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Effects of precipitate aging time on the cerium-zirconium composite oxides

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Abstract: Cerium-zirconium composite oxides with high performance were synthesized by a co-precipitation method, using zirconium oxychloride and rare earth chloride as raw materials. The effects of precipitate aging time on the properties of cerium-zirconium composite oxides were investigated. The prepared cerium-zirconium composite oxides were characterized by X-ray diffraction (XRD), BET specific surface area, pulsed oxygen chemical adsorption, H_2 temperature-programmed-reduction (H_2-TPR), scanning electron microscopy (SEM), etc. The results showed that the precipitate aging time caused great effects on the properties of cerium zirconium composite oxides. With the increase of aging time, the cerium zirconium composite oxides showed enhanced specific surface area, good thermal stability, and high oxygen storage capacity (OSC). The best performance sample was obtained while the precipitate aging time up to 48 h, with the specific surface area of 140.7 m^2/g, and OSC of 657.24 μmolO_2/g for the fresh sample. Even after thermal aged under 1000 ºC for 4 h, the aged specific surface area was 41.6 m^2/g, moreover with a good OSC of 569.9 μmolO_2/g.

Keywords: cerium-zirconium composite oxides; co-precipitation; precipitate aging time; thermal stability; rare earths

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In recent years, the emission of automotive exhaust gases (CO, HC_s and NO_x) has been strictly regulated. Automotive three-way catalyst is the effective measure and technology to address the current automotive emissions. Cerium oxide has the unique property of oxygen storage capacity (OSC) originated from the redox of Ce ion. It is demonstrated that the addition of zirconium results in the formation of cerium-zirconium solid solution with better texture properties, higher OSC, and higher thermal stability than pure ceria. Therefore the cerium-zirconium composite oxides are widely used as one of the key components in three-way catalysts (TWCs)[1–3]. Under alternative lean and rich fuel conditions, these oxides can store and release oxygen thereby enabling TWCs to remove the CO, HC and NO_x simultaneously with high efficiency. In order to pursue a good automotive catalyst, it is very necessary to develop the cerium zirconium composite oxides with high specific surface area, good thermal stability, high oxygen storage capacity and good oxygen mobility.

The composition of cerium zirconium composite oxide such as Ce/Zr mole ratio, foreign metals doping has effects on its structure, redox property and thermal stability. In addition, synthesis or preparation methods also cause different structure, physiochemical characterization and performance even with the same composition of cerium zirconium mixed oxides. Up to now, many kinds of synthesis methods and technologies have been investigated to develop a successful and advanced cerium zirconium solid solutions[4], such as co-precipitation[5], hydrothermal synthesis[6], sol-gel[7], templating[8], microemulsion[9] and so on. However the sol-gel, templating and microemulsion methods are all complicated, high cost and not easy to industrialization. In order to get a mass commercial production with low cost and easy operation, the co-precipitation method is the most choice because of its simple process and easy industrial scale up[10]. Rhone Poulenc Chimie[11] reported the cerium zirconium mixed oxides, having contents of zirconium of up to 60 mol.% and high specific surface areas at least greater than 80 m^2/g in a patent in 1995, were well suited as catalysts or catalyst supports for the treatment of vehicular exhaust gases. Okamoto presented a cerium zirconium mixed oxide with improved heat resistance in a patent in 2007, comprising of spherical particles from 5 to 20 nm in size and rod-like particles from 5 to 20 nm in diameter and 30 to 150 nm in length[12]. The cerium zirconium mixed oxides were synthesized by co-precipitation with ammonia as precipitant, and its catalytic application in three-way catalysts in some master/doctoral theses was further investigated[13,14]. It is very important and necessary to reveal the effects of the co-precipitation factors and to control the

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co-precipitation conditions such as pH, ion concentration, temperature, stirring, etc. for obtaining a good product. Letichevskya et al. investigated the role of preparation conditions in cerium zirconium mixed oxides co-precipitation, such as pH control, precipitate aging and Ce precursor, and it is revealed that the use of $Ce(NO_3)_3$ caused the formation of c-CeO_2 and t-ZrO_2 mixed oxide whereas a solid solution was achieved by using $(NH_4)_2Ce(NO_3)_6$[5]. In this study, with the rare earth chloride, zirconium oxychloride as raw metal materials, different cerium zirconium composite oxides were synthesized by a co-precipitation method, and the effects of the precipitate aging time on the physiochemical properties and OSC performance of cerium-zirconium composite oxide were revealed in detail.

1 Experimental

1.1 Synthesis

NaOH (Beijing Chemical Reagent Co., Ltd., chemical grade), $Ce_2(CO_3)_3$ (Baotou Hengyitong Rare Earth Co., Ltd., 99.9%), $ZrOCl_2·8H_2O$ (Zhejiang Shenhuabaike Co., Ltd., 99.99%), La_2O_3 (Jiangsu Yixingxinwei Co., 99.99%) and Nd_2O_3 (Jiangsu Yixingxinwei Co., 99.99%) were used. The $Ce_2(CO_3)_3$, La_2O_3 and Nd_2O_3 were dissolved by hydrochloric acid to get Ce^{3+}, La^{3+}, Nd^{3+} solution, respectively. The solid $ZrOCl_2·8H_2O$ was dissolved in water to get Zr^{4+} solution. The required amounts of the Ce^{3+}, Zr^{4+}, La^{3+}, Nd^{3+} solutions were mixed with a designed Ce/Zr/(La+Nd) molar ratio of 45/45/10. Then co-precipitation was carried out by dropping an sodium hydroxide solution to keep the pH at over 8. The obtained precipitate in a beaker was kept aging at about 60 ºC with a hot water bath for different time, such as for 0, 12, 24, 36 and 48 h respectively. After filtering and washing, the precipitate was dried at 120 ºC in air overnight and calcined in air at 600 ºC for 3 h to get the fresh samples. The samples are denoted as CZLN-0 h, CZLN-12 h, CZLN-24 h, CZLN-36 h, CZLN-48 h, respectively. Some fresh samples were put into a muffle and calcinated at 1000 ºC for 4 h to get the aged samples.

1.2 Characterization

X-ray powder diffraction (XRD) patterns of cerium zirconium composite oxides were recorded in a diffractometer (Netherlands PANalytical X'Pert PRO MPD) with a radiation of Cu Kα (λ=0.15418 nm) at a working voltage of 40 kV and a working current of 300 mA. The X-ray powder diffractograms were recorded between 10º and 90º (2θ) with a step of 0.02º.

Specific surface area, pore volume and pore size were measured using a Quadrasorb SI-KR/4MP automated surface area and pore size analyzer (Quantachrome Inc.). The samples were degassed under vacuum at 280 ºC for 3 h before specific surface area and pore size measurements.

The composition was analyzed using X-ray fluorescence technique. Scanning electron microscopy (SEM) was recorded on EDAX system (EDAX Inc.) at a voltage of 20 kV.

H_2-temperature-programmed reduction (H_2-TPR) of the samples was performed on a Chembet PULSAR TPR/TPD instrument (Quantachrome Inc.). In brief, the samples were firstly pretreated in a 5 vol.% O_2/Ar gas flow at 550 °C for 60 min, and followed by purging with He for 30 min at the same temperature and cooling down to room temperature in He flow. After that, a flow of 10% H_2/Ar was then switched into the system. The samples were subsequently heated up to 950 °C from room temperature at a rate of 10 °C/min.

Oxygen storage capacity (OSC) of the samples was measured using O_2 pulsed chemical adsorption method on Chembet PULSAR TPR/TPD instrument (Quantachrome Inc.). Briefly, the sample was firstly pretreated in 10% H_2/Ar gas flow at 800 °C for 60 min, followed by purging with He gas and cooling down to 500 °C. Being Kept at this temperature, the samples were oxidized by injecting periodically and automatically 289 μL pure O_2 pulses at an interval of about 5 min. OSC was calculated from the amount of O_2 consumption by samples, and expressed in micromoles of O_2 per gram of oxides[15].

2 Results and discussion

2.1 XRD and BET analysis

XRD provides the information about the crystal and phase structure of cerium zirconium samples. Fig. 1 shows the XRD patterns of the five cerium zirconium dried precipitates obtained at different precipitate aging times. All the diffractograms show the main reflections of a fluorite-structured materials, corresponding to the (111), (200), (220), (311), (331) planes, revealing that all the dried precipitates are crystallized. And the diffraction

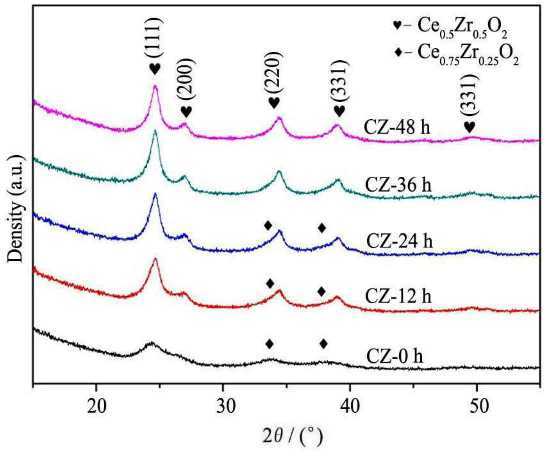

Fig. 1 XRD patterns of the dried precipitates for different precipitate aging time