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Short communication

Preparation of Pd/$(Ce_{1-x}Y_x)O_2$/γ-Al_2O_3/cordierite catalysts and its catalytic combustion activity for methane

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ABSTRACT

A series of $(Ce_{1-x}Y_x)O_2$ ($x = 0,0.15,0.35,0.5$) coatings on γ-Al_2O_3 pre-coated cordierite honeycomb were prepared by sol–gel method, and then palladium was loaded by aqueous solution impregnation deposition with $Pd(NO_3)_2$ as precursor. The structure and morphology of samples were evaluated and the catalytic combustion activity for methane was also discussed. $(Ce_{1-x}Y_x)O_2$ synthesized by sol–gel has a single-phase cubic fluorite structure. Increasing the Y/Ce ratio can significantly improve the inner surface morphology of the honeycomb channels and also the coating mechanical stability, and leads to a considerable improvement in the catalytic activity of the prepared catalysts for methane.

1. Introduction

With increasingly stringent requirements for protecting our environment, catalytic combustion of nature gas (methane) has attracted more and more attention [1]. Monolithic catalysts are widely used for catalytic combustion of methane and other organics. As a supporter, cordierite ceramic honeycomb (abbreviated to COR) has very small specific surface area (usually <1 m^2/g) [2], thus γ-Al_2O_3 coating is usually used as a transition layer to create a higher surface area [3], however, at high temperature, it is prone to transform into the θ-phase, finally into the α-form, which has a low specific surface area.

In order to prevent the transformation of γ-Al_2O_3 and also to enhance catalytic activities, some rare-earth element oxides (such as CeO_2, La_2O_3, and Y_2O_3) are commonly used as additives [4–6]. CeO_2 has been widely studied in recent years for catalytic application. CeO_2 has many advantages, such as: strong ability to store/release oxygen [7,8], high thermal and structure stabilities [9], and good ability to disperse the noble metal active component [10,11]. Doping divalent or trivalent ions in CeO_2 could improve its oxygen storage capacity [12,13]. Addition of Y to $(Ce,Zr)O_2$ solid solution could improve oxygen vacancies and promote the reduction of Ce^{4+} [14], and also improved the reduction–reoxidation properties of the active PdO species [15].

In this paper, $(Ce_{1-x}Y_x)O_2$ solid solution coatings were prepared by sol–gel method. The effect of Y/Ce ratio on the phase constitution, surface morphology, and mechanical stabilities was investigated and the catalytic performance of the prepared Pd/$(Ce_{1-x}Y_x)O_2$/γ-Al_2O_3/COR catalysts for methane was also discussed.

2. Experimental

2.1. Preparation of $(Ce_{1-x}Y_x)O_2$/γ-Al_2O_3/COR

A commercial honeycomb ceramic was cut into cuboid samples (6 mm × 6 mm × 30 mm) which were pretreated by conventional process. Then they were immersed in the γ-Al_2O_3 transition sol for 5 mins and the excess γ-Al_2O_3 sol inside the honeycomb channels was blown off, and then they were dried at 120 °C for 2 h and roasted at 550 °C for 2 h in a muffle furnace with flowing air. The amount of the loaded γ-Al_2O_3 coating can reach 12 wt.% – 15 wt.% after double repeating. The prepared samples above were labeled as γ-Al_2O_3/COR.

Ce and Y nitrates were used as Ce- and Y- precursors, and the mole ratios of Ce and Y was 1:0, 0.85:0.15, 0.65:0.35, and 0.5:0.5. The mixed aqueous solution of Ce- and Y- nitrates and citric acid was prepared with distilled water. Citric acid was added as a complexing agent in 1:2 M ratio with respect to the sum of the metal salts. The mixed solution were heated at 70 °C in a water bath and constantly stirred until a stable sol was obtained. The γ-Al_2O_3/CORs were impregnated in this sol for 5 min. The excess sol inside the channels need blow off.

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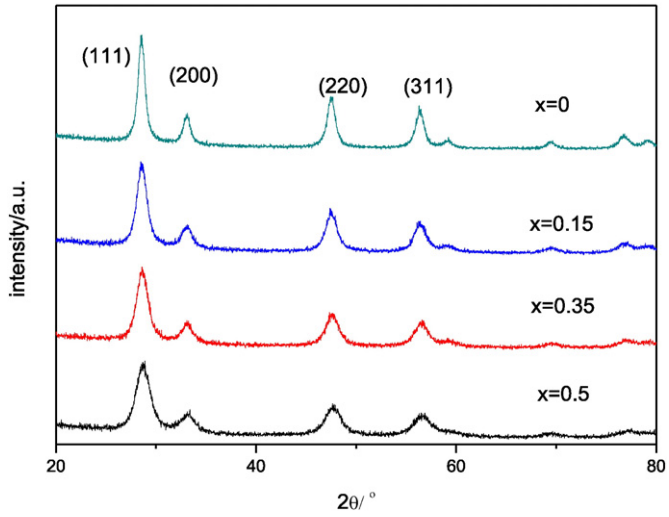

Fig. 1. XRD patterns of $(Ce_{1-x}Y_x)O_2$ (x = 0, 0.15, 0.35, 0.5) powders after calcination.

Table 1
Lattice constant and crystallite size of $(Ce_{1-x}Y_x)O_2$.

x	Lattice constant a/nm	Crystallite size D/nm
0	0.5413	11.8
0.15	0.5402	9.5
0.35	0.5395	8.8
0.5	0.5378	8.4

Subsequently, they were dried at 120 °C for 2 h in air and roasted at 550 °C for 2 h. This processed sample is labeled as $(Ce_{1-x}Y_x)O_2/\gamma$-Al_2O_3/COR.

2.2. Preparation of catalysts

Catalysts were prepared by a classical aqueous solution impregnation method, in which $Pd(NO_3)_2$ is as precursors. The $(Ce_{1-x}Y_x)O_2/\gamma$-Al_2O_3/CORs were completely impregnated in the Pd-solution for 30 min, and the excess aqueous solution inside the channels was blown off. Then they were dried at 120 °C for 2 h in air and roasted at 450 °C for 2 h. The final sample is labeled as $Pd/(Ce_{1-x}Y_x)O_2/\gamma$-$Al_2O_3$/COR.

2.3. Characterization

The XRD patterns of $(Ce_{1-x}Y_x)O_2$ dried gel powder were collected on a Bruker apparatus (D8-Discover), using Cu Kα radiation (λ = 1.5418 Å). The X-ray tube was operated at 40 kV and 30 mA and the scanning rate was 0.02°/step in the range of 20° ≤ 2θ ≤ 90°. The specific surface area was measured by N_2 adsorption at 77 K on ASAP 2000 M with the Brunauer–Emmet–Teller (BET) method. The surface morphology of the $(Ce_{1-x}Y_x)O_2$ coating was examined by XL30 environmental SEM.

Ultrasonic oscillating test was performed, to evaluate the cohesive strength of coating on the cordierite substrate, in a KQ-250B ultrasonic bath with a power of 220 W for 30 min. Before test, the dry sample was weighted as m_{before}, and after test, the sample was dried again, and then weighted as m_{after}. The mass losses of the coating was calculated using $\Delta W\% = (m_{before} - m_{after}) / m_{before} \times 100\%$.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed to measure the loading amount of palladium, cerium and yttrium in the prepared monolithic catalysts.

2.4. Catalytic activity evaluation

The catalytic combustion of methane on the $Pd/(Ce_{1-x}Y_x)O_2/\gamma$-$Al_2O_3$/COR catalysts was carried out in a conventional fixed-bed flow quartz micro-reactor (length = 400 mm, i.d. = 10 mm). A gas mixture

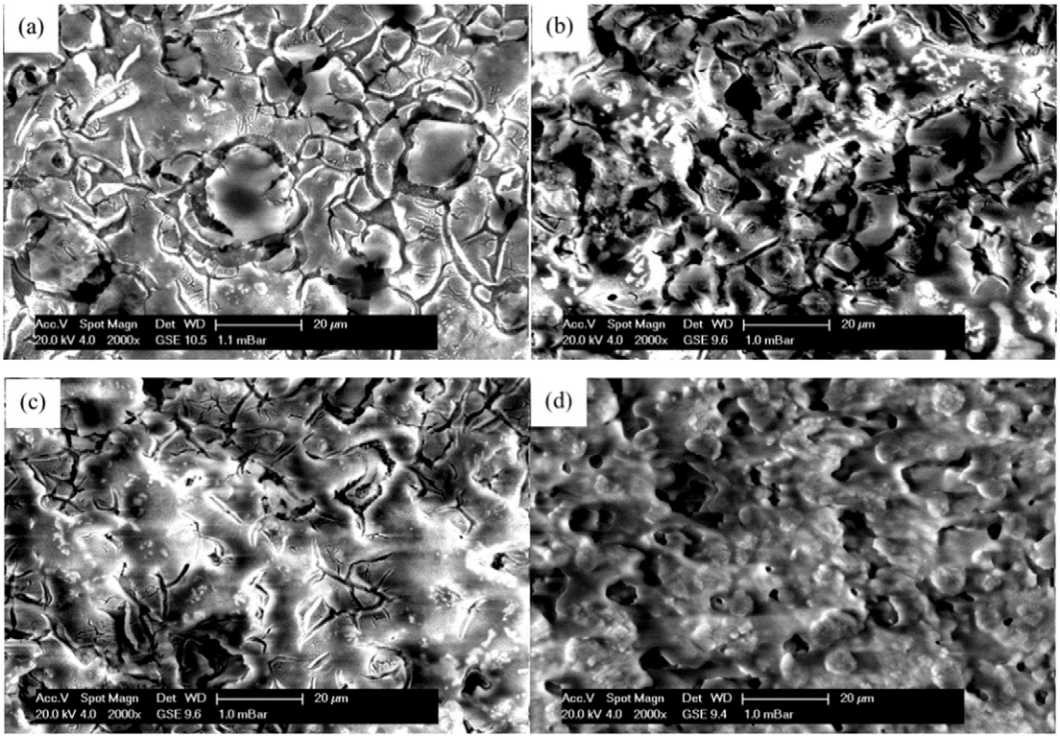

Fig. 2. The inner surface morphology of $(Ce_{1-x}Y_x)O_2/\gamma$-Al_2O_3/CORs (a) x = 0; (b) x = 0.15; (c) x = 0.35; (d) x = 0.5.