Fast Preparation of Nano-sized Nickel Particles under Microwave Irradiation without Using Catalyst for Nucleation

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Nano-sized nickel particles have been prepared through reduction of $Ni(OH)_2$ with ethylene glycol under microwave irradiation. Without using such a catalyst as Pt for nucleation, spherical nickel particles with a diameter of 6 ± 3 nm were produced within 5 min.

The preparation of nanocrystalline metals has received considerable attention in recent years for their applications in fields such as catalysis, photography, and electronic materials. Recently, monodisperse nickel powders have been prepared by using polyol process.[1–4] Monodisperse 1–2 μm Ni was prepared by reducing $Ni(OH)_2$ in ethylene glycol (EG). Heterogeneous nucleation using Pt or Pd was found to be effective for the production of smaller particles. A protective agent such as polyvinylpyrrolidone (PVP) was used to prevent sintering. All of previous works have been carried out by heating liquid reagents in an oil bath at about 200 °C except for a recent pioneering study of Wada et al.,[4] who used a microwave heating as a new heating method. They succeeded in preparing nickel nanoparticles having narrow size distribution through reduction of $Ni(OH)_2$ with EG under microwave irradiation. A clear difference in the particle sizes was found between their microwave irradiation and the conventional heating. They reported that average particle size was controlled between 5–8 nm by changing the irradiation time and irradiation power, which was one order of magnitude smaller than those obtained by the conventional heating.[3] It should be noted that the Ni particles formed via the microwave method are cube-shaped, whereas those prepared by the conventional method were spherical.

In this work, we prepared Ni nano-sized particles under microwave irradiation. $Ni(OH)_2$ was completely dissolved by the addition of a sufficient amount of H_2SO_4 solution. We found that Ni nano-sized particles having spherical structure could be prepared without using such a catalyst as Pt or Pd for nucleation.

A dispersion solution of $Ni(OH)_2$ (Kishida Chem. Ind. 240 mg) in EG (10 ml) and H_2O (10 ml) containing PVP (average molecular weight: 40000, 1.33 g) was placed in a glass vial. PVP acts as a stabilizer of small Ni metal particles. Solutions with and without the addition of a small amount of H_2PtCl_6 $6H_2O$ (1.6×10^{-6}) were prepared in order to examine the effects of Pt catalyst for nucleation. When $Ni(OH)_2$ was introduced into the solution and stirred, a light-green powder of $Ni(OH)_2$ was dispersed. If unresolved $Ni(OH)_2$ powder is present in solution, it will disturb accurate TEM measurements. Therefore, $Ni(OH)_2$ powder was completely dissolved by the addition of a sufficient amount of H_2SO_4 (5N 4 ml). The temperature of the microwave-irradiated mixture was measured by a gradual determination method, because thermometers or thermocouples could not be used. The microwave irradiation was turned off and a thermometer was immediately placed into the heated sample to measure an approximate temperature. When the dispersion solution was irradiated by microwave discharge (SANYO EMO-FR10 2.45 GHz) at 200 W, the temperature of the solution was raised to 423 K in 5 min and the color of the solution changed to light brown.

It is known that Ni metal particles are produced from the following reactions in the polyol process.[5]

$$CH_2OH\text{–}CH_2OH \xrightarrow{-H_2O} CH_3CHO \quad (1a)$$

$$2CH_3CHO \xrightarrow{Ni(II)} Ni + 2H^+ + CH_3COCOCH_3 \quad (1b)$$

The following six diffraction rings due to metal nickel (cubic form) were observed in the TEM diffraction pattern of products: (111), (200), (220), (311), (222), and (400). A TEM photograph and the size distribution histogram of nickel nanoparticles prepared by microwave heating without the addition of the Pt catalyst are shown in Figures 1 and 2, respectively. It is clear from Figure 2 that spherical nanoparticles with diameter of 6 ± 3 nm were produced and aggregated under the present experimental conditions. This particle size was slightly smaller and the distribution was narrower than the previous results of Wada et al. (4–12 nm).[4] In our TEM measurements, cube-shaped particles were not observed. When Ni nanoparticles were prepared with the addition of the Pt catalyst, a similar TEM photograph was obtained. This led us to conclude that the Pt catalyst has little effects for the nucleation of Ni nanoparticles under the microwave

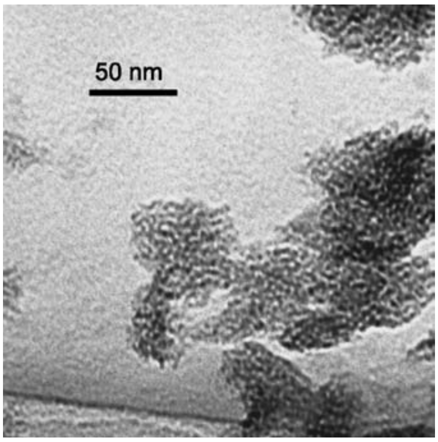

Figure 1. A TEM photograph of nickel nanoparticles prepared under microwave irradiation.

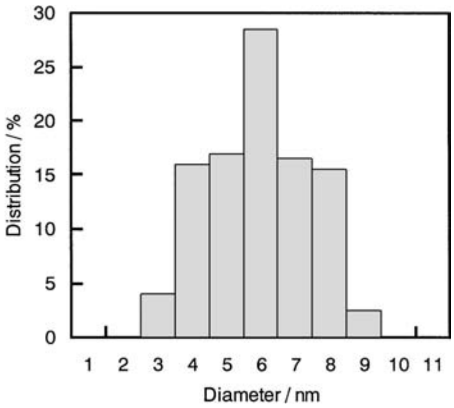

Figure 2. Size distribution of nickel nanoparticles.

heating.

UV-visible absorption spectra of reactant and product mixtures prepared without the addition of the Pt catalyst are shown in Figures 3(a) and 3(b), respectively. The reactant spectrum is composed of absorption peak of $Ni(OH)_2$ at 400 nm, which gives a green color of solution. The product spectrum consists of a strong peak at 210 nm and a weak peak at 350 nm, which can be ascribed to Ni nanoparticles by comparison with the reported spectroscopic data.[6] When UV-visible spectrum of products prepared with the addition of the Pt catalyst was measured, a similar spectrum was observed. This indicates that the same nickel nanoparticles were produced by using the Pt catalyst.

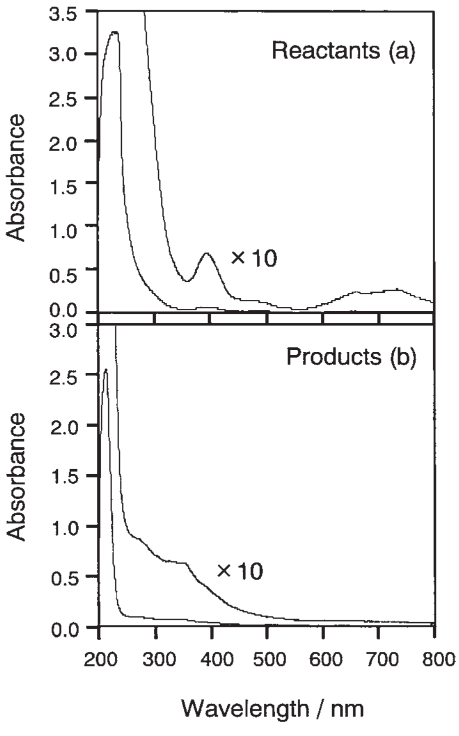

Figure 3. UV spectra of (a) reactants and (b) products of nickel nanoparticles prepared under microwave irradiation.

Hedge et al.[3] have studied the formation of Ni nanoparticles from the same $Ni(OH)_2$/EG/PVP system in an oil bath. They examined the effect of the addition of such a nucleation agent as Pd or Pt. The reaction time ranged from 50 min to 1 h 30 min. The average size of Ni particles prepared without using Pd or Pt was 135 nm. When $2 \times 10^{-3} - 2 \times 10^{-2}$ molar ratio of Pd or Pt was added, it reduced to 30–100 nm. In the present study using the microwave heating, the reaction time (5 min) is shorter than that in the oil-bath heating by factors of 10–18. The great reduction of the reaction time is an advantage of the microwave heating. Another advantage of the microwave heating for the preparation of nanoparticles is that the particle size of Ni is about one order of magnitude smaller than the conventional oil-bath heating.[5] It is known that the size of metal clusters depends on the speed of reduction of the metal precursors.[6] Microwaves provide fast heating and, thus, accelerate the reduction of the metal precursor. Therefore, rapid microwave heating leads to smaller sizes. An important finding in this study is that nucleation agent is unnecessary for the formation of Ni nanoparticles under the microwave heating. This indicates that nucleation of Ni occurs rapidly when the reduction rate of metal precursor is fast. In this study, spherical Ni particles were produced, which was different from the cubic-shaped particles obtained by Wada et al.[4] This difference must arise from different experimental conditions used here under the microwave heating.

In summary, fast preparation of Ni nanoparticles has been studied by the polyol method under the microwave irradiation. A great advantage of the microwave heating is that pure Ni particles with a small size of 6 ± 3 nm can be rapidly produced without using Pt or Pd catalyst for nucleation. We are planning to extend this technique as a new method for the preparation of metal nanoparticles.

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References

1 F. Fievet, J. P. Lagier, B. Blin, B. Beaudoin, and M. Fiflarz, *Solid State Ionics*, **32–33**, 198 (1989).
2 L. K. Kurihara, G. H. Chow, and P. E. Schoen, *Nanostruct. Mater.*, **5**, 607 (1995).
3 M. S. Hedge, D. Larcher, L. Dupont, B. Beaudoin, K. Tekaia-Elhsissen, and J. M. Tarascon, *Solid State Ionics*, **93**, 33 (1997).
4 Y. Wada, H. Kuramoto, T. Sakata, H. Mori, T. Sumida, T. Kitamura, and S. Yanagida, *Chem. Lett.*, **1999**, 607.
5 G. Carotenuto, G. P. Pepe, and L. Nicolais, *Eur. Phys. J. B*, **16**, 11 (2000).
6 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, **87**, 3881 (1991).