Synthesis of spherical cobalt oxide nanoparticles by a polyol method

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We report the synthesis of spherical cobalt oxide nanoparticles by a polyol method. To obtain spherical nanoparticles, water, polyvinylpyrrolidone (PVP), and cobalt acetate tetrahydrate were mixed in diethylene glycol and refluxed at 200°C. Spherical particles were not obtained in the absence of water or PVP, or when the mixture was refluxed at 180°C. The spherical nanoparticles were found to be composed of cobalt (II) oxide (CoO) with a small amount of cobalt oxyhydroxide (CoOOH). The synthesized spherical nanoparticles had good dispersibility in water, and Fourier transform infrared spectroscopy and thermogravimetry-differential thermal analysis measurements indicated that the nanoparticles had a core–shell structure, with a core of CoO and a polymer shell.

Key-words : Polyol method, Core–shell, Cobalt oxide, Spherical, Polyvinylpyrrolidone, Dispersibility

1. Introduction

Cobalt oxide (CoO, Co₃O₄, or Co₂O₃) is a common component in a number of pigments. To obtain a pigment with good printing properties, particles in the pigment should have good dispersibility. In ink-jet printing technology, very narrow lines of inks are drawn. Therefore, the dispersibility of nanoparticles has recently attracted attention. As the size of nanoparticles decreases, aggregation of the nanoparticles increases and, in general, the printing properties of a pigment including nanoparticles deteriorate.

Stable dispersions with cobalt oxide nanoparticles for the above-mentioned applications cannot be obtained by directly dispersing dried cobalt oxide nanoparticles into a dispersion medium, as the strong aggregation of the dried cobalt oxide nanoparticles must be addressed. In general, nanoparticles aggregate strongly after synthesis, unless aggregation prevention procedures (e.g., adding surfactant or polymer, increasing zeta potential of nanoparticles) are carried out, even if the synthesis process is a gas- or liquid-phase process. Once strong nanoparticle aggregates are formed, it is very difficult to disperse the nanoparticles.

It has been reported that particle aggregation can be resolved mechanically by using ceramic beads. In this case, any impurities included with the particles are considered problematic, as the impurities may adversely affect some properties of the particles. Further, in many cases, a dispersant is required. Therefore, cobalt oxide nanoparticles that disperse easily without mechanical treatment or addition of a dispersant need to be synthesized.

It is very difficult to break nanoparticle aggregates apart. Thus, before aggregation, that is, at the same time as the formation of the cobalt oxide nanoparticles, aggregation prevention should be carried out to obtain easily dispersed nanoparticles. When a dispersion medium in which a polymer is dissolved is used as the reaction solvent, the polymer should play the role of preventing aggregation, allowing stable cobalt oxide nanoparticles to be obtained. Even after such stable cobalt oxide nanoparticles are dried, they should be easily redispersed into a dispersion medium because of the aggregation prevention treatment.

A similar concept has been applied using sol–gel and hydrolysis methods to prepare inorganic or metal particles. However, there is no report in which this concept has been applied to a polyol method to obtain cobalt oxide nanoparticles.

In this technical report, as a first trial, we investigated whether cobalt oxide (CoO, Co₃O₄, or Co₂O₃) nanoparticles could be synthesized by a polyol method, which is similar to the process used by Izu et al. to synthesize cerium oxide nanoparticles. The polyol method has a number of advantages when compared with processes in aqueous solution, such as precipitation and hydrothermal methods; for example, an organic solvent (polyol) can be used, a reaction initiator is not needed, temperatures from 100°C to the boiling point of the polyol can be used, and no autoclave is needed. An initial characterization of the spherical nanoparticles obtained in this study was also carried out. Additionally, the dispersibility of the spherical nanoparticles in water was investigated qualitatively.

2. Experimental

Distilled water, polyvinylpyrrolidone (PVP, average molecular weight: 10,000; Sigma-Aldrich Co. LLC.), and cobalt acetate tetrahydrate [Co(CH₃COO)₂·4H₂O; Wako Pure Chemical Industries, Ltd.] were added to 30 mL of diethylene glycol (DEG; Wako Pure Chemical Industries, Ltd.). Water was added at a water/DEG ratio of 0.017:1 (v/v). In some experiments, no water was added. The concentration of PVP was 120 or 0 g/L. The concentration of Co(CH₃COO)₂·4H₂O was 0.10 mol/L. The mixture, which was a transparent solution, was heated to 180 or 200°C and maintained for 360 min at the same temperature under reflux until the transparent solution became a cloudy sol. To remove any unreacted chemicals, the product was centrifuged at 18000 rpm for at least 10 min and washed with water or ethanol. Before characterizing the obtained nanoparticles, they were dried at 80°C for at least 12 h.

Field emission scanning electron microscopy (FESEM; JSM-6335F, JEOL), X-ray diffraction (XRD; RINT 2100V/PC)
analysis, Fourier transform infrared (FTIR; FT/IR-610, Jasco Corp.) spectroscopy, and thermogravimetry-differential thermal analysis (TG-DTA; TG-DTA2010SA-II, Bruker Corp.) were used to characterize the prepared nanoparticles. The average particle size and standard deviation of the spherical nanoparticles were calculated by measuring the particles sizes of 100 spherical nanoparticles in FESEM images. To check the dispersibility of the nanoparticles, the dried nanoparticles (0.02 g) were added to water (2 mL) and ultrasonicated using an ultrasonic homogenizer for 9 min. To evaluate the dispersibility, the dispersions were compared visually.

3. Results and discussion

Cobalt oxide nanoparticles were prepared using a polyol method under various experimental conditions (Table 1). The SEM image of the dried powder of Sample 1-1 [Fig. 1(a)] shows many spherical nanoparticles. The average particle size obtained from the SEM image was 81.1 nm, with a coefficient of variation of 0.166. This result indicates that the size distribution of Sample 1-1 is very narrow and the sample is monodisperse. To evaluate reproducibility, Samples 1-2 and 1-3 were prepared under the same process conditions as Sample 1-1. The average particle size of the spherical particles in Samples 1-2 and 1-3 were 57.2 and 65.5 nm, respectively, with coefficients of variation of 0.137 and 0.105, respectively, as shown in Table 2. Thus, we can obtain spherical nanoparticles with sizes in the range of 57–80 nm, although we cannot currently control the average particle size within this range precisely. The factors that determine the average particle size will be determined in future studies. Samples 2–6 were prepared by varying the reflux temperature, water/DEG ratio, or content of PVP, and SEM images of the nanoparticles were obtained. The nanoparticles in Samples 2–6 were not spherical in shape, but more complicated, with agglomerates of various particle shapes [Fig. 1(b)] or angular particles with sizes of 10 μm or more. Therefore, the following conditions were needed to obtain spherical nanoparticles: reflux temperature of 200°C, addition of water to DEG, and PVP addition. PVP is indispensable for the formation of a shell, as PVP is one of the main components of the shell. Many nuclei are needed to obtain nanoparticles and a shell is considered to promote the formation of spherical particles. Thus, the temperature of 200°C and the presence of water may promote nucleation of particles or the formation of the shell.

Next, the XRD patterns of the dried powders of Samples 1-1, 1-2, and 1-3 were obtained. The XRD pattern of the dried powder of Sample 1-1 is shown in Fig. 2. The XRD patterns of Samples 1-2 and 1-3 were nearly identical to that of Sample 1-1. The XRD patterns revealed a NaCl structure, consistent with cobalt (II) oxide (CoO) (JCPDS 48-1719). However, small peaks corresponding to cobalt oxyhydroxide (CoOOH) (JCPDS 26-0480) were also observed in Sample 1-1. Therefore, the synthesized nanoparticles do not contain a single oxide phase, but include CoO with a small amount of CoOOH. From the peak width of Sample 1-1, the crystallite size of CoO was calculated to be 12–14 nm. This indicates that the spherical nanoparticles consist of several crystallites, which is similar to the composition of core–shell ceria nanoparticles.

The XRD pattern of Sample 2 was similar to that of Sample 1-1, which indicates that the reaction to form CoO from cobalt acetate occurred at 180°C. In contrast, the XRD patterns of Samples 5 and 6 showed broad peaks. These results indicated that Samples 5 and 6 include an amorphous phase, and that PVP may be needed to obtain crystalline CoO. In this study, the amorphous phase could not be identified, as only two peaks were observed. As only small amounts of powder were obtained for Samples 3 and 4 (less than 1/10 of that obtained for Sample 1-1), XRD analysis could not be carried out, although the amount of material was sufficient for SEM observations.

The characterizations by FTIR and TG–DTA were only carried out for Sample 1-1, which showed spherical shaped particles in SEM images. The IR spectrum of Sample 1-1 is shown in Fig. 3, with the IR spectra of Sample 5 and PVP shown for comparison. The absorption peak in the IR spectrum of Sample 1-1 at 1660 cm⁻¹ was not observed in the IR spectrum of Sample 5. However, an absorption peak of 1660 cm⁻¹ was also observed in the IR spectrum of PVP. PVP was not used during the preparation of Sample 5. Therefore, the peak at 1660 cm⁻¹ [sym (C=O)]

| Sample | Average particle size (nm) | Standard deviation (nm) | Coefficient of variation |
|--------|----------------------------|-------------------------|-------------------------|
| 1-1    | 81.1                       | 13.4                    | 0.166                   |
| 1-2    | 57.2                       | 7.8                     | 0.137                   |
| 1-3    | 65.5                       | 6.9                     | 0.105                   |

![Fig. 1](image1.png)  
(a) SEM images of the dried powders of (a) Sample 1-1 prepared with PVP and (b) Sample 6 without PVP.  
![Fig. 2](image2.png)  
Fig. 2. XRD patterns of the obtained nanoparticle samples.
stretch\(^{20}\)) was confirmed to correspond to PVP. Two other peaks at 1290 and 1420 cm\(^{-1}\) were also observed in the IR spectra of Sample 1-1 and PVP, which correspond to the C–N vibration and CH\(_2\) bending vibration of PVP, respectively.\(^{21}\) Therefore, the observation of these peaks in Sample 1-1 confirmed that PVP was incorporated into the nanoparticles in this sample. For Samples 1-1 and 5, the peaks at 2800–2900 cm\(^{-1}\) are attributed to CoO and/or ethylene glycol\(^{22},23\) and those at 1100 cm\(^{-1}\) are attributed to ethylene glycol.\(^{23}\) The broad peak in the 1200–1800 cm\(^{-1}\) region in Samples 1-1 and 5 is attributed to CoO.\(^{22}\) The peaks around 500 cm\(^{-1}\) for Sample 1-1 are attributed to CoO (500 cm\(^{-1}\)) and/or CoOOH (580 cm\(^{-1}\)).\(^{24}\)

The TG–DTA results for Sample 1-1 are shown in Fig. 4. A weight loss of 14% was observed when the sample was heated to 900°C owing to an exothermic reaction in the temperature range of 200–300°C. Cobalt (II, III) oxide (Co\(_3\)O\(_4\)) is more stable than CoO below 900°C in air.\(^{25},26\) Thus, during TG–DTA, it was considered that CoO changed to Co\(_3\)O\(_4\). Considering the weight increase corresponding to oxidation of CoO to form Co\(_3\)O\(_4\), the sample before TG–DTA was estimated to include organic substances with a weight of 19%. These organic substances were thought to be PVP, as observed by IR spectroscopy. The exothermic weight loss at around 200–300°C corresponds to the loss of PVP from the nanoparticles during combustion. Oxidation of CoO to form Co\(_3\)O\(_4\) could not be observed by TG–DTA owing to the strong PVP combustion reaction.

The dispersibility of two dispersions that were obtained by dispersing the dried powders of Samples 1-2 and 6 into water was investigated. The dried powder (0.02 g) of Sample 1-2 or 6 was dispersed in 2 mL of water, and the change in the dispersion was observed over time. After dispersing Sample 1-2 using an ultrasonic homogenizer, the dispersion was homogenously brown, with a small amount of sediment, as shown in Fig. 5(a). This result indicates that Sample 1-2 was well dispersed. However, in the case of Sample 6, mostly sediment was obtained, as shown in Fig. 5(b). This result means that the dispersibility of Sample 6 is less than that of Sample 1-2. After leaving the two dispersions for one night, most of Sample 1-2 remained dispersed, although some more sediment formed [Fig. 5(c)], while all of Sample 6 became sediment [Fig. 5(d)]. Thus, the sample prepared in the presence of PVP (Sample 1-2) showed significantly better dispersibility than the sample prepared without PVP (Sample 6). The improved dispersibility of Sample 1-2 may be the result of PVP on the surface of Sample 1-2, which has a affinity for water and provides steric hindrance that prevents particles from aggregating.

It has been reported that core–shell type nanoparticles consisting of a cerium oxide core and polymer shell are obtained by heating a mixture of cerium nitrate, PVP, and ethylene glycol at a temperature of 160°C or more.\(^{14},17\) Although different reactants were used in this study (cobalt acetate and DEG instead of cerium nitrate and ethylene glycol, respectively), similar spherical nanoparticles were obtained by a similar process. The XRD results indicate that the spherical nanoparticles obtained in this study include mostly CoO, and the IR and TG–DTA results indicate that the nanoparticles include polymer. Moreover, the good dispersibility of these nanoparticles indicates that there is steric hindrance between the particle surfaces. Therefore, these results imply that Sample 1 consists of core–shell type CoO nanoparticles, with a CoO core and polymer shell.

4. Conclusions

Spherical nanoparticles were obtained by refluxing a mixture of DEG, water, PVP, and cobalt acetate at 200°C. In contrast, when no water or PVP was added during the synthesis process,
non-spherical nanoparticles were obtained. Non-spherical particles were also obtained when the mixtures was refluxed at 180°C. Characterization of the obtained spherical nanoparticles revealed that the spherical nanoparticles consist of CoO with a crystallite size of 12–14 nm and a small amount of CoOOH. The FTIR spectrum of the nanoparticles indicated the incorporation of PVP into the nanoparticles, and TG-DTA revealed a weight loss of 19 wt% when the nanoparticles were heated to 900°C. Furthermore, the spherical nanoparticles showed better dispersibility in water than the sample synthesized without PVP. These results imply that the spherical nanoparticles have a core–shell structure consisting of a CoO core and polymer shell. The obtained CoO nanoparticles could be useful in inks to obtain narrow lines or fine features by ink-jet printing.

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