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Effect of synthesis method on the properties of ceria–zirconia modified alumina and the catalytic performance of its supported Pd-only three-way catalyst

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ABSTRACT

In this paper, five types of ceria–zirconia modified alumina (CZA) were prepared by co-precipitation with supercritical drying (CPS), co-precipitation with common drying (CPC), sol–gel (SG), micro-emulsion (ME) and impregnation (IM) methods, respectively. The corresponding supported Pd-only three-way catalysts (TWC) were also prepared and evaluated in the simulative gasoline engine exhaust. The influence of different preparation methods on the physicochemical properties of CZA mixed oxide and its supported TWC was characterized by X-ray diffraction (XRD), N_2 adsorption/desorption and transmission electron microscopy (TEM) techniques. The redox behavior was investigated with H_2 temperature-programmed reduction (H_2-TPR) experiments. The results reveal that the CZA mixed oxides derived from CPS and ME methods exhibit the relatively higher textural and structural properties as well as better redox behavior, which lead to the better catalytic activity and wider air-to-fuel operation window of the corresponding Pd-only three-way catalysts.

1. Introduction

In the past decades, environmental protection has attracted an increasing world wide concern. It is well-known that gasoline engine exhaust is one of the main sources for air pollution [1–6]. Three-way catalytic converter represents a well established technology for the abatement of NO_x, CO and hydrocarbon (HC) emission from gasoline engine-powered vehicles. However, as a result of the tightened legislations relating to automobile exhaust, the production of novel three-way catalyst (TWC) is required, which is the core of the catalytic converter.

Classical components of TWC usually include Rh, Pt, and/or Pd as active metal, Ce–Zr mixed oxide as the promoter, and high-surface area alumina as the support [7–11]. Recently, the use of Pd as the only active metal in TWC has received considerable attention considering the economic factor (the high cost and scarcity of Rh) and the availability of clean fuel as well as its excellent capability for low-temperature oxidation of carbon monoxide and hydrocarbons [3,9,12]. In practice, alumina is usually used as support in order to maintain favorable dispersion of active metal [13,14]. However, alumina supported palladium catalysts are not stable under high temperature in the catalytic converter [15,16]. The deactivation of PdO/Al_2O_3 catalysts is reported to be mainly due to a decrease in the surface area of alumina and the transformation of PdO to Pd at extreme high temperature [17]. For these reasons, addition of a promoter in order to increase the thermal stability of the catalyst is considered as an attractive alternative to enhance the performance of TWC [18,19]. Among the numerous potential promoters, ceria–zirconia is the best known [20–25]. On the one hand, the addition of ceria–zirconia into alumina would lead to the increased thermal stability of the support and catalyst. On the other hand, ceria–zirconia exhibits fast oxygen mobility and high oxygen storage capacity, which play an important role in the purification of gasoline engine exhaust.

Up to now, a great deal of attention has been paid to investigate the physicochemical properties of ceria-zirconia modified alumina (CZA), and it was found that the preparation procedure strongly affects the characters of CZA and the catalytic performance of its supported TWC [26–30]. In this paper, five different methods were adopted to synthesize CZA and the supported Pd-only three-way catalysts were also prepared. The samples were characterized from a structural and textural point of view with techniques such as X-ray diffraction (XRD), N_2 adsorption/desorption and Transmission electron microscopy (TEM) examination. The redox properties of the samples were investigated by means of H_2 temperature-programmed reduction (H_2-TPR). The catalytic performances of the corresponding TWCs were also investigated under the simulated automobile exhaust. Purpose of this work is to elucidate the optimal synthesis method for the development of a thermal stable TWC.

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2. Experimental procedures

2.1. Sample preparation

The five types of ceria–zirconia modified alumina mixed oxides (CZA) were synthesized using co-precipitation with supercritical drying (CPS), co-precipitation with common drying (CPC), sol–gel (SG), micro-emulsion (ME) and impregnation (IM) methods, respectively. The content of ceria–zirconia oxide was 18 wt.% with Ce/Zr molar ratio of 3:1 in the sample.

In the co-precipitation with supercritical drying technique, the ammonia solution was slowly added to quantitatively mixed aqueous solution of $Ce(NO_3)_3$, $ZrO(NO_3)_2$ and $Al(NO_3)_3$ under continuous stirring until pH = 9.5. The resulting precipitate was filtered, extensively washed with distilled water, and then washed with ethanol furthermore to replace the water in the precipitate considering that it would be dried under supercritical condition in ethanol (250 °C, 7.5 MPa) subsequently.

The co-precipitation with common drying method was performed by an addition of aqueous ammonia into the mixture of corresponding nitrates drop by drop under continuous stirring until pH value achieved 9.5. The obtained deposition was filtered and washed with distilled water followed by drying at 110 °C for 12 h.

In the sol–gel preparation procedure, the citric acid solution was slowly added to quantitatively mixed aqueous solution of $Ce(NO_3)_3$, $ZrO(NO_3)_2$ and $Al(NO_3)_3$ followed by evaporating at 80 °C until a spongy and transparent yellow gel was gained. Then the gel was dried at 110 °C for 12 h.

For micro-emulsion preparation method, cetyltrimethylammonium bromide (CTAB) was quantitatively mixed with butanol and cyclohexane with stirring until the mixture became transparent. The acquired microemulsion was divided into two parts. One was mixed with the corresponding nitrates, and the other one was mixed with solution of aqueous ammonia. Then, the microremulsion containing aqueous ammonia was added to the other mixture under vigorous agitation until the solution was suspended with formed colloidal particles. After aging at room temperature (20 °C) overnight, the precipitate was filtered, washed with deionized water and dried at 110 °C for 12 h.

With regard to the impregnation method, ceria and zirconia were deposited by impregnation of the γ-Al_2O_3 with an aqueous solution of $Ce(NO_3)_3$ and $ZrO(NO_3)_2$. Then the slurry was vaporized with water bath method at 100 °C followed by drying at 110 °C for 12 h.

All the dried samples mentioned above were calcined at 500 °C for 4 h to gain the so-called fresh supports. In briefly, they are marked as CZA-CPS, CZA-CPC, CZA-SG, CZA-ME and CZA-IM, respectively. The samples were also calcined at 1100 °C for 4 h to investigate the thermal stability, and the aged samples were labeled as CZA-CPSa, CZA-CPCa, CZA-SGa, CZA-MEa and CZA-IMa, correspondingly.

The supported Pd-only three-way catalysts were prepared by conventional wet impregnation method with an aqueous of H_2PdCl_4 as metal precursor. The impregnated samples were reduced with hydrazine hydrate to de-associate Pd^{2+} and Cl^- via the transformation of Pd^{2+} to Pd. Then the reduced sample was filtered and washed with a large amount of deionized water until no Cl^- ion was detected in the filtered solution (by $AgNO_3$ aqueous) considering that the appearance of Cl is harmful to the catalytic activity. The washed samples were dried at 100 °C for 12 h and then calcined at 500 °C for 2 h due to the active phase in TWC was metal oxide. In order to investigate their thermal stability, the catalysts were also calcined at 1100 °C for 4 h. The theoretical loading content of Pd for the catalyst was 0.5 wt.%. The catalysts obtained at 500 °C were denoted as Pd/CZA-CPS, Pd/CZA-CPC, Pd/CZA-SG, Pd/CZA-ME and Pd/CZA-IM, respectively. The corresponding aged catalysts were labeled with an additional suffix "*a*" similarly.

2.2. Catalytic activity test

The evaluation of three-way catalytic activity was performed in a fixed-bed continuous flow quartz reactor. The catalyst (0.2 ml) was held in the quartz tube by packing quartz wool at both ends of the catalysts bed, and the back-mixing in reactor is minimized by decreasing the dead volume of the reactor. The feed stream was regulated using special mass flow controllers and contained NO (0.1%)–NO_2 (0.03%)–HC (0.033%)–CO (0.68%)–O_2 (1.745%) with balance Ar at a GHSV of 24,000 h^{-1} referred to the catalyst volume and to a gas flow rate at room temperature (25 °C). The contents of CO, NO, NO_2 and total HC (C_3H_6 and C_3H_8) were recorded by a Bruker EQ55 FTIR spectrometer coupled with a multiple reflection transmission cell (Infrared Analysis Inc.) before and after the simulated gas passed the reactor. The air/fuel ratio (λ) is defined as $\lambda = (2V_{O_2} + V_{NO} + 2V_{NO_2})/(V_{CO} + 9V_{C_3H_6} + 10V_{C_3H_8})$ (V means concentration in volume percent unit), $\lambda = 1$ was utilized in all the activity measurements and the air/fuel ratio experiment was carried out at 400 °C with adjusting the concentration of O_2.

2.3. Characterization techniques

Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku D/Max-IIIB apparatus using Cu-Kα radiation operating at 45 kV and 40 mA with 0.02° step size scanning from 20° to 80° (2θ).

The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were determined by nitrogen physisorption at 77 K using a Coulter OMNISORP-100 apparatus after degassing the samples in vacuum ($<10^{-5}$ Torr) at 200 °C for 2 h.

Transmission electron microscopy (TEM) examinations were operated on a JEOL JEM-2010 electron microscope operating at 200 kV. Portions of 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. Bright-field micrographs were recorded over selected areas.

H_2 temperature programmed reduction (H_2-TPR) measurements were carried out on a GC-1690 chromatography (KeXiao Chemical Instruments Co., Ltd., China) to observe the reducibility of the samples. Prior to H_2-TPR measurement, 50 mg catalyst was pretreated at 300 °C in air for 0.5 h. The reducing gas was a mixture of 5 vol.% H_2 in Ar (40 ml/min), which was purified using deoxidizer and silica gel. The experimental temperature was raised at a constant rate of 10 °C per minute. The consumption of hydrogen during the reduction reaction was measured by a thermal conductivity detector (TCD), and the water formed during H_2-TPR was absorbed with 5A molecular sieve.

3. Results and discussion

3.1. Textual and structural characterization

3.1.1. XRD

The XRD patterns of the fresh and aged samples are presented in Fig. 1, and the relevant lattice parameters are summarized in Table 1. What should be pointed out is that only lattice parameters and crystallite sizes of the main crystallite phase (ceria–zirconia solid solution) are shown in Table 1. From Fig. 1(a), it can be seen that the fresh samples consist of low intensity peaks from two phases: γ-Al_2O_3 and a major phase of cubic CeO_2 with the fluorite structure. In Fig. 1, no reflections ascribed to pure zirconia are observed. In addition, Table 1 shows that the lattice parameter of $Ce_xZr_{1-x}O_2$ is smaller than pure CeO_2 (a = 5.41 Å). This is due to the lattice shrinkage caused by the introduction of Zr^{4+} (0.84 Å), which