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Regeneration of Co_3O_4-CeO_2 catalyst used for odor elimination in an offset printing factory

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Abstract

Deactivated ball-type Co_3O_4-CeO_2 catalyst used for odor elimination in an offset printing factory for a year was regenerated by soaking in water. The reaction yield of ethyl acetate to carbon dioxide increased, on regeneration, to 98% from 82% (used catalyst) at 350°C (new catalyst: almost 100%). Sulfur was found in the water (eluate) after soaking the deactivated catalyst; and it is suggested that sulfur, which generally works as a catalyst poison, is dissolved in the water, resulting in recovery of catalyst activity. In the case of ball-type Pt/Al_2O_3 catalyst, little catalyst deactivation was observed after a year of usage at 350°C; and it is considered that, in this case, the blocking of active sites is suppressed, since the sulfur adsorbed on platinum is easily burned and converted into gas.

Keywords*: *Co_3O_4-CeO_2 catalyst, offset printing factory, Pt/Al_2O_3 catalyst, odor elimination, recovery of catalyst activity, sulfur

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1. Introduction

In offset printing, a commonly used technique for printing flyers, newspapers, etc., an inked image is transferred from a plate to the printing surface. Components in the ink's oils chemically combine with oxygen in the atmosphere to form a solid ink film. Oxidation can be accelerated by the use of a drier. In the drying process, volatile organic compounds (VOCs) are released, causing atmospheric pollution and human health and odor problems (Browning, 1965; Lund, 1971).

Platinum, the most widely used catalyst for VOC elimination (Assal et al., 2017; Darif et al., 2016; Kajama, Shehu, Okon, Orakwe, & Gobina, 2016; Leclercq, Giraud, Bianchi, & Gaillard, 2014), is generally deposited on alumina. The authors (Somekawa, Yuliati, Ishikawa, Takanabe, & Domen, 2010; Somekawa et al., 2011; Somekawa, & Hagiwara, 2015) have already reported that Co_3O_4-CeO_2 catalyst could be used as a substitute for platinum-based catalyst in VOC treatment, and the former catalyst has shown high activity for various VOCs, especially ethyl acetate. The authors have developed the Co_3O_4-CeO_2 catalyst in both ball (Figure 1) and honeycomb form. Previous to the present study, ball-type Co_3O_4-CeO_2 and Pt/Al_2O_3 catalysts were tested in the field (offset printing factory) for a year, and showed good performance.

Generally, silicon and sulfur work as catalyst poisons, resulting in catalyst deactivation. In this study, the authors attempted to regenerate the catalysts used at the offset printing factory, by soaking them in water. The components causing catalyst deactivation were also investigated.

2. Materials and methods

2.1 Regeneration of used catalyst

As aforementioned, a VOC treatment field test was performed for a year in an offset printing factory, using ball-type Co_3O_4-CeO_2 and Pt/Al_2O_3 catalysts. In this study, we attempted to regenerate, and evaluated the resulting performance of, deactivated catalysts that had been used in the field test.

The used catalysts were regenerated by soaking in water. Roughly 10 g of each used catalyst was soaked in 150 mL of deionized water at room temperature for 3 days; after which, the catalyst was dried at 110°C for around 12 h in an oven. For comparison, new catalysts were treated in a similar manner.

Figure 1 Ball-type Co_3O_4–CeO_2 catalyst

2.2 Catalytic activity test

The catalytic activity tests were conducted using a flow reaction system (fixed-bed reactor) connected to bubble-type VOC gas generation equipment. Ethyl acetate, the evaluation VOC, was oxidized to carbon dioxide and water vapor in the presence of air. In order to ensure that the air contained a constant concentration of ethyl acetate (gas), dried air was passed through the bubbler containing ethyl acetate (liquid), inside a constant-temperature oven set at 40ºC. The dried-air flow rate was 4.64 liter/min (25°C, 1 atm). The catalyst (12.7 cm^3) was packed in a stainless steel reaction tube ($\varphi = 15$ mm). The air containing ethyl acetate flowed continuously through the reaction tube, which was placed in a furnace. A thermocouple was installed near the catalyst bed, to measure the temperature. The temperature range of the catalyst bed in the furnace was from room temperature to about 350ºC. The volume hourly space velocity, defined as the ratio of the gas flow rate to the catalyst bed volume, was 22,000 h^{-1}. The CO_2 concentration in the gas was analyzed online using a CO_2 gas monitor (Riken Keiki, RI-215D) with an infrared detector, and the reaction yield was obtained based on the concentration. The reaction yield was defined as 100% when all the treated ethyl acetate was converted into carbon dioxide. The concentration of ethyl acetate was determined using a gas chromatograph/mass analyzer (Agilent technology, 7890A/5975C). The concentration of ethyl acetate in the reaction tube inlet gas was 1,000 ppm.

2.3 Characterization

Scanning electron microscope-energy dispersive X-ray (SEM-EDX) spectrometer measurements were performed (JEOL, JSM-6490LA, JED-2300), to investigate the structure and constituent elements of the catalyst surface. The elements contained in the water (eluate) after soaking the catalyst were analyzed by induced coupled plasma-atomic emission spectrometry (ICP-AES, ICPS-8100, Shimazu), with the concentration inferred from the emission intensity. To elucidate the chemical-bond state of the catalyst surface, X-ray photoelectron spectroscopy (XPS) measurements were performed using an Ulvac-PHI Quantera II ESCA spectrometer with monochromatized Al Kα radiation.

3. Results and discussion

Figure 2 shows the ethyl acetate reaction yield for the used (deactivated) and regenerated catalysts. The yield for both new catalysts was almost 100% at 350°C. Actual treatment in the offset printing factory was performed at 350°C. After a year's usage of the Co_3O_4–CeO_2 catalyst, the yield decreased to 82% at 350°C. However, by soaking the used Co_3O_4–CeO_2 catalyst in water, the yield recovered to 98% at 350°C. In the case of the Pt/Al_2O_3 catalyst, the yield decreased to 94% at 350°C, after the year of treatment, and soaking the catalyst in water resulted in no observable recovery of catalyst activity at the same temperature.

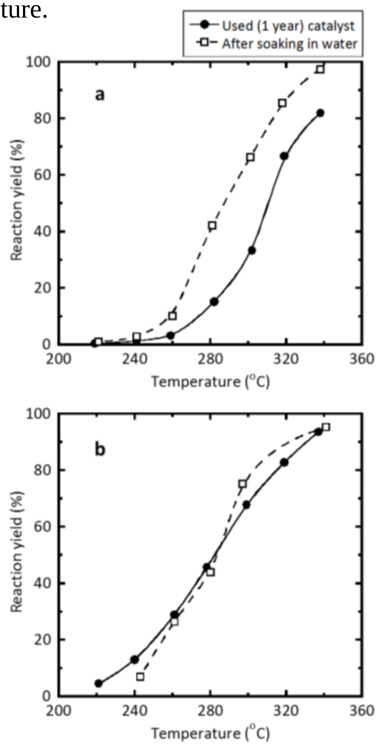

Figure 2 Reaction yield of ethyl acetate for used and regenerated (a) Co_3O_4–CeO_2 and (b) Pt/Al_2O_3 catalyst

The results of SEM-EDX analysis of the used catalysts are shown in Figure 3. SEM measurement revealed that the porosity of the used catalysts was not reduced, while EDX measurement detected elements constituting the catalyst (Co_3O_4–CeO_2 or Pt/Al_2O_3) and the ball-type cordierite carrier. Carbon was also detected in the carrier.

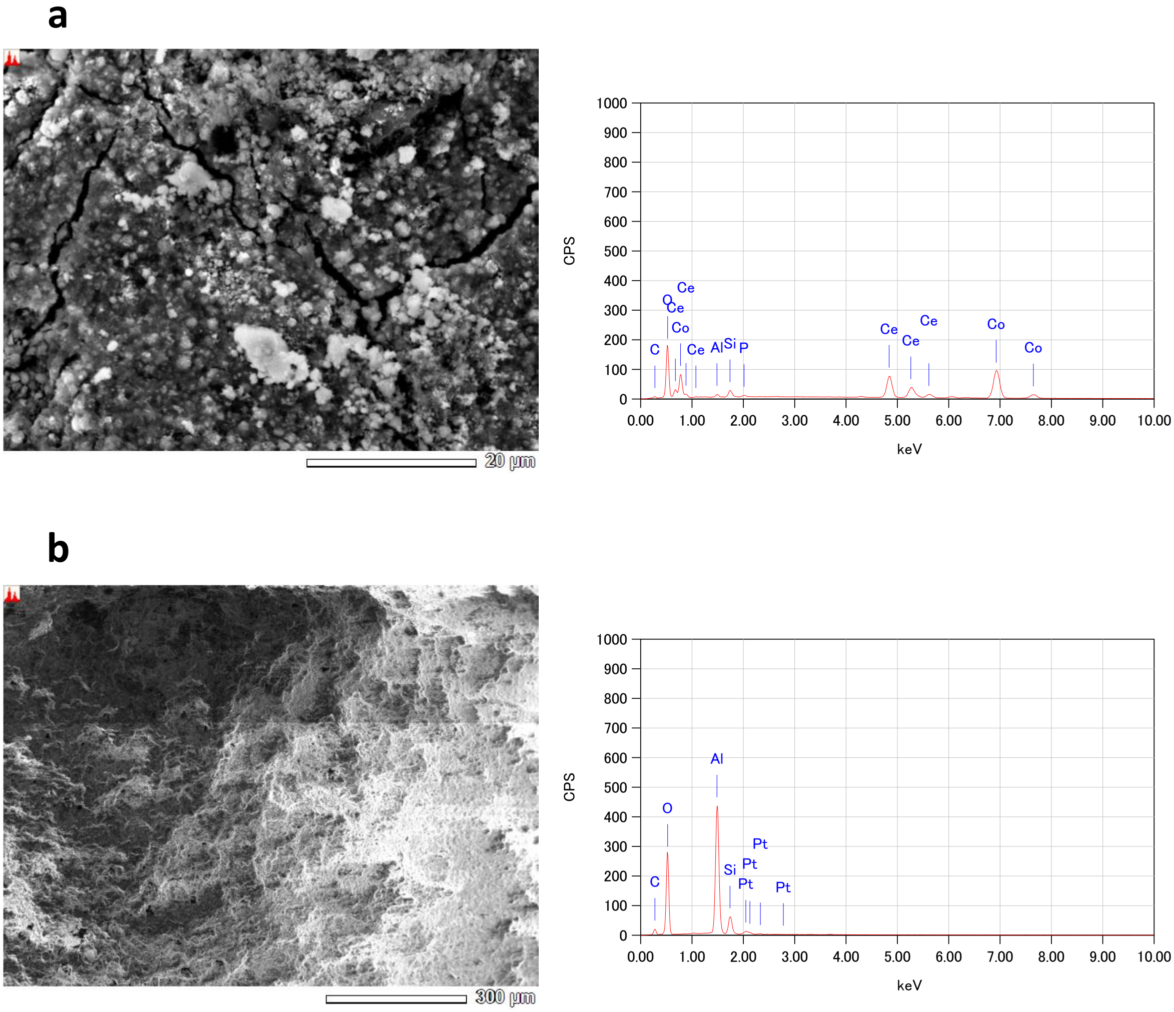

Figure 3 SEM-EDX characterization of (a) Co_3O_4–CeO_2 and (b) Pt/Al_2O_3 catalyst

In Figure 3, no trace components causing catalyst deactivation were detected, though a slight concentration of phosphorus (0.47 vol%) was detected on the used Co_3O_4-CeO_2 catalyst. The elements contained in the water (eluate), after soaking the new and used catalysts, were analyzed by ICP-AES. In addition to the eluted ingredients from the catalyst (Co_3O_4-CeO_2 or Pt/Al_2O_3) and ball-type cordierite carrier, sulfur was detected in the eluate of both used catalysts (Table 1). It is suggested that sulfur, which generally works as a catalyst poison, is dissolved in the water, resulting in a recovery of the catalytic activity of the Co_3O_4-CeO_2 catalyst. The state of sulfur on the used Co_3O_4-CeO_2 surface was analyzed by XPS, and Figure 4a shows the results, with the solid line indicating the result of moving-average smoothing. The intensity of the C 1s peak (at 284 eV) was used as a reference. The XPS spectra showed S 2p peak at around 169 eV, indicating that sulfur oxide was present on the surface (Sun et al., 1994). Thus, it is considered that the Co_3O_4-CeO_2 catalyst is regenerated by the dissolution of sulfur oxide in the water, which reduces its capacity for catalyst deactivation.

Table 1 Elemental analysis of the eluate by ICP-AES

	Concentration (mg/L)		
	1–10	10–100	> 100
Co_3O_4–CeO_2			
New catalyst	Na, Mg, Si, K, Co	–	–
Used catalyst	Na, Si, **S**, K	–	–
Pt/Al_2O_3			
New catalyst	Al, Si	Na, K	–
Used catalyst	B, Si	Na, **S**, K	–

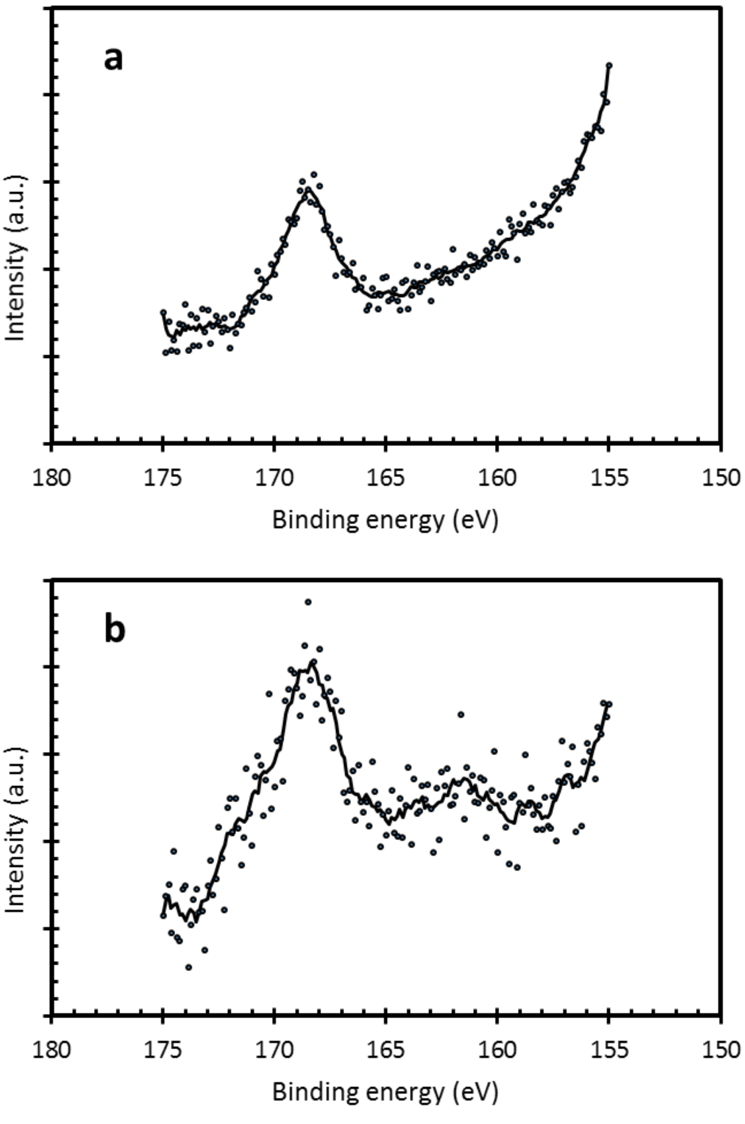

Figure 4 XPS spectra (S 2p) of used (a) Co_3O_4–CeO_2 and (b) Pt/Al_2O_3 catalyst

On the other hand, a greater concentration of sulfur was detected in the eluate of used Pt/Al_2O_3 catalyst (Table 1). Since alumina has a comparatively large surface area (S. Somekawa et al., 2011), comparatively more sulfur can adsorb on the surface. However, after a year of use, hardly any catalyst deactivation was observed at 350°C in this case, as aforementioned (Figure 2b). A slight peak was observed at around 162 eV in the XPS spectra (S 2p) of used Pt/Al_2O_3 catalyst (Figure 4b), which was attributed to Pt–S species (Sun et al., 1994). More sulfur oxide may have adsorbed on the alumina than on the platinum, as sulfur adsorbed on platinum is easily burned and converted into gas. (In the actual treatment in the offset printing factory, the temperature of the catalyst packing layer reached 450–500°C, through VOC combustion.) It is considered that catalyst deactivation due to blockage of active sites in the platinum is suppressed in the Pt/Al_2O_3 catalyst.

4. Conclusion

Ball-type Co_3O_4–CeO_2 catalyst used in an offset printing factory for a year was regenerated by soaking in water, and the reaction yield for the conversion of ethyl acetate to carbon dioxide increased from 82% (used catalyst) to 98% (regenerated catalyst) at 350°C (new catalyst: almost 100%). It is suggested that sulfur oxide, which generally works as a catalyst poison, is dissolved in the water (eluate), resulting in recovery of catalyst activity. In the case of Pt/Al_2O_3 catalyst, on the other hand, little deactivation had occurred at 350°C, after a year's usage in the same factory; and it is considered that the blockage of active sites is suppressed in this case, since the sulfur adsorbed on platinum is easily burned and converted into gas.

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