Synthesis of Ni Nanoparticles by Reduction of NiO Prepared with a Flow-through Supercritical Water Method

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Synthesis of Ni nanoparticles having an average diameter of 8.1 nm by reduction of NiO nanoparticles was carried out at 673 K. HCOOH was used as a reductant, which decomposes to CO and/or H_2 at higher temperatures. NiO nanoparticles having an average diameter of 3.8 nm were obtained from $Ni(NO_3)_2$ + KOH aqueous solution by a flow-through supercritical water method at 673 K and 30 MPa. Effect of HCOOH concentration on particle size and saturation magnetization was investigated.

Over the past ten years, a flow-through supercritical water (FT-SCW) method has been widely used for continuous production of metal oxide nanoparticles by hydrothermal synthesis.[1,2] This method uses high controllability of water properties (density, dielectric constant, and ion product) and also related factors (metal oxide solubility, ionic equilibria, and hydrothermal reaction rate) with temperature and pressure.[1] Very recently, we clarified the condition to obtain the nanoparticles having a desired particle size on the basis of the supersaturation degree evaluated by the estimated metal oxide solubility at given supercritical condition.[3] This method is basically environmentally sustainable process and is attracting considerable attention as an innovative technique for industrial production of metal oxide nanoparticles. In addition to the synthesis of metal oxides, high temperature water reaction fields, which include SCW condition, have also great possibility for forming size-controlled metal particles because SCW forms homogeneous mixture with reducing agents (H_2 and CO) and, therefore, reduction reaction of metal cations can be highly controlled.[4] However, synthesis of metal particles by reduction of metal cations in high-temperature water is difficult task because hydrothermal reaction (hydrolysis of metal cations and dehydration) occurs as a competitive reaction.[5–7] Some researchers have proposed methods for Ni synthesis such as the complexes formation of 1,10-phenanthroline[5] and ammonia,[6] and controlling pH to acidic condition[7] to prevent the hydrolysis. In addition, Ziegler et al. proposed a new method which used organic alkanethiol capping ligands to prevent the hydrolysis, to reduce Cu^{2+}, Cu_2O, or CuO and to stabilize Cu nanoparticle formation in SCW.[8] This method used the specific property that SCW forms homogeneous mixture with organic thiols. Although these methods promise metal particle synthesis in high-temperature water, they are complicated or require complex preparation of starting solutions.

In this work, we investigated a relatively simple route to Ni nanoparticles. NiO nanoparticles were prepared by the FT-SCW method. Considering that decomposition of HCOOH at higher temperatures produces reducing agents, CO and H_2,[9] preparation of Ni nanoparticles was carried out through the reduction of the NiO particles with HCOOH. We examined the effect of initial HCOOH weight and reaction time on size and magnetic saturation of the obtained particles.

Solutions for NiO synthesis were prepared by dissolving precise amounts of $Ni(NO_3)_2{\cdot}6H_2O$ (Wako Pure Chemicals, Japan) and KOH (Wako Pure Chemicals, Japan) in distilled and deionized water (resistivity $> 0.18\,M\Omega\,m$). The concentrations of $Ni(NO_3)_2$ and KOH in reactor were 0.01 and 0.02 mol/kg, respectively. HCOOH (+99% purity) was used for Ni synthesis.

NiO synthesis was performed by the FT-SCW method as described in our previous works.[2,3] In this work, reaction temperature and pressure were 673 K and 30 MPa, respectively. Reaction time was 1.0 s. Ni synthesis was performed by the following procedure at 673 K. Prepared NiO particles (1.12 g) and HCOOH (0.37–2.76 g) were loaded into a batch reactor (7.5 cm^3) made of SUS316. Molar ratio of HCOOH to NiO was changed from ca. 0.5 to 6. The temperature was measured with a K-type thermocouple that was inserted into the reactor. The air in the reactor was replaced with Ar by successive purging, and then the reactor was sealed. The reactor was heated by immersion into a temperature-controlled molten-salt bath at 673 K. Approximately 1 min was required for the batch reactor to reach the reaction temperature. Reaction time was 5–60 min, which includes heating up time. The reactor was quenched in a water bath, which was kept at room temperature.

The crystal structures of the products were analyzed by powder X-ray diffractometry (XRD, RINT-2200, Rigaku), using Cu Kα radiation. Observation of these products was performed by a transmission electron microscope (TEM, TECNAI-G2, FEI Co). Particle size distribution and average particles size with standard deviation (S.D.) were determined on the basis of the diameter of about 150–200 particles measured from TEM results. Concentrations of remaining Ni ion in the recovered aqueous solution were measured by inductively coupled plasma (ICP) emission spectroscopy (SPS-7800, Seiko). Conversion of Ni ion to NiO was defined as $(1 - C/C_0) \times 100$, where C and C_0 are molal concentrations of the metal species in the recovered and starting solutions, respectively. The magnetic properties of the Ni particles at room temperature were measured by a vibrating sample magnetometer (VSM, TEM-WF86R-153, Toei Kogyo Co. Ltd.).

Experimental conditions and results are summarized in Table 1. Figures 1–3 show XRD patterns, typical TEM images, and typical VSM results of the products, respectively. NiO nanoparticles having an average size of 3.8 nm was prepared by the

Table 1. Experimental conditions and results

Run No.	Reaction time /min	HCOOH /g	Crystal phase[a]	Average size /nm	S.D. /nm	Saturation magnetization /emu g^{-1}
1	—	—	NiO	3.8	8.1	—
2	5	0.69	Ni, (NiO)	4.9	1.6	18.3
3	30	0.69	Ni, (NiO)	5.2	1.2	33.5
4	60	0.69	Ni	6.1	2.1	37.8
5	30	0.37	Ni, (NiO)	5.0	1.3	2.1
6	30	1.38	Ni, (NiO)	6.7	1.5	32.5
7	30	2.76	Ni	8.1	3.8	36.3

[a] Species within parentheses indicate minor product.

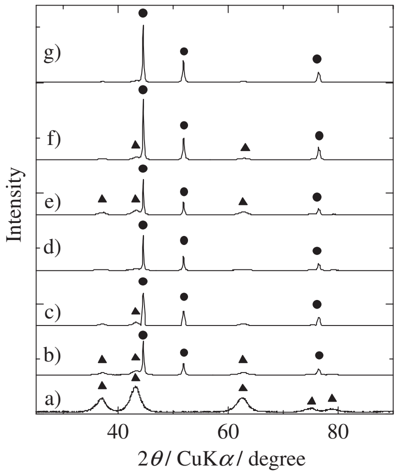

Figure 1. XRD patterns of the obtained particles by a) FT-SCW method and reduction of NiO b) for 5 min, c) for 30 min, d) for 60 min with 0.69 g of HCOOH, e) with 0.37 g of HCOOH, f) with 1.38 g of HCOOH, and g) with 2.76 g of HCOOH for 30 min. Circle and triangle denote Ni and NiO, respectively.

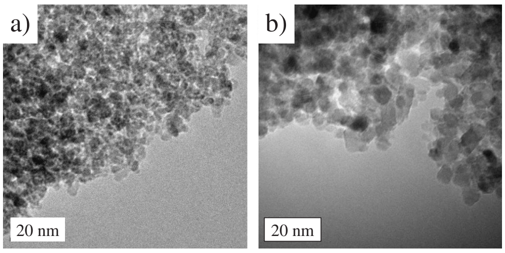

Figure 2. Typical TEM images of the obtained particles by a) FT-SCW method and b) reduction of NiO for 60 min with 0.69 g of HCOOH.

FT-SCW method as shown in Figures 1a and 2a. Conversion in this experiment was ca. 92%.

In the experiment of Ni synthesis, with increasing HCOOH weight from 0.37 to 2.76 g for 30 min, the peak intensity of the Ni phase increased and the peak of the NiO was disappeared at the condition using 2.76 g of HCOOH. In addition, the increase in HCOOH weight leads to the increase in particle size and saturation magnetization from 5.0 to 8.1 nm and from 2.1 to 36.3 emu/g, respectively. Then, with increasing reaction time from 5 to 60 min at constant HCOOH weight of 0.69 g, the peak intensity of the Ni phase also increased and Ni single phase particles were obtained for 60 min. The increase in reaction time leads to the increase in particle size and saturation magnetization from 4.9 to 6.1 nm and from 18.3 to 37.8 emu/g, respectively. The result suggests that the Ni synthesis occurs along the following steps. Because crystallinity of the primary produced NiO particles was relatively low, NiO particles grew up during heating-up period. After that reduction of NiO proceeded in parallel with HCOOH decomposition and Ni nanoparticles with higher saturation magnetization could be obtained.

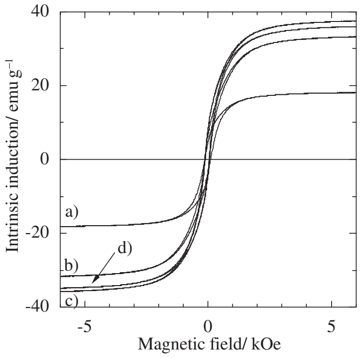

Figure 3. Typical VSM results of the obtained particles by reduction of NiO a) for 5 min, b) for 30 min, c) for 60 min with 0.69 g of HCOOH, and d) with 2.76 g of HCOOH for 30 min.

In conclusion, we have proposed a relatively simple synthesis method to obtain Ni nanoparticles. Ni particles were synthesized by reduction of NiO with HCOOH at 673 K, which was prepared by a flow-through supercritical water method. A detailed study of the preparation mechanism of Ni particles including decomposition behavior of HCOOH in the presence of NiO, which acts as a catalyst for HCOOH decomposition,[10] as well as the applicability for the synthesis of other metals is currently in progress.

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