



A new insight into the effects of barium addition on Pd-only catalysts: Pd-support interface and CO + NO reaction pathway



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ABSTRACT

The effects of barium addition on both fresh and aged Pd/Ce_{0.5}Zr_{0.5}O₂ catalysts were investigated. The activities of the catalysts were evaluated by CO + NO reaction and oxygen storage capacity (OSC). The features of palladium species and the properties of the supports were explored by X-ray diffraction (XRD), nitrogen physisorption, high-resolution TEM, CO chemisorption, X-ray photoelectron spectroscopy (XPS), and H₂ temperature-programmed reduction (H₂-TPR). The adsorption of CO and NO species during the reaction was especially characterized using *in situ* DRIFTS. The results reveal that barium addition decreases the activity of palladium on Ce_{0.5}Zr_{0.5}O₂, especially after ageing. During the ageing, barium reacts with Ce_{0.5}Zr_{0.5}O₂ forming barium zirconium oxides (xBaO·yZrO₂), which results in a barrier layer at the interface between palladium and ceria-zirconia. Such a layer consumes the beneficial Pd–ceria interface and blocks the migration of activated oxygen supplied from Ce_{0.5}Zr_{0.5}O₂ support to palladium, which results in the severe sintering of palladium during ageing and decreases the catalytic activity of the catalysts. In contrast, the activity of Pd/Al₂O₃ catalysts is improved by barium addition. The barium addition significantly suppresses the sintering of alumina, improves the dispersion of palladium and facilitates the adsorption of active surface nitrates during the reaction.

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1. Introduction

Three-way catalysts (TWCs) have been successfully used for the purification of automotive emissions by converting basic air pollutants like CO, HC and NO_x to their inactive products CO₂, H₂O and N₂ [1]. Conventional TWCs usually consist of precious metals such as Pt, Pd and Rh dispersed on alumina supports with rare earth oxides serving as the stabilizer and the promoters [2,3]. Recently, Pd-only TWCs have received considerable attention due to the high catalytic activity for HC oxidation and relatively low cost compared with other noble metals [4,5]. However, the Pd-only systems have a limitation for the NO_x reduction. Considerable efforts have focused on improving the de-NO_x catalytic activity of the Pd-only catalysts by componential modification. Alkaline earth metal oxide including barium oxide is one of the additives practically used in automotive catalysts [6,7]. Kobayashi et al. [6] observed that the presence of Ba species in the palladium catalysts increased the conversion of CO,

NO_x and hydrocarbons. Moreover, they explained that the addition of barium enhanced the basicity of catalysts and the electron density of palladium so as to improve the catalytic activity for NO reduction.

The resistance to thermal ageing is another main concern for the design of Pd-only catalysts [8]. It is therefore very important to understand the effects of high temperature ageing on additives modified catalysts and their deactivation phenomena, including the changes of the surface and interface properties. In some previous literatures, it is always accepted that barium addition can suppress the sintering of the catalysts [9,10]. For instance, alumina modified by barium is a thermally stable support material for the catalysts, since the presence of barium effectively inhibits the transition from γ -alumina to α -alumina [10]. And the mobility of atoms could also be reduced by barium, which suppressed the formation of larger particles during calcination [11]. Besides, the effects of alkaline earth metals on alumina supported palladium has been investigated in some other aspects: enhancement of thermal durability of alumina [10], suppression of hydrocarbon chemisorption [12], acceleration of NO_x chemisorption on palladium [13] and increase of palladium dispersion [14], etc.

Besides alumina as the supports, ceria-zirconia (CZ) mixed oxides generally exist in the three-way catalytic system, which act

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as an oxygen buffer in the exhaust purification [15] and can remarkably improve the thermal stability of Al_2O_3 due to the mutual interaction between CZ and Al_2O_3 [16]. Also, the palladium–ceria interaction at the palladium–ceria interface has been found to offer more active sites for oxygen activation, which would maintain the oxidative state and the adsorption properties of palladium to keep a high catalytic activity [17]. Additionally, the palladium–ceria interaction is beneficial to improve the resistance to thermal ageing of the Pd-only catalysts, which has been reported in our previous study [18]. The additives also influence the palladium–ceria interface as well as the palladium–ceria interactions [19,20]. Wang et al. [19] reported that the addition of La, Nd and Pr enhances the metal-support interaction between Pd and ceria, which can inhibit the sintering of active PdO species. For alkaline-earth metals, a recent work from Christou et al. [21] found that calcium is mainly concentrated on the surface of the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid material, causing a significant increase in the activation energy (kcal/mol) of surface oxygen diffusion and resulting in a substantial suppression of the bulk oxygen diffusion kinetics. Also, Tanikawa and Egawa [22] found that the barium addition reduces the supply of activated oxygen from ceria-zirconia mixed oxide to Pd particles and suppresses the interaction between Pd particles and the ceria-zirconia support in fresh catalysts. In spite of this, rare studies concerned the role of barium species at the interface between the palladium and the ceria-zirconia support, especially during high temperature ageing. What's the difference from the typical case in Pd/ Al_2O_3 system? These concerns draw our attentions.

In this work, the effect of barium addition on palladium catalyst supported on ceria-zirconia mixed oxides (PBCZ) is studied compared with that supported on alumina (PBA). The catalysts are further subjected to severe ageing at 1050 °C for 12 h in air with vapor. The catalytic activity of the catalysts are evaluated by CO + NO reaction and OSC measurement. The features of palladium species and the properties of the supports are explored by XRD, BET, TEM, CO chemisorption, XPS and H_2 -TPR. The adsorbed CO and NO species during the reaction are characterized using *in situ* DRIFTS.

2. Experiments

2.1. Catalyst preparation and characterization

The Pd/BaO/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (PBCZ) and Pd/BaO/ Al_2O_3 (PBA) catalysts were prepared by two-step incipient-wetness impregnation methods on commercial $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (CZ, $S_{\text{BET}} = 80 \text{ m}^2 \text{ g}^{-1}$, BASF) and Al_2O_3 (A, $S_{\text{BET}} = 150 \text{ m}^2 \text{ g}^{-1}$, BASF) with aqueous solution of $\text{Pd}(\text{NO}_3)_2$ and $\text{Ba}(\text{Ac})_2$ as precursors. The Ba precursor was firstly impregnated on the support materials with a barium loading ratio of 5 wt%, then the samples were dried at 110 °C for 12 h in air and calcined at 550 °C for 3 h in static air in a muffle. Subsequently, palladium precursor was impregnated on the oxides and calcined at 550 °C for 3 h in static air to obtain the fresh catalysts. The metal loading of Pd was 2 wt%. The 2 wt% Pd/CZ (PCZ) and Pd/ Al_2O_3 (PA) catalysts without barium were also prepared as the reference samples by the same procedures. All the fresh catalysts were aged in air with 10% steam at 1050 °C for 12 h to get the aged samples.

The specific surface area of the samples was measured using the N_2 adsorption at -196°C by the four-point Brunauer–Emmett–Teller (BET) method on an automatic surface analyzer (F-Sorb 3400, Gold APP Instrument). Prior to the measurements, the samples were degassed in vacuum at 200 °C for 2 h. The pore volumes of the catalyst were measured by nitrogen physisorption at liquid nitrogen temperature using a surface area and pore size analyzer (JW-BK122F, Beijing JWGB Sci. & Tech.). The catalysts were degassed at 200 °C for 2 h prior to the

measurements. The pore volumes for the samples were calculated by the BJH (Barrett–Joyner–Halenda) methods.

The powder X-ray diffraction (XRD) patterns were determined by a Germany Bruker D8 Advance diffractometer employing $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) operating at 40 kV and 40 mA. The diffractograms were recorded at 0.01° intervals in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with a scanning velocity of 6° min^{-1} (continuous scan). The crystal phase was identified with the help of the JCPDS cards. Step-scanning XRD was used to estimate the particle size of Pd species [23]. The data for step-scanning XRD were recorded in a step-scan mode with the step size of 0.02° and dwell time of 3 s per step in the range of $39^\circ \leq 2\theta \leq 43^\circ$. All the analysis of diffraction patterns were performed by using the program JADE that is provided by Materials Data Inc. (Livermore, CA).

Transmission electron microscope (TEM) images were taken using a JEOL 2100 TEM facility. The samples were crushed in an agate mortar and suspended in ethanol. After ultrasonic dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film. The mean Pd particle size was determined by measuring 50 particles for each sample.

The pulse CO chemisorption method (AutoChem II 2920, Micromeritics Co.) was used to measure the dispersion of Pd. Details of the procedure for CO chemisorption were described elsewhere [18]. The dispersion and particle size of palladium were calculated by the following equations [24,25]:

$$D_{\text{Pd}}(\%) = 100 \times \left[\frac{V_s/f}{(C_s \times W_s \times 22,414) \times M} \right]$$

$$d_{\text{Pd}} = \frac{6 \times C_a \times M \times 10^9}{\rho \times N_a \times D_{\text{Pd}}}$$

where D_{Pd} is the metal dispersion of Pd (%), V_s is the CO volume adsorbed (mL at STP), f is the stoichiometric factor (=1), C_s is Pd metal content (=2 wt%), W_s is the sample weight (g), M is the Pd atomic mass (=106.42 g/mol), d_{Pd} is the calculated particle size of palladium, C_a is the concentration of surface metal atoms ($=1.27 \times 10^{19} \text{ atoms/m}^2$) [25], ρ is the volumic mass ($=12.02 \times 10^6 \text{ g/m}^3$) [25] and N_a is the Avogadro constant ($=6.02 \times 10^{23}$).

H_2 temperature programmed reduction was performed on the Micromeritics AutoChem II 2920 apparatus. For each experiment, approximately 50 mg catalyst was placed in a U-shaped quartz tube and pretreated in flowing He at 300 °C for 30 min. After that the samples were cooled down to 0 °C. Then the samples were reduced in a flow of 10% H_2/Ar (50 mL min^{-1}) while ramping the temperature from 0 °C up to 800 °C while the TCD signal was recorded by the detector. Quantitative hydrogen consumptions were obtained by use of TPR calibration runs using a standard silver oxide sample (Micromeritics) in place of the catalyst. A reduced mass of silver oxide was used such that the absolute hydrogen consumption was in the same range as that determined for the various catalysts examined in this work.

The X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB 250Xi system equipped with a monochromatic Al $\text{K}\alpha$ X-rays (1486.8 eV) and samples were measured under ultrahigh vacuum ($\sim 10^{-9} \text{ Pa}$). Prior to the measurements, the samples were degassed in vacuum at room temperature for 1 h. Sample charging during the measurement was compensated by an electron flood gun. The electron take-off angle was 45° with respect to the sample surface. The analyzer was operated using an analysis area of approximately $500 \mu\text{m}$ in diameter. All binding energies were calibrated using the C 1s carbon peak (284.6 eV).

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