Applied Catalysis B: Environmental 187 (2016) 181–194

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Enhancing low-temperature activity and durability of Pd-based diesel oxidation catalysts using ZrO_2 supports☆

Mi-Young Kim[a,1], Eleni A. Kyriakidou[a], Jae-Soon Choi[a,*], Todd J. Toops[a], Andrew J. Binder[a], Cyril Thomas[b,c], James E. Parks II[a], Viviane Schwartz[d], Jihua Chen[d], Dale K. Hensley[d]

[a] *Fuels, Engines, and Emissions Research Center, Oak Ridge National Laboratory, Oak Ridge, TN, USA*
[b] *Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, Case 178, F-75252 Paris, France*
[c] *CNRS, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, Case 178, F-75252 Paris, France*
[d] *Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA*

ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form 6 January 2016
Accepted 10 January 2016
Available online 18 January 2016

Keywords:
Diesel oxidation catalyst
Palladium
Zirconia
Support
Sol-gel

ABSTRACT

We investigated the impact of ZrO_2 on the performance of palladium-based oxidation catalysts with respect to low-temperature activity, hydrothermal stability, and sulfur tolerance. Pd supported on ZrO_2 and SiO_2 were synthesized for a comparative study. Additionally, in an attempt to maximize the ZrO_2 surface area and improve sulfur tolerance, a Pd support with ZrO_2-dispersed onto SiO_2 was studied. The physicochemical properties of the catalysts were examined using ICP, N_2 sorption, XRD, SEM, TEM, and NH_3-, CO_2-, and NO_x-TPD. The activity of the Pd catalysts were measured from 60 to 600 °C in a flow of 4000 ppm CO, 500 ppm NO, 1000 ppm C_3H_6, 4% O_2, 5% H_2O, and Ar balance. The Pd catalysts were evaluated in fresh, sulfated, and hydrothermally aged states. Overall, the ZrO_2-containing catalysts showed considerably higher CO and C_3H_6 oxidation activity than Pd/SiO_2 under the reaction conditions studied. The good performance of ZrO_2-containing catalysts appeared to be due in part to high Pd dispersion resulting from strong Pd and support interaction. Another beneficial effect of strong interaction between Pd and ZrO_2 was manifested as a greater hydrothermal stability with good oxidation activity even after aging at 800 and 900 °C for 16 h. In contrast, Pd/SiO_2 suffered significant performance loss due to Pd particle coarsening. Although the Pd/ZrO_2-SiO_2 catalyst was not more active than Pd/ZrO_2, improved tolerance to sulfur was realized. Unlike the bulk ZrO_2 support, the ZrO_2-incorporated SiO_2 presented only weak basicity leading to a superior sulfur tolerance of Pd/ZrO_2-SiO_2. These results confirmed the potential of developing Pd-based oxidation catalysts with enhanced low-temperature activity and durability using ZrO_2-SiO_2 supports. Controlling morphology and accessible area of the dispersed ZrO_2 layer appeared critical to further maximize the catalytic performance.

1. Introduction

With ever tightening automotive emission standards, the role of oxidation catalysts becomes increasingly more important to remove CO and unburned hydrocarbons (HCs) from the engine exhaust gas as well as to enhance the performance of downstream NO_x control catalysts [1–3]. Moreover, as the efficiency of internal combustion engines is required to improve in response to US EPA's Corporate Average Fuel Economy (CAFE) mandates, the average exhaust gas temperature decreases making it more and more challenging to maintain high performance of aftertreatment catalysts. To comply with the future emission and fuel economy regulations, automotive catalysts should therefore achieve catalyst light-off (50% or higher conversion) at temperatures significantly lower than the current state of the art.

☆ Notice: This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

* Corresponding author.
E-mail address: choijs@ornl.gov (J.-S. Choi).
[1] Present address: Heesung Catalysts, 91, Somanggongwon-ro, Siheung-si, Gyeonggi-do 429-848, Republic of Korea.

http://dx.doi.org/10.1016/j.apcatb.2016.01.023
0926-3373/© 2016 Elsevier B.V. All rights reserved.

Despite recent progress made in the low-temperature catalyst development with novel formulations such as Au and Ag nanoparticles supported on metal oxides [4–7], critical challenges remain in implementing these novel materials into practice. For instance, new catalysts should be able to maintain high activity under harsh real automotive environments with good thermal stability and resistance to poisons [8,9]. Due to relatively good stability and activity, Pt and/or Pd supported on CeO_2-ZrO_2 added Al_2O_3 supports have been widely used as commercial oxidation catalysts [1,10]. The high affinity of Al_2O_3 toward sulfur, however, can lead to the formation of $Al_2(SO_4)_3$ with resultant performance degradation [11]. In addition, repeated high-temperature desulfation can lead to gradual sintering of metal components with resultant permanent activity loss. To further enhance the low-temperature activity and stability of Pt and Pd catalysts, recent research efforts have been devoted to developing novel approaches including the use of FeO_x as a support [12–14] and the encapsulation in core-shell nanostructures [15,16].

We have recently reported that Pt particles supported on ZrO_2-modifed SiO_2 were excellent CO oxidation catalysts with promising low-temperature activity, hydrothermal stability, and sulfur tolerance [17]. Covering SiO_2 surfaces with ZrO_2 via sol-gel method before Pt impregnation led to good dispersion and hydrothermal stability of Pt particles due to strong interaction between Pt and ZrO_2 phases. Furthermore, ZrO_2 incorporation generated surface acidity but negligible basicity, which explained the relatively low and weak sulfur uptake observed on Pt/ZrO_2-SiO_2. We also revealed that ZrO_2 increased the oxygen affinity of Pt leading to good catalytic activity of Pt/ZrO_2-SiO_2 in CO oxidation. In the present study, we extended this ZrO_2-incorporated SiO_2 support concept to Pd, a commonly-employed automotive catalyst that is traditionally less expensive than Pt by a factor of 2–3. For comparison, the catalytic properties of Pd/ZrO_2 and Pd/SiO_2 were studied. This paper will show that, as in the case of Pt, ZrO_2 incorporation on SiO_2 has positive effects on Pd as well with good metal dispersion, hydrothermal stability, sulfur tolerance, and CO and C_3H_6 oxidation activity. Directions for future research will be discussed to facilitate the development of strategies to maximize the potential of ZrO_2 supports.

2. Experimental

2.1. Preparation of Pd catalysts

Amorphous silica gel (Davisil Grade 635, pore size 60 Å, 60–100 mesh, Sigma-Aldrich) was used as a support for the preparation of Pd catalysts. ZrO_2 was incorporated on the silica surface following the procedure described in previous papers [17,18]. SiO_2 was first dehydrated with anhydrous ethanol (200 proof, ACS reagent, ≥99.5%, Sigma-Aldrich) and reacted at 80 °C for 3 h with zirconium(IV) *n*-propoxide (70% *w*/*w* in *n*-propanol, Alfa Aesar) dissolved in ethanol. The ratio between SiO_2, Zr precursor solution, and ethanol was 1: 2: 16 on a weight basis. The amount of Zr precursor molecules in the mixture corresponded to an average silanol concentration on the SiO_2 surface assumed to be 7.5 μmol/m^2 based on [19]. Since more than 1 silanol group would have reacted with a Zr precursor molecule during the sol-gel process, unreacted Zr precursor molecules were removed through ethanol washing. Subsequently, the filtrates were dried at 100 °C overnight and calcined at 500 °C for 2 h. The resulting ZrO_2-SiO_2 support was impregnated with a palladium (II) nitrate solution (12∼16 w/w, Alfa Aesar) by incipient wetness method to obtain a 1 wt% Pd loading. After the impregnation, the catalyst was dried at 100 °C in air and reduced in a flow of 10% H_2 in Ar at 500 °C for 2 h. The as-prepared catalyst was named as Pd/ZrO_2-SiO_2. For comparison, Pd catalysts supported on bare SiO_2 (Pd/SiO_2) and ZrO_2 (Pd/ZrO_2; ZrO_2 from Saint-Gobain) were also prepared by incipient wetness method (1 wt% loading).

2.2. Characterization

The Zr and Pd contents of the prepared catalysts were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; Optima 4300 DV, Perkin-Elmer, USA). The surface area and porosity of catalysts were determined using an automatic volumetric adsorption apparatus (Autosorb-1, Quantachrome, USA). The samples were evacuated at 200 °C for 2 h prior to exposure to nitrogen gas. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation and the pore volumes and average pore sizes were determined using the Barrett-Joyner-Halenda (BJH) method.

In powder XRD, the catalysts were ground into fine powder and placed on a zero background carbon plate of approximately 3.8 cm in diameter. The X-ray diffraction patterns of catalysts were recorded on a powder X-ray Diffractometer (XRD; X'Pert PRO, PANalytical, The Netherlands) operated at 45 kV and 40 mA using CuKα radiation ($K\alpha$ = 0.154178 nm) over a 2θ angle of 5–50 in a scan mode of 0.02° in 2s.

A Transmission Electron Microscope (TEM; LIBRA-120, Carl Zeiss, Germany) equipped with a LaB_6 filament was employed to examine the Pd dispersion. The acceleration voltage was 120 kV. The TEM samples were prepared by dropping ethanol suspension of Pd catalysts on a copper grid. The particle size of Pd was estimated from the digitized TEM image using analysis software (ImageJ, NIH, USA). The Scanning Electron Microscope (SEM; Merlin, Carl Zeiss, Germany) analyses were performed to examine the morphology of Pd catalysts, operating at an accelerating voltage of 30 kV. Elemental mapping analyses were also performed using Energy Dispersive X-ray Spectroscopy (EDS; Bruker Nano Gmbh with a XFlash 5030 detector, Germany) attached to the SEM.

NH_3- and CO_2-Temperature-Programmed Desorption (TPD) experiments were carried out with a flow reactor system. For each TPD experiment, 0.1 g of catalyst was placed between two quartz wool plugs in a U-shaped quartz tube (8 mm I.D.) and pretreated at 600 °C for 0.5 h in an Ar flow. After cooling to 100 °C, the catalyst was exposed to a flow of 2500 ppm NH_3 in Ar for 1 h, then to an Ar flow for 1 h. Desorption was carried out in an Ar flow from 100 to 600 °C with a temperature ramping rate of 10 °C/min. The total flow rate was 50 mL/min (STP) for all the steps. The procedure for the CO_2-TPD experiments was identical except that the adsorption was done in a flow of 1% CO_2 in Ar at 50 °C followed by a 1 h purge with the total flow rate of 100 mL/min (STP). Gas composition was continuously analyzed by a quadrupole mass spectrometer (RGA100, SRS, USA). The *m*/*z* values monitored were 15 for NH_3 and 44 for CO_2.

NO_x-TPD experiments were performed in a U-shaped quartz reactor (15 mm I.D.). The details were introduced in [20,21]. The catalysts were pretreated in a 20% O_2/He flow at 500 °C for 2 h with a flow rate of 100 mL/min. After cooling to room temperature, the catalysts were exposed to the adsorption mixture which consisted of 400 ppm NO and 8% O_2 in He. NO_x-TPD experiments were performed from room temperature to 560 °C at a heating rate of 3 °C/min under a mixture of 8% O_2 in He with a total flow rate of 230 mL/min (STP). The gas composition was continuously monitored at reactor outlet by a chemiluminescence NO_x analyzer (42C-HT, Thermo Environmental Instruments). The NO_x-TPD profiles were corrected for the weight loss due to dehydration of the samples.

2.3. Evaluation of catalytic performance in oxidation reactions

The catalytic performance of the prepared catalysts was evaluated for CO and C_3H_6 oxidation activity under simulated diesel