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Oxidation of toluene by Pt/Co_3O_4-CeO_2 catalyst prepared from pulverized cerium oxide

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Abstract

We prepared Pt/Co_3O_4-CeO_2 catalyst from pulverized cerium oxide, and evaluated the catalytic oxidation activity for toluene. Pulverization in a ball mill reduced the median diameter of the cerium oxide particles from 23.3 μm to 0.415 μm. Although the oxidation temperature of toluene hardly changed, even with pulverization of the cerium oxide, the deposition of carbon on the catalyst surface was reduced. The dispersibility of platinum on the surface after pulverization did not differ significantly from the case without pulverization. However, the pulverization increased the total external surface area of the cerium oxide particles from 0.66 $m^2\ g^{-1}$ to 16.7 $m^2\ g^{-1}$, and increased the contact area between the coke deposited on the surface and the cerium oxide, which influences soot combustion. Consequently, it is thought that the coke, which is unburned carbon like soot, became more oxidizable on the pulverized cerium oxide.

Keywords: *carbon deposition, cerium oxide, Co_3O_4-CeO_2, platinum, pulverization, toluene*

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1. Introduction

The estimated emission of volatile organic compounds (VOC) in Japan in 2016 was 671,567 tons (Ministry of the Environment, Government of Japan, 2018). The need to protect public health and prevent atmospheric pollution requires further reductions in emissions of VOC, the use of which results in the generation of photochemical oxidants and suspended particulate matter, which persist for many years.

The catalytic combustion method is widely used for the treatment of VOC (Khan & Ghoshal, 2000) in various industries and Pt/Al_2O_3 is conventionally used as a catalyst. Our group (Inoue et al., 2013; Inoue, Somekawa, Shinoda, Fujiwara, & Kawami, 2018) has already reported that the multiple oxide Co_3O_4-CeO_2 catalyst shows high activity for VOC oxidation, and this Co_3O_4-CeO_2 catalyst has been developed into ball-and honeycomb-type products (Kawami, 2016).

There are differences between Pt/Al_2O_3 and Co_3O_4-CeO_2 catalysts in the catalytic oxidation temperature for various VOC. Co_3O_4-CeO_2 catalyst showed high activity especially for ethyl acetate, but low activity for aromatic hydrocarbons such as toluene, in comparison with Pt/Al_2O_3 catalyst (Diehl, Barbier, Duprez, Guibard, & Mabilon, 2010; Papaefthimiou, Ioannides, & Verykios, 1998; Sawyer & Abraham, 1994). In order to increase the activity of both toluene and ethyl acetate, we attempted to support the platinum on Co_3O_4-CeO_2 catalyst. It was supported using chloroplatinic acid, a typical raw material for supporting platinum on alumina. However, the platinum and Co_3O_4-CeO_2 cohered, and the catalytic activity did not improve. Then, the platinum was supported using an aqueous solution of platinum colloid coated with polyvinylpyrrolidone dispersant. The platinum was directly supported on the Co_3O_4-CeO_2 catalyst, and both toluene and ethyl acetate could be oxidized at less than 250 °C (Inoue & Somekawa, 2019).

There are numerous reports on the effect of cerium oxide on soot combustion. Using thermogravimetric measurement, Nakamura, Hattori, Yokota, and Ozawa (2018) showed that soot and cerium oxide mixtures had a highly beneficial effect on soot combustion. Ivanova et al. (2016) measured the effect, on soot combustion, of cerium oxide films grown on stainless steel foil supports, and showed that cerium oxide was effective in lowering the soot combustion temperature. Using in situ microscopy, Muroyama, Asajima, Hano, Matsui, and Eguchi (2015) examined the oxidation behavior of a carbon black layer over cerium oxide substrate in air, and showed that the carbon layer disappeared from the periphery of the cerium oxide substrate with an increase in temperature.

In this study, we prepared Pt/Co_3O_4-CeO_2 catalyst from pulverized cerium oxide, and evaluated the oxidation activity for toluene. With pulverization, the total external surface area of the cerium oxide particles increased; and consequently, the coke deposited on the surface, which is unburned carbon like soot, became more oxidizable.

2. Materials and methods

2.1. Catalyst preparation

Co_3O_4-CeO_2 catalyst and Pt/Co_3O_4-CeO_2 (powder) was prepared from carbonate of cobalt and cerium as described by our previous report (Inoue & Somekawa, 2019).

In this study, after the cerium oxide was pulverized, Pt/Co_3O_4-CeO_2 catalyst was prepared. $Ce_2(CO_3)_3 \cdot 8H_2O$ (purity > 99.99 %, Kanto Chemical) was calcined for 1 h at 400 °C. The resultant cerium oxide was milled in a planetary ball mill (Pulverisette 7, Fritsch) at 2800 rpm. $CoCO_3$ (purity 87 %, Kanto Chemical) was calcined for 1 h at 400 °C. The resultant cobalt oxide and the pulverized cerium oxide were mixed in the mortar, and platinum was supported using platinum colloid (Tanaka Kikinzoku Kogyo; platinum nanoparticles coated with polyvinylpyrrolidone dispersant). Prepared mixture and an aqueous solution of the platinum colloid were stirred in a crucible for about 7 h at about 60 °C, and then dried at 180 °C. The dry matter was calcined for 1 h at 400 °C, after 5 h elevation from room temperature to 400 °C.

The molar ratio of cobalt to cerium in the multiple oxide was 1:1. The weight of platinum in the catalyst was 2 wt% (The weight was confirmed by fluorescent X-ray analysis).

2.2. Catalytic activity test

Catalytic activity test was carried out as described by our previous report (Inoue & Somekawa, 2019). Prepared gas (concentration of toluene: 0.4×10^3 ppm) flowed at a continuous 100 mL min^{-1} through a glass reaction tube within a furnace, at atmospheric pressure. The center of the reaction tube (ø 3 mm i.d.) was filled with catalyst (0.2 g) held in place by quartz wool plugs. A thermocouple installed near the catalyst bed measured the temperature. We evaluated the catalytic activity as follows. The temperature in the furnace was raised from room temperature to 400 °C for 1.5 h, while air flowed. The temperature was then held at 400 °C for 1 h, while the prepared gas containing toluene flowed. Then the temperature was lowered from 400 °C to 30 °C at 1 °C min^{-1}, while the prepared gas flowed, and the measurement plots in Figure 1 were obtained.

We also evaluated the deposition of carbon on the catalyst surface. Prepared gas containing toluene flowed continuously through the catalyst bed for 24 h at 150 °C, 170 °C, or 200 °C. The catalyst bed temperature was lowered to 30 °C, and then raised to 300 °C at 1 °C min^{-1} under air (not containing toluene) flow. The cokes deposited on the catalyst surface during the 24 h reaction were burned with the rising temperature, and converted into CO_2. In Figure 5, the generation of CO_2 was plotted while the temperature was increased from 30 °C to 300 °C.

The gaseous reaction products were analyzed with an in-line gas chromatograph equipped with thermal conductivity detectors (3000 Micro GC, Agilent Technologies). The OV-1 and PlotQ columns were used.

2.3. Characterization

The structure of the catalyst surface was determined through scanning electron microscope (SEM) measurements (JSM-6490LA, JEOL) and acceleration voltage was 15 kV. The particle diameter was measured by a laser diffraction method (laser micron sizer LMS-2000e, Seishin). Refractive index of particle was 1.520, dispersion medium was water, and refractive index of dispersion medium was 1.330. Total pore volume was estimated from the amount of nitrogen adsorbed (BELSORP-max, MicrotracBEL). Adsorption temperature was -196 °C and relative pressure was 0.980. The amount of CO adsorbed on the catalyst surface was measured by the CO pulse method (BEL-METAL-3SP, MicrotracBEL). The CO pulses were injected at 50 °C under helium gas, and the amount of CO adsorption was measured, with the CO being detected by a thermal conductivity detector. The weight of the catalyst sample was 0.06 g.

3. Results and discussion

Figure 1 shows the catalytic activities in the oxidation of toluene. The rate of conversion to CO_2 is defined as 100 % when all the molecules of toluene are oxidized to carbon dioxide and water vapor.

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \qquad (1)$$

Liotta et al. (2009) investigated the catalytic oxidation of toluene on a Co_3O_4-CeO_2 catalyst, as compared to the conventional Pt/Al_2O_3 catalyst. Co_3O_4-CeO_2 catalysts (Co_3O_4 loading: 5–70 %) achieved full toluene conversion at 275–450 °C, which was higher than the temperature (225 °C) required for complete oxidation on the Pt (1 %)/Al_2O_3 catalyst, at a weight hourly space velocity of 36 L g^{-1} h^{-1} and a toluene concentration of 1000 ppm. Co_3O_4-CeO_2 catalyst had lower toluene catalyzing activity than conventional Pt/Al_2O_3 catalyst. Our results show the same tendency; the complete oxidation of Co_3O_4-CeO_2 catalyst occurred at more than 300 °C (Figure 1a). However, the addition of supported platinum greatly decreased the oxidation temperature (Figure 1b), as mentioned earlier (Inoue & Somekawa, 2019). In addition, the catalytic activity of Pt/Co_3O_4-CeO_2 prepared using pulverized cerium oxide was evaluated, and found to be slightly improved (Figure 1c). SEM images confirmed that pulverization altered the particle shape of cerium oxide (Figures 2a, 2b), and the median particle diameter decreased from 23.3 μm to 0.415 μm after pulverization (Figure 3, Table 1). Figure 2c shows SEM image of Pt/Co_3O_4-CeO_2 prepared using pulverized cerium oxide. After mixing with cobalt oxide and calcination, the size of particles increased.

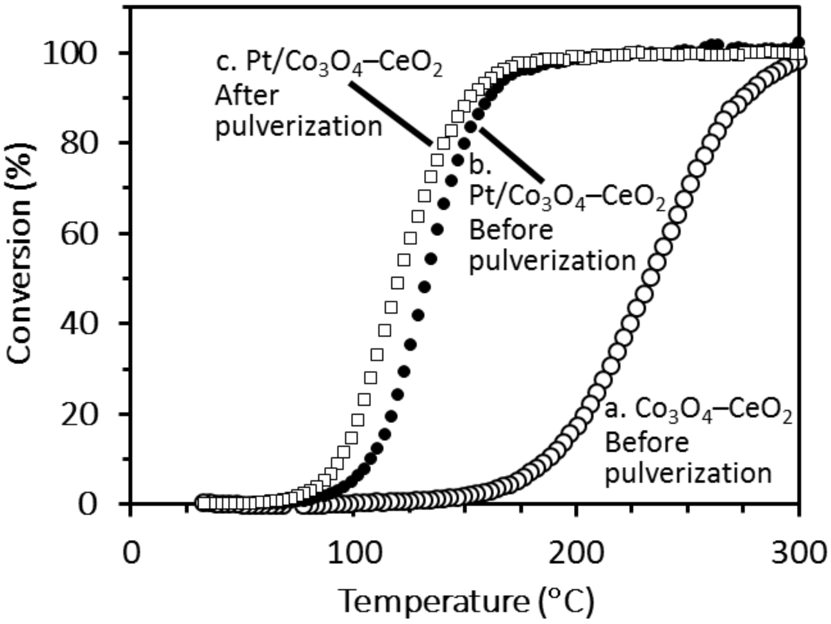
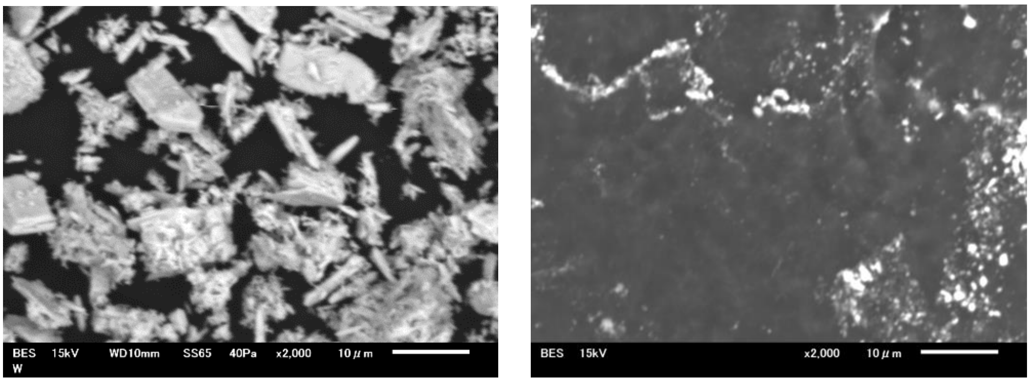


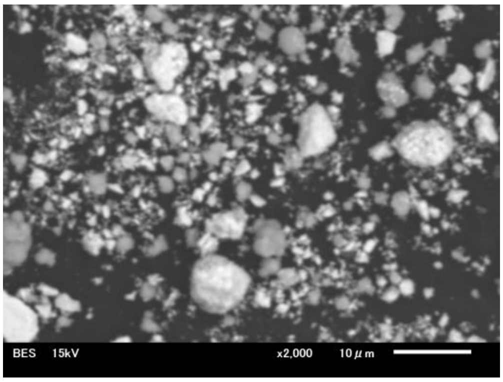
Figure 1 Catalytic activities for toluene oxidation

Table 1 Physical properties of cerium oxide and Co_3O_4-CeO_2 particles before and after pulverization

	Cerium oxide before pulverization	Cerium oxide after pulverization	Co_3O_4-CeO_2 after pulverization of cerium oxide
Median diameter (μm)	23.3	0.415	4.51
Total external surface area (m^2 g^{-1})	0.66	16.7	3.82
Total pore volume (cm^3 g^{-1})	0.0758	0.140	0.148



a. Cerium oxide before pulverization b. Cerium oxide after pulverization



c. Pt/Co_3O_4-CeO_2 prepared using pulverized cerium oxide

Figure 2 SEM images of cerium oxide (change in particle shape with pulverization) and Pt/Co_3O_4-CeO_2 prepared using pulverized cerium oxide

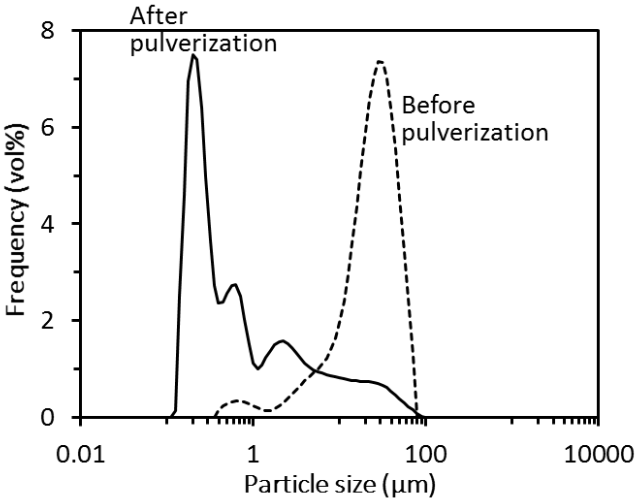


Figure 3 Particle size distribution of cerium oxide before and after pulverization

In order to clear the dispersibility of platinum, the amounts of CO adsorption were obtained by the CO pulse method (Figure 4). The amount of CO adsorption (platinum dispersibility) on Pt/Co_3O_4-CeO_2 prepared using pulverized cerium oxide did not differ significantly from the case without pulverization. Since the effect of the coating layer with polyvinylpyrrolidone dispersant is high, the cohesiveness of platinum particles on the surface did not change.

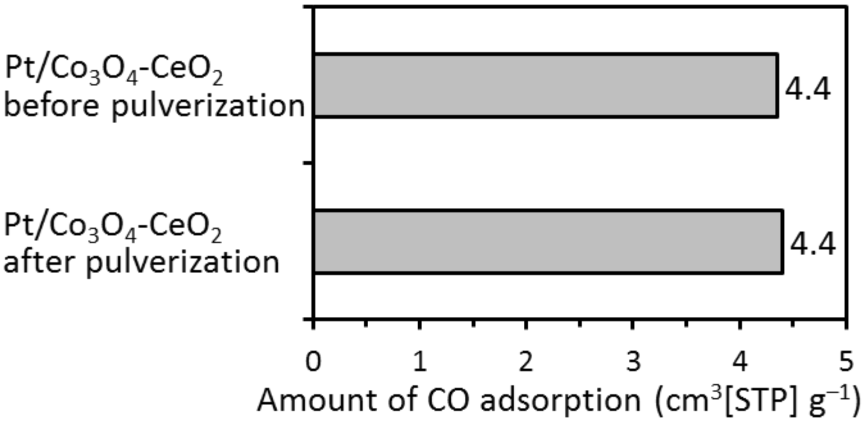


Figure 4 Amounts of CO adsorption using the CO pulse method

We also examined the deposition of carbon in this reaction. Prepared gas containing toluene flowed continuously through the catalyst bed for 24 h at 150 °C, 170 °C, or 200 °C. The bed temperature was lowered to 30 °C, and then raised to 300 °C at 1 °C min^{-1} under air (not containing toluene) flow. The cokes deposited on the catalyst surface during the 24 h reaction were burned with the rising temperature, and converted into CO_2. Figure 5 shows the generation behavior of CO_2. In the Pt/Co_3O_4-CeO_2 catalyst before the pulverization of cerium oxide, the CO_2 peaks appeared when the reaction temperature was lowered (at 170 °C and 150 °C). However, the peaks disappeared in the catalyst after pulverization; thus, the pulverization of cerium oxide clearly prevented the deposition of carbon in this reaction.

As noted above, cerium oxide has been shown to be effective in lowering the soot combustion temperature (Ivanova et al., 2016; Nakamura et al., 2018; Wang et al., 2017). It has proved suitable for oxidizing soot, owing to its capacity to store and release oxygen easily, while maintaining structural integrity (Soler et al., 2016). On the assumption that the cerium oxide and Co_3O_4-CeO_2 particles were spherical, we calculated the total external surface area of the particles, using the analysis software of the Seishin LMS-2000e laser micron sizer, and found that pulverization increased the surface area of the cerium oxide particles from 0.66 m^2 g^{-1} to 16.7 m^2 g^{-1} (Table 1). Total pore volume was measured by the nitrogen adsorption method. Pulverization also increased the total pore volume (Table 1).

The platinum dispersibility on Co_3O_4-CeO_2 prepared using pulverized cerium oxide did not differ significantly from the case without pulverization, as described above. Although the size (surface area) of platinum particles did not change, the external surface area of cerium oxide particles (space between the platinum particles) was increased after pulverization. Therefore, the contact area between cerium oxide and coke deposited on the surface was correspondingly increased. Consequently, it is thought that the coke, which is unburned carbon like soot, became more oxidizable on the pulverized cerium oxide.

4. Conclusion

We pulverized cerium oxide using a ball mill, and prepared Co_3O_4-CeO_2 catalyst. The platinum was directly supported on the Co_3O_4-CeO_2 using platinum colloid coated with dispersant. Pulverization reduced the median diameter of the cerium oxide particles from 23.3 μm to 0.415 μm, and reduced the deposition of carbon on the catalyst surface during the oxidation reaction. The degree of platinum dispersion on the surface after pulverization did not differ significantly from the case without pulverization. Pulverization increased the total external surface area of the cerium oxide particles from 0.66 m^2 g^{-1} to 16.7 m^2 g^{-1}, increasing the contact area between the coke deposited on the surface and the cerium oxide, which influences soot combustion. Consequently, it is thought that the coke, which is unburned carbon like soot, became more oxidizable on the pulverized cerium oxide.

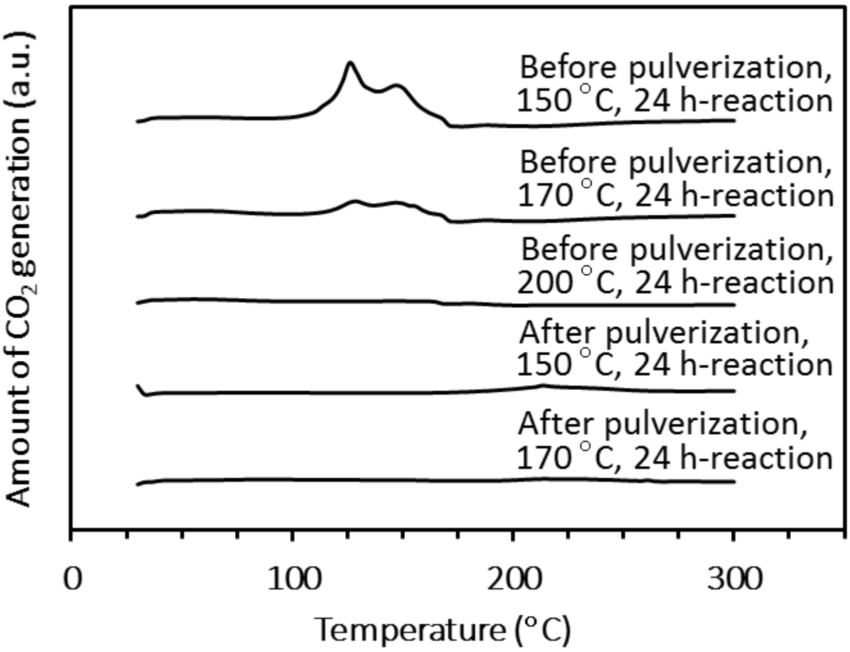


Figure 5 CO_2 generated by burning carbon deposited on Pt/Co_3O_4-CeO_2 catalyst

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