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Synthesis of La modified ceria–zirconia solid solution by advanced supercritical ethanol drying technology and its application in Pd-only three-way catalyst

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ABSTRACT

In this work, supercritical drying technology is investigated as a new method contrast with the conventional drying techniques to obtain La modified ceria–zirconia solid solution (CZL) with advanced textural/structural properties, and its supported Pd-only three-way catalysts (TWCs) were also prepared and studied. The results demonstrate that the CZL sample prepared by supercritical drying method shows relatively larger specific surface area, better thermal stability and higher redox properties, as well as the prominent oxygen storage capacity compared with samples prepared by conventional drying method. Moreover, it also exhibits remarkable porosity and wide pore size distribution due to the elimination of vapor–liquid interface in the process of supercritical drying, which is beneficial to the adsorption/desorption of pollutant in TWCs. The excellent structural/textural properties of the forenamed CZL support lead to the outstanding catalytic activity, wide air-to-fuel operation window of the corresponding three-way catalyst, indicating its tremendous potential possibilities.

1. Introduction

Ceria–zirconia solid solution has drawn great attention as an outstanding oxygen storage material in three-way catalysts (TWCs), which can reduce emissions of CO, HC (hydrocarbons) and NO_x simultaneously [1–6]. The major contributing factor is that ceria–zirconia solid solution shows a large concentration of surface and bulk oxygen-vacant sites, the fast exchange of surface oxygen with gas-phase oxygen species and the high diffusion rates of bulk oxygen toward its surface, which are caused by the presence of a rapid Ce^{4+}/Ce^{3+} redox couple [7–9].

Up to now, great deals of efforts have been paid to investigate the structure and properties of ceria–zirconia solid solution [10–14], and it was found that the catalytic performance of TWCs correlates to the specific surface area, thermal stability and oxygen exchange capacity (OSC) of samples. Strict restrictions on automotive emissions require higher catalytic activity at lower temperature, and the TWCs are located in positions closer to the engine manifold resultantly. However, the temperature in catalytic converter can rise to even above 1000 °C [15,16], at which the catalyst readily sinters, leading to the loss of specific surface area, oxygen storage capacity and further the decline of catalytic activity [17–19]. Several strategies such as the introduction of rare earth [9,20–23], base metals [13,24–26] and transition metals [27–31] have been recommended in order to improve the properties mentioned above.

On the other hand, the preparation procedure strongly affects the properties of the ceria–zirconia solid solution and the catalytic performance of its supported TWCs. Numerous synthesis routes including ball milling, co-precipitation, sol–gel, combustion, hydrothermal process and so on have been developed to prepare ceria–zirconia or ceria–zirconia-based materials [32–42]. However, both the lower specific surface area and inferior thermal stability are the main encumbrances faced by researchers, accounting for the adoption of common drying method. It is well known that when the removal of the solvent from sample is carried out conventionally in air or in vacuum, the highly porous texture may collapse due to the capillary force at a vapor–liquid interface.

In this paper, supercritical drying was applied as a new method contrast with the conventional drying techniques for the development of La modified ceria–zirconia solid solution (CZL) with higher specific surface area, larger OSC and better thermal stability. An important point, specifically addressed herein, is the investigation of the effects of drying method on the structural/textural properties of CZL and the effects on its supported Pd-only TWCs.

2. Experimental procedures

2.1. Sample preparation

The La modified ceria–zirconia solid solution samples were prepared as follows. The ammonia solution was slowly added to the quantitative mixed aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$, $ZrO(NO_3)_2{\cdot}6H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ under continuous stirring until pH value reached 9.0. The obtained slurry was aged at room

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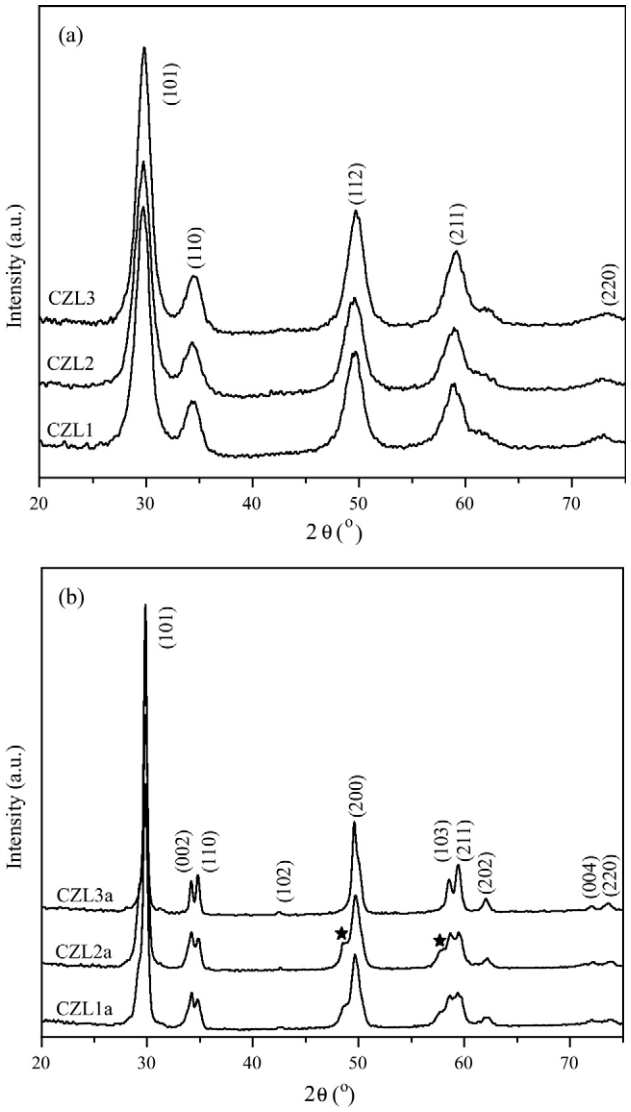

Fig. 1. XRD patterns of fresh (a) and aged (b) supports: (⋆) deteriorated Ce–Zr–La mixed oxide.

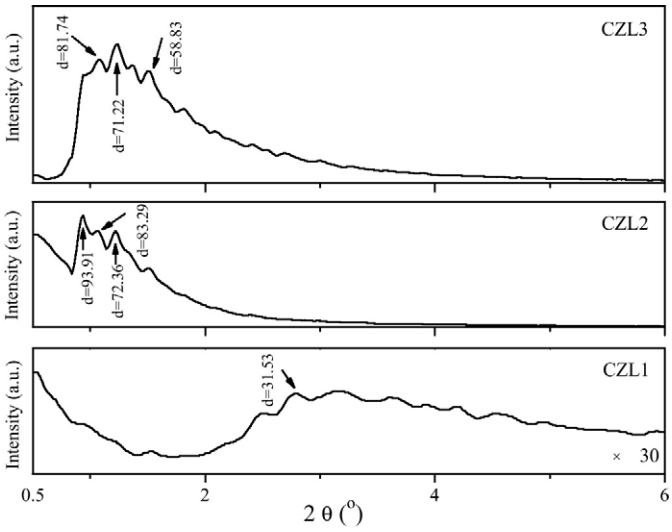

Fig. 2. Small-angle XRD patterns of all the fresh CZL*x* samples.

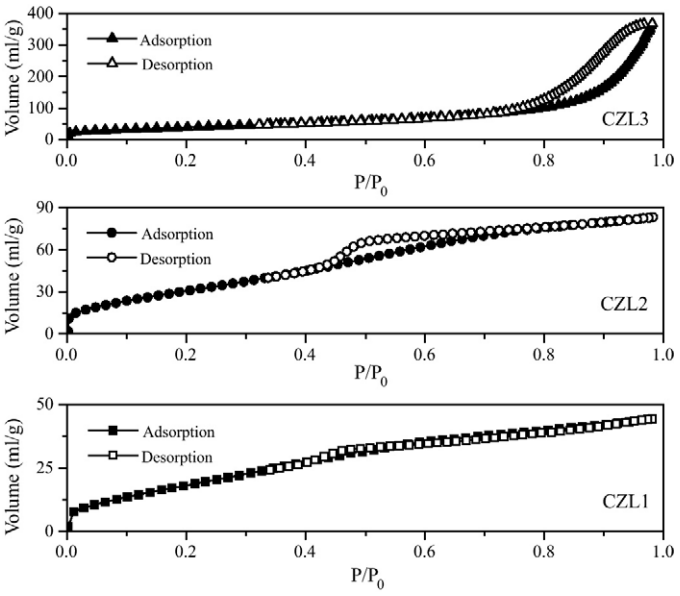

Fig. 3. Nitrogen adsorption/desorption isotherms of the fresh samples.

temperature (20 °C) for 12 h, and then was filtered with a large quantity of distilled water until pH value reached ca. 7. One-third of the resulting precipitate was separated, which was denoted as P1. The remainder precipitate was washed with ethanol furthermore to replace the water in the precipitate, and was divided into two parts, labeled as P2 and P3, respectively. P1 and P2 were dried at 100 °C for 12 h while P3 was dried under supercritical condition in ethanol (265 °C, 7.0 MPa). All of the dried samples were calcined at 500 °C for 4 h in static air (hereafter referred to as CZL1, CZL2 and CZL3, respectively), and then the materials were crushed and sieved to a size range of 40–60 mesh. A portion of the powders were further aged at 1100 °C in static air for 4 h to investigate the thermal stability of the samples, and the aged samples were denoted as CZL1a, CZL2a and CZL3a, correspondingly. The theoretical molar ratio of Ce:Zr is 1:4 and the theoretical additive content of La_2O_3 is 5 wt.% for CZL. All the La modified ceria–zirconia solid solution in this study was denoted as CZL*x* (*x* means the serial number of the sample) in brief, *x* = 1, 2, and 3.

The corresponding Pd/CZL*x* was prepared by conventional 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 transform 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 110 °C for 4 h and then calcined at 500 °C for 2 h in static air due to the active phase in TWC is metal oxide. In order to compare their thermal stability, the catalysts were also calcined at 1100 °C for 4 h (in static air). The academic loading content of Pd for all the catalysts is 0.5 wt.%. The catalysts obtained at 1100 °C are labeled as Pd/CZL1a, Pd/CZL2a and Pd/CZL3a, respectively.

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