Synthesis and Size Control of Ni Nanoparticles Using $\gamma$-Irradiation

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Abstract: Nickel nanoparticles have been prepared by the reduction of nickel chloride induced by $\gamma$-ray irradiation with a dose of 10~30 kGy and a dose rate of 3.9 kGy/hr at room temperature under atmospheric pressure. X-Ray diffraction (XRD) analysis revealed that the prepared particles of nickel had cubic phase. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and particle size analysis (PSA) indicated that these nickel nanoparticles had diameters of 10~15 nm and a narrow size distribution. Also, we have shown that a number of parameters, such as the concentrations of nickel ions and isopropyl alcohol, the irradiation dose, and the types of surfactants, can be used to control the size of the nickel nanoparticles.

Keywords: Ni nanoparticles, $\gamma$-irradiation, X-ray diffraction, size distribution

Introduction

The preparation of small magnetic particles, and the control of particle size within the nanometer regime of Ni, Co, and Fe have been the subject of intensive research efforts for decades because of their many technological applications in such fields as optics, electronics, catalysis, and magnetic materials [1-5]. A number of methods, such as the use of hydrogen arc plasma [6], rapid expansion of supercritical solutions [7,8], $\gamma$-ray irradiation [9], and sonochemical and thermal decomposition of organic metal complexes [10-12], have been developed for the preparation of metal nanoparticles. In particular, nickel nanoparticles have important applications as catalysts and as conducting and magnetic materials [13], but relatively few studies on the preparation of nickel nanoparticles have been reported to date.

In the last few years, $\gamma$-irradiation has been used extensively as a new method to prepare nanocrystalline metals, alloys, metal oxides, and composites [9,14-19]. Under irradiation, with isopropl alcohol as a hydroxyl radical scavenger, the aqueous system maintains an atmosphere that reduces high-valent metal ions to low-valency ones. In this manner, metal or metal oxide powders that have very small scales can be obtained [14,20]. In this system, the average particle size, as well as the particle size distribution, is strongly dependent on a number of parameters, such as the concentration of the reducible species, the irradiation dose, and the nature of the stabilizer and solvent, but the influence that these parameters have on the nickel nanoparticles has yet to be reported.

In this paper, we describe the preparation of nickel nanoparticles by the reduction of a solution containing NiCl$_2$ under $\gamma$-ray irradiation at room temperature at atmospheric pressure. In addition, the effects of various experimental conditions, such as the absorbed dose, the concentration of NiCl$_2$ and isopropyl alcohol, and the type of surfactants, are described.

Experimental

Starting Materials

Nickel chloride (NiCl$_2$) and isopropyl alcohol were obtained from Kanto Chemical (Kanto, Japan) and DC Chemical (Seoul, Korea), respectively. Triton X-100 and SDS (sodium dodecylbenzene sulfonate) were purchased from Merck (Darmstadt, Germany) and Showa Chemicals (Tokyo, Japan), respectively. NH-100 (polyoxyethylene alkylallylphenyl ether) and 565P (polyoxyethylene alkylaryl phosphate) were purchased from Hannong Chemical (Gunsan, Korea). All chemicals were used without further purification. The water used throughout this study was produced using a water purification system.

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Table 1. The Compositions of Various Ni Particles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NiCl₂ (M)</th>
<th>Isopropyl alcohol (mL)</th>
<th>Surfactant (M)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of NiCl₂</td>
<td>0.01</td>
<td>30</td>
<td>0.01 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>30</td>
<td>0.025 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>30</td>
<td>0.05 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>30</td>
<td>0.1 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>30</td>
<td>0.5 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td>Concentration of isopropyl alcohol</td>
<td>0.025</td>
<td>10</td>
<td>0.025 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>30</td>
<td>0.025 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>50</td>
<td>0.025 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>70</td>
<td>0.025 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td>Type of surfactants</td>
<td>0.025</td>
<td>30</td>
<td>0.025 (Triton X-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>30</td>
<td>0.025 (SDS)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>30</td>
<td>0.025 (NH-100)</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>30</td>
<td>0.025 (565P)</td>
<td>200</td>
</tr>
</tbody>
</table>

Preparation of Nickel Particles

The solutions were prepared by adding an aqueous NiCl₂ solution into a surfactant/water solution at the various compositions shown in Table 1. The same concentration of surfactant and NiCl₂ was always used in this experiment. To remove oxidative radicals, such as OH radicals, various amounts of isopropyl alcohol were added. Oxygen was removed from the solution by bubbling nitrogen gas through it for 30 min. The solutions were irradiated using gamma-rays from a ⁶⁰Co source at a dose of 10 ~ 30 kGy and a dose rate of 3.9 kGy/hr. The particles were then collected by centrifugation and washed repeatedly with ethanol and distilled water to remove any impurities. Finally, the particles were dried at 70°C for 10 h.

Characterization of Nickel Particles

The particles were characterized by X-ray diffraction (XRD, SIEMENS-D5000, Cu Kα, λ = 0.15418 nm), employing a scanning rate of 0.02°/sec in the 2θ range from 20 to 80°. The morphology and size of the particles were determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM images were recorded on a Carl Zeiss-EM 912 Omega energy-filtering transmission electron microscope, using an acceleration voltage of 120 kV. The samples used for the TEM observation were prepared by the dispersion of particles in ethanol followed by ultrasonic vibration for 5 min. The SEM images were recorded on a JEOL-JSM 6700F instrument working at 5~10 kV. A Microtrac-UPA 150 particle size analyzer was used to determine the size distribution of the Ni particles.

Results and Discussion

Formation of Ni Particles and their Structure

It is well known that the radiolysis of an aqueous solution generates many products [21]. Among these active species, the hydrated electron and the hydrogen atom are strong reductive species that can reduce nickel ions (Ni²⁺) in the solution to nickel (Ni⁰). Meanwhile, some oxidative species, such as hydroxyl radicals, must be scavenged by isopropyl alcohol because they inhibit the formation of the nickel particles. As radiolysis proceeds, the combination or aggregation reactions occur further. The principal reactions can be written in a simplified way [16]:

\[ \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H}_2 + \text{OH}^- \]
\[ \text{OH}^- + \text{CH}_3\text{CH}((\text{OH})\text{CH}_3) \rightarrow \text{H}_2\text{O} + (\text{CH}_3)\text{CH}((\text{OH})\text{CH}_3) \]
\[ \text{e}^- + \text{M}^n+ \rightarrow \text{M}^{n+} \] (reduction)
\[ \text{nM}^{n+} \rightarrow \text{M}_n \rightarrow \ldots \rightarrow \text{M}_{\text{agg}} \] (aggregation)

The XRD patterns of the prepared particles are shown in Figure 1. The as-prepared particles exhibited low crystallinity with a weak and wide diffraction peak at 44.5°. When heated at 400°C for 4 h under an argon atmo-
sphere, the XRD spectrum of the specimen showed three strong peaks at 44.5, 51.7, and 76.6°. All the peaks can be indexed to the cubic nickel phase by comparison with the data of the JCPDS file No. 04-0850. No oxides or hydroxides were observed. The particle size of the as-prepared nickel was estimated to be 12.3 nm from the Ni (111) peak at 2θ of 44.5° using the Scheerer equation. However, the heat-treated particles were larger than the non-heat-treated particles as a result of aggregation of the nanoparticles; we calculated their size to be 17.7 nm.

The size distributions and SEM and TEM images of the nickel nanoparticles are displayed in Figure 2. The particles were essentially very fine and had a narrow distribution with a mean diameter of 10.5 nm, as indicated by the PSA results. This analysis revealed that nanosized nickel particles could be obtained upon irradiation. In this study, a surfactant was used to form micelles in which the nickel ions were trapped during the irradiation step. Therefore, the particle size distribution of the nickel nanoparticles formed upon irradiation was influenced by the narrow size distribution of the micelles. The particle size characterized by PSA was confirmed by the SEM and TEM analyses. As shown in Figures 2(b) and 2(c), the particle sizes in the SEM and TEM images correspond to the values determined using the PSA.

**Effect of Preparation Conditions**

As has been determined previously, the size of the particles is dependent on the solution composition. The average diameters and distributions of the nickel particles obtained through PSA at various concentrations of NiCl₂ are shown in Figure 3. We observe that the average size and size distribution of the nickel nanoparticles increased

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Figure 2. The analysis of Ni nanoparticles: (a) size distribution determined using a particle size analyzer; (b) SEM image; (c) TEM image (sample preparation: concentration of NiCl₂, 0.025 M; irradiation dose, 30 kGy; isopropanol, 30 mL; concentration of Triton X-100, 0.025 M).
upon increasing the concentration of NiCl₂, in cases where the concentration of isopropyl alcohol and the irradiation dose were fixed. We confirmed that the particle size rapidly increased up to 0.1 M of NiCl₂, and then it slowly increased. The particles had an average diameter of 9.6 nm at a concentration of 0.01 M. We observed that the average particle diameter was 13 nm at 0.5 M, which was the highest concentration we studied. We believe that these results occur because more nickel atoms are reduced and become aggregated into larger particles as the concentration of Ni²⁺ increases [19].

The effect that the irradiation dose has on the sizes of the nickel particles was also investigated. All the other parameters, such as the concentrations of NiCl₂, isopropyl alcohol, and surfactant, were kept constant. It is known that the average diameters of nanoparticles increase upon increasing the irradiation dose with the same dose rate [22]. Ni²⁺ was reduced to form atomic Ni⁰ as a result of the emergence of e⁻ and the subsequent reduction of Ni²⁺. When absorbed dose increases, more active species, such as e⁻, are generated. The possibility of further aggregation of colloidal particles increases as the Ni concentration increases. Therefore, nickel particles of greater size are formed at higher irradiation doses, as shown in Figure 4.

Figure 5 shows the average diameters and distributions of the nickel particles obtained using various concentrations of isopropyl alcohol. The NiCl₂ solution concentration, irradiation dose, and surfactant were 0.025 M, 30 kGy, and Triton X-100, respectively. We confirmed that the average size and size distribution of the nickel nanoparticles increased upon increasing the concentration of isopropyl alcohol because the concentration of species, such as the hydroxyl radical, that prevent the formation of the particles was reduced.

SDS, NH-100, 565P, and Triton X-100 were used in this study as surfactants that could prevent aggregation. Figure 6 shows the influence of these surfactants on the particles' sizes. When SDS and Triton X-100 were used in the system, the diameters of the particles were about 10–12 nm. In addition, the particles formed using Triton X-100 possessed a remarkably narrow size distribution. On the other hand, the size and distribution of the particles using NH-100 and 565P were large and relatively wide.
Concentration of isopropanol (mL)

0 10 20 30 40 50 60 70 80

Figure 5. The (a) particle size and (b) distribution with respect to the concentration of isopropyl alcohol (sample preparation: concentration of NiCl₂, 0.025 M; irradiation dose, 30 kGy; concentration of Triton X-100, 0.025 M).

Conclusion

Nickel nanoparticles were prepared successfully by the γ-ray irradiation method using NiCl₂ as the nickel source. Small-sized nanoparticles having diameters ranging from 10 to 15 nm and a narrow size distribution were obtained. Various factors, such as the NiCl₂ concentration, the amount of isopropyl alcohol, the irradiation dose, and the nature of the surfactant, were investigated. We confirmed that increasing the NiCl₂, and isopropyl alcohol concentrations and absorbed dose increased the particle size and the size distribution. In addition, we have shown that Triton X-100, a stabilizer of the nickel particles, was the most suitable surfactant for preparing nanoparticles having a small size and distribution.

Acknowledgment

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Reference