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The effect of Nd on the properties of ceria–zirconia solid solution and the catalytic performance of its supported Pd-only three-way catalyst for gasoline engine exhaust reduction

Qiuyan Wang[a], Guangfeng Li[a], Bo Zhao[a,b], Renxian Zhou[a,*]

[a] Institute of Catalysis, Zhejiang University, 148 # Tianmushan Road, Hangzhou 310028, PR China
[b] School of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou 317000, PR China

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ABSTRACT

A series of ceria–zirconia–neodymia mixed oxides with different contents of neodymia and the supported Pd-only three-way catalysts before and after aging have been prepared and characterized. The influence of Nd doping on the structural/textural properties of ceria–zirconia (CZ) and the effect on the three-way catalytic performance are also investigated. The results demonstrate that the addition of neodymia results in the formation of ceria–zirconia–neodymia ternary solid solution (CZN) with better textural and structural properties as well as improved reducibility and redox behavior, leading to the promoted three-way catalytic activity and enlarged air/fuel operation window. The modified solid solution with 5 wt.% neodymia shows the preferable textural/structural properties considering that the capacity of foreign cation is limited in the crystal lattice of ceria–zirconia solid solution, and Pd/CZN5 shows the optimum three-way catalytic performance and wider air/fuel operation window, especially for the corresponding aged one.

1. Introduction

Air pollution mainly caused by exhausts from gasoline engine powered vehicles is one of the major environmental concerns and has drawn more and more attention in recent years [1,2]. Among the several techniques that have been developed for reducing gasoline engine exhaust, catalytic converter is regarded as the most promising solution [3–7]. As the key component in catalytic converter, three-way catalyst (TWC) has been successfully used for the control and suppression of automotive emission by converting basic air pollutants like carbon monoxide, hydrocarbons and nitrogen oxides simultaneously. Along with the more rigorous environmental regulations imposed on the automobile industry, more efficient TWC is required.

In the actual formulations of TWC, Pd exhibit excellent capability for low-temperature oxidation of carbon monoxide and hydrocarbons compared with Pt and Rh-supported catalysts [8,9]. On the other hand, Pd is relatively economical and abundant than Pt and Rh, especially than Rh. Therefore, Pd-only TWC has received considerable attention. Ceria–zirconia solid solution is widely employed as a promoter in TWC, and it represents the state-of-art of the so-called oxygen storage materials (OSM) [10–16]. Ceria–zirconia solid solution shows 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 towards its surface, all due to the presence of a rapid Ce^{3+}/Ce^{4+} redox couple. These important features, named oxygen storage capacity (OSC), provide a way to minimize fluctuation of the air-to-fuel (A/F) ratio at around 14.6 during engine operation. Under the transitions between lean and rich operating conditions, ceria–zirconia material stores or releases oxygen, thus ensuring that TWC work effectively within a narrow operating window near the stoichiometric A/F ratio [12,17–19].

In practice, the demand for decrease of cold-start emissions requires the catalyst to be located in positions closer to the engine manifold, where the temperature can rise even above 1000 °C [10,20–22]. As it is well-known, the exposure of catalysts to that high temperature will induce the sintering of both ceria–zirconia solid solution and active noble metal, causing the loss of OSC and the deactivation of TWC. Consequently, one of the recent requirements for developed TWC is the higher OSC and thermal stability under high temperature conditions. Until now, a great deal of research attention has been paid to the intrinsic structure and properties of ceria–zirconia solid solution [13–15,23–26], and it was found that the incorporation of other rare earth elements [2,7,27–31] is beneficial to increase the OSC and improve the thermal stability of ceria–zirconia mixed oxides. Nevertheless, summarizing the literature, the mechanism over these promoted properties of rare

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* Corresponding author. Tel.: +86 571 88273290; fax: +86 571 88273283.
E-mail address: zhourenxian@zju.edu.cn (R. Zhou).

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Table 1
Light-off temperature ($T_{50\%}$) and full-conversion temperature ($T_{90\%}$) of HC, CO, NO and NO_2 over all the fresh catalysts.

Sample	$T_{50\%}$ (°C)				$T_{90\%}$ (°C)			
	HC	CO	NO	NO_2	HC	CO	NO	NO_2
Pd/CZ	229	158	231	180	263	191	264	214
Pd/CZN3	226	167	210	174	257	199	263	205
Pd/CZN5	218	184	206	170	254	202	244	195
Pd/CZN8	224	186	188	165	255	205	224	185
Pd/CZN10	227	188	187	160	257	209	223	179

earth modified ceria–zirconia solid solution remains obscure, and research related to the effect of rare earth doping on the catalytic activity of TWC is little.

This work deals with a combined investigation of the effect of Nd doping on the structural/textural properties of ceria–zirconia solid solution and on the three-way catalytic performance of its supported Pd-only catalyst. A series of $Ce_{0.2}Zr_{0.8}O_2$ (CZ) modified with different neodymia contents were prepared and characterized by techniques such as X-ray diffraction (XRD), N_2 adsorption/desorption and X-ray photoelectron spectroscopy (XPS). The redox properties and OSC of the materials were studied by means of hydrogen temperature-programmed reduction (H_2-TPR), H_2–O_2 and CO–O_2 pluses. The catalytic activity of TWC was evaluated under the simulative automobile exhaust and the air/fuel ratio experiments were also carried out.

2. Experimental

2.1. Catalyst preparation

CZ and Nd modified CZ (CZN) supports were prepared by conventional coprecipitation method combined with supercritical drying technique. The detailed procedure was similar to literature [32]. The molar ratio of Ce:Zr is 1:4, and the additive content of neodymia is 3, 5, 8 and 10 wt.% for CZN, respectively. The fresh supports calcined at 500 °C are named as CZN*x* (*x* = 3, 5, 8, 10), where *x* means the content of neodymia. All the supports were also calcined at 1100 °C for 4 h to investigate the effect of doping on the thermal stability of CZ, and the aged supports are referred to as CZa and CZN*x*a, respectively. The corresponding Pd/CZ and Pd/CZN*x* catalysts were prepared by wet impregnation method. The as-received fresh catalysts were aged at 1100 °C for 4 h to investigate the thermal stability. The theoretical loading content of Pd for all the catalysts is 0.5 wt.%. The catalysts obtained at 1100 °C are labeled as Pd/CZa and Pd/CZN*x*a, respectively.

2.2. Catalytic activity test

The evaluation of three-way catalytic activity was performed on a Bruker EQ55 FTIR spectrometer coupled with a multiple reflection transmission cell (Infrared Analysis Inc.). The detailed information was also shown in [32].

The air/fuel ratio (λ) experiments were carried out at 400 °C. λ is defined as $(2V_{O_2} + V_{NO} + 2V_{NO_2})/(V_{CO} + 9V_{C_3H_6} + 10V_{C_3H_8})$ [32] (V means concentration in volume percent unit), and λ = 1 was used in all the activity measurements. The test of air/fuel operation window was carried out at λ = 0.9, 0.92, 0.95, 0.98, 1.0, 1.04, 1.07, 1.1 and 1.15, respectively [33–35].

2.3. Characterization techniques

The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI-Quantera SXM system equipped with a monochromatic Al Kα X-rays under ultra-high vacuum (6.7×10^{-8} Pa). Sample charging during the measurement was compensated by an electron flood gun. The XPS data from the regions related to C 1s, O 1s, Zr 3d, Ce 3d, Pr 3d and Pd 3d core levels were recorded for each sample. The binding energies were calibrated internally by the carbon deposit C 1s binding energy (BE) at 284.8 eV. The deconvolution method of XPS spectra is fitted by Gaussian function.

The oxygen storage capacity complete (OSCC) was measured using pulse injection technique with a CHEMBET-3000. The sample was first reduced with a flow of 10 ml/min H_2 at 550 °C for 1 h, then cooled to the testing temperature and purged by helium stream. The OSCC was measured by pulse injection of oxygen into the sample bed until no consumption of oxygen could be detected by TCD. The amount of oxygen consumed during the re-oxidation stage is referred as OSCC. All the gases employed in the experiment were high-purity (99.999%).

In addition, the characterization related to powder X-ray diffraction (XRD), N_2 adsorption/desorption, H_2-temperature programmed reduction (H_2-TPR) and dynamic oxygen storage capacity (DOSC) were also carried out according to the methods reported in literature [32].

3. Results and discussion

3.1. Catalytic performance

All the fresh and aged catalysts were evaluated in the simulative gasoline engine exhaust and the tail gas after reaction was detected by FTIR. The light-off temperature ($T_{50\%}$, the temperature at which 50% conversion is attained) and full-conversion temperature ($T_{90\%}$, the temperature at which 90% conversion is attained) of HC, CO, NO and NO_2 over all the fresh catalysts were summarized in Table 1. As reported in literature [9], the main chemical reactions taking place during the automobile exhaust treatment is as following:

Oxidation:

$$2CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O \quad \text{(unbalanced reaction)}$$

Reduction:

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

$$HC + NO \rightarrow CO_2 + H_2O + N_2 \quad \text{(unbalanced reaction)}$$

$$2H_2 + 2NO \rightarrow 2H_2O + N_2$$

Water–gas shift:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Steam reforming:

$$HC + H_2O \rightarrow CO_2 + H_2 \quad \text{(unbalanced reaction)}$$

From Table 1, it can be known that the introduction of Nd promotes the catalytic conversion of both NO and NO_2 obviously, the $T_{50\%}$ and $T_{90\%}$ of which decrease clearly with the increasing amount