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Preparation of cobalt nanoparticles by hydrogen reduction of cobalt chloride in the gas phase

Hee Dong Jang[a,*], Dae Won Hwang[b], Dong Pyo Kim[b], Heon Chang Kim[c], Byung Yoon Lee[d], In Bum Jeong[d]

[a]*Nano-Materials Group, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, South Korea*
[b]*Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Deajeon 305-764, South Korea*
[c]*Department of Chemical Engineering, Hoseo University, Asan 336-795, South Korea*
[d]*R/D center, Chang Sung Co., Incheon 405-100, South Korea*

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Abstract

Cobalt nanoparticles were produced by the hydrogen reduction of cobalt chloride vapor in a multistage tubular aerosol flow reactor. Reaction zone temperature, preheating temperature, mole fractions of $CoCl_2$ and H_2, and residence time were considered as key process variables for the control of particle size and size distribution. Ranging from 50 to 78 nm in average diameter, cobalt nanoparticles with narrow size distributions were synthesized throughout our experiments. All of the considered process variables affected the particle size and size distribution in the synthesis of cobalt nanoparticles. As the reaction zone temperature and the $CoCl_2$ mole fraction increased, the average particle diameter increased. But the average particle diameter decreased as the residence time of reactants increased.

Keywords: A. Metals; B. Nano structures; C. Chemical synthesis

1. Introduction

Metal particles smaller than 100 nanometers in primary particle diameter are generally considered as nanoparticles. Such metal nanoparticles often exhibit very interesting electronic, magnetic, optical, and chemical properties. For example, their high surface-to-volume ratios have large fractions of metal atoms at surface available for catalysis [1,2]. In the case of cobalt (Co) nanoparticles, they are expected to possess exceptionally high-density magnetic property, sintering reactivity, hardness levels, excellent

* Corresponding author. Fax: +82-42-861-9727.
E-mail address: hdjang@kigam.re.kr (H.D. Jang).

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impact resistance properties, etc. Many studies on synthesis and magnetic properties of nanoscale metal particles such as Fe, Au, Pd, and composites have been reported [3–6].

But only a few studies for the synthesis of Co particles by gas phase chemical reaction have been reported in the literature. The preparation of metal particles by gas phase chemical reaction becomes increasingly important mainly due to the easy control of process conditions, in turn particle size, particle crystal structure and purity [7]. Saeki et al. [8] prepared cobalt particles from the cobalt chloride ($CoCl_2$) both by gas–solid reaction and by gas–gas reaction. They found that the hexagonal crystal structured Co particles of several microns in diameter were produced by the gas–solid reaction while cubic Co nanoparticles by the gas–gas reaction. However, the effects of process variables on the control of the particle size and the crystal structure were not investigated in their study. Otsuka et al. [9] performed series of experiments to produce Ni, Co, Fe particles by the hydrogen reduction of $NiCl_2$, $CoCl_2$, and $FeCl_2$, respectively. Their main focus was the preparation of Ni particles ranging from 50 to 138 nm in particle diameter with process conditions, but the detailed discussions on the characteristics of the formation and growth of metal particles were not performed.

This paper presents a systematic experimental study on the preparation of Co nanoparticles by the gas phase reduction of $CoCl_2$ with hydrogen in a multistage tubular aerosol flow reactor. The characteristics of the formation and growth of cobalt nanoparticles in the gas phase are discussed. In our experiments, reaction zone temperature, preheating zone temperature, mole fractions of reactants, and residence time in the aerosol reactor were considered as key process variables for the control of particle size, size distribution, and crystal structure.

2. Experiments

A schematic drawing of our experimental apparatus is shown in Fig. 1. The apparatus consists of particle generation, particle collection, and off-gas treatment parts. A multistage tubular aerosol reactor, made of 155 cm long quartz, in the particle generation part is subdivided into a $CoCl_2$ evaporation zone, a reactant preheating zone, and a reaction zone. A detailed explanation of characteristics of the apparatus and experimental procedure were described in our previous paper [10].

The particle size and morphology were characterized by a transmission electron microscopy (TEM, Philips Model CM12). The average particle diameter and geometric standard deviation of the powders

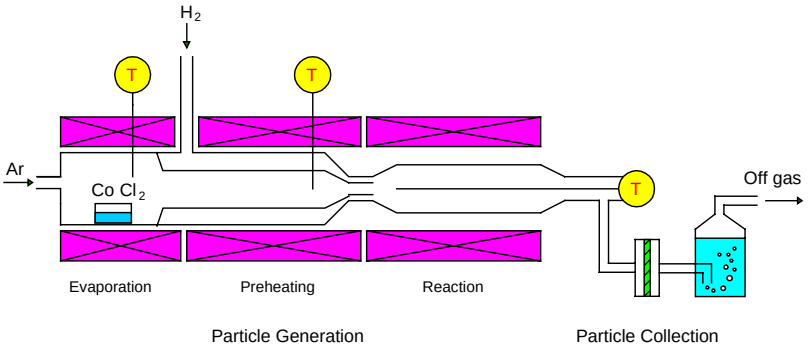

Fig. 1. Schematic drawing of experimental apparatus for the synthesis of Co nanoparticles.

were determined by counting more than 300 particles from TEM pictures [11]. X-ray diffractometer (XRD, Rigaku Co. Model RTP 300 RC) was used to obtain X-ray diffraction patterns of the powders.

3. Results and discussion

3.1. Effect of temperature

The overall reaction of $CoCl_2$ and H_2 in gas phase can be described as follows.

$$CoCl_2(g) + H_2(g) \rightarrow Co(s) + 2HCl(g)$$

Since the changes of Gibb's free energy for this reaction become negative at temperature above 500 °C [12], the reaction zone temperature was varied in the range of 800–950 °C. The effects of the reaction zone temperature on the conversion as well as on the particle diameter were investigated while fixing all other conditions (preheating temperature: 900 °C, $CoCl_2$ mole fraction: 0.0168%, total gas flowrate: 4 l/min). As the reaction zone temperature increased from 850 to 950 °C, the conversion monotonically increased from 72.5 to 99.9% and the average particle diameter also increased from 51 to 60 nm, as shown in Fig. 2. To explain the effects of the reaction zone temperature on the particle growth in the tubular aerosol reactor, two competing aspects need to be considered. Firstly, the rapidly increased nucleation rate at higher temperature produces much larger number of nuclei and sintering rate becomes high, then greatly enhancing the opportunity to grow into larger particles by high coagulation and sintering rate among nuclei [13]. Secondly, the residence time of the reactants in the reaction zone decreases at higher temperature due to volume expansion, providing the generated nuclei less chance to grow into larger particles by coagulation and sintering [14]. Since the particle diameter and the conversion monotonically increased with the reaction zone temperature, the particle growth mechanism in our experimental condition should be dominated by the first aspect.

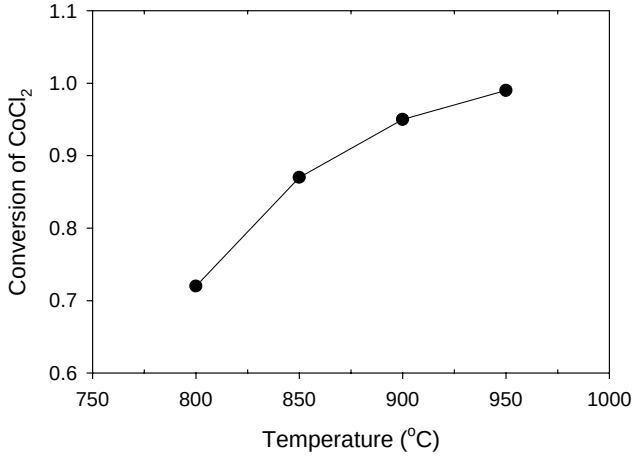

Fig. 2. Degree of conversion of $CoCl_2$ into Co increased as the temperature of reaction zone in the tubular aerosol reactor increased (preheating temperature: 900 °C, total gas flowrate: 4 l/min, $CoCl_2$ mole fraction: 0.0168%).

The preheating zone temperature was previously reported as one of the effective variables to control the particle diameter and size distribution. Jang and Jeong [14] reported that the smaller particle with narrower size distribution of titania powder could be synthesized by heating reactants up to the reaction zone temperature prior to entering the reaction zone. Here the effects of preheating temperature on the particle diameter and sized distribution were also investigated for cobalt nanoparticles. As the preheating zone temperature decreased from 900 to 800 °C by 50 °C while fixing the reaction zone temperature at 900 °C, the average particle diameter slightly decreased from 53 to 50 nm. However the geometric standard deviation of the powder increased from 1.34 to 1.45. When the preheating zone temperature is lower than the reaction temperature, the conversion can decrease and a temperature gradient can develop in the reaction zone. As a consequence, the particle diameter is expected to decrease due to lower conversion, and nuclei generated at the nozzle surface may act as seeds for heterogeneous nucleation resulting in wider size distribution of the powder. From these results the preheating zone temperature was found to be effective also for the synthesis of Co particles having smaller diameter and narrower size distribution.

3.2. *Effects of reactant concentrations*

As the concentration of aerosol precursor increases at the fixed reaction temperature and gas flow rate, the growth rate of nuclei by the coagulation and surface reaction becomes faster than the nucleation rate during the gas phase reaction. Thus, larger primary particles are generated at the higher precursor concentrations [15]. Nanometer-sized primary particles form aggregates in the gas phase because of interactive forces between particles. Such aggregates change into large particles when the temperature in the gas phase is high enough to sinter the aggregates [16,17].

Fig. 3 shows the effects of the $CoCl_2$ mole fraction on the particle size and size distribution at the constant conditions (preheating temperature: 900 °C, reaction zone temperature: 950 °C, total gas flowrate: 4 l/min). As $CoCl_2$ mole fraction increased from 0.0084 to 0.0862%, the average particle size

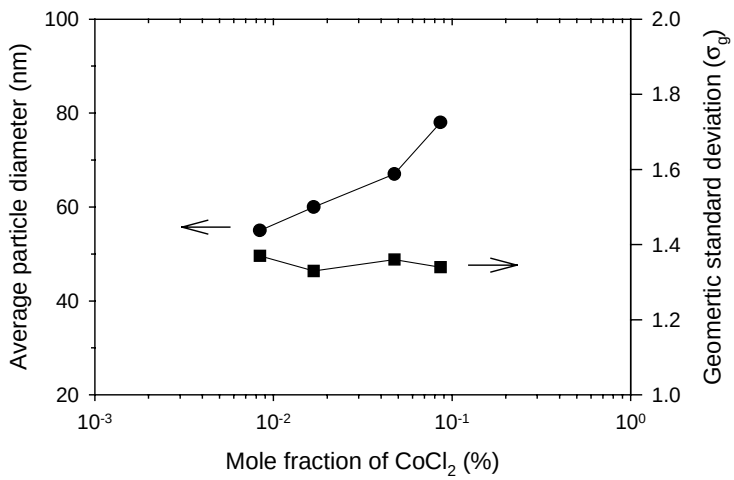

Fig. 3. As the mole fraction of $CoCl_2$ increased, average particle diameter increased but the geometric standard deviation of powder was not changed in the tubular aerosol reactor (preheating temperature: 900 °C, reaction temperature: 950 °C, total gas flowrate: 4 l/min).

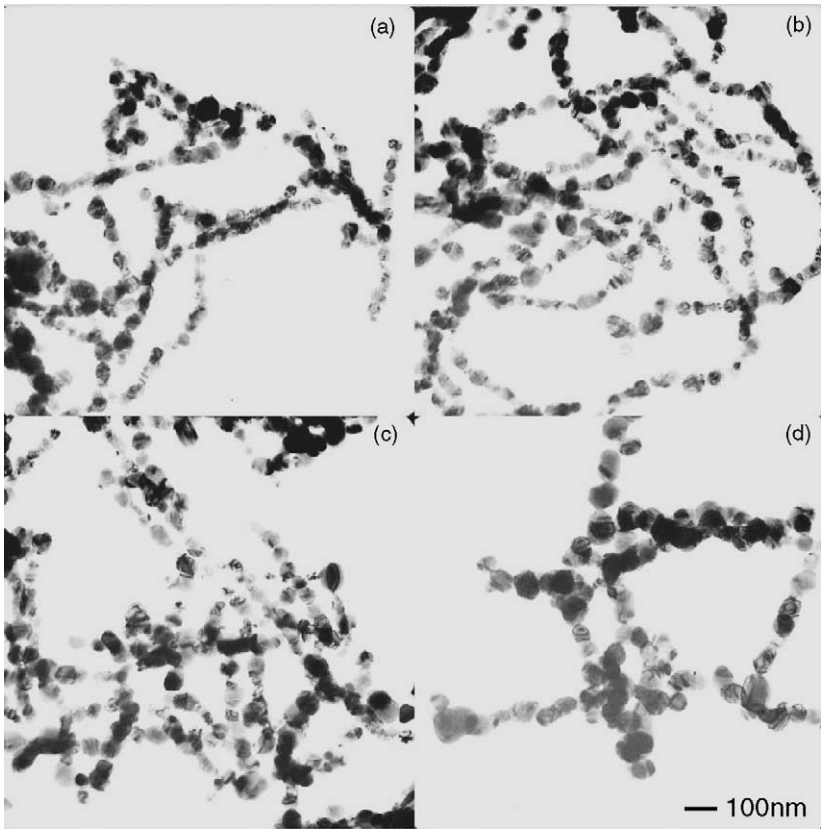

Fig. 4. TEM image of Co nanoparticles prepared at the different mole fraction of $CoCl_2$. Primary particles looked like single spherical crystals of nearly uniform size and the directional linkage of particles was observed.

of Co powders increased from 55 to 78 nm. However, the geometric standard deviation remained nearly constant around 1.35. Fig. 4 shows the TEM images of Co powders produced at the condition of Fig. 4. The morphology of Co particles was spherical in shape, primary particles seemed to be single crystals of nearly uniform size, and the directional linkage of particles due to magnetic interaction between particles was observed. By the XRD analysis as shown in Fig. 5, the crystal structure of the cobalt powders was cubic. The production rate of Co nanoparticles was 1 g/h at 0.0862% of $CoCl_2$ mole fraction.

As can be seen in Fig. 4, the increase in the number of larger particles with $CoCl_2$ concentration appears to indicate that they are produced by the coagulation, surface reaction, and sintering. However, smaller particles that seemed to be grown by the coagulation and surface reaction are observed at the low $CoCl_2$ concentration. If the sintering is dominant in the particle growth, it is expected that there should be many large particles at the low $CoCl_2$ concentration because the primary particle size is comparatively small at the low $CoCl_2$ concentration. Therefore, it is suggested that particle growth by the sintering is not dominant, and is only effective at the higher $CoCl_2$ concentrations in the present experimental condition.

The effects of the H_2 mole fraction on the particle size were also investigated while fixing all other conditions ($CoCl_2$ mole fraction: 0.0168%, total gas flowrate: 4 l/min, preheating temperature: 900 °C, reaction zone temperature: 900 °C). As the H_2 mole fraction increased from 12.49 to 49.99% by

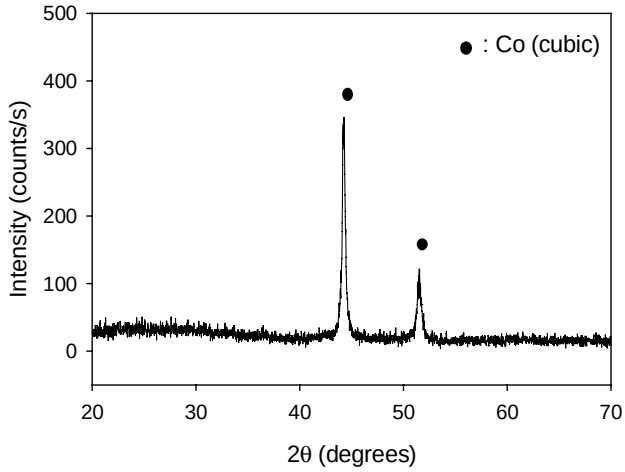

Fig. 5. X-ray diffraction pattern of product particles showed pure cobalt crystal having cubic structure.

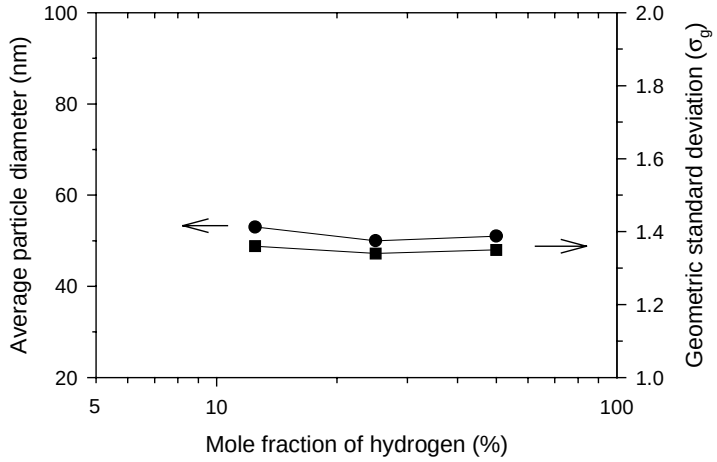

Fig. 6. Change of hydrogen flowrate at the fixed total flowrate was not effective on the average particle diameter and geometric standard deviation in the tubular aerosol reactor (reaction temperature: 900 °C, preheating temperature: 900 °C, total gas flowrate: 4 l/min, $CoCl_2$ mole fraction: 0.0168%).

varying the hydrogen flow rate from 0.5 to 2 l/min at the fixed total flowrate, the average particle diameter slightly decreased from 53 to 48 nm, as shown in Fig. 6. The alternation of the H_2 mole fraction, in the range of large excess H_2, gave small effect on particle size and distribution.

3.3. Effects of residence time

The effect of the residence time in the reaction zone was also investigated by varying the total gas flow rate from 3 to 5 l/min while fixing all other conditions (preheating temperature: 800 °C, temperature of reaction zone: 900 °C, $CoCl_2$ feed rate: 3×10^{-5} mol/min). As the residence time increased from 0.64 to 1.07 s, the particle size increased from 50 to 59 nm but the uniform size

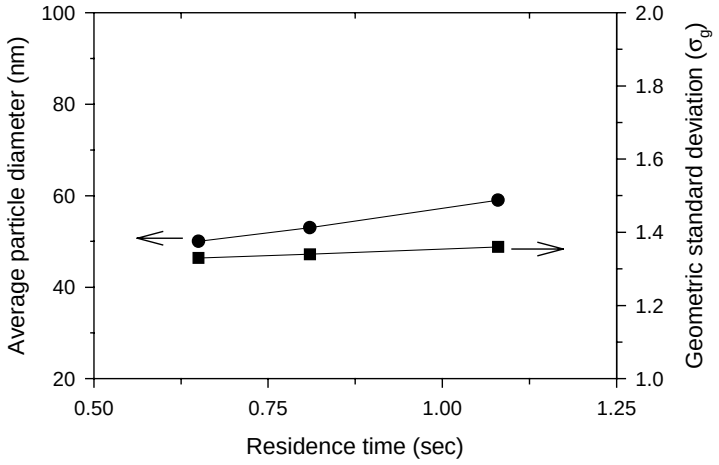

Fig. 7. As residence time of reactants in the reaction zone decreased, average particle diameter decreased but geometric standard deviation was nearly constant in the tubular aerosol reactor (reaction temperature: 900 °C, preheating temperature: 900 °C, $CoCl_2$ feed rate: 3×10^{-5} mol/min).

distribution was maintained, as shown in Fig. 7. This result is due to the reduction of possibility for the particles to grow by coagulation among small particles as the residence time decreases.

4. Conclusions

The synthesis of Co nanoparticles from $CoCl_2$ vapor by hydrogen reduction in the gas phase was investigated with a multistage aerosol reactor. Following important characteristics on the growth of cobalt nanoparticles were obtained.

1. As the reaction zone temperature increased, the particle diameter and the conversion of $CoCl_2$ monotonically increased. The increase of particle diameter with the reaction zone temperature was dominated by the high coagulation and sintering rate at higher temperature. The preheating of reactants was effective for the synthesis of Co nanoparticles having smaller diameter and narrower size distribution.
2. As the $CoCl_2$ mole fraction increased, the average particle diameter increased. The particle growth was not dominated by sintering.
3. As the residence time increased, the particle size increased. This is due to the reduction of possibility for the particles to grow by coagulation among small particles.
4. Throughout present experiments, spherical cobalt nanoparticles showing nearly uniform size were produced and the crystal structure was cubic.

Acknowledgements

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