

## Role of ZrO<sub>2</sub> in SO<sub>2</sub>-poisoned Pd/(Ce-Zr)O<sub>2</sub> catalyst for CO oxidation

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### Introduction

The diesel oxidation catalysts (DOC) play an important role in oxidation of CO, hydrocarbons, and soluble organics emitted from diesel engines. However, since DOC is located in front of the engine, it is prone to deactivation under high-temperature and hydrothermal environment in the form of the PGM sintering and the collapse of surface area [1]. In addition, the small amount of sulfur in fuel gives rise to the gradual deterioration of catalytic performance [2].

CeO<sub>2</sub> is a key component to lower light-off temperature in DOC due to its excellent oxygen-storage capacity (OSC). However, it is easily degraded by heat and sulfur poisoning. The addition of ZrO<sub>2</sub> to CeO<sub>2</sub> aids in improving the physicochemical properties [3], such as OSC and thermal stability. This research aims at understanding the role of ZrO<sub>2</sub> component in SO<sub>2</sub>-poisoned Pd/(Ce-Zr)O<sub>2</sub> catalysts for CO oxidation, especially focusing on the effect of SO<sub>2</sub> adsorption/desorption treatment on the catalyst and its CO oxidation activity.

### Materials and Methods

Two materials (CeO<sub>2</sub>, Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>) were used as the model supports. 2 wt% Pd was impregnated by applying incipient wetness method with Pd(NO<sub>3</sub>)<sub>2</sub> aqueous solution. The impregnated samples were dried at 100°C and then calcined at 500°C. The calcined catalysts were hydrothermally treated at 750°C with the addition of H<sub>2</sub>O. Those samples were designated as “HTA (hydrothermal aging)”.

In sulfur adsorption process, the HTA samples were exposed to SO<sub>2</sub> containing gases at 300 °C. The sulfur aging samples were named as “SA (sulfur aging)”. The SA samples were heated from room temperature to 750°C under lean gas condition to desorb SO<sub>x</sub>, which were designated as “DeSO<sub>x</sub>”. The amount of sulfur on the samples after SO<sub>2</sub> adsorption/desorption was measured by using elemental analysis. The state of Pd in the samples was extensively analyzed by using the various characterization methods such as HRTEM, XRD and CO chemisorption.

CO oxidation for HTA, SA and DeSO<sub>x</sub> samples were conducted in a fixed-bed quartz tubular reactor. The samples were blended with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to dissipate the heat during the reaction. The reactants include CO, NO, H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub> with N<sub>2</sub> balance. The catalyst in the reactor was heated from 80 °C to 400 °C at a rate of 2°C/min. ULTRAMAT 23 gas analyzer(SIEMENS) was applied to measure CO, SO<sub>2</sub> concentration of outlet gas during CO oxidation and SO<sub>2</sub> adsorption/desorption experiments.

### Results and Discussion

Figure 1a shows CO light-off curves of differently treated Pd/CeO<sub>2</sub> and Pd/(CeZr)O<sub>2</sub> catalysts. After hydrothermal treatment, Pd/(CeZr)O<sub>2</sub> sample has slightly better CO oxidation ability than Pd/CeO<sub>2</sub> one (square symbol). Note that there is not much difference

in Pd dispersion between these two hydrothermally treated samples. However, the gap between the light-off temperatures of two samples becomes larger upon sulfation treatment, indicating the severe deactivation of Pd/CeO<sub>2</sub> by sulfur exposure (circle symbol). Elemental analysis revealed that the amount of sulfur deposited on Pd/(CeZr)O<sub>2</sub> sample was about 60% of that on the Pd/CeO<sub>2</sub> one implying less affinity of ZrO<sub>2</sub> to sulfur species. The fact that the amount of sulfur is proportional to that of Ce strongly suggests that Ce is considered to be an active site for SO<sub>x</sub> adsorption. It is noticeable that the textural properties of two sulfated samples are deteriorated, attributed to the pore blockage by sulfates. However, after desulfation treatment, it was found that the surface area of Pd/(CeZr)O<sub>2</sub> sample was recovered to some extent, while that of Pd/CeO<sub>2</sub> was severely worsened. As a result, the difference of CO light-off temperatures between two deSO<sub>x</sub> samples remained significant (triangle symbol), as revealed in Figure 1(a).

Figure 1b shows SO<sub>2</sub> evolution during DeSO<sub>x</sub> treatment of two sulfated samples. During the ramping, most of sulfur species were desorbed as SO<sub>2</sub> with the peak at 710 °C for both samples. However, it must be pointed out that the amount of SO<sub>2</sub> desorbed from Pd/CeO<sub>2</sub> was much larger than Pd/(CeZr)O<sub>2</sub> sample, which was well corresponding to the elemental analysis result described above. It confirms that Zr plays a crucial role in inhibiting SO<sub>2</sub> adsorption on CeO<sub>2</sub> sites, thus leading to be less sensitive to SO<sub>2</sub> poisoning in CO oxidation. Combined CO oxidation activity and deSO<sub>x</sub> results unambiguously proved the beneficial role of Zr in sulfur poisoning on Pd/(CeZr)O<sub>2</sub> catalyst compared with Pd/CeO<sub>2</sub>.

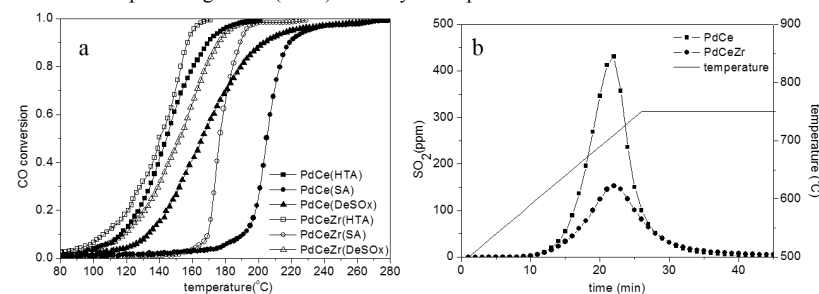


Figure 1. (a) Light-off curves of CO during CO oxidation for various Pd(2)/(CeZr)O<sub>2</sub> (open symbol) and Pd(2)/CeO<sub>2</sub> samples (filled symbol); (b) SO<sub>2</sub> desorption curve during deSO<sub>x</sub> treatment for sulfated Pd(2)/(CeZr)O<sub>2</sub> and Pd(2)/CeO<sub>2</sub> samples.

### Significance

The information about the role of ZrO<sub>2</sub> in Pd/(CeZr)O<sub>2</sub> catalyst related to SO<sub>2</sub> poisoning is of practical importance to develop a novel DOC catalyst with stronger sulfur resistance and improved CO oxidation activity.

### References

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