Preparation of La_2O_3-doped CeO_2–ZrO_2 Solid Solution with High Thermal Stability by Water-in-Oil Microemulsion

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Nanoparticles of the CeO_2–ZrO_2–La_2O_3 solid solution were prepared by the W/O microemulsion method. Ceria–zirconia–lanthana (Ce/Zr/La = 1/1/0.06, mol) sample calcined at 1000 °C for 4 h has higher surface area (126 m^2/g) and excellent thermal stability. Its particle size is 5–10 nm. The presence of lanthana in the sample can improve obviously the thermal stability of the CeO_2–ZrO_2 solid solution.

Materials containing ceria are attracting much attention because of their use as a promoter and oxygen storage/release material in the catalysts for the purification of emissions from automobiles.[1] A strong effort has been directed to increase the overall efficiency of CeO_2 in these applications and the properties of the ceria–zirconia mixed oxides are improved continually. The presence of ceria–zirconia enhances the redox and oxygen storage properties of catalyst,[2] improves its thermal stability and catalytic activity at lower temperature.[3] As a key material of the three-way catalyst, CeO_2 can release and uptake oxygen based on the following reversible reaction.[4]

$$\text{Oxygen storage: } x/2O_2 + CeO_{2-x} \rightarrow CeO_2,$$
$$\text{Oxygen release: } CeO_2 \rightarrow CeO_{2-x} + x/2O_2.$$

In the three-way catalyst, CeO_2 works as an oxygen buffer. CeO_2 stores oxygen when an engine is running in the fuel-lean condition and provides oxygen in the fuel-rich condition. One of the keys to this success is to choice the appropriate preparation method and to design suitable composition, which determines homogeneity at a molecular level and textural and morphological properties. Several methods have recently been described to prepare the CeO_2–ZrO_2 solid solution used in the catalysts, such as the high temperature firing or high-energy milling of the mixture oxides, coprecipitation and sol–gel methods.[5]

A microemulsion, a monodispersed system of water, oil and surfactant, is a single phase, isotropic and thermodynamically stable liquid solution. It provides a superior template and microenvironment for preparing nanomaterials. A novel preparation method of the La_2O_3-doped CeO_2–ZrO_2 solid solution with high surface area was developed by using water-in-oil (W/O) microemulsion.

The lanthana-doped CeO_2–ZrO_2 solid solution was prepared by the W/O microemulsion as follows. Cerium, zirconium, and lanthanum nitrates (Ce/Zr/La = 1/1/0.06, mol) were used to prepare an aqueous solution. A microemulsion (water in oil) was prepared by mixing an aqueous solution above with polyethylene glycol octyl phenyl ether/*n*-hexanol/ cycalohexane (1.0/1.6/2.3, volume) under stirring. This microemulsion was mixed with 30% aqueous ammonia under stirring, then stirring continually for 4 h until pH = 10.0. This suspension solution was aged overnight, then centrifuged, the solid was dried at 100 °C for 24 h and calcined at 600 °C for 4 h to obtain the yellow sample. For the comparison, the sample was also prepared with coprecipitation method, in which the precipitates were dried at 100 °C for 12 h and calcined at 600 °C for 4 h.

The results in Table 1 show the sample synthesized by microemulsion method has higher surface area and pore volume than that of sample prepared by coprecipitation. After calcined at 1000 °C for 4 h, the BET surface area of sample is about 126 m^2/g; if the sample (Ce/Zr = 1/1, mol) does not contain La_2O_3, its surface area is 35.5 m^2/g only. It is sure that the presence of La_2O_3 can promote obviously thermal stability of the sample at high temperature. Adding lanthana can also increase obviously its oxygen storage capacity (OSC). For the sample calcined at 600 °C for 4 h, the OSC of Ce–Zr–La–O is 0.26 mL O_2/g (198 m^2/g), and that of Ce–Zr–O is 0.15 mL O_2/g (115 m^2/g), which shows that the high surface area is in favor of increasing the OSC of catalyst.

The nitrogen adsorption isotherm of the CeO_2–ZrO_2–La_2O_3 sample calcined at 600 °C for 4 h is shown in Figure 1. It tallies with the adsorption isotherm of type IV, a typical pattern for the mesoporous sample, in which there is the capillary coacervation of uniform mesoporous pore.[6]

There are the diffraction peaks at $2\theta = 28.7°$, 33.3°, 47.8°, 56.8° and 77.1° in the XRD spectra of samples (Figure 2), which accords well with that of the CeO_2–ZrO_2 solid solution,[2,7] a cubic fluorite-type phase. The diffraction peaks of single oxide have not been observed. With increasing the calcination temperature, the diffraction peaks reinforce and the peak breadth narrows. The broad peaks are attributed to the small crystallites. The average particle size of sample can be estimated by the

Table 1. Pore volume and BET surface area of CeO_2–ZrO_2–La_2O_3 calcined at 600 °C for 4 h

	Method	
	Microemulsion	Coprecipitation
	Area/m^2/g	
Single point surface area	198.3 (126.2[a]) 115.3[b] (35.5[a,b])	56.0
Adsorption cumulative surface area of pore	213.3	64.5
Desorption cumulative surface area of pore	230.2	69.9
	Volume of pore/cm^3/g	
Adsorption pore diameter	0.83	0.24
Desorption pore diameter	0.84	0.26

[a] Calcined at 1000 °C for 4 h.; [b] Ce/Zr = 1/1 (mol) and no La.

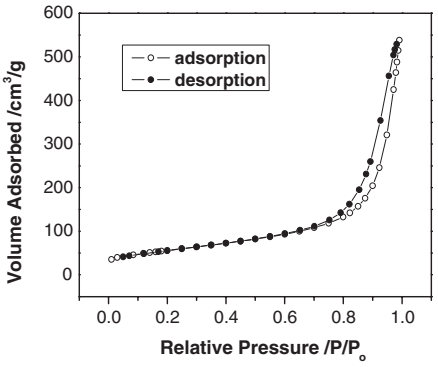

Figure 1. Nitrogen adsorption isotherms of CeO_2–ZrO_2–La_2O_3 calcined at 600 °C for 4 h.

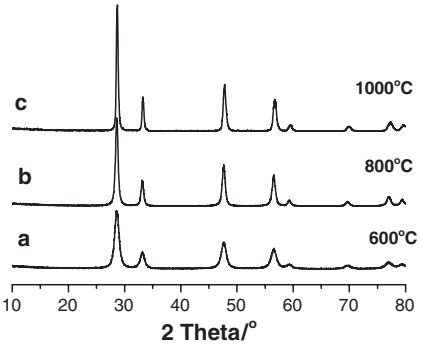

Figure 2. XRD patterns of CeO_2–ZrO_2–La_2O_3 calcined at 600 °C (a), 800 °C (b) and 1000 °C (c) for 4 h.

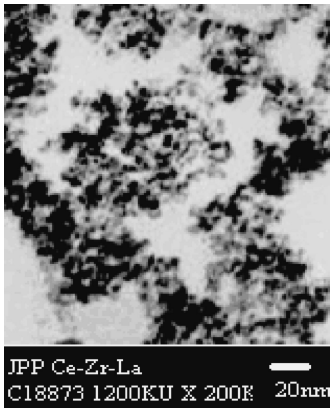

Figure 3. TEM photograph of CeO_2–ZrO_2–La_2O_3 calcined at 600 °C for 4 h.

line-broadening method.[8] The average particle sizes of the sample calcined at 600 and 1000 °C for 4 h are 6.8 and 10.5 nm, respectively. The results show that a high temperature makes the particles of sample grow up, and the sample prepared by the W/O microemulsion method has very high thermal stability. The presence of La_2O_3 can retard the splitting of a crystal phase of Ce–Zr–O into CeO_2 and ZrO_2 by La^{3+} inserting CeO_2–ZrO_2 lattice phase.

The TEM photograph of CeO_2–ZrO_2–La_2O_3 in Figure 3 shows that the particles of sample prepared by the microemulsion method are very fine and near-spherical, and its particle size is 5–10 nm. These observations are in accordance with the results obtained by the XRD spectra using the line-broadening method.

FT-IR spectra of the sample are shown in Figure 4. There are main infrared absorption bands at 3420 and 1634 cm^{-1}, that are the same as the absorption bands of the CeO_2–ZrO_2 solid solution.[9] It shows that the CeO_2–ZrO_2–La_2O_3 solid solution has formed. After the sample was calcined at 400–1000 °C, the absorption bands have shifted hardly, and the peak area decreases with a decrease of the surface area of sample. This is also proved that the sample prepared has very high thermal stability.

In conclusion, the La_2O_3-doped CeO_2–ZrO_2 solid solution with excellent thermal stability has been successfully synthesized in the polyethylene glycol octyl phenyl ether/*n*-hexanol/cyclohexane/water system, a W/O microemulsion using aqueous NH_3 solution as precipitation agent. The sample calcined at 1000 °C for 4 h exhibits fine nanoparticle (≈10 nm), the high surface area (≈126 m^2/g), which is superior to advanced CeO_2–ZrO_2 solid solution.[10]

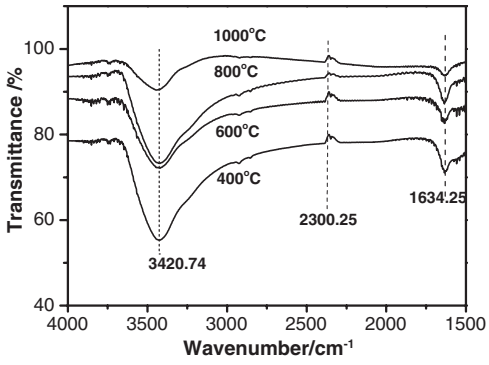

Figure 4. FT-IR spectra of CeO_2–ZrO_2–La_2O_3 calcined at 400–1000 °C for 4 h.

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