Preparation and characterization of nano-crystalline Ce_x-Zr_{1-x}-O_2 catalyst by SAS

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ABSTRACT

The nano-particles of amorphous precursor of Ce-Zr oxides were prepared by SAS process, with average size range was 40-90 nm. After calcinations, the Ce_x-Zr_{1-x}-O_2 nano-particles were formed, which consisted of 5-6 nm nano-crystallines, and showed the solid solution structure. Compared with the Ce_x-Zr_{1-x}-O_2 catalyst prepared by co-precipitation, the Ce_x-$Zr_{1-x}O_2$ catalyst prepared by SAS method indicated higher reduction ability and thermal stability, and could keep higher surface specific area after calcination. It was found that there existed strong co-antisolvents effect between the precursors of Ce and Zr oxides during the antisolvents process, which strongly influenced the molar ratio of Ce to Zr in the precursors.

Keywords Supercritical antisolvent (SAS) precipitation, Ce_x-Zr_{1-x}-O_2 nano-particles, nano-crystalline, solid solution

INTRODUCTION

Cerium oxide is an important environmental catalyst component to eliminate some toxic gases because of its high oxygen storage and transport capacity. However, CeO_2 nanoparticles could be easily sintered at higher temperature, resulting in the apparent decline of catalytic activity. After introduction of zirconia into ceria, not only the oxygen storage capacity and thermal resistance, but also the catalytic activity at lower temperature could be improved by the formation of ceria-zirconia solid solutions, thus which has attracted great interest in this fields [1].Although many methods, such as conventional co-precipitation, sol-gel technique, solution combustion, surfactant assistant approach, microemulsion [2-5], have been applied for the preparation of CeO_2-ZrO_2, the high dispersion uniformity of components becomes the most important index to obtain the ideal catalytic performance of Ce_x-Zr_{1-x}-O_2. In recent years the applications of supercritical antisolvent (SAS) procedure has been reported. As a promising micronization technology for the preparation of catalyst precursors, the products show controllable nano-particle size and rather narrow particle size distribution [6]. In this paper, the Ce_x-Zr_{1-x}-O_2 nano-particles are prepared by supercritical antisolvent process, and their physico-chemical properties are characterizaed.

MATERIALS AND METHODS

Zirconium nitrate pentahydrate (99%), cerium chloride (99%) and acetylacetonate (98%) were purchased from Pengxiang Chemicals Corp. China.

X-ray diffraction characterizations were performed on Rigaku D/MAX-2500 X-ray diffract meter with Ni-filtered Cu-Kα target. High-resolution transmission electron microscopy (HRTEM) characterizations were carried out on JEOL JEM-100CX□system. Thermogravimetric analyses (TGA) of the precursor were carried out on Mettler-toledo Star851e analyzer.The specific surface areas of the samples were measured on Micromeritics Tristar3000 adsorption analyzer. Temperature-programmed reduction (TPR) experiments for the cerium zirconium composite oxides were carried out on Micromeritics Autochem□2920 instrument. Element analyses were carried out on Varian VISTA－MPX with inductively coupled plasma - optic emission spectrometry (ICP-OES).

The precursors $Ce(acac)_3$ and $Zr(acac)_4$ were prepared by the SAS process discribed in [7], and were chosen as precursors of Ce_x-Zr_{1-x}-O_2. The methanol was chosen as solvent and $ScCO_2$ was chosen as antisolvent. The SAS experiments were carried out in a Thur SAS-50 experimental apparatus. The Ce_x-Zr_{1-x}-O_2 nanoparticles were obtained by the calcination of precursor at 873K for 2 hours.

RESULTS AND DISCUSSION

1 Characterization of nano-particles

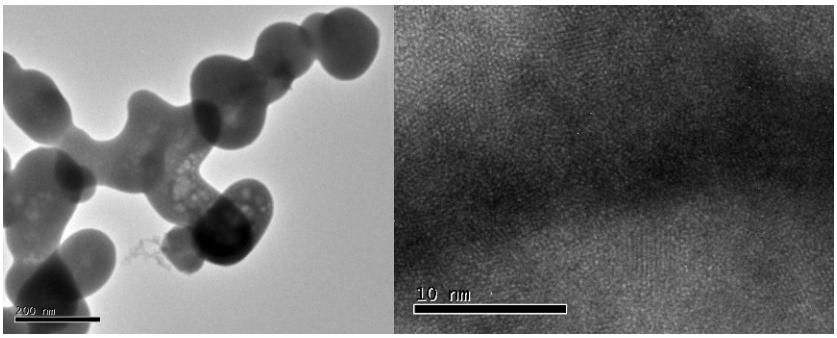

Figure1 HRTEM photographs of $Ce(acac)_3$-$Zr(acac)_4$ nano-particles prepared by SAS method

Figure 1 showed the HRTEM photographs of precursor $Ce(acac)_3$-$Zr(acac)_4$ nano-particles prepared by SAS method. The particles exhibited fairly smooth spherical form with diameter range of about 40-90 nm, which was similar to those for CeO_2 precursor reported by Z. R. Tang [8]. The precursor indicated also the amorphous phase structure, exhibiting the characters of short-range order in the crystal and long-range disorder as a whole, which fact was approved by the XRD characterization results (as shown in Figure 2).

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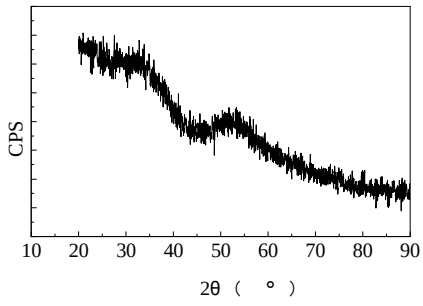

Figure 2 XRD pattern of $Ce(acac)_3$-$Zr(acac)_4$ nano-particles prepared by SAS method

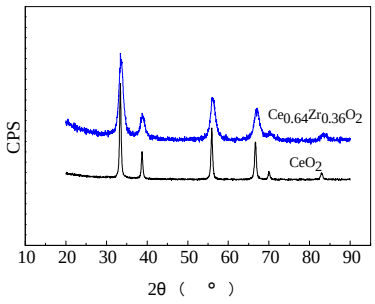

Figure 3 XRD patterns of $Ce_{0.64}$-$Zr_{0.36}$ O_2 nano-particles prepared by SAS method

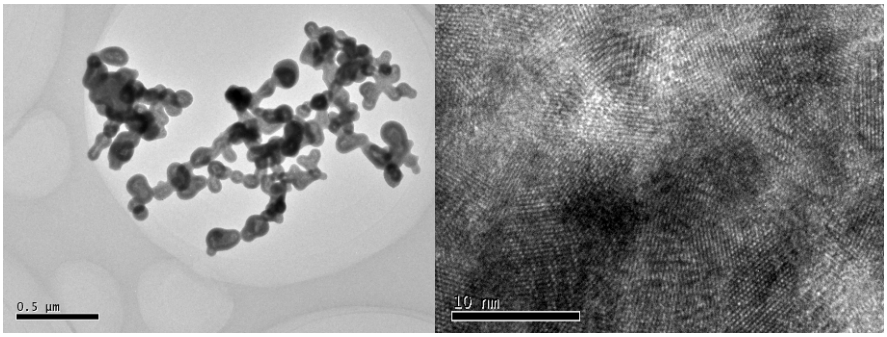

Figure 4 HRTEM photographs of $Ce_{0.64}Zr_{0.36}O_2$ nano-particles prepared by SAS method

The Ce_x-Zr_{1-x}-O_2 nanoparticles with the average size of 70nm were obtained via the calcinations of precursor, Figure 4 indicated that the amorphous structure of precursor was transformed to the well crystlline structure during the calcination, in which 5~6 nm nano-crystallines were dispersed.. The Ce_x-Zr_{1-x}-O_2 nanoparticles showed the characteristic fluorite structure of CeO_2, the ZrO_2 nano-particles might be well dispersed into the fluorite lattice cell of CeO_2 after the calcination, thus the solid solution was generated (as shown in Figure 3.).

2 Co-antisolvent effect of multi-components system

For the SAS process of multi-components system, every single component experienced the antisolvent effect, therefore, there existed the co-antisolvent effect, which could considerably affect the disperson and relative ratio of compontents in the composed nano-particles. In this work, the effect of temperature on co-antisolvent of $Ce(acac)_3$ and $Zr(acac)_4$ was investigated. Table 1 showed the influence of temperature on Ce/Zr molar ratio in the prepared precursor by SAS. It was indicated that the temperature had different antisolvent effect on the two precursors during SAS process. At 318K, Ce/Zr molar ratio reached to the minimum value (1.28 mol/mol), which was far above the initial Ce/Zr molar ratio in feed (1.11 mol/mol), indicating the $Zr(acac)_4$ always presented weaker antisolvent effect than $Ce(acac)_3$ in the experimental temperature range, and the co-antisolvent effect between two precursors was changed with temperature.

Table 1 The influence of temperature on Ce/Zr molar ratio in precursors[a]

Temperature /K	Ce/Zr molar ratio (ICP) /mol/mol
313	1.67
318	1.28
323	1.39
328	1.62

a：Fixing other experimental conditions: pressure 15MPa ; solution flow rate 2 $ml \cdot min^{-1}$; CO_2 flow rate 30 $g \cdot min^{-1}$; initial Ce/Zr molar ratio in feed 1.11 mol/mol

3 Reducibility and thermal stability

Unlike the samples prepared by co-precipitation method, the Ce_x-Zr_{1-x}-O_2 nano-particle catalyst prepared by the SAS method exhibited only single reduction peak centred at 600℃ and more H_2 comsumption, implying that surface and bulk reduction of cerium zirconium composite oxides material could occur at the same temperature. The main reason was probably that the Ce_x-Zr_{1-x}-O_2 prepared by SAS method was made up with lots of homogeneous dispersed microcrystallites which inhibited better unformity.

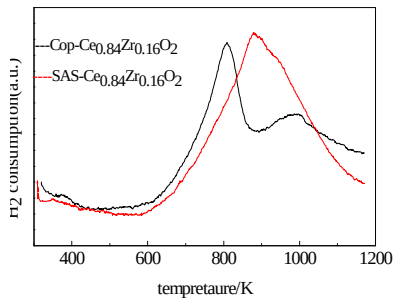

Figure 5 H_2-TPR data of cerium zirconium composite oxides prepared by SAS and precipitation method

The thermal stability was an important property for the CeO_2-based catalyst material, especially when used in the three-way catalysts. The BET surface area data in Table 2 showed that the nano-particle samples prepared by SAS method indicated much better thermal stability than those obtained by co-precipitation method. It was found that, after calcination at high temperature, the BET surface area of Ce_x-Zr_{1-x}-O_2 nano-particle prepared by SAS method was changed only slightly, whereas the BET surface area of the samples prepared by co-precipitation method dropped sharply from 23.03 $m^2 \cdot g^{-1}$ to 0.091 $m^2 \cdot g^{-1}$.

Table 2 The effect of calcination temperature on the specific surface area of Ce_x-Zr_{1-x}-O_2 samples

Preparation method	BET surface area[a] /$m^2 \cdot g^{-1}$	
	After calcination at 873K,2hrs	After alcination at 1173K,2hrs
SAS process	9.35	10.68
Co-precipitation	23.03	0.091

CONCLUSION

The nano-particles of amorphous precursor of Ce-Zr composite oxide was prepared by SAS with the average size range of 40-90nm. After calcinations, the 70nm size Ce_x-Zr_{1-x}-O_2 nano-particles were formed, which consisted of 5-6nm nano-crystalline. XRD test results showed that the Ce_x-$Zr_{1-x}O_2$ solid solution structure was generated after the calcination of precursor.

It was found that there existed strong co-antisolvents effect between the Ce and Zr precursors during the supercritical antisolvents process, which could strongly affect the molar ratio of Ce to Zr in the precursors.

Compared with the Ce_x-Zr_{1-x}-O_2 particle samples prepared by the co-precipitation method, the Ce_x-$Zr_{1-x}O_2$ nano-particle catalyst prepared by SAS method showed higher reduction ability, oxygen storage capacity and thermal stability.

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