Low-Temperature Complete Combustion of Volatile Organic Compounds over Novel Pt/CeO₂-ZrO₂-SnO₂/γ-Al₂O₃ Catalysts

Keisuke Yasuda,^{1,2} Atsuki Yoshimura,¹ Atsushi Katsuma,¹ Toshiyuki Masui,¹ and Nobuhito Imanaka^{*1}

¹Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

²Japan Society for the Promotion of Science, 8 Ichibancho, Chiyoda-ku, Tokyo 102-8472

Received December 6, 2011; E-mail: imanaka@chem.eng.osaka-u.ac.jp

Catalytic combustion of volatile organic compounds (VOCs) such as ethylene, toluene, and acetaldehyde over novel $Pt/CeO_2-ZrO_2-SnO_2/\gamma-Al_2O_3$ catalysts prepared by a coprecipitation method was investigated. The introduction of a small amount of SnO_2 within the CeO_2-ZrO_2 lattice as a promoter was considerably effective to enhance the oxygen release and storage abilities of the catalysts, so that complete oxidation of VOCs was markedly activated. This improvement of the reducibility of the catalyst can be ascribed to the simultaneous reduction of Ce^{4+} and Sn^{4+} in the $CeO_2-ZrO_2-SnO_2$ solid solutions. By the optimization of the composition and the Pt amount, complete oxidation of ethylene, toluene, and acetaldehyde was realized at temperatures as low as 55, 110, and 140 °C over a $Pt(10 \text{ wt }\%)/Ce_{0.68}Zr_{0.17}Sn_{0.15}-O_{2.0}(16 \text{ wt }\%)/\gamma-Al_2O_3$ catalyst, respectively.

Volatile organic compounds (VOCs) include a wide range of organic chemical compounds such as alkenes, aldehydes, ketones, aromatics, and other light-weight hydrocarbons. They are emitted into the atmosphere from both anthropogenic and biogenic sources (mainly vegetation). The anthropogenic VOCs are released in a variety of processes such as exhaust gases from the internal combustion engine, power generation plants, and chemical processing plants. VOCs are recognized as major sources of air pollution including photochemical smog, ground-level ozone, suspended particulate matter, and sick building syndrome, and are considered to be detrimental to human health and the environment.^{1,2}

Among a large number of VOCs, toluene is widely used as an organic solvent for paints, printing inks, adhesives, and antiseptics due to its excellent ability to dissolve substances, and acetaldehyde is well-known as a raw material to produce synthetic resins and rubbers. However, they have unpleasant odors and cause sick building syndrome by evaporating into the atmosphere. Ethylene is an important feedstock for the manufacture of many organic products in the petrochemical industry. Furthermore, it is a plant hormone released from fruits to control physiological process such as seed germination and the blooming of flowers. During postharvest storage of fruits and vegetables, however, it induces negative effects enhancing the senescence, ripening, and softening.³ To protect our health and the environment and to maintain agricultural products fresh away from such noxious influences, it is necessary to remove the VOCs released into the atmosphere as much as possible.

Up to now, several technologies such as flame combustion,⁴ catalytic combustion,⁵ catalytic destruction using ozone and plasma,⁶ photocatalytic decomposition,⁷ adsorption processes,⁸ and biological treatment⁹ have been developed to eliminate VOCs. Among these methods, catalytic combustion is one of the most promising processes for VOCs abatement because VOCs can be completely oxidized to harmless carbon dioxide

and steam over the catalyst at moderate temperatures, leading to minimal negative side effects such as NO_x production.⁵ However, it is extremely difficult to accomplish complete combustion of VOCs at low temperatures and, actually, the catalyst has to be heated at least up to 150 °C.^{10–12} Thus, it is considerably important to develop a novel active catalyst that can realize complete oxidation of VOC at temperatures as low as possible.

In our previous studies, we found that dibismuth trioxide (Bi₂O₃) doping into the CeO₂–ZrO₂ lattice was significantly effective to enhance the oxygen release and storage properties of CeO₂-ZrO₂ solid solutions.¹³⁻¹⁵ In addition, a Ce_{0.64}Zr_{0.16}-Bi_{0.20}O_{1.9} solid exhibits a remarkable low-temperature reduction behavior below 100 °C when it is supported on a high surface area γ -Al₂O₃ support.^{16,17} In order to establish complete oxidation of VOCs at moderate temperature, novel catalysts, in which CeO_2 -ZrO₂-Bi₂O₃ is employed as a promoter in the conventional Pt/γ -Al₂O₃ catalyst, were prepared. As a result, we demonstrated that the Pt/CeO₂-ZrO₂-Bi₂O₃/ γ -Al₂O₃ catalysts can completely oxidize ethylene, toluene, and acetaldehyde at temperatures as low as 65,^{18–21} 120,^{20–22} and $150 \,^{\circ}C$,²¹ which are dramatically lower than those of the conventional catalysts, respectively. These significantly high catalytic activities of the Pt/CeO₂-ZrO₂-Bi₂O₃/ γ -Al₂O₃ catalysts will be attributed to the appearance of electronic conduction associated with the simultaneous reduction of both Ce^{4+} and Bi^{3+} ions.

In this study, we have focused on tin dioxide (SnO₂) applied for gas sensing element, which has been well-known as a typical n-type semiconductor with electronic conduction.²³ Tin ion has both tetravalent (+4) and divalent (+2) states, and Ce_{1-x}Sn_xO₂ solid solutions, in which Ce⁴⁺ sites in CeO₂ were partially substituted with Sn⁴⁺ ions, have been reported to possess excellent oxygen storage and release properties compared with those of CeO₂ and SnO₂.²⁴⁻²⁶ Therefore, introduction of a small amount of SnO₂ as the substitute for Bi₂O₃ into the CeO₂–ZrO₂ lattice will be reasonably effective in enhancing the reducibility of the catalyst. Accordingly, $Pt/CeO_2-ZrO_2-SnO_2/\gamma-Al_2O_3$ catalysts were prepared by coprecipitation and the oxidation activities for several VOCs were investigated.

Experimental

The CeO₂–ZrO₂–SnO₂/ γ -Al₂O₃ supports were prepared by a coprecipitation method. Tin(II) oxalate $(Sn(C_2O_4))$ was dissolved into a mixture of γ -Al₂O₃ powder (DK Fine, AA-300), aqueous solutions of $1.0 \text{ mol } L^{-1} \text{ Ce}(NO_3)_3$ and $0.1 \text{ mol } L^{-1}$ $ZrO(NO_3)_2$ in a stoichiometric ratio. The CeO₂-ZrO₂-SnO₂ content was adjusted to be 16 wt % of the total support and the molar ratio of Ce:Zr:Sn were controlled to be 80:20:0, 76:19:5, 72:18:10, 68:17:15, and 64:16:20, respectively. The pH of the aqueous mixture was adjusted to 11 by the dropwise addition of aqueous ammonia (5%). After stirring for 12h at room temperature, the resulting precipitate was collected by filtration, washed several times with deionized water, and then dried at 80 °C for 6 h. The sample was heated at 600 °C for 1 h in an ambient atmosphere. Supported platinum catalysts (Pt/CeO₂- $ZrO_2-SnO_2/\gamma-Al_2O_3$) were prepared by impregnating the $CeO_2 - ZrO_2 - SnO_2 / \gamma - Al_2O_3$ supports with a platinum colloid stabilized with PVP (Tanaka Kikinzoku Kogyo Co., Ltd.). After impregnation, the catalyst was dried at 80 °C for 12 h and then finally calcined at 500 °C for 4 h. The amount of Pt in the catalyst was adjusted in the range of 5-12 wt %. In addition, the Pt(7 wt %)/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.9}(16 wt %)/ γ -Al₂O₃ catalyst was also prepared by a similar procedure for comparison.²²

The compositions of the catalysts were analyzed with an X-ray fluorescence spectrometer (XRF; Rigaku, ZSX-100e). The crystal structures of the catalysts were identified by X-ray powder diffraction (XRD; Rigaku, SmartLab) analysis using CuKa radiation (40 kV, 30 mA). Brunauer-Emmett-Teller (BET) specific surface area was measured using nitrogen adsorption at -196 °C (Micromeritics Tristar 3000). X-ray photoelectron spectroscopy (XPS; ULVAC 5500MT) was performed at room temperature using Mg K α radiation (1253.6 eV). The effect of charging on the binding energies was corrected with respect to the C1s peak at 284.6 eV. The temperature-programmed reduction (TPR) measurements were carried out under a flow of pure H_2 (80 mL min⁻¹) at a heating rate of 5°C min⁻¹ using a gas chromatograph with a thermal conductivity detector (TCD; Shimadzu GC-8AIT). Following the TPR experiments, the total oxygen storage capacity (OSC) was measured using a pulse-injection method at 427 °C (700 K). The total OSC value was estimated as the uptake of O_2 from the O_2 pulse by comparing the TCD signals obtained with and without the catalyst. Dynamic OSC measurements were also performed by increasing the temperature in a stepwise manner between 50 and 300 °C. The catalyst was first heated in a flow of He (100 mL min⁻¹) at each temperature, and then pulses of H_2 (0.2 mL) and O_2 (0.2 mL) were alternately injected over the catalyst. The average amount of oxygen incorporated into the catalyst was evaluated as the dynamic OSC by comparing the peak area detected by the TCD with that obtained in the absence of the catalyst.

The oxidation activity for VOCs was tested in a conventional fixed-bed flow reactor consisting of a 10 mm diameter quartz glass tube. The feed gas was composed of 0.09 vol %



Figure 1. XRD patterns of the Pt(7 wt %)/Ce_{0.8(1-x)}-Zr_{0.2(1-x)}Sn_xO_{2.0}(16 wt %)/ γ -Al₂O₃ (0 $\leq x \leq$ 0.20) catalysts.

toluene (space velocity (S.V.) = $12000 L kg^{-1} h^{-1}$), 1 vol % acetaldehyde (S.V. = $10000 L kg^{-1} h^{-1}$), or 1 vol % ethylene (S.V. = $12000 L kg^{-1} h^{-1}$) in air balance. Prior to the measurements, the catalysts were heated at $200 \,^{\circ}$ C for 2 h in a flow of Ar (20 mL min^{-1}) to remove water molecules adsorbed on the surface of the catalyst. The catalytic activity was evaluated in terms of VOCs conversion. The gas composition after the reaction was analyzed using a gas chromatograph with TCD (Shimadzu GC-8AIT) and a flame ionization detector (FID; Shimadzu GC-8AIF).

Results and Discussion

Figure 1 shows XRD patterns of the Pt(7 wt %)/Ce_{0.8(1-x)}-Zr_{0.2(1-x)}Sn_xO_{2.0}(16 wt %)/ γ -Al₂O₃ (0 $\leq x \leq$ 0.20) catalysts. The XRD patterns of the catalysts contain diffraction peaks of only the cubic fluorite-type oxide, metallic platinum, and γ -Al₂O₃ and no crystalline impurities were observed. The inset shows the enlargement of the pattern in the 2 θ range from 54 to 60°. The diffraction peaks assigned to the cubic fluorite structure slightly shifted to higher angles with increasing the Sn⁴⁺ content, suggesting that Ce⁴⁺ (ionic radius: 0.097 nm)²⁷ and Zr⁴⁺ (ionic radius: 0.084 nm)²⁷ in CeO₂–ZrO₂ were partially substituted with smaller Sn⁴⁺ (ionic radius: 0.081 nm)²⁷ to form solid solutions.

The composition and BET specific surface area of the $Pt(7 \text{ wt } \%)/Ce_{0.8(1-x)}Zr_{0.2(1-x)}Sn_xO_{2.0}(16 \text{ wt } \%)/\gamma$ -Al₂O₃ ($0 \le x \le 0.20$) catalysts are summarized in Table 1. The compositions of the catalysts were confirmed by the XRF analysis to be in good agreement with their stoichiometric values within the experimental errors. The BET specific surface area of the catalysts decreased with increasing Sn content, probably due to the lower melting point of SnO₂ (1630 °C)²⁸ compared to CeO₂ (2445 °C)²⁹ and ZrO₂ (2710 °C).²⁹

Figure 2 presents the temperature dependencies of toluene oxidation over the Pt(7 wt%)/Ce_{0.8(1-x)}Zr_{0.2(1-x)}Sn_xO_{2.0}-(16 wt%)/ γ -Al₂O₃ (0 $\leq x \leq$ 0.20) catalysts. It was confirmed that only CO₂ and H₂O were produced by the complete

Table 1. Composition and BET Surface Area of the Pt(7 wt %)/Ce_{0.8(1-x)}Zr_{0.2(1-x)}Sn_xO_{2.0}(16 wt %)/ γ -Al₂O₃ (0 $\leq x \leq 0.20$) Catalysts

	BET
Catalyst composition	surface area
	$/m^{2}g^{-1}$
$Pt(7 \text{ wt } \%)/Ce_{0.79}Zr_{0.21}O_{2.0}(17 \text{ wt } \%)/\gamma-Al_2O_3$	158
$Pt(7 \text{ wt }\%)/Ce_{0.75}Zr_{0.20}Sn_{0.05}O_{2.0}(17 \text{ wt }\%)/\gamma-Al_2O_3$	155
$Pt(7 \text{ wt }\%)/Ce_{0.71}Zr_{0.19}Sn_{0.10}O_{2.0}(16 \text{ wt }\%)/\gamma-Al_2O_3$	151
$Pt(7 \text{ wt }\%)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 \text{ wt }\%)/\gamma-Al_2O_3$	149
$Pt(7wt\%)/Ce_{0.64}Zr_{0.16}Sn_{0.20}O_{2.0}(17wt\%)/\gamma\text{-Al}_2O_3$	147



Figure 2. Temperature dependencies of toluene oxidation over the Pt(7 wt %)/Ce_{0.8(1-x)}Zr_{0.2(1-x)}Sn_xO_{2.0}(16 wt %)/ γ -Al₂O₃ (0 $\leq x \leq$ 0.20) catalysts.

oxidation of toluene, and no toluene-derived compounds were detected as by-products with a gas chromatography mass spectrometer. The toluene oxidation activity was significantly enhanced by the incorporation of SnO₂ into the CeO₂–ZrO₂ lattice as a promoter, and the highest activity was obtained for the Pt(7 wt %)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 wt %)/ γ -Al₂O₃ catalyst, over which the complete oxidation of toluene to carbon dioxide and steam was confirmed at 120 °C.

The temperature dependencies of the oxidation activity of the catalysts with different amount of Pt in the Pt/Ce_{0.68}Zr_{0.17}-Sn_{0.15}O_{2.0}(16 wt %)/ γ -Al₂O₃ catalysts are shown in Figure 3. The optimum amount of Pt to bring the highest activity to the catalysts was approximately 10 wt %, and, as a result, toluene was completely oxidized at a temperature as low as 110 °C. For catalysts containing larger amounts of Pt, the efficacy of the metal (Pt) dispersion was decreased by agglomeration and particle growth of the Pt particles. As a result, it can be concluded that excess amounts of Pt cause deterioration in the catalytic activity in these systems. A similar result was observed in the case of toluene oxidation over the Pt/CeO₂–ZrO₂–Bi₂O₃/ γ -Al₂O₃ catalysts, and agglomeration of the platinum particles was ascertained by the transmission electron micrographs.²²

Figure 4a depicts the temperature dependencies of toluene oxidation over the Pt(10 wt %)/Ce_{0.79}Zr_{0.21}O_{2.0}(16 wt %)/ γ -Al₂O₃ (Pt/CZ/Al₂O₃), Pt(7 wt %)/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.9}-(16 wt %)/ γ -Al₂O₃ (Pt/CZB/Al₂O₃), and Pt(10 wt %)/Ce_{0.68}-Zr_{0.17}Sn_{0.15}O_{2.0}(16 wt %)/ γ -Al₂O₃ (Pt/CZS/Al₂O₃) catalysts. The amount of Pt(7 wt %) on the Pt/CZB/Al₂O₃ catalyst was



Figure 3. Temperature dependencies of toluene oxidation over the $Pt(5-12 \text{ wt }\%)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 \text{ wt }\%)/\gamma-Al_2O_3$ catalysts.

optimized for the most effective toluene oxidation.²² The toluene catalytic activity was remarkably promoted by the Bi₂O₃ or SnO₂ doping into the CeO₂–ZrO₂ lattice as a promoter. Among these catalysts, the highest activity was obtained for the Pt/CZS/Al₂O₃ catalyst, over which the toluene oxidation activity appeared from 70 °C and the complete oxidation of toluene was realized at a temperature as low as 110 °C, which is the lowest temperature ever reported. The reason for the composition dependence of the oxidation activity of the catalyst can be ascribed to the different reducibilities of the supports, as discussed in detail later. Furthermore, the temperature dependencies of acetaldehyde and ethylene oxidation over the Pt/CZ/Al₂O₃, Pt/CZB/Al₂O₃, and Pt/CZS/Al₂O₃ catalysts are shown in Figures 4b and 4c, respectively. Total oxidation of acetaldehyde and ethylene into CO₂ and steam was confirmed by gas chromatography-mass spectrometry as in the case of toluene. Also for acetaldehyde and ethylene oxidation, the introduction of CeO₂-ZrO₂-SnO₂ as the promoter was highly effective to enhance the catalytic activity. As a result, the complete oxidation of acetaldehyde and ethylene on the Pt/CZS/Al₂O₃ catalyst was realized at temperatures as low as 140 and 55 °C, respectively.

The oxidation state of Sn in the Pt/CZS/Al₂O₃ catalyst was confirmed by XPS analysis. The XPS of Sn 3d core-level is shown in Figure 5. The binding energies of Sn $3d_{3/2}$ (494.7 eV) and Sn $3d_{5/2}$ (486.3 eV) can be assigned to Sn⁴⁺ in SnO₂³⁰ while no peaks that would suggest the presence of other oxidation states of Sn were observed.

As mentioned above, the results in Figure 4 suggest that the oxidation activity of the catalyst depends on the reducibility of the catalyst support. Indeed, we demonstrated that the CO oxidation activity is correlated with the reducibility of the support.³¹ Temperature-programmed reduction profiles using hydrogen (H₂-TPR) were measured for comparison of the reduction behavior of the Ce_{0.79}Zr_{0.21}O_{2.0}(16 wt %)/ γ -Al₂O₃ (CZ/Al₂O₃), Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.9}(16 wt %)/ γ -Al₂O₃ (CZB/ Al₂O₃), and Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 wt %)/ γ -Al₂O₃ (CZS/ Al₂O₃) supports as shown in Figure 6. The profile of CZ/ Al₂O₃ did not exhibit any noteworthy reduction peak in the temperature range below 200 °C. In contrast for CZB/Al₂O₃, the reduction initiated from 60 °C and a significant reduction



Figure 4. Temperature dependencies of (a) toluene, (b) acetaldehyde, and (c) ethylene oxidation over the Pt/CZ/ Al₂O₃, Pt/CZB/Al₂O₃, and Pt/CZS/Al₂O₃ catalysts.

peak was observed at 97 °C. This promotion of the reduction can be attributed to the high reducibility of Bi_2O_3 and the formation of oxide anion vacancies by partially replacing the Ce^{4+} and Zr^{4+} sites with Bi^{3+} ion to form solid solutions, leading to the enhancement of the oxide anion conductivity.^{16,17} In the case of CZS/Al₂O₃, furthermore, the oxygen release began at a temperature as low as 30 °C, and a specific reduction peak was observed at 95 °C. Accordingly, the introduction of SnO₂ into the CeO₂–ZrO₂ lattice was remarkably more effective than that of Bi_2O_3 to enhance the reducibility of the support at lower temperatures, corresponding to high oxidation activity in the low-temperature region below



Figure 5. XPS of the Sn 3d core-level of the Pt/CZS/Al₂O₃ catalyst.



Figure 6. TPR profiles of the CZ/Al₂O₃, CZB/Al₂O₃, and CZS/Al₂O₃ samples.

80 °C. In addition, the total oxygen storage capacity (OSC) relevant to the overall reducibility of the catalyst was evaluated by injecting oxygen into the sample reduced by the TPR experiments. As a result, the total OSC value of CZS/Al₂O₃ was 198 µmol-O₂ g⁻¹, which is significantly higher than those of CZ/Al₂O₃ (107 µmol-O₂ g⁻¹) and CZB/Al₂O₃ (130 µmol-O₂ g⁻¹). The improvement of the oxygen release and storage abilities can be attributed to the enhancement of the redox activity by the synergistic effects of Ce⁴⁺/Ce³⁺ and Sn⁴⁺/Sn^{2+, 24-26}

The total OSC expresses the maximum oxygen storage capacity, while the dynamic OSC is correlated to the most reactive and readily available oxygen species on or near the surface of the catalyst. The dynamic OSC, which is defined as the amount of oxygen released and stored by every reduction and oxidation cycle in a short time-scale, can be estimated by alternating pulse injections of H₂ and O₂ every 20 s. As demonstrated in Figure 7, the responses of the CZS/Al₂O₃ sample to rapid reduction and oxidation was considerably higher than those of the CZ/Al₂O₃ and CZB/Al₂O₃ samples at each temperature. In particular, the dynamic OSC value of the CZS/Al₂O₃ sample (0.565 μ mol-



Figure 7. Dynamic oxygen storage capacities of the CZ/ Al₂O₃, CZB/Al₂O₃, and CZS/Al₂O₃ samples.

 $O_2 g^{-1}$) at 50 °C was more than twice as high as that of the CZB/Al₂O₃ sample (0.260 µmol-O₂ g⁻¹) as shown in the enlargement of Figure 7, corresponding to high oxidation activity for ethylene in the low-temperature region around 50 °C. It is suggested that the redox activity on the surface of the catalyst is enhanced by the incorporation of SnO₂ into the CeO₂–ZrO₂ lattice. From these results, we conclude that the VOCs oxidation activity is strongly correlated with the reducibility of the support, and, as a result, complete oxidation of VOCs can be realized at lower temperatures over the Pt/CeO₂–ZrO₂/ γ -Al₂O₃ and Pt/CeO₂–ZrO₂–Bi₂O₃/ γ -Al₂O₃ catalysts.

Conclusion

Complete oxidation activities of VOCs such as ethylene, toluene, and acetaldehyde were evaluated over the Pt/CeO₂– ZrO₂–SnO₂/ γ -Al₂O₃ catalysts prepared using a coprecipitation method. These VOCs were completely oxidized into CO₂ and steam (H₂O) over the Pt/CeO₂–ZrO₂–SnO₂/ γ -Al₂O₃ catalysts at low temperatures without the formation of by-products. The oxidation activity is correlated with the reducibility and oxygen storage capacity of the catalyst support, and these properties are significantly enhanced by the introduction of SnO₂ into the CeO₂–ZrO₂ lattice. As a result, complete oxidation of ethylene, toluene, and acetaldehyde was realized at temperatures as low as 55, 110, and 140 °C on a Pt(10 wt %)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}-(16 wt %)/ γ -Al₂O₃ catalyst, respectively.

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