

Continuous solvothermal synthesis of cobalt oxide nanoparticle using a high temperature high pressure water-ethanol mixed solvent

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1. Introduction

Continuous hydrothermal synthesis of metal oxide nanoparticles (NPs) using supercritical water has been widely researched as an environmentally benign method for producing high-crystalline functional metal oxide NPs. With the drastic decrease of water density and permittivity, along with the temperature and pressure increase of water to a supercritical state (374°C, 22.1 MPa), solubility of metal oxides sharply decreases, which leads to NP formation that result from the high degree supersaturation. Apart from supercritical water, supercritical ethanol is a widely utilized solvent for solvothermal synthesis of NPs [1]. In comparison to water, ethanol has a lower critical temperature and pressure (241°C, 6.14 MPa), which provides a benign condition for NP synthesis. It is reported that ethanol can work not only as solvent, but also as a surface modifier during the synthesis process of NPs [2]. Furthermore, because of ethanol's reduction environment, in addition to metal oxide nanoparticles, metal nanoparticles are also synthesized in supercritical ethanol [3]. Based on the characteristics of supercritical ethanol mentioned above, it becomes possible to change the critical point, acid/base property, and oxidation/reduction property of a high temperature and high pressure water/ethanol mixture solvent, by only changing the water-ethanol ratio of the solvent. It is reported that barium titanate nanoparticles are synthesized with the crystallinity of 90% [4] and that the crystallization of yttrium aluminum garnet nanoparticles are promoted by the mix of ethanol into water [5]. Therefore, the crystallinity or the size [6] of NPs can be changed by the solvent mixture. There is little research focusing on the oxidation/reduction property changes in a water-ethanol mixture that may cause changes to the composition of synthesized nanoparticles. Furthermore, how the property changes of the water-ethanol ratio in a mixed solvent affect the synthesis of NPs also needs to be explored.

The purpose of this research is to elucidate the effect of mixing ethanol into water for the synthesis of metal oxide nanoparticles at a high temperature and high pressure condition. Synthesis of cobalt oxide NPs was selected as a model reaction because cobalt oxide has a different valence number (CoO , Co_3O_4 , Co_2O_3) and shape. Therefore, the size and valence number of NPs may be affected by the variation of the water/ethanol ratio.

2. Experiment

In this research, cobalt oxide nanoparticles have been synthesized using a simple, custom-built, continuous-flow reactor as shown in Fig. 1. In this process, a water-ethanol mixture was heated by the oven and then fed into the swirl mixer from line 2 and 3. A cobalt precursor $\text{Co}(\text{NO}_3)_2$ aqueous solution was also simultaneously pumped into the mixer from line 1. Experiments were conducted at different reaction times (5 s, 10 s, 20 s) from the mixer to the inlet of the cooling tube. The temperature and pressure of the reaction part were fixed at 250°C, 20 MPa respectively. The water/ethanol (w/e) ratio of the solvent ranged from 1/0~0.2/0.8 by changing the flow rate of the influent 2~5. After the experiment, the effluent containing NPs was filtered and the NPs were vacuum dried for 24 h.

TEM and XRD were used to analyze the particle size, shape, and composition of synthesized nanoparticles. UV-vis was used to measure the concentration of cobalt ions in the effluent.

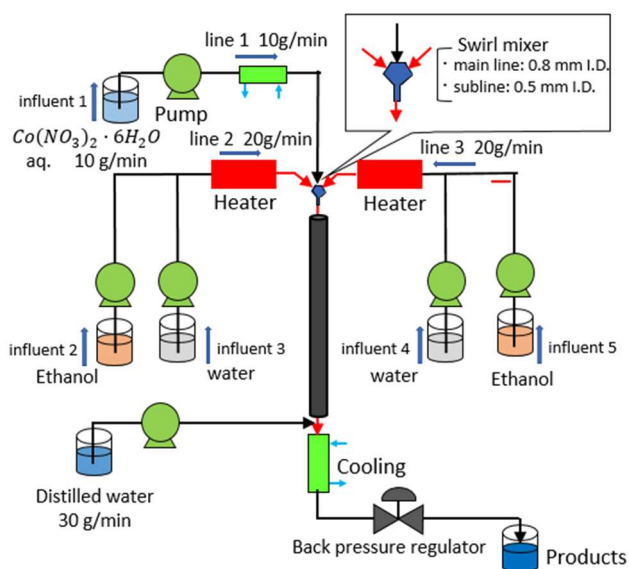


Fig. 1. Continuous flow reactor

3. Results and Discussion

3.1 Co ions conversion

When using only water as the solvent, no NP formation was confirmed at each reaction time. However, when using the water-ethanol mixture and when the molar ratio of ethanol became equal to or higher than 0.2, cobalt oxide NP formation occurred.

As seen in Table 1, at 5 s, Co had a higher conversion at a 0.3 molar ratio of ethanol than at 0.2. This was also observed at 10 s, where the conversion of Co at a 0.3 molar ratio of ethanol was higher than at 0.2 and 0.4. At 20 s, the conversions of Co at a 0.8/0.2 and 0.7/0.3 w/e ratio were both almost 100%.

Table 1. Conversion of Co ions in Cobalt oxide NPs synthesis at different w/e ratio, 250°C, 20 MPa

conversion	5 s	10 s	20 s
0.8/0.2 w/e	89.35%	91.14%	91.38%
0.7/0.3 w/e	97.90%	97.97%	98.55%
0.6/0.4 w/e		92.28%	
0.5/0.5 w/e	58.08%	64.57%	95.06%
0.4/0.6 w/e	32.24%	37.45%	41.51%
0.2/0.8 w/e		31.62%	59.26%

3.2 Results in lower ethanol ratio range

The TEM images of samples synthesized in A) 0.8/0.2, B) 0.7/0.3, C) 0.5/0.5, w/e ratios are shown in Fig. 2. As can be seen in Fig.2a, d, g, cubic NPs were synthesized at the condition of a 0.8/0.2 w/e ratio at each reaction time. Under the condition of a 0.7/0.3 w/e ratio, cubic NPs were also synthesized at each reaction time (Fig.2b, e, h). According to Fig.2c, f, i, under the condition of a 0.5/0.5 w/e ratio, some octagonal and round particles were produced.

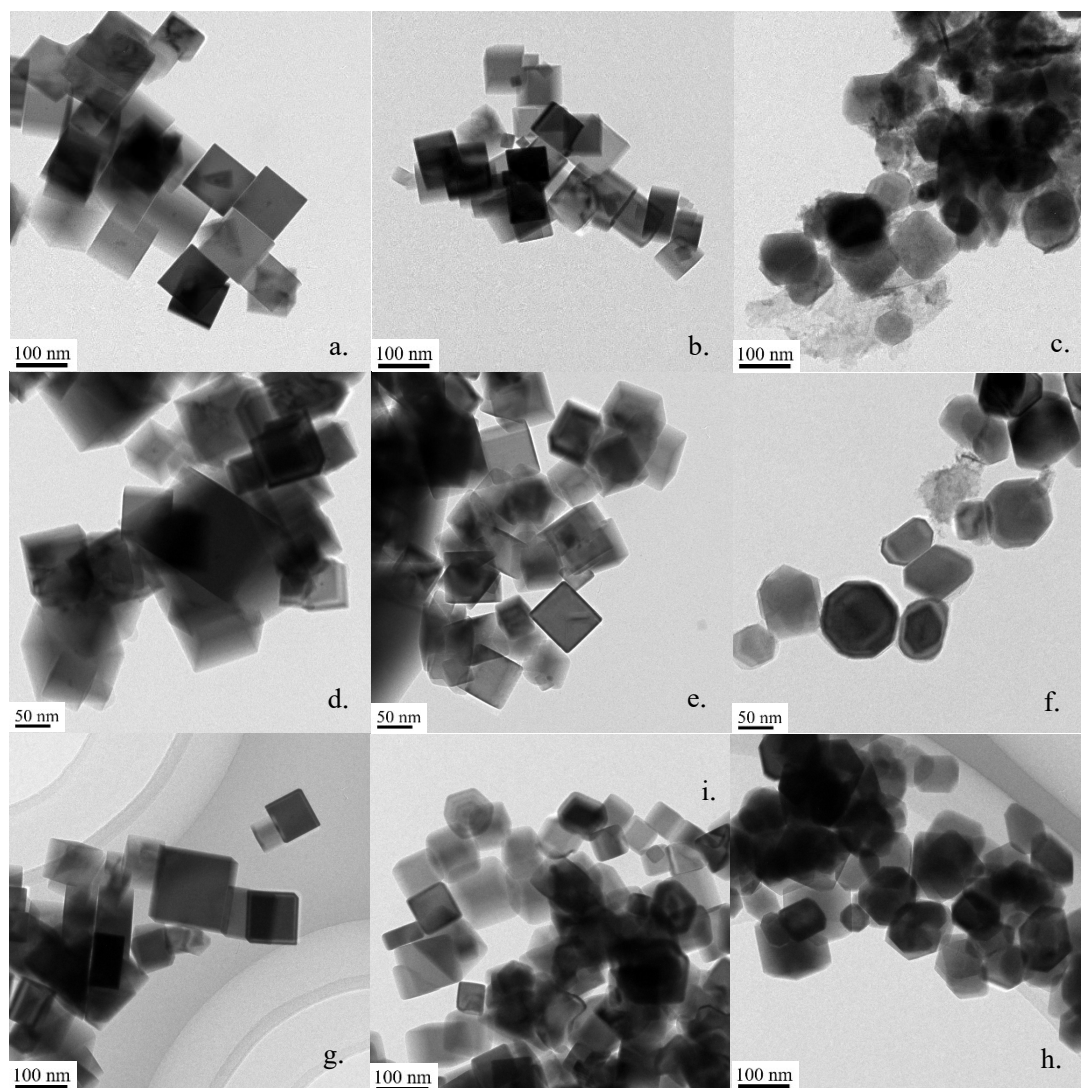


Fig 2. TEM images of NPs synthesized at different w/e ratio and reaction time. a, d, g) 0.8/0.2. b, e, i) 0.7/0.3. c, f, h) 0.5/0.5, a, b, c) 5 s, d, e, f) 10 s, g, i, h) 20 s.

Figure 3 shows the XRD results of samples synthesized in w/e ratios of 0.8/0.2, 0.7/0.3, 0.6/0.4, and 0.5/0.5 at 10 s. All samples showed similar peaks, which indicates that Co_3O_4 NPs were synthesized under all of the conditions. NPs synthesized in w/e ratios of 0.8/0.2, 0.7/0.3, 0.6/0.4 had the same lattice constant, which was slightly smaller than that of the samples synthesized in a 0.5/0.5 w/e ratio.

Figure 4 shows the size distribution of NPs synthesized in w/e ratios of 0.8/0.2, 0.7/0.3, and 0.5/0.5 at 5 s, 10 s, and 20 s. NPs in a 0.7/0.3 w/e ratio had the smallest particle size at each reaction time.

Based on the results in the last two sections, it can be seen that Co in a 0.7/0.3 w/e ratio has a higher conversion than Co in a 0.8/0.2 w/e ratio. Additionally, the particle size of NPs synthesized in a 0.7/0.3 w/e ratio is smaller than that of NPs in a 0.8/0.2 w/e ratio. According to the classical nucleation theory, the higher supersaturation degree of metal ions tends to promote the nucleation process, and at a lower supersaturation degree condition the crystal growth process dominates the NPs synthesis. Compared to water, ethanol has a lower permittivity, which may cause lower solubility of Co ions in the solvent. Under the high temperature and high pressure condition (250°C, 20MPa), the solubility of Co ions decreases with the ratio of ethanol in the mixed solvent increasing, which may cause a higher supersaturation degree of cobalt ions. This results in a higher conversion of the cobalt precursor and smaller particle size of Co_3O_4 nanoparticles.

Octagonal and round particles synthesized in a 0.5/0.5 w/e ratio condition had a lattice constant that was larger than that of the cubic particles, but also had similar XRD patterns. This indicates that the crystal structure of the octagonal and round particles differ from the cubic particles. When considering the conversion result in Table 1, unlike the 0.8/0.2 and 0.7/0.3 w/e ratios that had the same conversions at all reaction times (5, 10, 20 s), the conversion at a 0.5/0.5 w/e ratio rose drastically from 10 to 20 seconds. This shows that the reaction rate of NP synthesis at a 0.5/0.5 w/e ratio is slower than the lower ethanol condition. However, the slower growth of the (1.1.1) face of NPs at a 0.5/0.5 w/e ratio needs further research.

3.3 Results in higher ethanol ratio range

The XRD results of samples synthesized in w/e ratios of 0.5/0.5, 0.4/0.6, and 0.2/0.8 at 10 s are shown in Fig.5. At a 0.5/0.5 w/e ratio Co_3O_4 nanoparticles are synthesized, and at a 0.4/0.6 w/e ratio both Co_3O_4 and CoO peaks are observed, indicating the synthesis of Co_3O_4 and CoO. Additionally, when the ethanol ratio is increased to 0.8, only CoO peaks are observed. The lattice constant of Co_3O_4 and CoO synthesized at a 0.4/0.6 w/e ratio are the same as Co_3O_4 at a 0.5/0.5 w/e ratio and

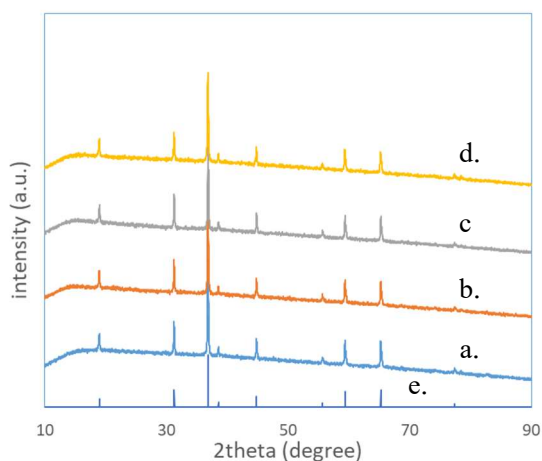


Fig 3. XRD results for Cobalt oxide NPs synthesized at lower w/e ratio, 250°C, 20 MPa, 10s. a. 0.8/0.2, b. 0.7/0.3, c. 0.6/0.4, d. 0.5/0.5, e. peaklist of Co_3O_4 .

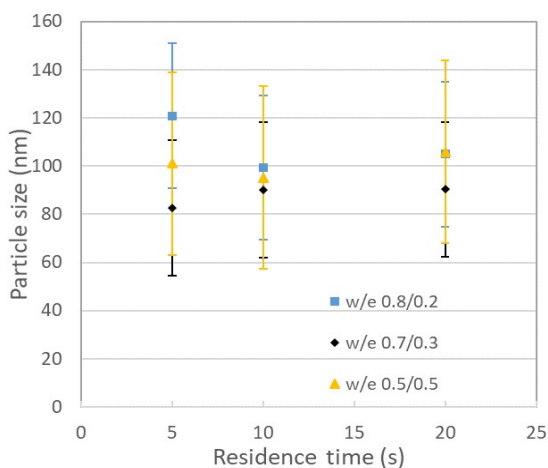


Fig 4. Particle size of Cobalt oxide NPs synthesized at 0.8/0.2, 0.7/0.3, 0.5/0.5 w/e ratio, 5s, 10s, 20s reaction time.

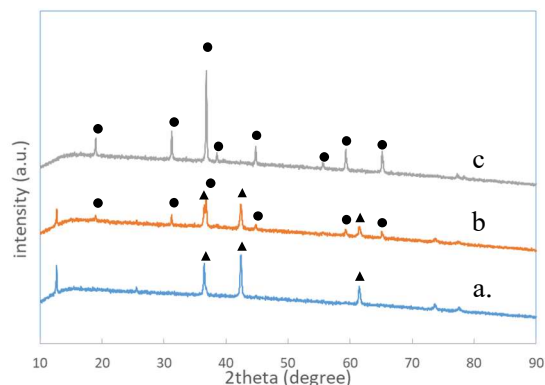


Fig 5. XRD results for Cobalt oxide NPs synthesized at higher w/e ratio, 250°C, 20 MPa, 10s. a. 0.2/0.8, b. 0.4/0.6, c. 0.5/0.5. (●): Co_3O_4 ▲: CoO

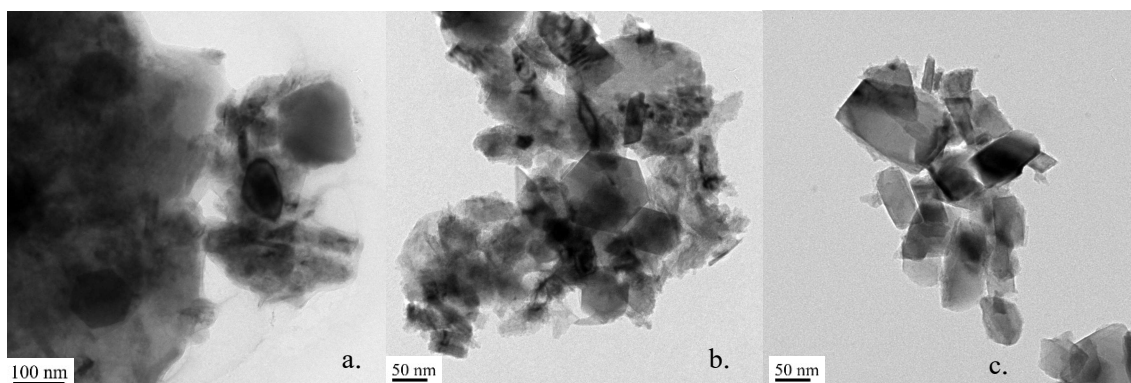


Fig 6. TEM images of Cobalt oxide NPs synthesized at a) 0.4/0.6, 5 s. b) 0.4/0.6, 10 s. c) 0.2/0.8, 10 s.

CoO at a 0.2/0.8 w/e ratio respectively. Figure 6 shows the TEM images of samples synthesized at different reaction times and w/e ratios. In Fig. 6a, some amorphous materials can be observed; whereas in Fig. 6b, two kinds of NPs can be observed. In comparison to Fig. 6a and Fig. 6b, the CoO NPs synthesized at a 0.2/0.8 w/e ratio (Fig. 6c) have a more clear crystal structure. This could also be indicated by the sharper and higher XRD result of the 0.2/0.8 w/e ratio sample in Fig. 5.

Figure 7 shows the XRD results of samples synthesized at a 0.4/0.6 w/e ratio and at a reaction time of 5 s, 10 s, and 20 s respectively. At 5 s, both Co_3O_4 and CoO peaks are not clear, which indicates that amorphous materials may be produced at this condition. This is consistent with the results shown in Fig. 6a. When the reaction time is extended to 10 s, clear Co_3O_4 and CoO peaks appeared in the XRD pattern. As shown in the TEM image in Fig. 6b, both Co_3O_4 and CoO NPs can be observed. When reaction time was set to 20s, the peaks of Co_3O_4 became sharper than that of shorter reaction time, and the peaks of CoO became broader. This indicates that at a 0.4/0.6 w/e ratio, CoO NPs appeared at the 10 s reaction time and almost disappeared at 20 s.

Based on the results in this section, it is indicated that at 250°C 20 MPa, a water-ethanol mixed solvent with a higher ethanol ratio (over 0.5 molar ratio) can provide a more reductive environment for Cobalt oxidant NPs synthesis. The disappearance of CoO in the condition of a 0.4/0.6 w/e ratio and 20 s reaction time shows that CoO may play the role as an intermediate material during the Co_3O_4 NPs synthesis process.

4. Conclusion

In this study, the syntheses of cobalt oxide NPs in a water-ethanol mixing solvent were conducted at 250°C 20 MPa from an ethanol molar ratio of 0 to 0.8 at different reaction times. The mixing of ethanol with water at a relatively low ratio and at a high temperature and high pressure caused lower solubility of cobalt ions. This resulted in a higher supersaturation of cobalt ions, thus enhancing the formation of nanoparticles. For similar reasons, as ethanol ratio increased from 0.2 to 0.3, the cobalt ions had a higher conversion and synthesized nanoparticles with smaller particle size. When the ethanol ratio was increased to 0.5, the reaction rate of NP synthesis and growth of (1 1 1) face of NPs became slower, which caused the shape of NPs to change from cubic to octagonal and round. When the ethanol ratio rose from 0.5 to 0.8, the redox potential of the mixed solvent changed and resulted in a more reductive environment for Co NPs synthesis. Conclusively, the composition of the nanoparticles was changed, and metal oxides with a lower valent number were synthesized.

Reference

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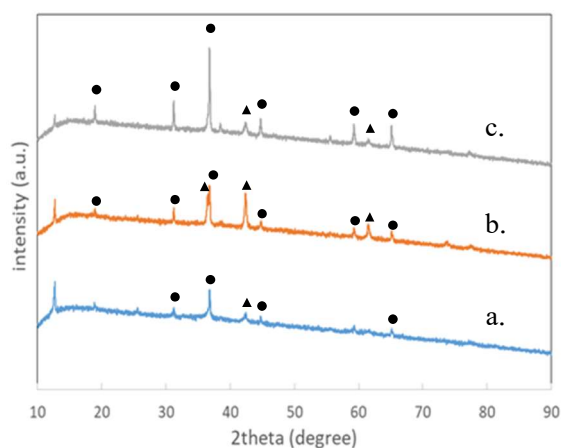


Fig7. XRD results for Cobalt oxide NPs synthesized at different reaction time, 250°C, 20 MPa, 0.4/0.6 w/e ratio. a. 5 s, b. 10 s, c. 20 s. (●: Co_3O_4 ▲: CoO)