Effective p-cresol removal through catalytic liquid-phase oxidation under moderate conditions using Pt/CeO$_2$-ZrO$_2$-SnO$_2$/SBA-16 as a catalyst

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1. Introduction

Over recent decades, the use of phenolic compounds in industrial processes has been expanded by reason of the vital precursors in many strategic chemical reactions [1–3]. Consequently, phenolic compounds have become known as pollutants frequently encountered in the wastewater of many industries. Among these phenols, cresols (o-, m-, p-cresol) are widely employed by various manufacturers, including petrochemical, refinery, and coking plants [4–6]. Among their direct applications, saponified cresol disinfectant has been used in medical, livestock-related, and industrial environments. Since they are reported to be accumulated in the ground water, removal of cresols from wastewater streams is crucial [5–7]. Among the three cresol isomers, p-cresol has the highest toxicity and causes heart, kidney, and liver damage [8–10]. In addition, p-cresol has a greater permeability effect on skin than the other cresols [11]. This makes p-cresol the priority pollutant to be removed from the wastewater streams of various industries.

Although the removal of p-cresol was reported to be handled by biological treatment [5,9,12] and adsorption [6,13,14], these processes face several drawbacks; e.g. requiring temperature and pH maintenance for microorganisms and replacement of adsorbents. Chemical oxidation using an oxidizing agent (ozone or hydrogen peroxide) was also demonstrated to decompose cresol effectively, but this requires a strong, constant input of hazardous additives [3,4,7]. Liquid-phase oxidation with oxygen gas over catalysts (generally denoted as "catalytic wet-air oxidation") is an effective method for cresol removal employing a simple, sustainable, and environmentally friendly technique [4,15]. According to a previous study, complete p-cresol removal was realized with an Ag/Al$_2$O$_3$-ZrO$_2$ catalyst at a temperature of 160°C and under 1.6 MPa pressure [16]. Unfortunately, the operating conditions for its practical application are severe; therefore, improvement of the catalytic activity is necessary to realize effective p-cresol removal under moderate reaction conditions (below 100°C and under atmospheric pressure).

Ceria (CeO$_2$) is a material famous for its extensive use in the catalyst field, since it has the ability to release and store active oxygen species due to the reversible redox behaviors of Ce$^{4+/3+}$ ions [17–19]. The introduction of zirconia (ZrO$_2$) into the CeO$_2$ lattice, that is, CeO$_2$-ZrO$_2$ solid solution, has been reported to increase its oxygen storage capacity, and it has been applied as an automotive exhaust catalyst [20–23]. In wastewater treatment, CeO$_2$-ZrO$_2$ has also been used for catalytic oxidation of phenolic compounds [24]. In our previous studies, we demonstrated that the introduction of tin oxide (SnO$_2$) into the CeO$_2$-ZrO$_2$ lattice led to a further increase of its oxygen release and storage capabilities because a synergy between the valence changes of Sn$^{4+/2+}$ with those of...
Ce\(^{4+/3+}\) could trigger its reducibility [25–27]. In this study, we focused on the CeO\(_2\)-ZrO\(_2\)-SnO\(_2\) solid solution as the promoter, in which the active oxygen species is effectively supplied from inside the lattice to an activator, and, thus, both the operating temperature and pressure can be expected to be lowered.

Based on this concept, we prepared Pt loaded onto a CeO\(_2\)-ZrO\(_2\)-SnO\(_2\)/SBA-16 catalyst (SBA-16: mesoporous silica, Santa Barbara Amorphous No. 16), where Pt was the activator and SBA-16 was a support with a large surface area, and investigated the catalytic activity for p-cresol removal. For the composition of the CeO\(_2\)-ZrO\(_2\)-SnO\(_2\) promoter, the optimum Ce/Zr ratio in the CeO\(_2\)-ZrO\(_2\) system was confirmed to be 4 [28] and the doping amount of SnO\(_2\) in the Ce\(_{0.8(1-x)}\)Zr\(_{0.2(1-x)}\)Sn\(_{0.15}\)O\(_2\) solid solution was optimized as \(x = 0.15\) to provide an effective oxygen supply [26]; we therefore selected the composition of Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_2\).

2. Experimental

SBA-16 was synthesized using the hydrothermal method [25]. Pluronic F-127 (1.6 g) was dissolved in 0.2 mol·L\(^{-1}\) (90 mL) hydrochloric acid, and 1,3,5-tri-methylbenzene (1.1 mL) was then added. After stirring at 35°C for 3 h, tetraethyl orthosilicate (7.1 mL) was added to the mixture, which was then stirred further at the same temperature for 20 h. Subsequently, the mixture was treated hydrothermally inside a Teflon bottle in a sealed brass vessel at 140°C for 24 h. The precipitates were separated by filtration and dried at room temperature for 12 h. The dried sample was then calcined at 400°C for 4 h under air flow.

Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_2\) (16 wt%)/SBA-16 was synthesized using the co-precipitation method. Stoichiometric amounts of 1.0 mol·L\(^{-1}\) Ce(NO\(_3\)\(_2\))\(_2\) aqueous solution, 0.1 mol·L\(^{-1}\) ZrO(NO\(_3\)\(_2\))\(_2\) aqueous solution, and SnC\(_2\)O\(_4\) were mixed in the water solvent. After stirring of the mixed solution at room temperature for 30 min, the prepared SBA-16 powder was added. The ammonia solution (5.6 vol%) was added dropwise to the mixture to adjust the pH to 11, followed by stirring at room temperature for 12 h. The precipitates obtained were collected by suction filtration, and then calcined at 900°C for 1 h. For purposes of comparison, Ce\(_0.8\)Zr\(_{0.2}\)O\(_2\) (16 wt%)/SBA-16 (same ratio of Ce:Zr = 4:1 in Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_2\)), Ce\(_{0.82}\)Sn\(_{0.18}\)O\(_2\) (16 wt%)/SBA-16 (same ratio of Ce:Sn = 4:1 in Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_2\)), and CeO\(_2\) (16 wt%)/SBA-16 were also synthesized by a similar process. Hereafter, Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_2\) (16 wt%)/SBA-16, Ce\(_{0.82}\)Zr\(_{0.2}\)O\(_2\) (16 wt%)/SBA-16, Ce\(_{0.82}\)Sn\(_{0.18}\)O\(_2\) (16 wt%)/SBA-16, and CeO\(_2\) (16 wt%)/SBA-16, and SBA-16 are denoted as CZSn/SBA, CZ/SBA, CSn/SBA, C/SBA, and SBA, respectively.

Pt(7 wt%)/Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_2\) (16 wt%)/SBA-16 (Pt/CZSn/SBA) was prepared using the impregnation method. CZSn/SBA was mixed with a colloidal solution of Pt stabilized with polyvinylpyrrolidone in ethanol (Pt: 4.0 wt%) in water, and stirred at room temperature for 6 h. The mixture was then heated at 180°C to evaporate the solvent, and subsequently calcined at 500°C for 4 h. Pt was also loaded onto the other prepared samples by the same method to produce Pt(7 wt%)/Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\) (16 wt%)/SBA-16 (Pt/CZ/SBA), Pt(7 wt%)/Ce\(_{0.82}\)Sn\(_{0.18}\)O\(_2\) (16 wt%)/SBA-16 (Pt/CSn/SBA), Pt(7 wt%)/CeO\(_2\) (16 wt%)/SBA-16 (Pt/C/SBA), and Pt(7 wt%)/SBA-16 (Pt/SBA).

The sample composition was confirmed by X-ray fluorescence (XRF; Supermini200, Rigaku) analysis. The BET (Brunauer-Emmett-Teller) specific surface area was measured by nitrogen gas adsorption (Tristar 3000, Shimadzu). The prepared catalysts were characterized by X-ray powder diffraction (XRD; SmartLab, Rigaku) measurement using Cu K\(_\alpha\) radiation (40 kV, 30 mA). The oxidation state of Pt in the samples was investigated by X-ray photoelectron spectroscopy (XPS) analysis. The peak position of the obtained spectrum was refined by the peak attributed to C 1s (284.6 eV), and spectrum fitting was then performed using a Gaussian-Lorentzian line shape with a Shirley background. The Pt dispersion of the catalysts was measured by the CO pulse-injection method at 50°C (Belcat-B; MicrotracBEL). The catalyst particles were observed directly by transmission electron microscopy (TEM; H-800, Hitachi). Temperature-programmed reduction (TPR; Belcat-B, MicrotracBEL) measurements were performed under a flow of 5 % H\(_2\) − 95 % Ar (50 mL·min\(^{-1}\)) at a heating rate of 5° C·min\(^{-1}\). Thermogravimetric-differential thermal analysis (TG-DTA; DTG-60AH, Shimadzu) was carried out at a 10°C·min\(^{-1}\) heating rate from room temperature to 500°C under air flow.

The catalytic liquid-phase oxidation of p-cresol was conducted using an open-vessel batch reactor equipped with an ethanol-cooled condenser (4°C) to suppress evaporation. The prepared catalyst (0.1 g) and 1000 ppm p-cresol aqueous solution (10 mL) were mixed in the reactor and heated in the oil bath at 40 or 80°C under atmospheric pressure. After a preset reaction time, the liquid phase was separated using a centrifuge (Allegra 64R Centrifuge, Beckman Coulter), and the p-cresol concentration in the liquid sample was evaluated by gas chromatography-mass spectrometry (GC-MS; GCMS-QP2010 Plus, Shimadzu). Here, 1000 ppm naphthalene solution in methanol was added to the liquid sample as an internal standard. The catalyst used was heated at 400°C for 1 h under air flow, prior to the reusability test. The p-cresol removal percentage is given by the following equation:

\[
(p - \text{Cresol removal percentage}) = \left(1 - \frac{C}{C_0}\right) \times 100 \%
\]

where \(C\) and \(C_0\) are the p-cresol concentrations after and before the reaction, respectively. Furthermore, the
apparent rate constant \((k)\) was estimated from the following pseudo-first-order reaction model:
\[
\frac{dC}{dt} = -kC
\]

### 3. Results and discussion

#### 3.1. Catalysts characterization

Table 1 shows the measured compositions determined by XRF and the BET surface area of the catalysts. The measured compositions were in good agreement with the feed value within the experimental error. The Pt and promoter loading caused a decrease in the surface area compared to that of SBA. The surface areas of the catalysts with the promoter were almost the same.

Figure 1 shows XRD patterns of the prepared catalysts. In the case of Pt/SBA, the diffraction peaks were assigned only as SBA and Pt. For the catalysts with the promoter, four additional peaks corresponding to the cubic fluorite-type structure were observed. In comparison with Pt/C/SBA, the peaks corresponding to the cubic fluorite-type structure of Pt/CZ/SBA and Pt/CSn/SBA were shifted toward higher angles due to partial replacement of the \(\text{Ce}^{4+}\) (0.111 nm; coordination number (CN) = 8) [29] site by \(\text{Zr}^{4+}\) (0.098 nm; CN = 8) [29] or \(\text{Sn}^{4+}\) (0.095 nm; CN = 8) [29]. In the case of Pt/CZSn/SBA, since both \(\text{ZrO}_2\) and \(\text{SnO}_2\) were doped into the \(\text{CeO}_2\) lattice, the peaks of the cubic fluorite-type structure were shifted further toward higher angles.

Figure 2 shows XPS spectra of the Pt 4f core level of the prepared catalysts, whose fitting parameters are shown in Table S1. The Pt 4f\(_{7/2}\) and 4f\(_{5/2}\) peaks of all the prepared catalysts can be assigned as Pt\(^{2+}\) (ca. 75.6 and ca. 72.2 eV) and Pt\(^0\) (ca. 74.2 and ca. 70.8 eV). The Pt\(^{2+}/(\text{Pt}^{2+}+\text{Pt}^0)\) ratios are summarized in Table 2. While Pt/SBA has the lowest Pt\(^{2+}\) ratio, the presence of promoters led to an increase in the Pt\(^{2+}/(\text{Pt}^{2+}+\text{Pt}^0)\) ratio. Among the catalysts with promoters, Pt/CZSn/SBA has the highest Pt\(^{2+}/(\text{Pt}^{2+}+\text{Pt}^0)\) ratio, followed by Pt/CSn/SBA, Pt/CZ/SBA, Pt/C/SBA, and Pt/SBA. Table 2 also shows the Pt dispersion of the catalysts. The catalysts with promoters exhibited higher Pt dispersion compared to Pt/SBA, although the introduction of the promoters decreased their surface areas. In addition, the highest Pt dispersion was obtained for Pt/CZSn/SBA, which possessed the highest Pt\(^{2+}/(\text{Pt}^{2+}+\text{Pt}^0)\) ratio,

| Catalyst         | Feed composition          | Measured composition          | Surface area (m\(^2\) g\(^{-1}\)) |
|------------------|---------------------------|-------------------------------|-----------------------------------|
| Pt/CZSn/SBA      | Pt(7.0 wt%)/Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_{2}(16\text{ wt%})/\text{SBA-16}\) | Pt(6.6 wt%)/Ce\(_{0.68}\)Zr\(_{0.17}\)Sn\(_{0.15}\)O\(_{2}(16\text{ wt%})/\text{SBA-16}\) | 257                              |
| Pt/Cn/SBA        | Pt(7.0 wt%)/Ce\(_{0.82}\)Zr\(_{0.18}\)O\(_{2}(16\text{ wt%})/\text{SBA-16}\) | Pt(6.7 wt%)/Ce\(_{0.82}\)Zr\(_{0.18}\)O\(_{2}(15\text{ wt%})/\text{SBA-16}\) | 292                              |
| Pt/CZ/SBA        | Pt(7.0 wt%)/Ce\(_{0.82}\)Zr\(_{0.20}\)O\(_{2}(16\text{ wt%})/\text{SBA-16}\) | Pt(6.7 wt%)/Ce\(_{0.82}\)Zr\(_{0.20}\)O\(_{2}(16\text{ wt%})/\text{SBA-16}\) | 279                              |
| Pt/C/SBA         | Pt(7.0 wt%)/Ce\(_{0.82}\)O\(_{2}(16\text{ wt%})/\text{SBA-16}\) | Pt(6.6 wt%)/Ce\(_{0.82}\)O\(_{2}(17\text{ wt%})/\text{SBA-16}\) | 279                              |
| Pt/SBA           | Pt(7.0 wt%)/SBA-16        | Pt(6.8 wt%)/SBA-16            | 456                              |
| SBA              | -                         | -                             | 648                              |

Figure 1. XRD patterns of Pt/SBA, Pt/C/SBA, Pt/CZ/SBA, Pt/CZn/SBA, and Pt/CZSn/SBA.
suggesting that the oxidation of Pt inhibited the agglomeration of the Pt particles. The TEM images shown in Figure 3 confirmed that the Pt particle size of Pt/CZSn/SBA (ca. 8 nm) was slightly smaller than that of Pt/SBA (ca. 13 nm); that is, the Pt aggregation might have been suppressed by introducing the CZSn promoter.

The generation of oxidized Pt might be related to the redox of the promoter, in which the reducibility of CeO$_2$ is reported to cause oxidation of Pt through the following reaction: Pt$^0$ + 2Ce$^{4+}$ → Pt$^{2+}$ + 2Ce$^{3+}$ [30]. Thus, TPR analyses were performed to investigate the reducibility of the promoters, and the TPR profiles are presented in Figure 4. While the profile of SBA did not show any reduction peaks at below 500°C, C/SBA possessed a broad peak tail at above 400°C due to the reduction of Ce$^{4+}$. Clear broad peaks were observed at 338°C and 448°C for CSn/SBA and CZ/SBA, respectively. The decrease in the reduction temperature of CSn/SBA was caused by a synergistic redox reaction between Ce$^{4+/3+}$ and Sn$^{4+/2+}$ ions [31]. Zr$^{4+}$ ions are generally introduced into CeO$_2$ to increase its oxygen release and storage capacities due to an increase in oxide ion diffusivity [32], which leads to a lowering of the reduction temperature. For CZSn/SBA, the peak are split into two, and the reductions at 305°C and 375°C correspond to the surface and bulk reductions of Ce$^{4+}$ ions, respectively [25]. Among the samples, CZSn/SBA exhibited the lowest onset temperature, i.e. the highest reducibility, owing to the effects of both of SnO$_2$ and ZrO$_2$. Based on the onset temperature of the first reduction peak, the order of the redox properties was postulated as CZSn/SBA > CSn/SBA > CZ/SBA > C/SBA > SBA. This order is similar to the Pt$^{2+}/$(Pt$^{2+}$+Pt$^0$) ratio, suggesting that the high redox properties of the promoter facilitated Pt oxidation by supplying Pt with active oxygen from inside the promoter lattice.

### 3.2. Catalytic performance

The catalytic performance in liquid-phase oxidation of p-cresol was evaluated at 80°C under atmospheric pressure. Figure 5(a) shows the p-cresol removal percentages as the reaction time functions of Pt/CZSn/SBA, Pt/CSn/SBA, Pt/CZ/SBA, Pt/C/SBA, Pt/SBA, and Pt/CZSn/SBA.

| Catalyst     | Pt$^{2+}/$(Pt$^{2+}$+Pt$^0$) ratio | Pt dispersion (%) |
|--------------|----------------------------------|------------------|
| Pt/CZSn/SBA  | 0.40                             | 9.04             |
| Pt/CSn/SBA   | 0.36                             | 8.96             |
| Pt/CZ/SBA    | 0.34                             | 8.63             |
| Pt/C/SBA     | 0.30                             | 8.28             |
| Pt/SBA       | 0.22                             | 7.98             |

Figure 3. TEM images of Pt/CZSn/SBA and Pt/SBA.
SBA, where the removal percentages were estimated from the GC-MS spectra (Figure S1). Here, the Pt and CZSn loading amounts were optimized (Table S2). In the absence of the catalysts, a slight degradation of p-cresol (<10%) was observed, and the removal percentage was gradually increased as a function of time. This phenomenon was caused by evaporation of p-cresol during the stirring at 80°C, whereas no p-cresol removal was observed when stirring at 40°C. For SBA (Figure 5(a)), the p-cresol removal percentage was constantly higher than in the absence of catalysts by ca. 6%, owing to adsorption onto the SBA support. Loading Pt with an oxidation ability drastically increased the p-cresol removal percentage compared to SBA. The introduction of the promoters further enhanced the removal percentage. Of particular note, the Pt/CZSn/SBA catalyst exhibited the highest performance for p-cresol removal and completely removed p-cresol after the reaction for 4 h. This reaction condition is sufficiently moderate, i.e. conducted at a temperature as low as 80°C and under atmospheric pressure, compared to the previous catalyst (160°C, 1.6 MPa [16]).

According to the previous reports, acetic acid is generated in the final stage of catalytic liquid-phase oxidation of phenolic compounds, and remains as a by-product because it is one of the most refractory organic compounds. For prepared catalysts, however, the GC-MS spectra (Figure S1) showed no peaks of any by-product, including acetic acid, except for p-cresol and naphthalene.

In catalytic liquid-phase oxidation of phenolic compounds, the carbonaceous deposit generally forms on the catalyst surface [33–35]. The amount of the carbonaceous deposit was estimated from the TG-DTA measurement for the Pt/SBA and Pt/CZSn/SBA catalysts used after a 4 h catalytic reaction (Figure S2). The amount of the carbonaceous deposit for the Pt/SBA used was 4.2 mg, suggesting that 61% of the removed p-cresol was converted to carbonaceous material. For Pt/CZSn/SBA, the amount of the carbonaceous deposit was 3.4 mg; that is, the conversion ratio of the carbonaceous deposit on the removed p-cresol was calculated as 39%, which is obviously lower than in the case of Pt/SBA (61%). Therefore, the carbonaceous material deposition was probably suppressed by use of Pt/CZSn/SBA, because Pt supported on CZSn seems to have contributed to the complete oxidation of p-cresol due to the effective supply of active oxygen species from the CZSn promoter.

In order to confirm that the p-cresol removal proceeded catalytically, moreover, the reaction was performed at 40°C for 4 h using Pt/CZSn/SBA or SBA. Typically, lowering the reaction temperature causes deactivation of a catalyst and an increase in the adsorption amount. In the case of Pt/CZSn/SBA, the p-cresol removal percentage at 40°C was determined to be

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**Figure 5.** (a) Catalytic performances for p-cresol oxidation using the prepared catalysts and (b) plots of $-\ln(C/C_0)$ vs. reaction time.
20%, which is lower than that at 80°C (100%). On the other hand, the percentage of SBA removed at 40°C (8%) was higher than that at 80°C (6%). These phenomena clearly indicate that Pt/CZSn/SBA decomposed p-cresol catalytically.

For further investigation of the catalyst properties, the apparent reaction rate was estimated from the plot of $-\ln(C/C_0)$ vs. reaction time, as shown in Figure 5(b). Since the linear plots were obtained, the apparent rate constant of each catalyst was estimated from the pseudo-first oxidation reaction. The order of the apparent rate constant was Pt/CZSn/SBA (0.76(5) h$^{-1}$) > Pt/CZ/SBA (0.55(2) h$^{-1}$) > Pt/Cs/SBA (0.53(6) h$^{-1}$) > Pt/C/SBA (0.44(1) h$^{-1}$) > Pt/SBA (0.35(1) h$^{-1}$). This trend was similar to that of the Pt$^{2+}$/(Pt$^{2+}$+Pt$^0$) ratio; i.e. the surface Pt$^{2+}$ ions contributed substantially to enhancement of the apparent rate constant, and Pt/CZSn/SBA exhibited the highest catalytic activity. Here, previous studies reported that oxidized Pt (Pt$^{2+}$) is effective for the oxidation of phenolic compounds compared to metallic Pt [30,36–39]. Although the oxidation of p-cresol is involved in the reduction of Pt$^{2+}$ to Pt$^0$, the reoxidation of Pt$^0$ might be facilitated by a continuous supply of active oxygen species from the promoter. The promoter is also considered to be oxidized by dissolved oxygen molecules, which can be supplied from atmospheric air owing to the open-vessel batch reactor. In fact, the Pt 4f XPS spectrum remained unchanged even after reaction at 80°C for 4 h (Figure S3). In addition, no metal leaching from Pt/CZSn/SBA catalyst was observed, and the results showed effective removal of as much as 94% of the p-cresol after reaction for 4 h.

4. Conclusions

For effective p-cresol removal from industrial wastewater, a Pt/CoO$_2$-ZrO$_2$-SnO$_2$/SBA-16 catalyst has been prepared by supporting the Pt activator and the CeO$_2$-ZrO$_2$-SnO$_2$ promoter on an SBA-16 support. The introduction of ZrO$_2$ and SnO$_2$ into the CeO$_2$ lattice enhanced its redox properties, which caused generation of oxidized platinum ions (Pt$^{2+}$) by providing an effective supply of active oxygen species from inside the lattice. Since the Pt$^{2+}$ ion has a high oxidation capability with respect to phenolic compounds compared to metallic Pt, catalytic activity for p-cresol removal was improved with the increase in the amount of Pt$^{2+}$. The highest catalytic performance was obtained for the Pt/CoO$_2$-ZrO$_2$-SnO$_2$/SBA catalyst, and p-cresol was completely removed after a reaction of 4 h at 80°C under atmospheric pressure.

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Disclosure statement

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