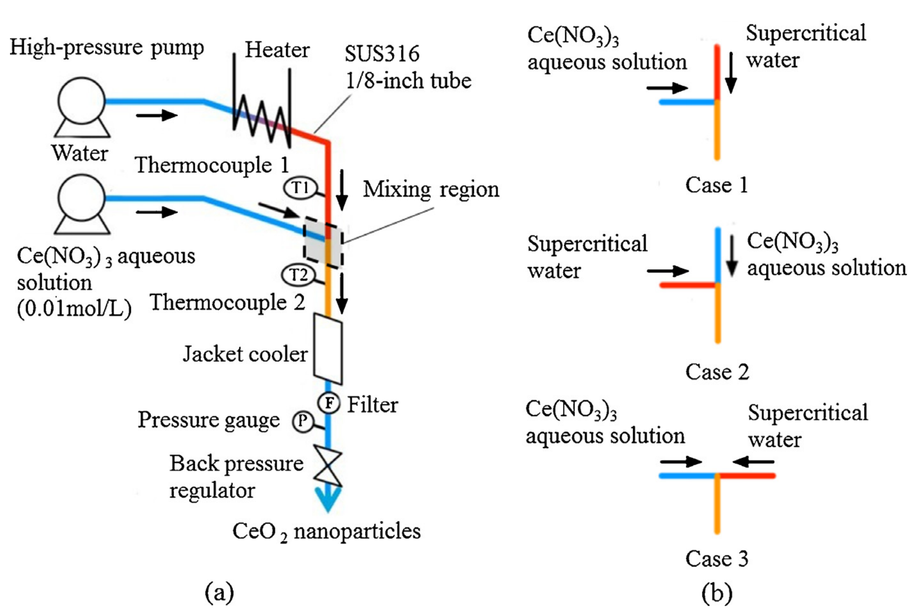

Fig. 1. Schematic diagram of tubular flow reactor used to synthesize nanoparticles.