

Structure and properties of cerium zirconium mixed oxide prepared under different precipitate aging processes

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Abstract: Oriented attachment and Ostwald ripening are two aging mechanisms of precipitation particles which may result in different crystallization mechanism of precipitates during the aging process. In this work, the effects of different aging process on the structure and properties of cerium zirconium mixed oxides were investigated. The results indicated that the mixed structure of 11.48% CeO₂ phase and 88.52% Ce_{0.26}Zr_{0.62}(LaPr)_{0.12}O₂ solid solution phase were obtained under oriented attachment aging process. The rod-like CeO₂ phase coexisted with spherical Ce_{0.26}Zr_{0.62}(LaPr)_{0.12}O₂ solid solution phase, which improved the surface area (64 m²/g) and pore volume (0.32 mL/g) of cerium zirconium mixed oxides after 1000 °C 4 h thermal treatment. However, through controlling the aging process, the Ce_{0.35}Zr_{0.55}(LaPr)_{0.10}O₂ solid solution with homogenous phase structure was generated by Ostwald ripening aging process, exhibiting higher oxygen storage capacity (501 μmol O₂/g) and H₂ consumption per gram (1378.3 μmol H₂/g).

Keywords: cerium zirconium mixed oxides; Ostwald ripening; oriented attachment; co-precipitation; rare earths

The solid solution ceria-zirconia based composites serve as key component in three-way catalysts (TWCs) and have allured a lot of attention which can purify automobile exhaust such as CO, NO_x and hydrocarbons (HC) in the meantime. The addition of TWCs promoter, ceria-zirconia oxygen storage material, can broaden the operating window and enhance the TWCs efficiency under different operating conditions. This is because ceria-zirconia based solid solution has high surface area and large concentration of bulk oxygen vacancy, oxygen species to conduct fast exchanging among gas-phase, surface oxygen and bulk oxygen at high diffusion rates, which are caused by the presence of a rapid Ce⁴⁺/Ce³⁺ redox couple^[1-3].

Nowadays, automobile exhaust emission is one of main pollution source of atmospheric contamination, as a consequence, more and more stringent emission regulations are set up, and also that will spread all over the world. Further efforts are needed to research and exploit higher performance of ceria-zirconia-based oxygen material in the automotive catalyst catering to the need of pollution management. Up to now, extensive research has been conducted about the relationship between cerium zirconium oxygen storage materials and the catalytic performance of TWCs^[4-8], and it was found that the catalytic performance of TWCs correlates to the specific surface area, thermal stability and oxygen storage capac-

ity (OSC) of samples. It is generally known that TWCs is a device installed in positions closer to the engine manifold resultantly which purify exhaust gases. However, the temperature in catalytic converter can rise to even above 1000 °C^[9], at which the catalyst readily sintered after a period of time, leading to the loss of specific surface area, oxygen storage capacity and further reducing the service life of TWCs^[10,11]. Several strategies such as the introduction of rare earths^[3,12-15], base metals^[16,17] and transition metals^[18,19] have been recommended in order to improve the properties mentioned above.

On the other hand, the preparation procedure strongly affects the properties of the cerium zirconium oxygen storage materials and the catalytic performance of its supported TWCs. Numerous synthesis routes including high-energy ball milling, co-precipitation, sol-gel, combustion, hydrothermal process and so on have been developed to prepare ceria-zirconia or ceria-zirconia-based materials^[20-28]. Yet, the most straightforward method is co-precipitation owing to its simple processing and being easy to industrialize. Researchers have carried out extensive studies on pH values, temperature, precipitator and the valence of raw material^[29]. However, in our recent studies, the precipitate aging process also has great effects on physicochemical properties of cerium zirconium composite oxides^[30].

Oriented attachment process and Ostwald ripening

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process are common mechanisms in the precipitate aging processing^[31]. The oriented attachment formation mechanism usually occurs on asymmetric particles in the hydrothermal reactions without intense disturbance, and it depends on the effective collision among nuclei during the reaction. In Ostwald ripening process, the small hydroxide particles dissolve and re-precipitate on big particles in the hydrothermal reactions^[32–35]. Crystal particles possessing the same crystallographic orientation are liable to generate oriented attachment growth pattern, which is beneficial to obtaining rod-like particles and exposed (110) crystal planes with excellent surface activity and moderate stability^[36].

In this paper, cerium zirconium mixed oxides were prepared by co-precipitation with different aging processes, oriented attachment and Ostwald ripening. The effects of aging processing on the composition, structure and properties of cerium zirconium mixed oxides were studied. Understanding different aging process will provide important guidance to prepare powder material in solution.

1 Experimental

1.1 Sample preparation

The raw materials were well-mixed and composed by chloride CeCl_3 , LaCl_3 , PrCl_3 and ZrOCl_2 at the molar ratio of $\text{Ce/Zr}/(\text{La+Pr})=35/55/10$. Then raw materials and precipitant aqueous solution NaOH were added dropwise to the beaker at the same time, controlling the reaction temperature at $80\text{ }^\circ\text{C}$ and the pH value at 10. The obtained precipitate slurry was divided into three portions, of which one was directly filtered and washed with de-ionized water until no pH change was detected^[28] and Cl^- contents were controlled under 100 ppm by measuring the electrical conductivity of washing water until it is below $50\text{ }\mu\text{s}/\text{cm}$ and not changing, another was kept aging at $80\text{ }^\circ\text{C}$ water bath environment with intense stirring corresponding to Ostwald ripening process, the last one was aging at $80\text{ }^\circ\text{C}$ water bath environment without stirring corresponding to oriented attachment process. After aging 48 h, the precipitate was filtered and washed with the same method. Then the related obtained precipitates were dried at $100\text{ }^\circ\text{C}$ in air for 24 h and denoted as CZ-d, CZOR-d and CZOA-d, respectively. And then the fresh samples were calcined in static air at $600\text{ }^\circ\text{C}$ for 3 h, the heating rate was $10\text{ }^\circ\text{C}/\text{min}$. The samples were denoted as CZ, CZOR and CZOA, respectively. A portion of fresh samples were further calcined at $1000\text{ }^\circ\text{C}$ for 4 h in static air condition (the heating rate was also $10\text{ }^\circ\text{C}/\text{min}$) getting the aged samples and denoted as CZ-a, CZOR-a and CZOA-a, respectively.

1.2 Characterization techniques

Powder X-ray data (XRD) of cerium zirconium mixed

oxides were collected on a diffraction instrument (Netherlands PANalytical X'Pert PRO MPD) operated at 40 kV and 40 mA, using $\text{Cu K}\alpha$ radiation ($\lambda=0.15418\text{ nm}$). The powder X-ray data were collected from 10° to 90° (2θ) with a 0.02° step size. The XRD data were further analyzed by Rietveld refinement method using Fullprof if it is necessary.

The BET surface area, pore volume and pore diameter distribution of the samples were measured at $-196\text{ }^\circ\text{C}$ with nitrogen as an absorbent using a Quadrasorb SI-KR/4MP interfaced to a computer (Quantachrome Inc.). The samples were carried out degassing treatment under vacuum at $280\text{ }^\circ\text{C}$ for 3 h before textural properties measurements.

The surface chemical composition and state of different samples were analyzed by X-ray photoelectron spectroscopy (XPS) technology on a Thermo Escalab 250xi X-ray photoelectron spectrometer under $6.7\times 10^{-8}\text{ Pa}$ vacuum condition. The energy source type is monochromatic $\text{Al K}\alpha$ X-rays and energy step size is 1 eV. The C 1s, O 1s, La 3d, Ce 3d, Pr 3d and Zr 3d core levels XPS data were recorded and peaks were identified on the equipped data system. The binding energies positions were adjusted internally by the carbon deposit C 1s binding energy (BE) at 284.8 eV. The XPS spectra peak-differentiation-imitating was fitted by Gaussian function.

Temperature-programmed reduction (TPR) of the samples were carried out in a Chembet PULSAR TPR/TPD instrument (Quantachrome Inc.). Firstly, the samples were pretreated in 5 vol.% O_2/Ar flow at $550\text{ }^\circ\text{C}$ for 30 min, and then in order to blow away the residual oxygen He was switched into the pipeline to sweep the samples for 30 min. The flow of 10% H_2/Ar was then switched into the system until the temperature decreased to ambient automatically. The samples were subsequently heated up to $950\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$.

OSC measurements of all the fresh samples were carried out using a flow reactor system, pulse chromatographic technique on Chembet PULSAR TPR/TPD instrument (Quantachrome Inc.). Briefly, the sample was reduced in 10% H_2/Ar at $800\text{ }^\circ\text{C}$ for 60 min firstly, and then for blowing away the residual hydrogen, helium gas was switched into and the temperature cooled down to $500\text{ }^\circ\text{C}$. OSC was calculated by the consumption of each automatic titration peaks, and expressed in micromoles of O_2 per gram.

2 Results and discussion

2.1 Structural properties

Fig. 1 shows the XRD patterns of the three cerium zirconium dried precipitates obtained by different aging processes. The major peak of the XRD pattern of CZ-d sample was seriously wide with less obvious diffraction

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