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Catalytic Oxidation Process and Thermal Characteristics of Toluene and Butyl Acetate Vapor in an Oven

Kenichiro Inoue

Tokyo Metropolitan Industrial Technology Research Institute, 2-4-10 Aomi, Koto-ku, Tokyo 135-0064, Japan

E-mail: inoue.kenichiro@iri-tokyo.jp

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Abstract

Toluene vapor and butyl acetate vapor were oxidized at 523 K in an oven using the Pt/Co_3O_4-CeO_2, Pt/Al_2O_3, and Co_3O_4-CeO_2 catalysts and a comparison of activity and thermal characteristic among three different catalysts was conducted. The conversion into CO_2 was estimated from the change in temperature of a catalyst bed during the oxidation reaction. A relation between heat capacity of the gas and amount of solvent molecule oxidized was clarified. In the oxidation with Pt/Al_2O_3 catalyst, the butyl acetate could not be completely oxidized, and part remained. Butanol and butanal were formed as by-products of the butyl acetate in the oven, which contained moist air. In the oxidation with Co_3O_4-CeO_2 catalyst, although no butyl acetate remained, some toluene remained and the amount of butanol and butanal increased somewhat after passage over the catalyst bed. By using a catalyst that combined platinum and Co_3O_4-CeO_2 with the original method, both the toluene and butyl acetate were almost completely oxidized at 523 K.

Keywords: *by-products; Co_3O_4-CeO_2, lower heating value; platinum; specific heat*

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1. Introduction

A lot of toluene and butyl acetate solvent is used with paint and printing ink. In 2021, Japan's estimated emissions (Ministry of the Environment, Government of Japan, 2023) for toluene were 8403, 5640, and 2930 tons in the fields of automobile painting (new cars and repairs), painting buildings, and gravure ink, respectively. The values for butyl acetate were 1461, 1190, and 253 tons in the fields of automobile painting, painting metal products, and gravure ink, respectively. Organic solvent vapor emissions must be controlled because of their influence on human health and air pollution. One control technology in such fields is catalytic combustion. Although a Pt/Al_2O_3 catalyst is widely used, the author's group has developed a Co_3O_4-CeO_2 catalyst (Inoue et al., 2018).

Table 1 shows catalytic oxidation temperature of aromatic hydrocarbon and ethyl acetate (acetic ester). Papaefthimiou et al. (1997, 1998) reported that the ethyl acetate molecule was the most difficult to oxidize on a Pt/γ-Al_2O_3 catalyst. Delimaris, & Ioannides (2009) reported that the complete conversion of toluene requires high temperature in a CeO_2 catalyst (Table 1), and they explained, "we do not have any plausible explanation for the peculiar behavior of CeO_2 in toluene oxidation". The results as shown in Table 1 indicate that benzene and toluene are easily oxidized at a lower temperature in a Pt/Al_2O_3 catalyst, and ethyl acetate is easily oxidized in a Co_3O_4-CeO_2 (CeO_2) catalyst. The author's group supported platinum over a Co_3O_4-CeO_2. A platinum colloid coated with poly-vinylpyrrolidone dispersant was used for a raw material because the cohesion occurred in the case of a typical raw material, chloroplatinic acid. In this way, the author's group could oxidize both aromatic hydrocarbon and acetic ester concurrently at lower temperature (Inoue, & Somekawa, 2019a; Inoue, & Somekawa, 2019b; Inoue et al., 2021).

In Japanese painting and printing plants, the installation of equipment for the catalytic treatment does not advanced since the costs are high and the installation area is large (Mizukoshi et al., 2010). Then, in a previous study, the author studied a process for treating the vapor of paint thinner in a baking oven using the oven's own heat. The gas containing aromatic hydrocarbon and acetic esters could be treated in the oven at 523 K by using a Pt/Co_3O_4-CeO_2 catalyst (Inoue, 2022). The oxidation and hydrolysis of the solvent molecules diffused in the oven generate the by-products. However, the knowledge about the catalytic oxidation of by-products for each solvent component has not been provided because the paint thinner, which had a mixed solvent composition, was used in previous work (Inoue, 2022). In addition, the behavior of heat generation with the progress of oxidation reaction has not been examined. In this work, toluene vapor and butyl acetate vapor were oxidized individually at 523 K in the abovementioned oven and the comparison of activity and thermal characteristic among the Pt/Co_3O_4-CeO_2, Pt/Al_2O_3, and Co_3O_4-CeO_2 catalysts was conducted.

2. Objectives

1) The estimation of CO_2 production using the changes of the bed temperature. The relation between heat capacity of the gas and amount of solvent molecule oxidized is clarified.

2) The comparison on the activity and restraint of the by-products among three different catalysts.

3. Materials and methods

A previous study examined a process for treating organic solvent vapor in baking oven using the oven's own heat. Figure 1 shows schematic illustration of catalytic oxidation setup. The setup is here the same as in the previous work (Inoue, 2022). The set temperature of the oven (internal volume: 303 L) was 523 K (maximum temperature). The space velocity and the gas flow rate were 5000 h^{-1} and 0.32 L min^{-1} (296 K), respectively.

Table 1 Oxidation temperature of aromatic hydrocarbon and ethyl acetate (acetic ester)

	Catalyst	Benzene or toluene	Ethyl acetate	Concentration and space velocity
Sawyer, & Abraham (1994)	Pt/Al_2O_3	–	563 K (around 85% conversion)	1100 ppm, 48,000 h^{-1}
Papaefthimiou et al. (1997, 1998)	Pt/Al_2O_3	Benzene: around 493 K (exceed 95% conversion) Activation energy: 96±6 kJ mol^{-1}	Around 593 K (exceed 95% conversion) Activation energy: 121±11 kJ mol^{-1}	150–250 ppm, 30,000 h^{-1}
Liotta et al. (2009)	Pt/Al_2O_3	498 K (full toluene conversion)	–	1000 ppm, weight hourly space velocity: 36 L g^{-1} h^{-1}
	Co_3O_4-CeO_2 (Co_3O_4 loading: 5–70 %)	548–723 K (full toluene conversion)	–	
Delimaris, & Ioannides (2009)	CeO_2	Toluene: higher than 673 K (complete conversion)	Above 553 K (complete conversion)	Toluene: 600 ppm, ethyl acetate: 1800 ppm, 50,000 h^{-1}

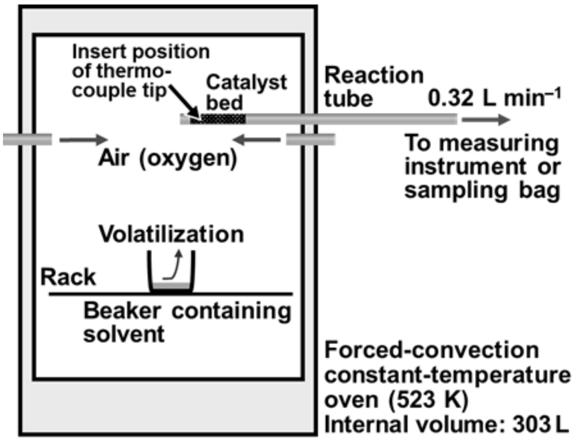


Figure 1 Schematic illustration of catalytic oxidation setup using a constant-temperature oven.

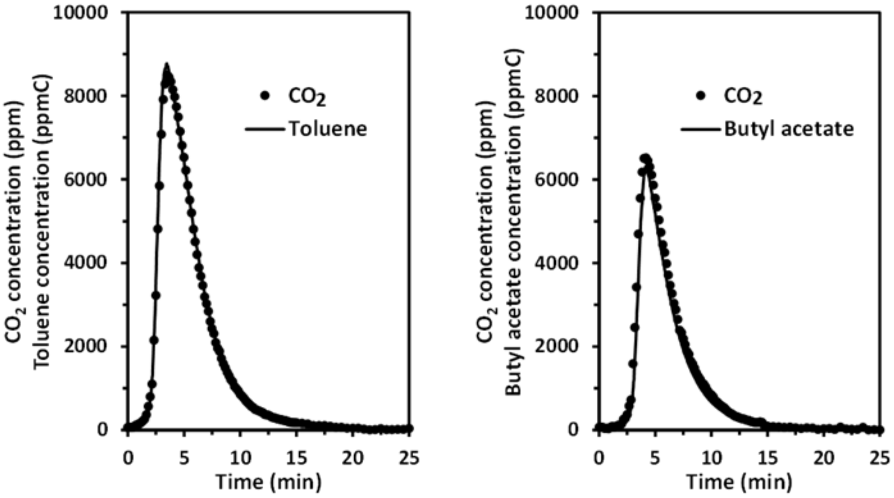


Figure 2 The CO_2 concentration in the gas passed through Pt/Co_3O_4-CeO_2 catalyst bed in the tube (plot) and the toluene or butyl acetate concentration in the gas passed through the empty tube (continuous line).

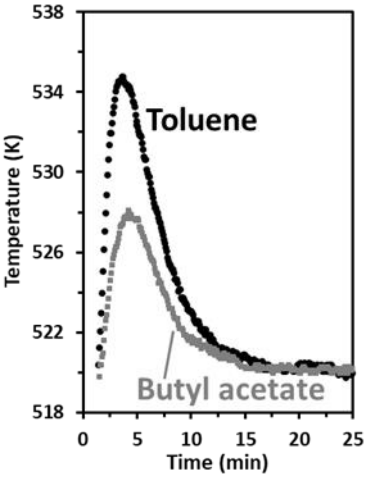


Figure 3 Change of temperature during the oxidation reaction with Pt/Co_3O_4-CeO_2 catalyst.

In this work, a thermocouple was inserted in the catalyst bed and the change in temperature during the oxidation reaction was measured. The loading length of the catalyst bed was 76 mm, and the tip of thermocouple was inserted at a position around 15 mm from the inlet of the bed. The temperature in the catalyst bed was measured using a type K thermocouple (AS ONE) and a data logger (ADL12N, AS ONE). A beaker containing 2 mL of toluene or butyl acetate (special grade reagent, Kanto Kagaku) was placed in the oven at 0 min, and the concentration and temperature of the gas were measured over a period of 0–25 min. For the analysis of residue and by-product components after reaction, the beaker containing 1 mL of toluene or butyl acetate was placed in the oven at 0 min, and the gas that passed through the reaction tube was collected in a sampling bag (Tedlar bag, GL Sciences; suction flow rate: 0.32 L min^{-1}, 296 K) over a period of 2–14 min. The measuring method of the gas is also the same as in the previous work (Inoue, 2022).

Used catalysts were ball-type Pt/Co_3O_4-CeO_2, Pt/Al_2O_3 (commercial grade), and Co_3O_4-CeO_2 (around 4 mm diameter). The prepared method for Co_3O_4-CeO_2 and Pt/Co_3O_4-CeO_2 was described in the author’s previous report (Inoue et al., 2021). In order to clear a state of platinum supported on the surface, high-angle annular dark-field scanning transmission electron microscopy image and bright-field scanning transmission electron microscopy image were obtained by electron microscope (ARM200F, JEOL). Since the ball-type catalyst used in this study could not be measured, the Pt/Co_3O_4-CeO_2 powder (Inoue, & Somekawa, 2019b) and the sample which crushed a Pt/Al_2O_3 supported on a honeycomb carrier (commercial grade) (Inoue et al., 2021) were used. The acceleration voltage was 200 kV. The measurement sample was prepared by wet dispersion method.

4. Results and discussion

4.1. Change in temperature of catalyst bed and conversion into CO_2

A beaker containing toluene or butyl acetate was placed in an oven maintained at 523 K and gas containing the generated vapor flowed into the reaction tube. Figure 2 shows the CO_2 concentration (plot) in the gas passed through Pt/Co_3O_4-CeO_2 catalyst bed in the tube. The toluene or butyl acetate concentration in the gas passed through the empty tube is also shown in the same figure (continuous line). The toluene and butyl acetate were measured in ppmC, namely parts per million on the basis of the number of carbon atoms. In both solvent vapors, the plots and continuous line were almost in agreement. This means they were almost completely oxidized into CO_2 and H_2O with the Pt/Co_3O_4-CeO_2 catalyst at 523 K.

A thermocouple was inserted in the catalyst bed and the change of temperature during the oxidation reaction was measured. A rise in temperature with toluene and butyl acetate oxidation was confirmed (Figure 3).

To estimate CO_2 generation from the change in temperature, the specific heat of the air at the catalyst bed temperature when there is no reaction was obtained. Generally, the specific heat values of a combustion gas and air differ by only around several percent (Tanaka et al., 2003). Therefore, the specific heat of air was employed in this study. The specific heat is shown with the following quadratic relationship for the temperature (McQuillan et al., 1984). In addition, the air density needed for conversion to the specific heat of a gas volume base is found from the following quadratic relationship (McQuillan et al., 1984):

$$C_\mathrm{p} = 1030.5 - 0.19975\,T + 3.9734 \times 10^{-4}\,T^2, \quad (1)$$

$$\rho = \frac{351.99}{T} + \frac{344.84}{T^2}, \quad (2)$$

where C_p is specific heat at constant pressure ($\mathrm{J\ kg^{-1}{\cdot}K^{-1}}$), T is the catalyst bed temperature when there is no reaction (K), and ρ is the air density ($\mathrm{kg{\cdot}m^{-3}}$). In Figure 3, the gas temperature of the catalyst bed was around 520 K when there was no reaction. The catalyst bed was kept at a temperature slightly lower than 523 K, which is the set temperature of the constant-temperature oven. At this temperature, the specific heat in the gas volume base and normal states is shown with the next equation:

$$C_{\mathrm{p,\ vol.\ base}} = \frac{\rho C_\mathrm{p} T}{273.15 \times 1000}, \quad (3)$$

where $C_{\mathrm{p,\ vol.\ base}}$ is specific heat at constant pressure ($\mathrm{kJ\ Nm^{-3}\ K^{-1}}$). The heat capacity of gas flowing for one minute is calculated from the change in temperature (T_n - T) by the oxidation reaction shown in Figure 3:

$$q=C_{\mathrm{p,\ vol.\ base}}\times r\times(T_{\mathrm{n}}-T), \qquad (4)$$

where q is the heat capacity of gas (kJ min^{-1}), r is the gas flow rate (Nm^3 min^{-1}), and T_{n} is the temperature of the catalyst bed during the oxidation reaction (K). Meanwhile, the heat capacity of the gas flow per minute is expressed based on the solvent vapor concentration and the lower heating value:

$$q=\frac{1000\ r\times(C\times10^{-6})}{273.15\times0.0821}\times\mathrm{LHV}, \qquad (5)$$

where C is the toluene or butyl acetate concentration (ppm), and LHV is the lower heating value (kJ mol^{-1}), which does not include the latent heat of condensation. The lower heating value was calculated from the standard enthalpy of the formation of toluene (g), butyl acetate (g), CO_2 (g), and H_2O (g) (National Institute of Standards and Technology, 2023). The lower heating values of toluene and butyl acetate were 3772 and 3246 kJ mol^{-1}, respectively. Based on the relations of Eq. (1)–Eq. (5), the concentration of the generated CO_2 was estimated from the change of temperature in the catalyst bed:

$$C_{\mathrm{CO_2}}=0.0821\times nk\rho C_{\mathrm{p}}T(T_{\mathrm{n}}-T)\times\frac{1}{\mathrm{LHV}}, \qquad (6)$$

where $C_{\mathrm{CO_2}}$ is the CO_2 concentration (ppm), n is the number of carbon atom(s) in a solvent molecule (–), k is a constant (–). When the toluene and butyl acetate were completely oxidized, 7 and 6 mol of CO_2 are generated, respectively, from 1 mol of toluene and butyl acetate. Therefore, the number of carbon atom(s) in a solvent molecule n was multiplied. The specific heat and the lower heating value were calculated as being uniform without depending on temperature. The temperature of each plot in Figure 3 was substituted into Eq. (6) and fitting to a CO_2 generation curve was performed. The results of the fitting are shown in Figures 4a and 4b. The constant k values were 10.5 and 14.9 in the toluene and butyl acetate, respectively. If there is no heat radiated into the neighboring area or loss caused by heat conduction to the solid wall during the oxidation reaction, the k value approaches to 1. With the heat radiation loss at the thermocouple insertion position, the value k became higher. In particular, because the reaction tube outside the oven was not thermally insulated in this experimental system to aim at the simple device, the heat radiation is easy to advance. Similar fitting results for the Pt/Al_2O_3 and Co_3O_4-CeO_2 catalysts are shown in Figures 4c–4f. The change in the bed temperature could be used to estimate the CO_2 concentration. The catalytic oxidation activity of the toluene for Pt/Al_2O_3 (Figure 4c) and of the butyl acetate for Co_3O_4-CeO_2 (Figure 4f) was high and the values of k were 10.5 and 16.1, respectively. However, the conversion of the butyl acetate into CO_2 for Pt/Al_2O_3 (Figure 4d) and of the toluene for Co_3O_4-CeO_2 (Figure 4e) decreased greatly, and the k values changed to 16.6 and 18.5, respectively.

Figure 5 shows the relation between total heat capacity of the gas and total amount of substance of toluene or butyl acetate molecule oxidized in the gas over a period of 0–25 min calculated from Figure 4. With increase of the amount oxidized, the heat capacity also increased, and the relation was concluded by a straight line. On the other hand, when the amount oxidized decreased the heat radiation loss increased. The next section examines the residue and the by-products in the gas where the conversion to CO_2 was lower.

4.2 Residue and by-products after reaction

The gas that passed through the tube was collected and analyzed using gas chromatography/mass spectrometry. The total ion chromatograms in the oxidation of toluene and butyl acetate are shown in Figures 6 and 7, respectively. For the Co_3O_4-CeO_2 catalyst, the toluene peak area showed that 28.9 % remained compared with the value without the catalyst (peak a, chromatograms 3, 4 in Figure 6). For the Pt/Al_2O_3 catalyst, the butyl acetate peak area showed that 21.1 % remained compared with the value without the catalyst (peak e, chromatograms 2, 4 in Figure 7). It was confirmed that aromatic hydrocarbons are easily oxidized in the Pt/Al_2O_3 catalyst and acetic esters are easily oxidized in the Co_3O_4-CeO_2 catalyst.

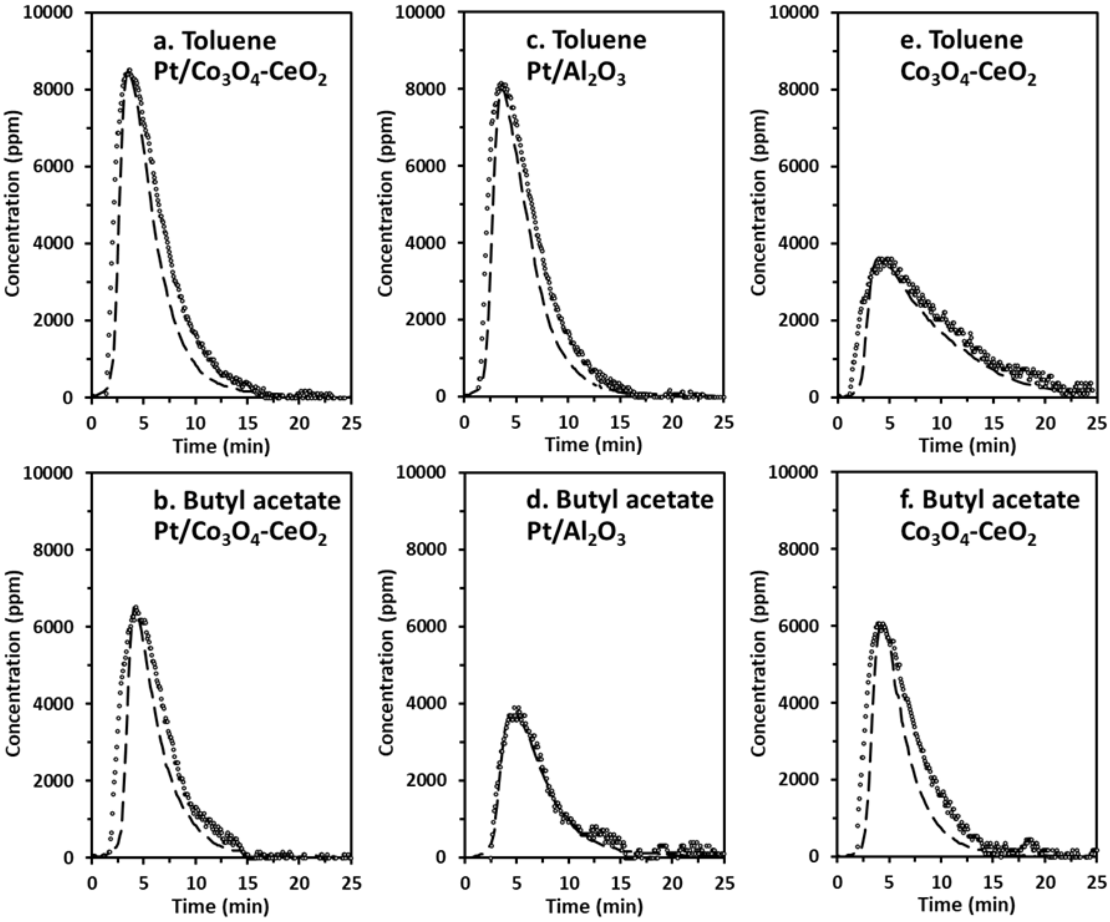


Figure 4 CO_2 generation curve (dashed line) and the fitting curve (plot) calculated from the temperature change of the catalyst bed with oxidation based on Eq. (6).

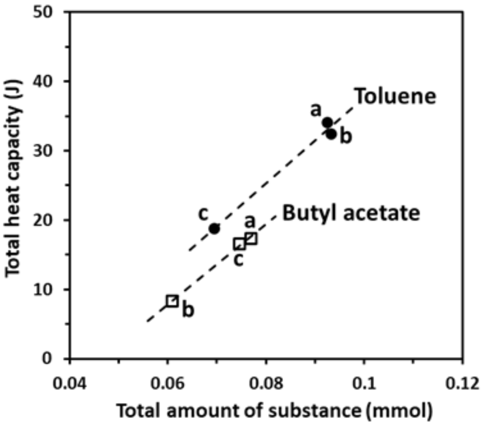


Figure 5 Relation between total heat capacity of the gas and total amount of substance of solvent molecule oxidized in the gas over a period of 0–25 min.
a: Pt/Co_3O_4-CeO_2, b: Pt/Al_2O_3, c: Co_3O_4-CeO_2

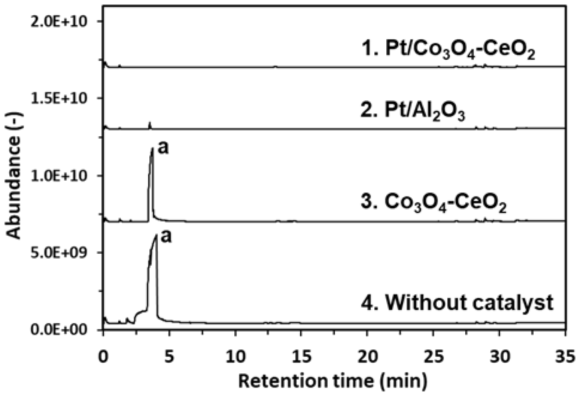


Figure 6 Total ion chromatograms in the oxidation of toluene.
a: toluene

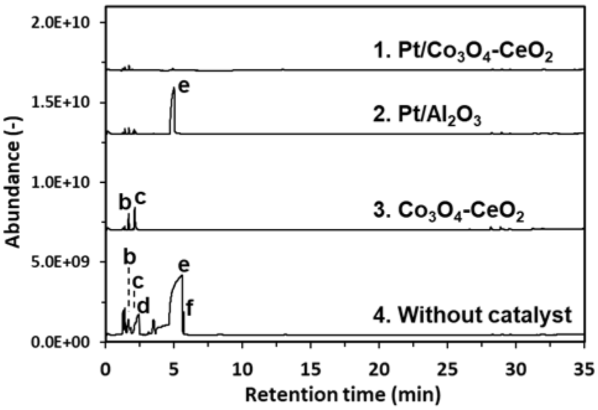


Figure 7 Total ion chromatograms in the oxidation of butyl acetate.
b: butanal, c: butanol, d: acetic acid, e: butyl acetate, f: 2-buten-1-ol acetate

Some butyl acetate by-products were clearly detected in the gas from the empty tube (chromatogram 4 of Figure 7). These by-product components were identified by an NIST MS library search. Although 2-buten-1-ol acetate was generated (peak f, chromatograms 4 of Figure 7), this peak disappeared with catalytic oxidation. The hydrolysis of ethyl acetate advances the generation of acetic acid and ethanol (Delimaris, & Ioannides, 2009; Papaefthimiou et al., 1998; Sawyer, & Abraham, 1994). In this work, since butyl acetate was used, acetic acid (peak d, chromatogram 4 of Figure 7) and butanol (peak c) were detected in the gas from the empty tube. The hydrolysis of butyl acetate was caused by moist air in the oven.

Papaefthimiou et al. (1997) observed the homogeneous gas-phase oxidation of butanol in a stream of 150 ppm butanol in air with a 30 cm^3 min^{-1} gas flow. They showed that the reaction proceeds via the formation of butanal (butanol → butanal → CO_2). The conversion of butanol to butanal started at temperatures as low as 453 K and reached maximum at around 533 K. The CO_2 product appeared at 513 K and the complete conversion of butanol to CO_2 was achieved homogeneously at around 613 K. In this study, the butanal (peak b, chromatogram 4 of Figure 7) was generated with oxidation of the butanol (peak c) at 523 K and the peak height ratio of butanal to butanol was 1.28:1. The results that both components existed and the amount of butanal was more than that of butanol accorded.

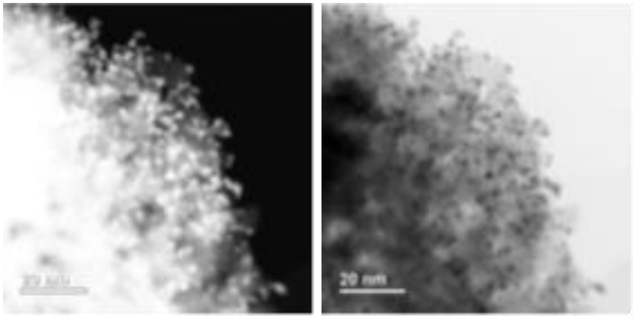
The butanol peak height in the Co_3O_4-CeO_2 catalyst increased to 1.85 times compared with that without the catalyst (peak c, chromatograms 3, 4 of Figure 7). The butanal peak height in the Co_3O_4-CeO_2 catalyst increased to 1.05 times compared with that without the catalyst (peak b, chromatograms 3, 4 of Figure 7). Since the peaks of butanol (peak c) and acetic acid (peak d) appeared almost simultaneously, here the comparison was made using peak height rather than peak area. With the Co_3O_4-CeO_2 catalyst oxidation, although the peaks of butyl acetate and acetic acid disappeared, the amount of the butanol and butanal as by-product increased somewhat compared with before the catalytic reaction. By using the Pt/Co_3O_4-CeO_2 catalyst, the components of these by-products were barely detected, and both toluene and butyl acetate were almost completely oxidized at 523 K.

Figure 8 shows the scanning transmission electron microscopy image of Pt/Co_3O_4-CeO_2 and Pt/Al_2O_3. In the Pt/Co_3O_4-CeO_2 catalyst, the projected area diameter of platinum was around 2.6 nm (number of samples: 158, standard deviation: 0.61). In this study, the platinum colloid coated with polyvinylpyrrolidone dispersant was used for supporting of platinum on the Co_3O_4-CeO_2, mentioned earlier. However, in comparison with the Pt/Al_2O_3 catalyst (commercial grade), the fact to be superior in particle size (surface area of particles) and dispersibility was not recognized. The catalytic activity increased with not the property of platinum particle, but combination effects of platinum and Co_3O_4-CeO_2. Actually, the activity for ethyl acetate of the Pt/Al_2O_3 catalyst prepared by platinum colloid raw material did not be improved (Inoue, & Somekawa, 2019b). Furthermore, in this study, it was revealed that the combination with platinum could also oxidize butanol and butanal generated on the Co_3O_4-CeO_2 in the presence of moisture.

5. Conclusion

The catalytic oxidation of toluene and butyl acetate vapor was conducted at 523 K in an oven. As the oxidation reaction progressed, the temperature of the catalyst bed increased. From the relation between the specific heat of air and the lower heating value of the solvent, fitting to a CO_2 generation curve was performed. The change in the bed temperature could be used to estimate the CO_2 concentration. A relation between heat capacity of the gas and amount of solvent molecule oxidized was clarified. In the oxidation reaction with Co_3O_4-CeO_2 catalyst, part of the toluene remained. Although the butyl acetate did not remain, the amounts of butanol and butanal, which were generated as by-products in the presence of moisture in the air, increased somewhat. By using a catalyst that combined platinum and Co_3O_4-CeO_2, and that was prepared using the author's original method, both toluene and butyl acetate were almost completely oxidized at 523 K.

Pt/Co_3O_4-CeO_2



Pt/Al_2O_3

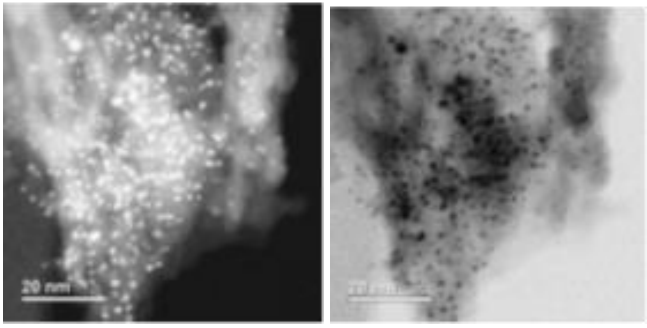


Figure 8 High-angle annular dark-field scanning transmission electron microscopy image (left) and bright-field scanning transmission electron microscopy image (right) of Pt/Co_3O_4-CeO_2 and Pt/Al_2O_3.

6. Acknowledgment

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