

Catalytic properties of Pd/CeO₂ and Pd-Cu/CeO₂

Saki Shigenobu,¹ Hajime Hojo,² Hisahiro Einaga²

¹*Interdisciplinary Graduate School of Engineering, Kyushu University*

Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

²*Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University*

Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

Abstract

The effect of adding Cu to Pd catalysts (Pd/CeO₂, Pd/TiO₂, Pd/Al₂O₃) on their catalytic properties was investigated. The low-temperature oxidation activity of Pd/CeO₂ was superior to that of Pd/TiO₂ and Pd/Al₂O₃, and the Cu addition enhanced the CO oxidation activity in all temperature ranges. The structural changes of Pd/CeO₂ before and after sulfur poisoning were investigated by *in situ* XAFS. The sulfidation of the CeO₂ support was promoted by the Pd deposition.

1. Introduction

Regulations on factory and vehicle emissions are becoming increasingly stringent worldwide to achieve a sustainable society. Pd catalysts are a key material to purify these exhaust gases. However, there is a strong need to reduce the amount of Pd used because Pd is scarce and expensive. Furthermore, catalyst poisoning by sulfur content (e.g., SO₂ and H₂S) is an important issue in the industrial exhaust gas purification process. Because the catalytic performance of Pd catalysts after sulfur poisoning is seriously affected, therefore, it is necessary to develop a Pd catalyst with high activity and resistance to sulfur poisoning.

One way to improve the activity of the noble metal catalyst is to add transition metals. Our previous studies revealed that the co-deposition of transitional metals enhances the activity of TiO₂-supported noble metals for CO oxidation.^[1] In this study, we focused on Cu, which has high redox properties and attempted to improve the catalytic activity of Pd catalysts by the addition of Cu. Understanding the sulfur poisoning mechanism is essential for designing catalysts that are highly resistant to sulfur poisoning. However, the process has not been clarified. *in situ* X-ray absorption fine structure (XAFS) measurements can investigate the local structure of catalyst

under reaction condition. Therefore, *in situ* XAFS measurements under SO₂ gas flow were carried out to investigate the local structure change to elucidate the sulfur poisoning process.

2. Experimental

2.1. Catalyst preparation

Pd catalysts (Pd/TiO₂, Pd/Al₂O₃, Pd/CeO₂) and Pd-Cu co-deposition catalysts (Pd-Cu/TiO₂, Pd-Cu/Al₂O₃, Pd-Cu/CeO₂) were prepared by impregnation methods. For the preparation of catalysts, Pd(NO₃)₂ · 4NH₃ and (CH₃COO)₂Cu · H₂O were dissolved into water. The solution was added dropwise to the powders of catalyst support and evaporated to dryness at 60°C. The catalyst samples were dried, calcined, and then reduced in H₂ flow. The Pd loading was set to 1 wt %.

2.2. Catalysts characterisations

Catalytic CO oxidation was carried out with a fixed bed flow reactor. Catalyst samples were loaded in a U-shaped glass flow reactor, which was placed in a furnace for catalyst heating. Reaction gases (CO 0.5 %, O₂ 0.25 %, He-balance) were fed to the reactor with a flow rate of 100, 300 mL/min. The concentrations of CO₂ and CO were determined using GC-TCD. Prior to the reaction, the catalyst was heated at 300 °C in a He flow for 1 h. Reaction temperature was

set in the range of 90 to 250°C.

XAFS spectra were obtained using an *in situ* XAFS measurement cell at Kyushu University beamline (SAGA-LS BL-06). The catalysts were contacted with SO₂ containing gas (500 ppm of SO₂) at 500°C and then cooled down to room temperature for spectra measurements under the flow of He. Data reduction was performed with the software Athena and Artemis.

3. Results and discussion

Figure 1 shows the effect of Cu addition on the CO oxidation activity of the Pd catalyst. The light-off temperature of Pd/Al₂O₃ and Pd/TiO₂ was 150°C and 120°C, respectively. The CO oxidation activity of Pd/CeO₂ was higher than that of Pd/Al₂O₃ and Pd/TiO₂ in the low-temperature region (<180°C). The addition of Cu on Pd/CeO₂ enhanced the activity in both the low and high-temperature ranges. Pd-Cu/CeO₂ showed the highest CO oxidation activity. FTIR spectra of Pd/CeO₂ showed the peak of linearly coordinated CO on Pd around and bridge coordinated CO around. Both peaks of linearly coordinated CO and bridge coordinated CO on Pd-Cu/CeO₂ decreased significantly in the presence of CO oxidation reaction gas. This behavior is due to the desorption of CO on Pd by the CO oxidation reaction. Therefore, the addition of Cu to the Pd/CeO₂ promoted oxidative desorption of CO which had been adsorbed on Pd sites at low temperature.

Figure 2 shows the Ce L₃-edge XANES spectra of CeO₂ and Pd/CeO₂ in the presence of SO₂. CeO₂ and Pd/CeO₂ showed a peak attributed to Ce⁴⁺. The reduction of Ce⁴⁺ to Ce³⁺ occurred by SO₂. The change of peak to Ce³⁺ under SO₂ flow was remarkable for Pd/CeO₂. This shows the reduction of the support CeO₂ by SO₂ was promoted by the Pd deposition. When the reaction gas was changed to O₂ at 500°C, the XANES spectra did not change. This indicates that sulfurized CeO₂ support was not reoxidized by O₂. In addition, the peak of sulfide did not detect in Pd L₃-edge XANES spectra. This means no sulfide was formed on Pd by SO₂.

4. Conclusions

Pd/CeO₂ showed high CO oxidation activity at low temperature, and the oxidation activity of Pd-Cu/CeO₂ was enhanced in all temperature ranges. FTIR studies suggested that the addition of Cu enhances CO desorption on Pd by CO oxidation reaction. Therefore, the activity of CO oxidation was improved at low temperature. *in situ* XAFS analysis showed that the support CeO₂ of Pd/CeO₂ was more reduced by SO₂ than that of CeO₂ which did not supported Pd. The support CeO₂ reduced by SO₂ were not reoxidized by O₂.

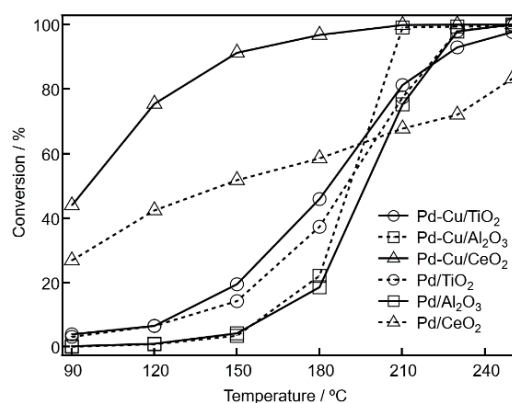


Figure 1. CO oxidation activity of Pd catalysts and Pd-Cu catalysts

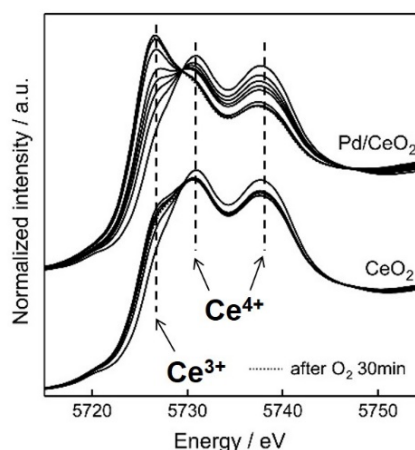


Figure 2. Ce L₃-edge XANES spectra of CeO₂ and Pd/CeO₂ under the flow of 500 ppm SO₂
Measurement time
CeO₂ : 20,40,60,80 min
Pd/CeO₂ : 20,40,60,80,120,240 min

Reference

[1] H. Einaga, R. Shiranita, H. Saito, and S. Hata, Chem. Lett., 44, 1786, 2015.