Chinese Journal of Catalysis 36 (2015) 639–648

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

Article

The effect of Pd precursor on Pd/$Ce_{0.67}Zr_{0.33}O_2$ catalysts for automotive emission control

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ARTICLE INFO

Article history:
Received 29 October 2014
Accepted 12 December 2014
Published 20 April 2015

Keywords:
Palladium precursor
Three-way catalyst
Noble metal-support interaction
Light-off catalytic performance

ABSTRACT

A Pd/CZ(NO) catalyst prepared with $Pd(NO_3)_2$ as the metal precursor exhibited the best catalytic performance for HC and CO elimination because of a higher oxygen storage capacity, abundant small Pd_n clusters and a strong Pd-support interaction that facilitated electron transfer from PdO_x particles to the CZ support. A Pd/CZ(NH) catalyst prepared with $Pd(NH_3)_4(NO_3)_2$ as the metal precursor exhibited good performance for NO and NO_2 elimination due to a higher Pd dispersion, abundant bigger Pd_n clusters and oxidized/metallic Pd coexistence. A Pd/CZ(Cl) catalyst prepared with H_2PdCl_4 as the metal precursor exhibited low catalytic activity due to a low Pd dispersion, weak Pd-support interaction, and the trace amount of CeOCl which inhibited oxygen vacancy creation. However, it showed good thermal stability, and benefited when an aging treatment removed the residual chlorine species and also promoted the interaction between PdO_x and the support.

1. Introduction

Three-way catalysts (TWCs) are extensively used to diminish pollutant emissions from gasoline automotives. The classical components of these systems are Rh, Pt, and Pd as active metals and Ce-Zr mixed oxide as promoter. The use of Pd as a single active metal in TWCs has recently gained increasing attention due to the high cost and scarcity of Rh and its high activity for oxidation reactions [1–5]. Since the simultaneous conversions of HC, CO, and NO_x are strongly affected by the oxygen partial pressure, Ce-Zr mixed oxides with an inherent property to release or adsorb oxygen have been widely used. Ceria is recognized as the chief oxygen storage material because of its facile redox cycling through the Ce^{3+}/Ce^{4+} cycle. It also has the ability to increase the thermal and structural stability of the catalyst carrier [6]. The introduction of zirconia into the ceria lattice can significantly increase the oxygen vacancies in the fluorite lattice by charge compensation, facilitate oxygen diffusion or transport and enhance the thermal stability of the solid solution [7]. Better results are obtained with $Ce_xZr_{1-x}O_2$ with x ranging from 0.6 to 0.8 [8,9]. It is well known that several factors influence the catalytic performance of supported Pd catalysts, such as the nature of the support, physicochemical properties of the metal particles, and metal-support interaction [1,3,10]. Among these factors, the configuration of the noble metal particles and noble metal-support interaction are considered to be two important factors affecting the amount and nature of the active sites [11]. Wang et al. [12,13] reported the effect of rare earth element (La, Nd, Pr, Sm and Y) doping on the three-way catalytic performance of Pd/$Ce_xZr_{1-x}O_2$ catalyst and showed that the addition of La or Pr promoted the interaction between PdO_x species and $Ce_xZr_{1-x}O_2$, resulting in increased thermal stability and oxygen storage capacity (OSC). In addition, we have studied the effects of CeO_2-ZrO_2 presence

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This work was supported by the National High Technology Research and Development Program of China (863 Program, 2011AA03A406) and Zhejiang Leading Team of Science and Technology Innovation (2009R50020).

DOI: 10.1016/S1872-2067(14)60264-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 4, April 2015

in Pd/Al_2O_3 catalysts on the redox behavior of PdO_x and their combustion activity [14]. The interaction between Ce-Zr and PdO_x controlled the growth of PdO_x particles and inhibited the decomposition of PdO to Pd^0, and the reoxidation ability of Pd^0 to PdO was greatly improved. Therefore, it increased thermal stability and the catalytic performance of the $Pd/Ce\text{-}Zr/Al_2O_3$ catalyst for methane combustion. Owing to the complexity of the large number of chemical reactions of TWCs, some arguments exist with regard to both the best configuration of the noble metal particle and the noble metal-support interaction.

The nature of the noble metal precursor utilized in the preparation of the catalyst is also considered to affect the noble metal-support interaction. Baylet et al. [15] studied the influence of the Pd precursor on the activity for CH_4 combustion and reported that using $Pd(acac)_2$ as the metal precursor gave a higher dispersion (> 30%), smaller Pd particle size (< 3 nm) and better catalytic performance than when using $Pd(NO_3)_2$. Panprant et al. [16] investigated the effects of the Pd precursor on hydrogenation and reported that using $PdCl_2$ as a precursor led to smaller Pd particles (< 4.5 nm), higher dispersion (> 26%) and hydrogenation activity than the catalysts prepared with $Pd(NO_3)_2$ or $Pd(OOCCH_3)_2$ precursors. However, the mechanism and the interaction between Pd precursor and the support are still not clear, and need to be further studied. On the other hand, for different reactions, the configuration of the noble metal particle and the different interaction between metal and the support also have a different effect on the catalytic performance.

The scope of this paper is to investigate the effect of the configuration of the noble metal particle and the metal-support interaction on the catalytic performance of TWC in automobile emission control. $Ce_{0.67}Zr_{0.33}O_2$ supported Pd catalysts that used three different Pd precursors, H_2PdCl_4 (chlorine-containing), $Pd(NO_3)_2$, and $Pd(NH_3)_4(NO_3)_2$ (chlorine-free), were prepared by impregnation. Their physical and chemical properties were characterized by X-ray diffraction (XRD), CO chemisorption, X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), H_2-temperature program reduction (H_2-TPR) and in situ diffuse reflectance infrared transform spectroscopy (DRIFTS). These techniques helped acquire some insight into what improved the catalytic performance for HC, CO and NO_x conversion in automobile exhaust.

2. Experimental

2.1. Catalyst preparation

$Ce_{0.67}Zr_{0.33}O_2$ (CZ, S_{BET} = 111 m^2/g) was prepared by the co-precipitation method [17]. Three $Pd/Ce_{0.67}Zr_{0.33}O_2$ catalysts with 1.0 wt% loading were prepared with CZ using H_2PdCl_4, $Pd(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ as metal precursor by incipient wetness impregnation at 30 °C. The samples were dried at 110 °C for 4 h and then calcined at 500 °C in air for 2 h. The sample prepared from the H_2PdCl_4 precursor was designated as Pd/CZ(Cl), and that prepared from $Pd(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ precursors were designated as Pd/CZ(NO) and Pd/CZ(NH). TWCs are frequently exposed to very high temperature above 1000 °C in the application, which is the main reason resulting in decreased catalytic performance [18,19]. Therefore, the catalysts were also treated at 1000 °C for 4 h to get aged catalysts designated as Pd/CZ(Cl)-a, Pd/CZ(NO)-a and Pd/CZ(NH)-a, respectively.

2.2. Catalytic performance test

The three-way catalytic performance tests were carried out in a fixed bed continuous flow reactor at atmospheric pressure. 0.2 ml catalyst (0.3–0.45 mm, 0.276 g) was used. The reaction mixture containing NO (0.121%), NO_2 (0.034%), C_3H_6 (0.067%), C_3H_8 (0.033%), CO (0.748%), O_2 (0.745%) and balance Ar was fed to the reactor at a GHSV of 43000 h^{-1}. The total flow rate was 143 ml/min. The effluent gas was analyzed by an online Fourier transform infrared spectrophotometer (BRUKER EQ55) equipped with a multiple reflection transmission cell (Infrared Analysis Inc.; path length 10.0 m). All spectra were taken at a resolution of 2 cm^{-1} using 128 scans [20].

2.3. Characterization techniques

XRD measurement was performed on an ARL X'TRA X-ray diffractometer (Thermo Electron Co.), operating at 40 kV and 40 mA with Ni-filtered Cu K_α radiation. The dispersion of Pd was calculated on the basis of CO chemisorption at room temperature [21–23] using a CHEMBET-3000 apparatus (Quantachrome Co.). The catalyst was first reduced under H_2. CO chemisorption experiments were also performed with a Nicolet 6700 FTIR fitted with a MCT detector following the same pretreatment. The spectrum was recorded after CO adsorption at 30 °C. The dispersion (D) and palladium particle size (d) were calculated as [9,21,22]:

$$D\ (\%) = 100 \times [(V_s \times f) / (C_s \times W_s \times 22414)] \times m \quad (1)$$

$$d\ (\text{nm}) = 6 \times 105 \times m / (\rho_{Pd} \times D \times S_{Pd}) \quad (2)$$

where V_s is the CO volume adsorbed (ml at STP), f is the stoichiometric factor (= 1), C_s is Pd metal content (wt%), W_s is the sample weight (g), m is the Pd atomic mass (106.42 g/mol), D is Pd metal dispersion (%), n is Avogadro's number (6.02×10^{23}), S_{Pd} is molar surface area of Pd assuming an equidistribution of the low index faces (S = 47780 m^2/mol for Pd metal) and ρ_{Pd} is palladium density (12 g/cm^3).

XPS analysis was performed on a Thermo ESCALAB 250 spectrometer with Al K_α radiation (1486.6 eV) operating at 150 W and with an energy pass of 20 eV. The surface charging effect was corrected for by fixing the C 1*s* peak at a binding energy of 284.8 eV. HRTEM analysis was carried out on a TECNAI G220 apparatus operated at 200 kV. XEDS analysis was used to record elemental maps to find the chemical composition. The sample for the HRTEM study was first dispersed in ethanol and deposited onto a perforated carbon film supported on a copper grid.

The oxygen storage capacity complete (OSCC) measurement was carried out using a CHEMBET-3000 apparatus (Quantachrome Co.). The sample (100 mg) was first reduced under H_2 (10 ml/min) at 550 °C for 60 min, and then cooled