

Enhancing Durability and Low-Temperature Activity of Pd-based Diesel Oxidation Catalysts Using ZrO₂ Supports

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Introduction

Automotive oxidation catalysts will need to achieve high conversion of hydrocarbons (HCs) and carbon monoxide at increasingly low exhaust temperatures (e.g., 90+% below 150 °C) due to continued gain in internal combustion engine efficiency. Despite recent progress made in low-temperature catalyst development (e.g., Au and Ag nanoparticles combined with Cu, Mn, or Fe), critical challenges remain in implementing these novel materials into practice. For instance, new catalysts should maintain performance under harsh automotive environments with good thermal stability and resistance to poisons. Higher precious metal loading (e.g., Pt) can improve the low-temperature performance of current commercial catalysts, but that approach is cost-prohibitive. We have recently reported that Pt dispersed on ZrO₂-coated SiO₂ supports are excellent CO oxidation catalysts with good hydrothermal stability and sulfur tolerance [1]. In this study, we extended this ZrO₂-coated support concept to Pd, a popular metal due to its cost-competitiveness compared to Pt. Emphasis was put on determining the impact of ZrO₂ incorporation between Pd and SiO₂ on CO and C₃H₆ oxidation performance, hydrothermal stability, and inhibition of CO conversion by co-reactants of NO and C₃H₆.

Materials and Methods

Catalysts were prepared by impregnating 1 wt% Pd on ZrO₂-incorporated SiO₂ (Pd/ZrO₂-SiO₂) as described in [1], ZrO₂ (Pd/ZrO₂) and SiO₂ (Pd/SiO₂). The catalysts were characterized and evaluated for performance after calcination at 600 °C for 1 h, and hydrothermal aging at 800 and 900 °C for 16 h in a flow of 10% O₂ + 5% H₂O + Ar. The physicochemical properties were examined using ICP, N₂ sorption, XRD, TEM, and NO_x-TPD [1,2]. CO and C₃H₆ oxidation performance was measured from 60 to 600 °C at 5 °C/min (total flow rate 100 mL/min; 4000 ppm CO + 500 ppm NO + 1000 ppm C₃H₆ + 4% O₂ + 5% H₂O in Ar balance).

Results and Discussion

Strong interaction between metal and support led to a high Pd dispersion on ZrO₂ (83 m²/g) in contrast with Pd supported on relatively “inert” SiO₂ (402 m²/g). This explains in part significantly superior activity of Pd/ZrO₂ compared to Pd/SiO₂ (Figure 1) despite the large difference in surface area. Strong interaction between Pd and ZrO₂ was also manifested as remarkably high thermal stability as shown by good oxidation performance even after aging at 900 °C for 16 h. On the other hand, Pd/SiO₂ suffered significant performance loss due to Pd particle coarsening (XRD and TEM results not shown). These results suggest that, as in the case of Pt [1], coating a thin layer of ZrO₂ over high surface area SiO₂ can further increase the catalyst performance by combined effects of strong metal interaction of ZrO₂ and high surface area of SiO₂. Indeed, compared to Pd/SiO₂, Pd/ZrO₂-SiO₂ showed considerably higher CO and

C₃H₆ oxidation performance in all states studied. Note that despite the higher total surface area, the activity of Pd/ZrO₂-SiO₂ was lower than that of Pd/ZrO₂. This could be due to the difference in accessible ZrO₂ surface area: 55 m²/g for Pd/ZrO₂-SiO₂ vs. 83 m²/g for Pd/ZrO₂ estimated using a NO_x-TPD method (Figure 2) [2]; a higher ZrO₂ surface area leading to a higher Pd dispersion (TEM results not shown). The results indicate the possibility of further controlling Pd dispersion via ZrO₂-coating of SiO₂. In this talk, we will also discuss the impact of ZrO₂ on the interplay between CO, C₃H₆, and NO oxidation as well as adsorptive properties.

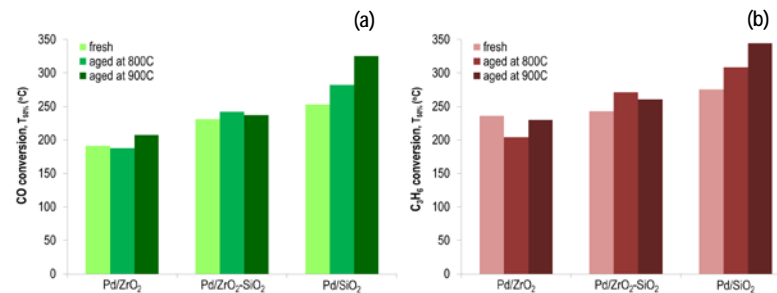


Figure 1: Light-off temperature of Pd/ZrO₂, Pd/ZrO₂-SiO₂, and Pd/SiO₂ catalysts in fresh and aged states: (a) CO and (b) C₃H₆ oxidation (catalyst loading=50 mg in all cases)

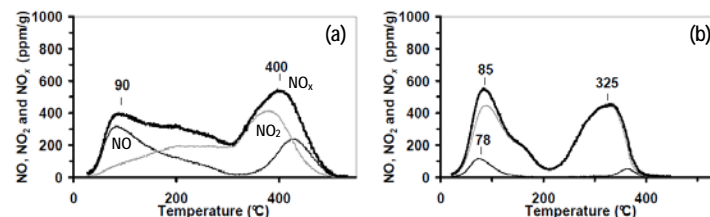


Figure 2: NO_x-TPD profiles obtained with fresh catalysts: (a) Pd/ZrO₂ and (b) Pd/ZrO₂-SiO₂. Adsorption at RT in a flow of 400 ppm NO + 8% O₂ + He balance; Temperature-Programmed Desorption from RT to 560 °C at 3 °C/min in a flow of 8% O₂ + He balance.

Significance

This work confirms the potential of developing Pd-based oxidation catalysts with enhanced durability and low-temperature activity using ZrO₂-SiO₂ supports. Controlling morphology and accessible area of the coated ZrO₂ layer appears critical to maximize the catalytic performance.

References

- Kim, M.-Y.; Choi, J.-S.; Toops, T.; Jeong, E.-S.; Han, S.-W.; Schwartz, V.; Chen, J. *Catalysts* **2013**, *3*, 88.
- Law, H. Y.; Blanchard, J.; Carrier, X.; Thomas, C. *Journal of Physical Chemistry C* **2010**, *114*, 9731.