**FULL PAPER**

**Growth mechanism and CO oxidation catalytic activity of raspberry-shaped Co₃O₄ nanoparticles**

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Raspberry-shaped Co₃O₄ nanoparticles has a great potential as a CO oxidation catalyst in a wide temperature range because of a high stability and a low-temperature oxidation activity. In this study, primary particle sizes, morphology and crystallite sizes were controlled by changing a synthesis time to enhance the CO oxidation activity and to reveal growth mechanism of the raspberry structure. The primary particle sizes increased while decreasing crystallite size, indicating crystal orientation and particle growth of Co₃O₄ nanoparticles were occurred in multistage, and a single-crystal-like structure formed in the hydrothermal treatment for 3.0 h. Long-time hydrothermal treatment for 12.5 h caused decomposition of the crystallographic orientation and the raspberry structure. H₂-temperature programmed reaction analysis indicated that crystal orientation among multiple Co₃O₄ nanoparticles improved a mobility of bulk oxygen species, and our previous findings that 93% of CO conversion rate for the raspberry-shaped Co₃O₄ nanoparticles was confirmed analytically by the high oxygen mobility in the early 3.0 h-hydrothermal treatment.

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1. Introduction

Carbon monoxide (CO) oxidation catalysts have been in great demand in automotive industry and industrial processes to convert toxic CO gasses to non-toxic CO₂ gasses. Among the CO oxidation catalysts, rare and expensive metals such as Pt, Au and Pd have been extensively studied and widely used in the industry because of their high CO oxidation activity in a wide temperature range.¹⁻⁹ On the other hand, alternative catalysts without the noble metals have been developed in order to move toward a sustainable society. The challenge for alternative materials was to give an activity from −80°C to room temperature. Since Xie et al. reported that tricobalt tetroxide (Co₃O₄) nanobelts achieved 100% CO conversion even at −77 and 25°C under moist normal feed gas,¹⁰ Co₃O₄ nanocrystals have been actively studied as a promising alternative catalyst to the rare metals. Recently, Murayama and Baidya, and their groups have developed highly stable and active cobalt oxide-based catalysts by addition of dopants, and furthermore, they have updated the theory of the unusual catalytic behavior of Co₃O₄ based catalysts.¹¹⁻¹² Previously, We have proposed morphological control approach to enhance stability while maintaining CO oxidation activity by synthesizing raspberry-shaped Co₃O₄ nanoparticles.¹³ Various types of Co₃O₄ nano-architectures showed specific catalytic reactivities;¹⁴⁻²² however, the large surface energy of nanoscale materials causes them to sinter under high temperature. The raspberry-shaped Co₃O₄ nanoparticles formed by self-accumulation of numerous 7⁻8 nm Co₃O₄ nanoparticles in hydrothermal reaction achieved high structural stability. The accumulation was promoted by bridging adsorption of sulfate ions among the Co₃O₄ nanoparticles, resulting in the formation of unique nanostructure which was maintained after the CO oxidation test at 350°C, and nearly 100% CO conversion was achieved in a temperature range from room temperature to 350°C. Comparing Co₃O₄ nanocubes and non-spherical Co₃O₄ nanoparticles, the raspberry Co₃O₄ showed the highest CO conversion rate (93%) around at 25°C, and the analysis of surface states by H₂-temperature programmed reaction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS) suggested that abundance of oxygen vacancies and Co²⁺ in the single nanoscale (<10 nm) surface contributed to the high oxidation activity in the wide temperature range. It is therefore conceivable that decreasing the size of primary particles, which are structural components of raspberry shaped Co₃O₄ particles, will enhance the CO oxidation activity.
Herein, raspberry-shaped Co$_3$O$_4$ nanoparticles were hydrothermally synthesized by changing synthesis time from 0.5–24.0 h and the size, morphology and crystallographic structure was controlled. The surface state was investigated by N$_2$-adsorption, H$_2$-TPR and XPS analysis. The CO oxidation activity was evaluated in a fixed-bed continuous-flow reactor with a reaction gas mixture (0.5% CO and 1% O$_2$ diluted in He). Additionally, we expected to be able to reveal the self-accumulation process of cobalt oxide particles forming the raspberry-like structure by observing a change in the microstructure during the hydrothermal reaction.

2. Experiment

2.1 Hydrothermal synthesis of raspberry-shaped Co$_3$O$_4$ nanoparticles

All chemicals were used as received. Co(CH$_3$COO)$_2$·4H$_2$O was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Ethylene glycol and Na$_2$SO$_4$ were supplied by Kishida Chemicals Co., Ltd. (Osaka, Japan). Cobalt glycolate was synthesized by dissolving Co(CH$_3$COO)$_2$·4H$_2$O (4.98 g, 0.02 mol) in 50 mL ethylene glycol$^{10}$). Distilled water (6.16 mL), cobalt glycolate solution (2.3 mL) and Na$_2$SO$_4$ solution (1.54 mL, 0.5 mol·L$^{-1}$) were transferred into a 25 mL polytetrafluoroethylene (PTFE) container (HUT-25, San-ai Kagaku, Aichi, Japan). The PTFE container was placed in an autoclave (HU-25, San-ai Kagaku, Aichi, Japan). The autoclave was then heated at 180 °C for 0.5–24.0 h in an aluminum heating unit (HHE-19G-U4, San-ai Kagaku, Aichi, Japan) under autogenous pressure and magnetic stirring at 300 rpm. Subsequently, the autoclave was removed from the heating unit, and the solution was cooled to room temperature under continuous magnetic stirring. The hydrothermally treated solution was then transferred into a 50 mL centrifugation tube and centrifuged at 13000 g. After discarding the clear supernatant, the precipitates were washed with distilled water. This centrifugation and washing process was repeated three times. Finally, a black powder was obtained by drying at 60 °C for 12 h in air.

2.2 Characterization and CO oxidation test

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex600-NB diffractometer equipped with Co-K$_\alpha$ radiation at 40 kV and 10 mA. The particle size and morphology were determined by transmission electron microscope (TEM; JEM2100F, JEOL, operating at 200 kV). An average particle size was estimated from the sizes of 100 particles in the TEM image.

Catalytic activity for CO oxidation was evaluated in a fixed-bed continuous-flow reactor. The reaction gas mixture (0.5% CO and 1% O$_2$ diluted in He) was fed through 30 mg of the catalyst, which had been pretreated in situ by flowing He gas at 300 °C for 0.5 h. The steady-state catalytic activity was measured every 20 °C as the temperature decreased from 400 to 25 °C. The effluent gas was analyzed via on-line gas chromatography with thermal conductivity detection in thermal conductivity detector [TCD; Shimadzu C-R8A (Kyoto, Japan)]; Shimadzu C-R8A (Kyoto, Japan). Catalytic activity was evaluated in terms of CO conversion to CO$_2$. The reducibility of the catalysts was evaluated via H$_2$-TPR, which was conducted from room temperature to 500 °C under flowing 5% H$_2$/Ar (30 cm$^3$·min$^{-1}$) at a heating rate of 10 °C·min$^{-1}$. H$_2$ consumption was monitored via TCD. The surface compositions of the catalysts were evaluated via Surface Science Instruments XPS, SSX-100 with Al-K$_\alpha$ radiation ($\lambda = 1486.6$ eV).

3. Results and discussion

3.1 Hydrothermal synthesis of raspberry shaped nanoparticles

The reaction time of hydrothermal synthesis greatly affected the structure of raspberry shaped Co$_3$O$_4$ nanoparticles, which is helpful to understand the formation process. Figure 1(a) showed synthesis time dependency for the XRD patterns of cobalt oxide nanoparticles synthesized by hydrothermal treatment for 0.5, 1.0, 1.5, 3.0, 6.0, 12.5, 24.0 h. The obtained materials were labelled as

![Fig. 1. (a) Powder XRD patterns of cobalt oxide nanoparticles synthesized by hydrothermal treatment for 0.5, 1.0, 1.5, 3.0, 6.0, 12.5 and 24.0 h; (b) Synthesis time dependency for crystallite sizes estimated from the FWHM of (311) peaks.](image-url)
xh-Co (where x refers to the synthesis time). The peaks around at 2θ = 22.0, 36.3, 42.9, 44.9, 52.3, 65.4, 69.9 and 77.2° in all samples were attributed to typical spinel Co₃O₄ crystal structures (PDF#04-016-4508). XRD pattern of the 0.5 h-Co sample had several peaks at 2θ = 11.9, 13.2, 17.7, 38.5, and 40.5° in addition to the peaks of Co₃O₄, and they were kinds of cobalt compounds but could not be identified as specific compounds. The unknown peaks disappeared with increasing synthesis time from 0.5 to 1.0 h. Crystallite sizes of Co₃O₄ were estimated from the full width at half maximum (FWHM) of (311) peaks and summarized in Table 1. In the time range from 1.0 to 6.0 h, there was no significant change in the crystallite sizes. As the time increased from 6.0 to 24.0 h, the crystallite size decreased from 34.2 to 20.2 nm.

Table 1. Structural characteristics of the hydrothermal synthesized cobalt oxide nanoparticles

| Synthesis time (h) | TEM Observations | XRD Measurements |
|-------------------|------------------|------------------|
|                   | Average Primary Particle Size (nm) | Average Secondary Particle Size (nm) | FWHM (deg.) | Crystallite Size (nm) |
| 0.5               | —                | 90.2             | 0.236       | 34.2                |
| 1.0               | 6.8              | 99.3             | 0.218       | 37.1                |
| 1.5               | 6.7              | 91.6             | 0.253       | 32.0                |
| 3.0               | 8.1              | 88.1             | 0.233       | 34.7                |
| 6.0               | 8.9              | 98.0             | 0.236       | 34.2                |
| 12.5              | 11.2             | 101.2            | 0.270       | 30.0                |
| 24.0              | —                | —                | 0.400       | 20.2                |

Figure 2 shows TEM images of the synthesized cobalt oxide particles. Our previous report showed the raspberry structure formed by self-accumulation of Co₃O₄ nanoparticles with the bridging adsorption of ligands. Although the raspberry-shaped Co₃O₄ nanoparticles were composed of multiple Co₃O₄ nanoparticles, it was considered that they had single-crystal-like structure because of their uniform lattice fringes and fast fourier transform (FFT) patterns. The crystallographic orientation must be induced by an oriented attachment of Co₃O₄ nanoparticles. TEM image for 0.5 h-Co precisely indicated the accumulation of nanoparticles. Dispersed particles (indicating with red allows) with a diameter of 10–20 nm were observed in addition to raspberry shaped nanoparticles in the 0.5 h-Co sample. These 10–20 nm nanoparticles were not observed in the 1.0 h-Co sample. According to XRD patterns, it can be speculated that the dispersed particles in the 0.5 h-Co sample were reaction products in their accumulation process. In the time range from 0.5 to 12.5 h, the morphology and size of primary particles which are constituents of the raspberry structure changed as shown in Figs. 2(b)–2(f). It was difficult to define the primary particles in the raspberry structure because the primary particles were integrated into a larger secondary particle immediately via the oriented attachment. Therefore, size of particles on outer surface was measured as the size of primary particles. In contrast to the decrease of crystallite sizes, sizes of secondary particles remained around the same in the time range from 0.5 to 12.5 h.
sizes, the sizes of primary particles increased from 6.8 to 11.2 nm with increase of synthesis time from 1.0 to 12.5 h, whereas the secondary particle size, which is the overall size of the raspberry-shaped particles, did not change with approximately 100 nm in size (Table 1). Since the primary particles were integrated to the secondary particles while maintaining the crystallographic orientation, the crystallite size is larger than the primary particle size. Small gaps appeared among primary particles in 6.0 h-Co and 12.5 h-Co samples, suggesting the primary particles grown by a dissolution–precipitation process. Finally, the raspberry structure was completely decomposed by long hydrothermal treatment for 24.0 h as shown Fig. 2(g). Lattice fringes and an FFT pattern of 24.0 h-Co sample [Fig. 2(h)] indicated the decomposed raspberry Co3O4 was polycrystal. In general, the crystallite size increase with increase of particle size; however, the collapse of the crystallographic orientation of nanoparticle within the raspberry-like structure caused the decrease of crystallite size with increase in the primary particle size. From these results and previous reports,13),27),28) we concluded the growth mechanism of the raspberry-shaped Co3O4 nanoparticles as shown in Fig. 3. Firstly, cobalt oxide nanoparticles formed by decomposition and oxidation of cobalt glycolates, and they dispersed with the adsorption of sulfate ions. Secondly, the nanoparticles were self-accumulated by oriented attachment and bridging adsorption of the sulfate ions29) among multiple nanoparticles. In early stage of the oriented attachment, crystal orientation of nanoparticles was rotating to match and align their planes before disappearing their grain interface.25),30) In the middle of hydrothermal treatment, the accumulated Co3O4 nanoparticles grew while maintaining the crystallographic orientation via dissolution–reprecipitation process and atomic diffusion in neighboring particles. Then, long-time hydrothermal treatment caused the further growth of the primal particles and made the attached Co3O4 nanocrystals split, resulting in decomposition of the raspberry-structure and the crystallographic orientation.

3.2 Surface analysis and catalytic activity

Controlling the synthesis time, we could obtain various types of the raspberry-shaped Co3O4 nanoparticles. The surface states and oxygen species which affect the CO oxidation activity were examined using H2-TPR and XPS for 1.0 h-Co, 3.0 h-Co, 12.5 h-Co and 24.0 h-Co which showed significant differences in morphology, particle size and crystallite size. The H2-TPR curves of all samples showed reduction peaks in the temperature range of 20–150, 200–380 and 400–500 °C. The minor reduction peak at around 80 °C is attributed to the active species on the surface, and two major peaks are corresponded to reduction of internal or surface Co3O4 to CoO and CoO to metallic Co.31)–33) The peaks centered around at 80 and 330 °C shifted to lower temperature with increase of the synthesis time from 1.0 h to 12.5 h, and the peak position shifted to higher temperature for 24.0 h-Co [Figs. 4(a) and 4(b)]. In contrast, the high-temperature peaks for 1.0 h-Co, 12.5 h-Co and 24.0 h-Co around at 440 °C shifted to higher temperature compared with 3.0 h-Co [Fig. 4(c)]. Furthermore, the peak around at 440 °C was weaker for the 12.5 h-Co and 24.0 h-Co than for the other samples, but instead, the hydrogen uptake of 12.5 h-Co and 24.0 h-Co at 490–500 °C was larger than the others. These results suggest a movement of bulk oxygen was hindered in 1.0 h-Co,

![Fig. 3. Schematic for the growth mechanism of raspberry-shaped Co3O4 nanoparticles.](image)

![Fig. 4. H2-TPR curves of 1.0 h-Co, 3.0 h-Co, 12.0 h-Co and 24.0 h-Co in the temperature range of (a) 20–200 °C, (b) 200–400 °C and (c) 400–500 °C.](image)
The 3.0 h-Co particles had the single-crystal-like structure formed by oriented attachment; bulk oxygen move easily in the Co$_3$O$_4$ crystal because of no grain boundaries among the attached particles. In contrast, the oriented attachment of Co$_3$O$_4$ nanoparticles in the 1.0 h-Co were not completed as described in the formation process, and the crystallographic orientation of 12.5 h-Co and 24.0 h-Co decomposed as shown in Figs. 2(f)–2(h), and grain boundary among the particles will hinder the bulk oxygen movements. Figure 5 shows XPS spectra of the O 1s and Co 2p core level for 1.0 h-Co, 12.5 h-Co and 24.0 h-Co. The broad peak in O 1s [Fig. 5(a)] was divided to several peaks, and the peaks at lower binding energy attributed to lattice oxygen (O$_{\text{Lattice}}$) and adsorbed water (O$_{\text{Water}}$). The O$_{\text{Lattice}}$ peak for 12.5 h-Co was further divided into two peaks, suggesting a presence of lattice oxygen ions having different bonding states. The O 1s peaks contain minor peaks at the higher binding energy of 534 eV. Sexton et al. reported the peaks at higher energy appeared when the CoO was reduced the atomic ratio of O/Co less than 1, meaning that minor peaks at higher binding energy would be appeared when the oxygen is removed from cobalt oxide. Therefore, the minor peaks at around 535 eV were attributed to oxygen vacancy (O$_{\text{Vacancy}}$). The fraction of O$_{\text{Lattice}}$, O$_{\text{Vacancy}}$, O$_{\text{Water}}$ and the Co$^{3+}$/Co$^{2+}$ ratio were estimated from Fig. 5 and summarized in Table 2. The fraction for 3.0 h-Co was estimated from XPS spectra in the previous report. The 3.0 h-Co showed highest O$_{\text{Vacancy}}$ fraction and smallest O$_{\text{Lattice}}$ fraction. It was hard to identify O$_{\text{Vacancy}}$ peak in XPS spectrum for 24 h-Co. Although there was no significant difference for the Co$^{2+}$/Co$^{3+}$ fractions between 1.0 h-Co and 3.0 h-Co, the Co$^{2+}$ fraction for 12.5 h-Co was much smaller and the Co$^{2+}$ fraction for 24.0 h-Co was much higher than the others.

Murayama and Baidya et al. revealed that cobalt species in octahedral site are active species and high reduction potential of Co$^{3+}$/Co$^{2+}$ couple in MnCo$_2$O$_4$ correlated to the unique CO oxidation activity of octahedral Co species at very low temperature. Our XPS and H$_2$-TPR analysis indicated 3.0 h-Co have higher reducibility and abundance of O$_{\text{Vacancy}}$ which will enhance CO oxidation activity. From this points of view, 3.0 h-Co must have shown higher CO oxidation activity than the others. In order to confirm our expectation, CO oxidation activity of each cobalt oxide catalyst was evaluated.

Figure 6 shows the CO conversion rates of 1 h-Co, 3.0 h-Co, 12.5 h-Co and 24.0 h-Co samples evaluated while decreasing the temperature. All samples showed 100% CO conversion at above 300 °C. The CO conversion rates of 1.0 h-Co, 12.5 h-Co and 24.0 h-Co began to decrease at 150 °C, and eventually reached 61, 78 and 10% at 25 °C, respectively. In contrast, the 3.0 h-Co retained 100% CO conversion rate at 150 °C and showed the highest CO oxidation rate of 93% at 25 °C. We considered that the crystallographic orientation of the raspberry-shaped Co$_3$O$_4$ nanoparticles is one of the reasons to enhance CO oxidation activity. Liotta et al. revealed a relationship among surface and bulk oxygen mobility and catalytic activity for ceria-based catalysts, and higher mobility of lattice oxygen reacting with propene to form CO$_2$ contributed to enhance the oxidation activity in a Co$_3$O$_4$–CeO$_2$ system. H$_2$-TPR analysis [Fig. 4(c)] for the raspberry-shaped nanoparticles supposed the mobility of bulk oxygen species was higher for the 3.0 h-Co than the others because of their complete oriented attachment.

![Fig. 5.](image-url)

Fig. 5. (a) O 1s XPS spectra and (b) Co 2p spectra of 1.0 h-Co, 12.5 h-Co and 24.0 h-Co.

| Sample  | O$_{\text{Lattice}}$ (%) | O$_{\text{Water}}$ (%) | O$_{\text{Vacancy}}$ (%) | Co$^{3+}$/Co$^{2+}$ |
|---------|-------------------------|------------------------|--------------------------|---------------------|
| 1.0 h-Co | 31                      | 58                     | 11                       | 0.12                |
| 3.0 h-Co | 21                      | 50                     | 29                       | 0.14                |
| 12.5 h-Co | 39                     | 48                     | 13                       | 0.56                |
| 24.0 h-Co | 47                     | 53                     | —                        | 0.05                |

Table 2. Fraction of lattice oxygen (O$_{\text{Lattice}}$), oxygen vacancy (O$_{\text{Vacancy}}$), adsorbed water (O$_{\text{Water}}$) and the Co$^{3+}$/Co$^{2+}$ ratio estimated from XPS spectra.
CO oxidation activity increases as the primary particle size changing the reaction time. We had hypothesized that the raspberry-shaped Co$_3$O$_4$ nanoparticles synthesized with Thus, the highest oxidation activity was achieved in the temperature range.13) Accordingly, in addition to the abundance of O$_{\text{vacancy}}$ the single-crystal-like structure of the raspberry-shaped Co$_3$O$_4$ particles promoted O$_{\text{Lattice}}$ mobility and CO oxidation activity.

4. Conclusion

We revealed that the raspberry-shaped Co$_3$O$_4$ nanoparticles formed by an oriented attachment and multistage particle growth of cobalt oxide nanoparticles in a hydrothermal treatment. The rotating of crystal orientation in the oriented attachment process was completed in 3.0 h and the single-crystal-like structure was obtained. The long-time hydrothermal treatment caused the decomposition of the raspberry structure and crystal orientation. Sizes of primary particles and crystallite for the raspberry-shaped Co$_3$O$_4$ nanoparticles were successfully controlled by changing the reaction time. We had hypothesized that the CO oxidation activity increases as the primary particle size decreases; however, the raspberry Co$_3$O$_4$ nanoparticles treated for 3.0 h showed higher CO oxidation rate (93%) than the sample treated for 1.0 h (61%) even though the primary particle sizes decreased from 8.1 to 6.8 nm. H$_2$-TPR analysis indicated 3.0 h-treated sample showed the highest mobility of bulk oxygen species. Considering that bulk oxygen migration was hindered by grain boundary, the high mobility of bulk oxygen was achieved by the formation of single-crystal-like structure in the raspberry-shaped nanoparticles obtained for 3.0 h-hydrothermal treatment. Thus, in addition to the tiny particle size which produces an abundance of oxygen vacancy, we concluded that the crystallographic orientation of Co$_3$O$_4$ nanoparticles in the raspberry structure is key factor to enhance the CO oxidation activity.

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