Catalytic combustion-type CO sensor applying Pt loaded CeO$_2$–ZrO$_2$–ZnO solid solution

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A catalytic combustion-type carbon monoxide gas sensor was fabricated by employing a Pt-loaded cerium oxide–zirconium oxide–zinc oxide solid solution as the oxidizing catalyst. Since the present catalyst can completely oxidize CO at temperature as low as 25°C. As a result, the sensor with this catalyst exhibits superior performance for the CO detection at 60°C, a temperature which is substantially lower than that (>400°C) required for the operation of sensors with the conventional CO oxidation catalyst of Pt/Al$_2$O$_3$ or Pd/Al$_2$O$_3$.

Key-words : Gas sensor, Carbon monoxide, Catalytic combustion-type, Low-temperature operation, Rare earth oxide

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1. Introduction

Carbon monoxide (CO) is one of well-known toxic gases causing serious damage for health when it is inhaled, even at relatively low concentrations. Exposure to high concentration of CO gas (especially over 0.15%) can be fatal because the binding ability of the CO molecule to hemoglobin is approximately 250 times higher than that of O$_2$. Since CO is colorless and odorless gas, smart detection tool is required to prevent an accident of CO poisoning. The settlement of compact and inexpensive CO gas sensors at sites with the potential for elevated CO gas concentrations is so effective to prevent such accidents. Therefore, the development of compact CO gas sensors is desired.

Until now, various types of compact CO gas monitoring devices have been developed, such those based on semiconductor,\textsuperscript{1,2) potentiostat\textsuperscript{3) and catalytic combustion.\textsuperscript{4,5) Semiconductor-type CO gas sensors are based on electrical resistance changes caused by CO gas adsorption on the semiconductor surface and exhibit stable performance. However, they have a potential drawback of poor selectivity caused by the adsorption of the ambient gas species with CO on the semiconductor surface. Potentiostat-type CO sensors exhibit selective CO detection, but the liquid electrolyte in the device eventually evaporates and cannot operate over prolonged time of periods. In contrast, catalytic combustion-type CO gas sensors are consist of only solid component, that is, a Pt coil combined with CO oxidation catalyst, realizing a simple detection system. Therefore, they are capable of stable and rapid sensing performance over long periods. Similar to the semiconductor-type sensors, catalytic combustion-type sensors detect CO gas via resistance change of the Pt coil. Since this resistance change is resulted from the heat generated by combustion of CO gas on the catalyst loaded on the Pt coil, selective CO gas detection can be achieved by employing an appropriate catalyst that oxidizes only CO gas over a given temperature range. However, there is a fatal problem for the conventional catalytic combustion-type CO gas sensors. Although the conventional sensors used Pt or Pd loaded Al$_2$O$_3$, (Pt/Al$_2$O$_3$ or Pd/Al$_2$O$_3$) as the CO oxidizing catalyst, these catalysts require high temperatures over 400°C to completely oxidize CO gas. At such elevated temperatures, burnable gases are all oxidized, and as a result, the selectivity of the conventional catalytic combustion-type sensors is poor. To solve this problem, it is necessary to employ novel CO oxidation catalyst that can lower the operation temperature of the sensor where CO can only be oxidized.

In our previous studies on the environmental remediation catalysts, we developed Pt loaded CeO$_2$–ZrO$_2$–MO$_3$ (M = Bi, Sn, Zn) solid solutions supported on γ-Al$_2$O$_3$ which exhibited high oxidation performance for various volatile organic compounds\textsuperscript{6) at lower temperatures than those for previously reported catalysts. We therefore considered that the Pt loaded CeO$_2$–ZrO$_2$–MO$_3$ solid solution might also effectively oxidize CO gas at relatively low temperatures, and based on this strategy, we have demonstrated that the catalytic combustion-type sensor applied the Pt loaded CeO$_2$–ZrO$_2$–SnO$_2$ solid as the CO oxidizing catalyst exhibited reproducible and linear response toward CO gas concentration at 70°C.\textsuperscript{7}

In the present study, we selected Pt loaded CeO$_2$–ZrO$_2$–ZnO as a new CO oxidizing catalyst. ZnO is also known as an excellent semiconducting material similar to SnO$_2$, and enough CO oxidizing activity is also expected for the Pt loaded CeO$_2$–ZrO$_2$–ZnO solid as same as the Pt loaded CeO$_2$–ZrO$_2$–SnO$_2$. Here, we devised the catalytic combustion-type CO sensor incorporating the 10 wt % Pt/Ce$_{0.76}$Zr$_{0.19}$Zn$_{0.05}$O$_{1.95}$ and investigated its CO sensing performance.

2. Experimental

The Ce$_{0.76}$Zr$_{0.19}$Zn$_{0.05}$O$_{1.95}$ solid solution was prepared via sol–gel method. After mixing a stoichiometric amount of aqueous solutions of 1.0 mol dm$^{-3}$ Ce(NO$_3$)$_3$, 0.1 mol dm$^{-3}$ ZrO(NO$_3$)$_2$·2H$_2$O and 1.0 mol dm$^{-3}$ Zn(NO$_3$)$_2$, polyvinylpyrrolidone (PVP) was added into mixed solution. After the solution was stirring at 80°C for 6 h, the solvent was removed at 180°C and the resulting powder was dried at 80°C for 6 h. The obtained powder was heated at 350°C for about 8 h to remove residual carbon without occurring any solid state reactions. After then, obtained powder was calcined at 500°C for 1 h in atmospheric air. The 10 wt %
Pt/Ce0.76Zr0.19Zn0.05O1.95 was obtained by impregnating the Ce0.76Zr0.19Zn0.05O1.95 solid support with a colloidal platinum solution stabilized with PVP. The catalyst was subsequently dried at 80°C for 6 h and then calcined at 400°C for 4 h in air to remove PVP and ethanol.

Sample characterization was performed using X-ray fluorescence (Rigaku, ZSX100e) and X-ray powder diffraction (XRD) (Rigaku, SmartLab). The CO oxidation activity was investigated using a conventional fixed-bed flow reactor, by flowing 1,000 ppm CO in air at a rate of 67 cm³ min⁻¹ over 0.2 g of catalyst, equivalent to a space velocity (S.V.) over the catalyst of 20,000 cm³ h⁻¹ g⁻¹. Prior to these activity measurements, the catalyst was heated at 200°C for 2 h under an argon flow. The oxidation activity was evaluated by the average amount of the approximately-constant CO conversion at each temperature maintained for over half an hour. The gas composition after the reaction was analyzed by using a gas chromatograph with a thermal conductivity detector (TCD; Shimadzu, GC-8AIF).

The catalytic combustion-type CO gas sensor was fabricated using a coil formed from 30 µm diameter Pt wire. A quantity of the 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst was dispersed in ethylene glycol to form a slurry. The slurry was carefully put onto Pt coil by using a small ink brush, and the coil was subsequently heated at approximately 150°C for 10 min by applying voltage to the Pt coil to drive off the ethylene glycol and sinter the catalyst. Above process was repeated until the amount of catalyst loaded on the Pt coil reached to ca. 0.6 mg, which is considered to be an enough quantity of catalyst fully covers the Pt coil. The performance of the sensor was assessed with an electrometer (Advantest, R8240) to measure the DC voltage generated while the Pt coil by using oxygen migrated from inside of the lattice to surface by using oxygen migrated from inside of the lattice to surface. Regardless of the CO gas concentration, the total gas conductivity detector (TCD; Shimadzu, GC-8AIF).

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3. Results and discussion

Figure 1 shows the XRD pattern of the 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 solid. Only peaks assigned to the cubic fluorite-type oxide and metallic Pt were observed with no crystalline impurities. The diffraction peaks assigned to the cubic fluorite-type structure were shifted slightly to higher angles as compared to the pattern for the mother solid of Ce0.76Zr0.19O1.95, suggesting that the Ce⁴⁺ (ionic radius: 0.097 nm) and Zr⁴⁺ (0.084 nm) ions presented in CeO₂–ZrO₂ (calculated average ionic radius of 0.8Ce⁴⁺–0.2Zr⁴⁺: 0.0944 nm) have been partially substituted with smaller Zn²⁺ ions (0.09 nm) to form a solid solution. Furthermore, we have confirmed the composition of the synthesized solid by X-ray fluorescence analysis, and the cationic ratio in the solid prepared is almost identical to the expected one from the mixing ratio of the reactants. From this result, it was confirmed that the 10 wt % Pt loaded cerium oxide–zirconium oxide–zinc oxide (10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95) solid solution was successfully obtained.

Figure 2 depicts the CO conversion properties of the 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst. The 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst shows CO oxidizing activity even at −30°C and complete oxidation is realized at such a low temperature of 25°C. Since the sensor with 10 wt % Pt/Ce0.68Zr0.17Sn0.15O2.0 solid7) which exhibited a complete CO oxidation at 65°C realized a sensor operation at 70°C, the catalytic combustion-type CO sensor with the 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst can be also expected to operate at low temperatures. Such higher CO oxidation activity of 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst compared with the 10 wt % Pt/Ce0.68Zr0.17Sn0.15O2.0 catalyst is considered to be caused by the high amount of oxide ion vacancy in the solid which is produced by the lower valence state of Zn (+2) compared to that of Sn (+4). High amount of oxide ion vacancy would accelerate the oxidation reaction on the catalyst surface by using oxygen migrated from inside of the lattice to the surface.

Figure 3(a) presents a representative sensor response curve obtained when the CO gas concentration was varied from 0 to 500 ppm and vice versa in a step-by-step manner at the temperature of 70°C. The sensor signal [(Rgas – Rair)/Rair] changed smoothly and reproducibly with varying CO gas concentration. The response time calculated from the response curve was estimated at approximately 3–4 min, which was similar to the sensor with the 10 wt % Pt/Ce0.68Zr0.17Sn0.15O2.0 solid.7) Figure 3(b) shows the CO gas concentration dependence of sensor signal obtained at 70°C. The sensor signal changed linearly with varying CO gas concentration, and the same value was obtained for identical CO gas levels both in increasing and in decreasing the concentration, suggesting that the sensor response is both stable and reproducible. These results show that the sensor incorporating the 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 solid as the CO oxidation catalyst can detect CO gas quantitatively at 70°C.

Because the operation temperature of the sensor is expected to lower by applying the 10 wt % Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst from the result of CO oxidizing performance (Fig. 2), we
investigated the sensing performance at 60°C at which the sensor with 10 wt% Pt/Ce0.76Zr0.19Zn0.05O1.95 solid could not show a meaningful response in its sensor signal. Figure 4 depicts the CO gas concentration dependencies of sensor signal obtained at 60 and 70°C. Even at 60°C, a linear deviation in sensor signal was clearly observed, similar to the case at 70°C, although electrical noise (The noise is presented as bars in Fig. 4.) was higher than that at 70°C (In the case for the electrical noise at 70°C, the bars are also shown in Fig. 3. However, they are hindered in the marks because of too small deviation.). Moreover, the sensitivity is almost the same as that at 70°C, indicating that the present sensor can operate even at 60°C which is 10°C lower than the threshold temperature of the previous sensor with the 10 wt% Pt/Ce0.68Zr0.17Sn0.15O2.0 solid. This is because the higher CO oxidizing performance of the 10 wt% Pt/Ce0.76Zr0.19Zn0.05O1.95 catalyst compared with the 10 wt% Pt/Ce0.68Zr0.17Sn0.15O2.0 catalyst as displayed in Fig. 2. While the sensor with 10 wt% Pt/Ce0.76Zr0.19Zn0.05O1.95 is expected to operate at further lower temperature than 60°C, we could not measure a sensor signal because of high electrical noise. The electrical noise of the sensor is originated by Pt coil, and therefore, it is expected that the sensor operation at around room temperature by using the potential materials with low electrical resistance instead for Pt at room temperature or by lowering electrical resistance of Pt coil.

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