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Structure and oxygen storage capacity of Pd/Pr/CeO_2-ZrO_2 catalyst: effects of impregnated praseodymia

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Abstract: Praseodymium (Pr) was impregnated to CeO_2-ZrO_2 solid solution by an impregnation method. The as-obtained Pr modified CeO_2-ZrO_2 was impregnated with 1 wt.% Pd to prepare the catalysts. The structure and reducibility of the fresh and hydrothermally aged catalysts were characterized by X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS), CO chemisorption and H_2 temperature-programmed reduction (H_2-TPR). The oxygen storage capacity (OSC) was evaluated with CO serving as probe gas. Effects of impregnated Pr on the structure and oxygen storage capacity of catalysts were investigated. The results showed that the aged Pr-impregnated samples had much higher OSC and better reducibility than the unmodified ones. The scheme of structural evolutions of the catalysts with and without Pr was also established. Partial of the impregnated Pr diffused into the bulk of CeO_2-ZrO_2 during ageing, which inhibited the sintering, and increased the amount of oxygen vacancies in CeO_2-ZrO_2 support. Furthermore, those impregnated Pr species which covered on the surface of the support obstructed the strong metal-support interaction between Pd and Ce so as to reduce the encapsulation of Pd as well as the back spill-over of the oxygen during the catalytic process.

Keywords: CeO_2-ZrO_2; praseodymia; sintering; covering; oxygen storage capacity; rare earths

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CeO_2-ZrO_2 (CZ) solid solution is widely used in three-way catalysts (TWCs) as an oxygen storage material (OSM)[1–3]. Nowadays, Zr-rich CeO_2-ZrO_2 solid solution (0.5<Zr ratio<0.8) is the most extensively used OSM in TWCs due to their large oxygen migration channel and high oxygen storage capacity (OSC) per mole of cerium[4,5]. Developing more thermally stable oxygen storage materials with improved performance is one of the recognized needs to fulfill the rigorous regulations on emission control.

Dopant modification is a common method to optimize the composition and the structure of ceria in order to improve both the OSC and the structural stability of the OSMs. Some trivalent rare earth cations, such as La^{3+}, Y^{3+}, Pr^{3+}, and Nd^{3+}, have been widely studied as selected dopants[6–11]. The doping of these cations can stabilize the fluorite-related structure of ceria and introduce lattice defects, leading to the improvement of bulk oxygen mobility and thermal stability of ceria. Praseodymium ion has a similar ionic radius to Ce ion, and it also keeps a stable fluorite-related structure. It is therefore used as one of important additives in commercial CZ[12,13].

In comparison to dopant modification, surface modification shows its superiority in improving the stability and the service lifetime of CZ. In our previous work, we have found that the impregnated Sr on the surface of CZ was effective for retarding the sintering of CZ particles and restricting the phase segregation and grain growth during severe hydrothermal ageing process, so that the Sr impregnated CZ presented a better OSC performance than the Sr-doped CZ after ageing treatment[14]. Furthermore, the highly-enriched Sr species existing on the surface of the aged CZ interrupted the interaction between precious metal and CZ for charge transfer, and consequently it maintained the precious metal at a relatively high oxidation state[15]. Such effects would be in favor of catalysis reactions which were sensitive to the valence of precious metal.

In this work, we introduced praseodymia as an additive to the Zr-rich CZ by an impregnation method, which is aiming at investigating the effects of surface impregnated Pr on the structure and OSC of CZ, especially after the high-temperature hydrothermal ageing treatment. To make sense for application in Pd-only three-way catalysts, 1 wt.% Pd was loaded on the supports. The schemes of structural evolutions of the catalysts with and without Pr were also established.

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1 Experimental

1.1 Catalyst preparation

Fresh Ce$_{0.30}$Zr$_{0.70}$O$_2$ (CZ) was prepared by an oxidative co-precipitation method, which had been reported in our previous work[14]. Pr-loaded CZ (PCZ) was obtained by impregnating the aqueous solution of Pr(NO$_3$)$_3$ on CZ and subsequently calcinating at 700 ºC for 3 h for the decomposition of Pr(NO$_3$)$_3$. The theoretical mass percentage of Pr$_6$O$_{11}$ in PCZ was 3%. To obtain the Pd-loaded catalysts, CZ and PCZ were impregnated by the aqueous solution of Pd(NO$_3$)$_2$ and submitted to calcination at 700 ºC for 1 h, and the as-obtained catalysts were denoted as Pd/CZ and Pd/PCZ, respectively. The mass percentage of PdO in both catalysts was 1%. The ageing treatment was performed at 1050 ºC in 10% steam/air flow for 5 h, and the aged catalysts were named as Pd/CZa and Pd/PCZa, respectively.

1.2 Characterizations

The X-ray diffraction (XRD) analysis was conducted on a Japan Science D/max-RB diffractometer employing Cu Kα radiation (λ=0.15418 nm). The X-ray tube was operated at 45 kV and 150 mA. The X-ray powder diffractograms were recorded at 0.02° intervals in the range $20° \leq 2\theta \leq 80°$ with 2 s count accumulation per step. The crystal phase was identified with the help of the JCPDS cards. The average crystallite size of CZ was estimated according to Debye-Scherrer equation.

The specific surface area of the samples was measured using the N$_2$ adsorption at –196 ºC by the four-point Brunauer-Emmett-Teller (BET) method on an automatic surface analyzer (F-Sorb 3400, Gold APP Instrument). Prior to the measurements, the samples were degassed in vacuum at 200 ºC for 2 h.

Palladium particle size was calculated based on the data of CO chemisorption tested by Micromeritics Auto Chem II 2920 apparatus with a thermal conductivity detector (TCD). For each experiment, approximately 100 mg catalyst was placed in a U-shaped quartz tube (i.d.= 10 mm) and reduced in a flow of 10% H$_2$/Ar (50 mL/min) while ramping the temperature up to 350 ºC at the rate of 10 ºC/min, and then held at 350 ºC for 30 min in flowing He (50 mL/min) for proper degassing. After that the sample was cooled down to 25 ºC, the loop gas of 10% CO/He (20 mL/min) was pulsed over the sample and the TCD signal was recorded until the peak area became constant.

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 UHV (6.7×10^8 Pa). Sample charging during the measurement was compensated by an electron flood gun. The electron taking off angle was 45º with respect to the sample surface. The binding energy was calibrated internally by the carbon deposit C 1*s* binding energy (B.E.) at 284.8 eV.

H$_2$ temperature programmed reduction (H$_2$-TPR) was performed on the Micromeritics Auto Chem II 2920 apparatus. Prior to the reduction measurement, 50 mg sample was pretreated in He at 300 °C for 30 min and then cooled down to 0 ºC. Then the samples were reduced in a flow of 10% H$_2$/Ar (50 mL/min) while ramping the temperature from 0 ºC up to 800 ºC while the TCD signal was recorded by the detector. Quantitative hydrogen consumptions were obtained by use of TPR calibration runs using a standard silver oxide sample (Micromeritics) in place of the catalyst. A reduced mass of silver oxide was used so that the absolute hydrogen consumption was in the same range as that determined for the various catalysts examined in this work.

The Raman spectra of the samples were obtained at ambient condition on a confocal micro-Raman apparatus (IDSpec Aurora, China) using Ar$^+$ laser with a CCD detector. Pure powder supported on a sheet glass was used without any pretreatment and the wavelength of laser was 532.0 nm and the exposure time was 20 s while the spectra were recorded.

1.3 Oxygen storage capacity measurement

OSC measurements were carried out in a flow reactor system, designed for powder samples and equipped with solenoid valves for rapid introduction of 4%CO/He pulses. Typically, 25 mg powders were loaded into a quartz tube reactor and a total gas flow rate of 300 mL/min was employed. The channels at 28(CO), 32(O$_2$), 44(CO$_2$), 4(He) and 40(Ar) *m*/*z* in the outlet gas were detected by an on-line mass spectrometer (Omnistar 200, Switzerland) at 0.1 s intervals. After heating in He to the operating temperature and an 5 min O$_2$ pre-treatment, two modes were carried out in order, with an outgassing process under pure He for at least 10 min before each regime: (i) transient regime (dynamic): CO (5s, 4% in He)- O$_2$ (5s, 2% in He) cycles (CO-O$_2$ cycles, 0.1 Hz); (ii) the successive CO pulse regime: CO (5s, 4% in He)-He (40s, pure He) cycles. Total gas flow during the test was 300 mL/min. Dynamic OSC was calculated from the amount of CO$_2$ produced in one CO-O$_2$ cycle under dynamic mode[16]. It could be used to reflect the oxygen storage/release property of such materials under variable atmosphere. The successive CO-pulse test was consisted of 10 cycles of 5s CO/He injection with 40s He-flow outgassing between two CO pulses. The OSC in each pulse was quantified by integrating the concentration of CO$_2$ produced in each CO/He pulse.

2 Results

2.1 Oxygen storage capacity

Concerning the application temperature of TWCs, the OSC performance was typically investigated at 400 and