

Study of Pt–Rh/CeO₂–ZrO₂–M_xO_y (M = Y, La)/Al₂O₃ three-way catalystsGuo Jiaxiu^{a,c}, Shi Zhonghua^{b,*}, Wu Dongdong^b, Yin Huaqiang^{a,c}, Gong Maochu^b, Chen Yaoqiang^{b,c,*}^a College of Architecture and Environment, Sichuan University, Chengdu 610065, China^b College of Chemistry, Sichuan University, Chengdu 610064, China^c National Engineering Research Center for Flue Gas Desulfurization, Chengdu 610065, China

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ABSTRACT

CeO₂–ZrO₂–M_xO_y (M = Y; La) mixed oxides, prepared by co-precipitation method and characterized by Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), Raman spectra (RM) and oxygen pulse reaction, were comparatively investigated to elucidate the combinational effects of Y and/or La oxide promoters on the catalytic activity and anti-aging performance of monolithic cordierite honeycomb catalysts with low Pt and Rh content. The catalytic activities, water-gas shift (WGS) and steam reforming reaction (SR) were studied under a simulated gas mixture. The catalysts were also characterized by H₂-temperature-programmed reduction (H₂-TPR) and O₂-temperature-programmed desorption (O₂-TPD). The results showed that the prepared CeO₂–ZrO₂–M_xO_y oxides have a face-centered cubic fluorite structure and are nanosize. La³⁺ ions can significantly improve thermal stability and efficiently retard CeO₂–ZrO₂ crystal sintering and growth. Doped CeO₂–ZrO₂ with Y³⁺ and La³⁺ has 105 and 60 m²/g surface area and 460 and 390 μmol/g OSC before and after aging. The T₅₀ of fresh Pt–Rh/CZY/LA is 170 °C for CO, 222 °C for C₃H₈ and 189 °C for NO, and shift to 205, 262 and 228 °C after hydrothermal aging, which are better than those of Pt–Rh/CZY/LA or Pt–Rh/CZL/LA. WGS and SR are relate to the OSC of oxygen storage materials and absorbed oxygen species on the catalyst surface and affect the three-way catalytic activities of catalysts. The reductive property of noble metals and the dissociatively adsorbed O₂ on the surface of catalysts are closely related to the catalytic activities.

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1. Introduction

The automotive three-way catalysts (TWCs) are widely used to eliminate the exhaust gases from gasoline vehicles, especially CO, NO_x and unburned hydrocarbons (HC). After many years of development, the most frequently used components in TWCs are ceria-based oxides owing to its high oxygen storage capacity. In the case of ceria–zirconia, the doped ZrO₂ can improve mobility and diffusion of bulk oxygen of CeO₂ [1,2] and make bulk reaction process become active, which can enhance the conversion of CO and HC under reduction conditions and NO_x under oxidation conditions. A large number of investigations have revealed that the bulk oxygen mobility and oxygen vacancy number play key roles in the whole oxygen storage/release process, especially at “real”

working conditions [3]. The introduction of small amounts of dopants has been suggested to be a powerful tool in designing innovative catalytic materials with oxygen storage/release capacities. However, the loss of the oxygen storage capacity (OSC) due to aging at high temperature is one of the major deactivation pathways for the TWCs. Thermal stabilization of the OSC component is a major objective for developing advanced TWCs. As a rule, Ce_{1–x}Zr_xO_{2–x} with $\chi = 0.2$ –0.4 shows the highest OSC [4], but the cerium–zirconium component with lower CeO₂ content possesses superior textural properties [5]. This will raise a problem of conserving and stabilizing the fluorite structure. A stabilizing effect can be exerted by rare-earth ions [6,7]. Y³⁺ doping into the CO₂–ZrO₂ lattice increases the concentrations of oxygen vacancies and Ce³⁺ ions [8]. La³⁺ ions can increase the active component dispersion and active sites, resulting in decreasing the light-off temperature of catalysts and improving the conversion of NO_x [9,10]. A successful commercial TWC application must meet the requirements of high thermal stability and activity, especially 1000 °C. In this paper, Y³⁺ and/or La³⁺ ions were added into the CeO₂–ZrO₂ to form ceria–zirconia-based mixed oxides with nanosize, and these mixed

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oxides were used to prepare three-way catalysts with low Pt and Rh content. The properties of catalysts were systematically investigated by three-way activities, water-gas shift (WGS) and stream reforming (SR).

2. Material and methods

2.1. Materials

Aqueous ammonia (30% NH₃), ammonium carbonate (AR) and hydrogen peroxide (30%, w/w) were purchased from Chengdu Kelong Chemical Reagent Factory in Chengdu. Pseudo-boehmite was purchased from SD-AL Co., Ltd. Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, CP), cerous nitrate hexahydrate (Ce(NO₃)₃·6H₂O, CP), yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O, CP) and zirconyl nitrate pentahydrate (ZrO(NO₃)₂·5H₂O, CP) were purchased from Leshan Wutongqiao Dongfeng Chemical Factory in Sichuan. Rhodium chloride (RhCl₃) and chloroplatinic acid (H₂PtCl₆) were purchased from Bright Optoelectronics Co., Ltd. in Chengdu. All chemicals were used as received without further purification. The de-ionized water used throughout the experiments was prepared using an Eco purelab water system.

2.2. CeO₂-ZrO₂-M_xO_y preparation and characterization

The samples of Ce_{0.35}Zr_{0.55}Y_{0.10}O₂ (CZY), Ce_{0.35}Zr_{0.55}La_{0.10}O₂ (CZL) and Ce_{0.35}Zr_{0.50}Y_{0.075}La_{0.075}O₂ (CZYL) were prepared by co-precipitation method from the following chemicals: Ce(NO₃)₃·6H₂O; ZrO(NO₃)₂·5H₂O; Y(NO₃)₃·5H₂O; and La(NO₃)₃·5H₂O, at nominal compositions. The precursors were mixed in an aqueous solution with 0.02 mol/L metal salt solution. A mixed solution of 3 mol/L ammonia and 3 mol/L ammonia-carbonate aqueous solution was used as precipitant. The resulted metal salt solution and precipitant were simultaneously added drop-wise to a new container with the pH value maintained at 10. The precipitates were aged at 90 °C for 3 h with vigorous agitation, and then filtered. The obtained cake was washed with distilled water, spray-dried, and calcined at 600 °C in a muffle furnace for 5 h. These samples were calcined at 1000 °C for 5 h to compare their thermal stabilities.

The N₂ adsorption isotherms of the samples at −196 °C were obtained on a ZXF-06 automatic surface analyzer (Xibei Chemical Institute, China). Samples were degassed at 350 °C for 2 h in a vacuum to desorb surface impurities. The adsorption isotherm data were used to calculate the surface area (*S*_{BET}) of each sample using the Brunauer–Emmett–Teller (BET) equation at relative pressures between 0.05 and 0.35. The crystal structures of the samples were determined using an X-ray diffractometer (XRD) (DX-2000, Dandong Fangyuan Instrument Co., China) with Cu Kα radiation ($\lambda = 0.15406$ nm). The X-ray tube was operated at 40 kV and 25 mA. The samples were scanned within the 2θ range of 10–90° at a scanning rate of 0.03°/s. The crystalline phases were identified by comparing them with reference data from the International Center for Diffraction Data (JCPDs). Particle size calculations were performed using peak-broadening analysis. Laser Raman spectra were recorded using a LabRAM HR Raman spectrometer (HORIBA Jobin Yvon Co., France) with a 30 mW Ar ion laser (532 nm).

The 200 mg sample was reduced from room temperature (RT) to 550 °C in flowing pure H₂ (40 mL/min) before the OSC measurement. The samples were then maintained at this temperature for 45 min, cooled to 200 °C, and purged with pure N₂ (20 mL/min). OSC was measured by injecting oxygen pulses (82 μmol of O₂ per g of sample) into the sample bed until no more oxygen consumption was detected by the thermal conductivity detector (TCD).

2.3. Catalyst preparation and performance evaluation

The 3 wt% La₂O₃ stabilized γ -Al₂O₃ calcined at 1000 °C for 5 h was labeled as LA (BET surface area of 114 m²/g). The Pt and Rh-loaded CeO₂-ZrO₂-M_xO_y and LA catalyst powders were prepared by impregnating CeO₂-ZrO₂-M_xO_y and LA powders with RhCl₃ and H₂PtCl₆ aqueous solutions, respectively. All catalyst powders were dried at 105 °C overnight and calcined at 550 °C for 3 h in a muffle furnace. The two resulting catalyst powders were mixed at a certain proportion, added with some distilled water, and ball-milled to obtain homogeneous slurry. The slurry was spread on a honeycomb cordierite (2.5 cm³, Corning, Shanghai) and the excess was blown away using compressed air. This process was repeated several times to achieve a Pt and Rh loading of 0.70 g/L. The coated honeycomb cordierite was dried at 105 °C for 4 h and calcined at 550 °C for 3 h in a muffle furnace. Finally, monolithic catalysts were obtained, and then denoted as Pt-Rh/CZY/LA, Pt-Rh/CZL/LA, and Pt-Rh/CZYL/LA, respectively. These fresh catalysts were hydrothermal aged for 5 h at 1000 °C in a tubular oven under a mixed gas with 10% of H₂O and 90% of 5%H₂-95%N₂ (v/v) mixture, and then the aged catalysts were obtained.

The three-way catalytic activity was evaluated in a multiple fixed bed continuum flow micro-reactor with a gas mixture which simulated the exhaust from a gasoline engine (Fig. 1). The gases were controlled using mass flow controllers before entering the blender. The gas space velocity (SV) was 34,000 h^{−1}. A λ -value of 1.0 was utilized in all activity measurements. The λ -value of the simulated exhaust represents the ratio of available to needed oxygen for a complete conversion of the components to CO₂, H₂O and N₂. The λ -value is defined as oxidants/reductants factor $\lambda = (2O_2 + NO)/(10C_3H_8 + CO)$. The CO, C₃H₈ and NO contents in the stimulated gas before and after the micro-reactor were analyzed on-line using a FGA-4100 five-component analyzer (Fushan Analysis Instrument Co., Ltd., China). The curves about the relationship between conversion and temperature/ λ were obtained. The WGS and SR were measured onto the same apparatus. The curves about the relationship between CO or C₃H₈ conversion and temperature were obtained. The stoichiometric simulated exhaust contained adjustable O₂, 0.86% CO, 0.06% C₃H₈, 0.12% NO, 12% CO₂, 10% H₂O and N₂ as the balance. The WGS reaction simulated exhaust contained 10% CO, 10% H₂O and N₂ as the balance. The SR reaction simulated exhaust contained 0.06% C₃H₈, 10% H₂O and N₂ as the balance. For the activity experiments, the reactor was heated from RT to 550 °C at a rate of 10 °C/min, maintained 60 min in the simulated exhaust, and then cooled to anticipated temperature.

The conversion of CO, C₃H₈ and NO was calculated using the following formula:

$$\text{Conversion (\%)} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

where *C*_{in} is the component concentration in the original simulated mixture before the micro-reactor, and *C*_{out} is the concentration after the micro-reactor.

2.4. Catalyst characterization

The temperature-programmed reduction of H₂ (H₂-TPR) and desorption of O₂ (O₂-TPD) experiments were performed in a quartz tubular micro-reactor. The 100 mg sample was pretreated under a N₂ flow (20 mL/min) for TPR from RT to 400 °C before the H₂-TPR measurements, maintained at this temperature for 40 min, and then cooled to RT. The reduction reaction was performed using a 5%H₂-95%N₂ (v/v) mixture at a heating rate of 10 °C/min from RT to 800 °C. The 100 mg sample was initially pretreated first in pure N₂ (20 mL/min) at 400 °C for 45 min before performing an O₂-TPD experiment, and then purged with 10%O₂-90%N₂ (v/v) mixture

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