Impact of ZrO2 Supports on the Durability and Low-Temperature Performance of Pd-based Diesel Oxidation Catalysts

Mi-Young Kim1, Eleni A. Kyriakidou1, Jae-Soon Choi*1, Todd J. Toops1, Cyril Thomas2, Andrew J. Binder1, James E Parks II1, Viviane Schwartz2, Jihua Chen1

1Oak Ridge National Laboratory, Oak Ridge, TN, USA
2UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, Paris, France
*chojis@ornl.gov

Introduction

Future diesel oxidation catalysts (DOC) will need to perform effectively at increasingly low exhaust temperatures; this so-called “150 °C challenge” (i.e., achieve over 90% conversion below 150 °C) arises from continued improvements in diesel engine efficiency. Recently, there has been progress made in designing catalytic materials with enhanced low-temperature oxidation performance (e.g., Au and Ag nanoparticles combined with Cu, Mn, or Fe). However, significant technical barriers exist for implementing these novel materials into practice. For instance, these novel materials tend to lose performance rather quickly under harsh reaction environments typical to automotive emissions control due to hydrothermal aging and poisoning. Alternatively, increasing 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 work, we extended this ZrO2-coated support concept to Pd, a popular metal due to its cost-competitiveness compared to Pt. Specifically, we assessed the impact of ZrO2 supports on CO and C3H6 oxidation, sulfur tolerance, and hydrothermal stability.

Materials and Methods

Catalysts were prepared by impregnating 1 wt% Pd on ZrO2-incorporated SiO2 (Pd/ZrO2-SiO2), ZrO2 (Pd/ZrO2) and SiO2 (Pd/SiO2). The physicochemical properties were examined using ICP, N2 sorption, XRD, TEM, and NH3-, CO2-, and NOx-TPD [1,2]. Catalytic performance was measured under the following conditions: temperature increased from 60 to 600 °C at 5 °C/min, total flow rate 100 mL/min, 0.4% CO / 0.05% NO / 0.1% C3H6 + 10% O2 + 5% H2O in Ar balance. The performance of Pd catalysts was evaluated in fresh, sulfated, and hydrothermally aged states, and compared with that of a commercial DOC.

Results and Discussion

As shown in the NH3 TPD profiles (Figure 1), ZrO2 presents acidic surfaces which strongly interact with Pd. Thus, incorporating ZrO2 onto relatively inert SiO2 significantly improved the Pd dispersion as in the case of Pt [1]. This explains in part significantly superior activity of Pd/ZrO2-SiO2 (and Pd/ZrO2) compared to Pd/SiO2 (Figure 2). Overall, Pd/ZrO2-SiO2 showed considerably higher CO and C3H6 oxidation performance than Pd/SiO2 in all states studied and under certain conditions outperformed a Pd/ Pt commercial DOC. Strong interaction between Pd and ZrO2 was also manifested as greater thermal stability as shown by good oxidation performance even after aging at 800 and 900 °C for 16 h (results not shown). In contrast, Pd/SiO2 suffered significant performance loss due to Pd particle coarsening. Note that despite the higher total surface area, Pd/ZrO2-SiO2 was less active and thermally less stable than Pd/ZrO2. This could be due in part 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 NOx-TPD method [2]. A higher and more complete coverage of SiO2 by ZrO2 could have led to a higher dispersion and stability of Pd. Contrary to the bulk ZrO2, the ZrO2 on SiO2 presented only weak basicity (CO2 TPD in Figure 1), which explains the greater S-tolerance of Pd/ZrO2-SiO2 (results not shown).

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.

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References