Development of Novel Micro Swirl Mixer for Producing Fine Metal Oxide Nanoparticles by Continuous Supercritical Hydrothermal Method

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Abstract: Novel micro swirl mixers were developed to synthesize nanoparticles, and the effect of their mixing performance on the characteristics of the synthesized nanoparticles was determined. The results were compared with those obtained using simple T-shaped mixers under the same reaction conditions. The synthesis of NiO, whose characteristics depend on the mixing performance of the mixer, was chosen as a model reaction. Initial investigations highlighted that the average particle size decreased from 32 to 23 to 20 nm as the inner diameter of the swirl mixers was decreased from 3.2 mm (Swirl mixer, SM-3.2) to 0.8 mm (Micro swirl mixer, MSM-0.8) to 0.5 mm (Micro swirl mixer, MSM-0.5), respectively. On the other hand, a similar decrease in the average particle size from 34 to 20 nm was observed with a decrease in the inner diameter of the T-shaped mixers from 1.3 mm (Tee union, T-1.3) to 0.3 mm (Micro tee union, T-0.3), respectively. Further, narrow particle size distributions were observed with a decrease in the inner diameter of each mixer. Furthermore, a computational fluid dynamics (CFD) simulation indicated an excellent mixing mechanism, which contributed to the improvement in the heating rate and the formation of nanoparticles of smaller size with a narrow particle size distribution. The result presented here indicates that the micro swirl mixers produce high-quality metal oxide nanoparticles. The size of the obtained particles with improved size distributions was comparable to that of the particles obtained using the T-shaped mixers, although the inner diameter of the swirl mixers was larger. Therefore, preliminary evidence suggests that the swirl flow mixers have the ability to produce rapid and homogeneous fluid mixing, thus controlling the particle size.

Key words: micromixer, swirl mixer, supercritical hydrothermal synthesis, nanoparticle, simulation, NiO

1 INTRODUCTION

Metal oxide nanoparticles have been attracting much attention as catalysts in oil chemistry because of their large surface area. Several synthesis methods such as sol-gel, spray pyrolysis, thermal decomposition, and hydrothermal/solvothermal synthesis have been used to produce metal oxide nanoparticles. However, these methods require extremely high temperatures, long reaction times, a concentrated base solution, surfactants, and organic solvents for preparing the nanoparticles. Further, in some cases, additional processes such as calcination and comminution are necessary. A continuous supercritical hydrothermal method has been proposed for producing metal oxide nanoparticles. In this method, the initial aqueous solution of metal salts is heated to a supercritical state at the reaction temperature (e.g., 400°C and 30 MPa) by mixing it with pre-heated water in a T-shaped mixer using flow-through apparatus. The high temperature results in a high hydrothermal reaction rate. Further, the low dielectric constant of water is one of the major controlling factors of the solubility of metal oxides, and it aids the synthesis of nanoparticles with small and narrow size distributions under supercritical water conditions. Because water and metal salts are used as the...
reaction media and starting materials, this method is an eco-friendly process for producing small-sized metal oxide particles. However, the practical application of this method has still not been realized because it causes problems such as large particle formation and wide size distribution in some cases. It is well known that the formation of small and homogeneous distributed nanoparticles requires high supersaturation, because the rate of homogeneous nucleation depends on the degree of supersaturation. Thus, the rapid heating method to supercritical state which is low solubility condition of metal oxides is a key technology. At present, main task for the practical application of this method is the development of a new type of mixer that can rapidly heat the starting solution to obtain small-sized nanoparticles with a narrow size distribution. In this work, a novel micro swirl mixer with a further increased heating rate was developed to produce nanoparticles with a small and uniform size distribution by micro-\textit{ization}. Continuous supercritical hydrothermal synthesis was carried out using swirl mixers and the conventional T-shaped mixers having different inner diameters (ID). The NiO nanoparticles synthesized from Ni(NO\textsubscript{3})\textsubscript{2} were assessed to discuss the effect of mixer type and ID on the particle size, because, in our previous work, we found that the effect of heating rate greatly influenced the particle size and size distribution of the nanoparticles\textsuperscript{10}. In addition, a computational fluid dynamics (CFD) simulation was carried out to compare the heating profiles of each mixer. On the basis of experimental and CFD simulation results, the effectiveness of the micro swirl mixer was evaluated.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

Ni(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O (purity>98.0\%, Kanto Chemical Co., Inc.) was used for NiO synthesis, without further purification. The de-ionized water was produced through two steps; distillation and ion exchange. The starting solution was prepared by dissolving Ni(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O into de-ionized water. The concentration of Ni(NO\textsubscript{3})\textsubscript{2} in the starting solution was 0.02 mol/kg.

2.2 Apparatus

A schematic representation of the apparatus is shown in Fig. 1. Two high-pressure double-plunger pumps were used for the supercritical water (SCW) feed and quench water feed (Pump 1 and Pump 3, Nihon Seimitsu Kagaku Co., Ltd; NP-KX-500, maximum pressure: 35 MPa, maximum flow rate: 100 g/min). Another high-pressure double-plunger pump was used for the starting solution feed (Pump 2, NP-AX-25, maximum pressure: 35 MPa, maximum flow rate: 30 g/min). The pressures throughout the process (P1-P4) were measured using a pressure transducer (Nagasato Keiki Co., Ltd., KH-15, measurement error: 0.5% FS.). The temperatures of the outer surface of the tubes (T2-T4, T6-T10) were measured by K-type thermocouples, which were fastened to the tubes. A detailed diagram representing the components around mixing point 1 of the SCW and the starting solution (MP1) are shown in Fig. 1(a) T-shaped mixer and (b) swirl mixer. Two types of T-shaped mixers, a union tee for a 1/16 inch tube (ID = 1.3 mm, Swagelok company, SS-100-3, T-1.3) and a low dead volume union tee for a 1/16 inch tube (ID = 0.3 mm, Swagelok company, SS-1F03GC, T-0.3), were used for the T-shaped mixer of MP1. In addition, three types of swirl mixer, a relatively large diameter swirl mixer with a conical swirling zone (maximum ID = 3.2 mm, SM-3.2) and micro swirl mixers with no conical swirling zone (ID = 0.8 mm, MSM-0.8 and ID = 0.5 mm, MSM-0.5). Cross sectional diagrams of the mixers used in this work are shown in Fig. 2. In the case of the swirl mixer, a supercritical water stream was separated by the equal distribution device, which was made using the small channel tubes with the same pressure drop length. The performance of the equal distribution device was checked to measure the stream temperatures, T2a and T2b. The separated supercritical water streams were set to an incline of 60° with respect to the starting solution stream, and separated supercritical water steams were displaced small gap (less than 1 mm) each other with respect to the mixer’s center axis. The swirl flow was formed by the separated, inclined, and displaced supercritical water streams, and resulted only from the fluidic force; no mechanical parts were involved. These mixers were covered with glass wool for heat insulation. Again, a 1/16 (ID = 0.8 mm) and a 1/8 inch...
Development of Novel Micro Swirl Mixer for Producing Fine Metal Oxide Nanoparticles


A 1/16 inch tube with an ID = 0.8 mm was used for the SCW stream connection. Furthermore, a 1/16 inch tube with an ID = 0.5 mm was used for the SCW stream connection. The value of the ID for the main stream in the micro swirl mixer was designed to have connection tubes with diameters of 0.8 mm or 0.5 mm for the smooth stream configuration. These inner diameters were mainly used for the 1/16 inch tube. Expanded or reduced sections formed unexpected accumulation space due to the circular vortex. In all cases, the tube, following mixing point 1 (MP1), was connected to the coiled reactor, made of 1/8 inch tube (ID = 1.8 mm, Length = 1.5 m), and the end of the reactor tube was connected to a 1/8 inch tube tee union (ID = 2.3 mm), forming mixing point 2 (MP2). The reactor was placed in an electric furnace. A compact coil and shell type cooler was used to cool the effluent from MP2 down to room temperature, including the products, was recovered after depressurization by BPR, to atmospheric pressure. No filters were used in this experimental apparatus; hence, all of the products were collected in the effluent. Detailed experimental conditions are listed in Table 1. The system pressure (P4) was adjusted to 30 MPa via BPR. Temperatures upstream of MP1 (T2) and near to the reactor (T4, T6-T8) were set to 463 and 400 °C, respectively. T2 was calculated from the mass and heat balances, based on the flow rates of the SCW and the starting solution, as well as the temperatures of the reactor (400 °C) and the starting solution (15 °C). The flow rate of the starting solution was 16 g/min, and the flow rate of the water for the SCW was 44 g/min. The flow rate of the quench water was 65 g/min. The residence time was calculated to be 1.3 s on the basis of flow rate, reactor volume, and solution density, at 400 °C and 30 MPa. The solution density was taken from the pure water density because of the low Ni(NO₃)₂ molality in the reactor. The Reynolds number following mixing at MP1 changed from 9,100 to 96,600, at 400 °C and 30 MPa.

2.3 Procedure and condition

In a typical execution, the starting solution was fed by Pump 2, flowed into MP1 and mixed with the SCW, which was fed by Pump 1. The mixed solution was heated to a given temperature (400 °C), and passed through the reactor, and then cooled down to room temperature by mixing with Quench water fed by Pump 3 in MP2 and passing through the compact cooler. The cooled effluent, including products, was recovered after depressurization by BPR, to atmospheric pressure. No filters were used in this experimental apparatus; hence, all of the products were collected in the effluent. Detailed experimental conditions are listed in Table 1. The system pressure (P4) was adjusted to 30 MPa via BPR. Temperatures upstream of MP1 (T2) and near to the reactor (T4, T6-T8) were set to 463 and 400 °C, respectively. T2 was calculated from the mass and heat balances, based on the flow rates of the SCW and the starting solution, as well as the temperatures of the reactor (400 °C) and the starting solution (15 °C). The flow rate of the starting solution was 16 g/min, and the flow rate of the water for the SCW was 44 g/min. The flow rate of the quench water was 65 g/min. The residence time was calculated to be 1.3 s on the basis of flow rate, reactor volume, and solution density, at 400 °C and 30 MPa. The solution density was taken from the pure water density because of the low Ni(NO₃)₂ molality in the reactor. The Reynolds number following mixing at MP1 changed from 9,100 to 96,600, at 400 °C and 30 MPa.

2.4 Analysis

A transmission electron microscope (TEM, FEI Company, TECNAI-G2) was used to observe the produced particles. A TEM grid was prepared as follows. The effluent, including the particles, was diluted 5 times by ethanol. A few drops of the mixed solution were put on the grid (Okenshoji Co., Ltd, High Resolution Carbon Substrate, carbon thickness < 15 nm, STEM 100-Cu grids #10-1013). The grid was dried...

Table 1 Experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>T-1.3</th>
<th>T-0.3</th>
<th>SM-3.2</th>
<th>MSM-0.8</th>
<th>MSM-0.5</th>
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<td>SCW feed [g/min]</td>
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<td>44</td>
<td>44</td>
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<td>44</td>
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<tr>
<td>Solution feed [g/min]</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Residence time [s]</td>
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<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Mixer i.d. [mm]</td>
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<td>0.3</td>
<td>3.2</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Re [-]</td>
<td>22,300</td>
<td>96,600</td>
<td>9,100</td>
<td>36,200</td>
<td>58,000</td>
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in an oven at 60°C for 12 h. The particles had a tabular shape. The size was evaluated based on the equivalent area diameter using measurements of the long and short lengths of each particle. The average particle size (Size) and standard deviation (S.D.) were obtained by measuring the diameters across 300 particles. The particles were separated by vacuum filtration using a membrane filter (MILLIPORE nitrocellulose filter, 25 nm pore size, 90 mm filter size). The concentration of Ni²⁺ in the filtrate was measured by an inductively-coupled plasma atomic emission spectrometry (ICP-AES, Seiko Instruments Inc., SPS7800). The reaction conversion was estimated by comparing the concentration before and after the reaction. The separated particles on the filter were collected and dried in an oven at 60°C for 12 h. The dried particles were milled using an agate mortar for crystal characterization. A powder X-ray diffractometer (XRD, Rigaku, RINT-2200VK/PC, 60 kV, 3 kW) was used to perform the crystal structure analysis. The source of the X-radiation was CuKα, and the scan rate was set to 2º/min. The weight loss was estimated on the basis of the thermogravimeter and differential thermal analysis measurements (Bruker AXS Inc., TG-DTA 2010 SAT) at temperatures of up to 600°C and a heating rate of 10°C/min.

### 3 RESULTS AND DISCUSSION

The powder-XRD patterns of products are shown in Fig. 3. All products were NiO single-phase crystal compared, with the Powder Diffraction File (PDF# 44-1159). The experimental results of the weight loss and the conversion are listed in Table 2. The weight loss values of the products, between 100 and 600°C, measured by TG-DTA analysis, were very low, ranging from 1.1 to 1.6 wt.-%. The conversions obtained by ICP were in the range between 77 and 86%. The results indicate that the hydrothermal synthesis of high crystalline NiO progresses rapidly within a very short residence time (1.3 s).

The photographs of the synthesized NiO, taken by TEM, are shown in Fig. 4. The crystals appeared to have a rhombic shape with a thin plate-like structure. The particle size and size distribution varied with different mixer types and IDs. The size distributions of the products are shown in Fig. 5. The average particle size (AS) and standard deviation (SD) and maximum frequency of the size distribution (MF) are summarized in Table 2. In the case of T-shaped mixers, the AS and SD decreased from 34 to 20 nm and from 11 to 8 nm, respectively, with the ID decreasing from 1.3 to 0.3 mm. Further, MF increased from 7 to 13 %. In the case of swirl mixers, AS and SD decreased from 32 to 20 nm and from 15 to 8 nm, respectively, with ID decreasing from 3.2

### Table 2 Experimental results

<table>
<thead>
<tr>
<th></th>
<th>T-1.3</th>
<th>T-0.3</th>
<th>SM-3.2</th>
<th>MSM-0.8</th>
<th>MSM-0.5</th>
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<tr>
<td>Size [nm]</td>
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<td>32</td>
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<td>20</td>
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<tr>
<td>S.D. [nm]</td>
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<td>8</td>
<td>15</td>
<td>9</td>
<td>8</td>
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<tr>
<td>Max. frequency [%]</td>
<td>7</td>
<td>13</td>
<td>9</td>
<td>13</td>
<td>15</td>
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<tr>
<td>Conversion [%]</td>
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<td>77</td>
<td>86</td>
<td>81</td>
<td>77</td>
</tr>
<tr>
<td>Weight loss [%]</td>
<td>1.3</td>
<td>1.6</td>
<td>1.6</td>
<td>1.3</td>
<td>1.1</td>
</tr>
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</table>

Fig. 3 XRD patterns of the products using (a) T-1.3, (b) T-0.3, (c) SM-3.2, (d) MSM-0.8, and (e) MSM-0.5.

Fig. 4 TEM photographs of the products using (a) T-1.3, (b) T-0.3, (c) SM-3.2, (d) MSM-0.8, and (e) MSM-0.5.
Development of Novel Micro Swirl Mixer for Producing Fine Metal Oxide Nanoparticles


Fig. 5 Size distribution diagrams.

to 0.5 mm. Further, MF increased from 9 to 15%. These trends in the particle size, with decreasing ID, are considered to reflect the micronization effect, because of the Reynolds number, as shown in Table 1, as well as the increasing heating rate. We next discuss the differences between the T-shaped mixer and the swirl mixer, in terms of the resulting characteristics of the products. AS, SD, MF and conversion, when using swirl mixers with an ID = 0.5, were 20 nm, 8 nm, 15%, and 77%, respectively. Similar values were observed when using conventional T-shaped mixers with an ID = 0.3 mm, in spite of increases in ID and decreases in the Reynolds number, from 96,600 to 58,000, as shown in Tables 1 and 2. A similar trend was observed between the swirl mixers with an ID = 3.2 and the conventional T-shaped mixers with an ID = 1.3 mm. These results imply that the use of the swirl flow contributes to rapid and homogeneous fluid mixing, producing small and narrowly distributed particles. From a practical application standpoint, it is better to reduce the pressure drop at the mixing device. The swirl mixers produce small and homogeneous nanoparticles, compared to T-shaped mixers, even if the ID of swirl mixers is larger than that of a T-shaped mixer. Therefore, swirl mixers deliver an advantage in terms of pressure drop reduction.

Steady state calculations, by CFD simulation, were performed using GAMBIT ver. 2.4.6 and FLUENT ver. 6.3.26 (ANSYS, Inc), to compare the heating profiles of each mixer. The mesh number at the fluid section was approximately 140,000. The mesh number at the metal section was between 830,000 and 1,300,000, depending on the mixer shape. Other simulation details are as described, in detail, in our previous study. The temperature contour diagrams of the mixed fluid’s y-z surface are shown in Fig. 6. The colors represent temperature, from 15°C (blue) to 470°C (red). The temperature distribution of the mixed fluid’s y-z surface decreased with increasing distance from the mixer center. In the case of T-shaped mixers, the starting solution (low temperature fluid) drifted to the bottom of the fluid channel as a result of the supercritical water mixing from the upper side. In the case of swirl mixers, the separated and displaced supercritical water streams formed the swirl flow. The maximum and minimum temperature profiles of the y-z surface, as analyzed on each mixer, are shown in Fig. 7. In both the cases of the T-shaped mixers (Fig. 7(a)) and the swirl mixers (Fig. 7(b)), the difference between the maximum and minimum temperatures decreased sharply with increasing distance from the mixer center and with decreasing ID. Further, the temperature difference when using the swirl mixers, with IDs = 0.5 and 3.2, decreased to 10°C at distances of 2.5 mm and 11 mm from the mixer center, respectively. Similar trends were observed when using the T-shaped mixers, with IDs = 0.3 and 1.3, in spite of the increase in ID and the decrease in the Reynolds number. These results support the experimental trends in AS, SD, MF and conversion. This suggests that the micro swirl mixer would contribute to the production of small and homogeneous nanoparticles.

4 CONCLUSION

This study demonstrated the successful construction of micro swirl mixer that, by a continuous supercritical hydrothermal synthesis method, contributes to the formation of metal oxide nanoparticles having smaller size and a nar-
row size distribution. As mixing is the dominant driving force behind the smaller size of formed NiO nanoparticles, the swirl mixer was used to examine the effect of mixing on the structural characteristics of the synthesized particle. The results were compared with those obtained using a T-shaped mixer. It was observed that the average particle size decreased with the ID of mixers containing a micro channel. This was determined based on the high Reynolds number flow under the same synthesis conditions. Again, in comparison to T-1.3, a smaller particle size can be obtained by SM-3.2, even though the ID of SM-3.2 is larger than the T-1.3. Similarly, subsequent investigation using the MSM-0.5 mixer also revealed that the produced particles are comparable to those obtained using a T-0.3 mixer, even if the ID of the MSM-0.5 is larger. Moreover, the maximum frequency of the size distribution was largest when the MSM-0.5 mixer was in action. The initial experimental results highlight the possibility of an improved hydrothermal process using a micro swirl mixer, under eco-friendly conditions.

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