Preparation and characterization of high specific surface area CeO0.5Zr0.5O2 mixed oxide
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Received 29 May 2003; revised 8 September 2003

A high specific surface area CeO0.5Zr0.5O2 mixed oxide has been prepared by means of a co-precipitation method with Ce(NO3)3 and Zr(NO3)4 as raw materials. Experimental results show that specific surface area of the Ce0.5Zr0.5O2 mixed oxide is largely affected by the amount of surfactants added, pH and ageing time. Specific surface area was up to 279.69 m2/g at 70% of surfactants, pH 9.5, ageing time 120 h and calcination at 923 K for 2 h. Analysis by FT-IR indicates that the remaining surfactants are removed after calcination at 923 K for 2 h. There are two weightless phenomena in the TG curve and two heat-absorptive peaks in the DTA curve. The first heat-absorptive peak is the desorption process of adsorbed water and acetone at 373 K and weightless ratio of 7.43%, and the second peak is the decomposition of the surfactants at 773 K. The N2 adsorption-desorption experiment indicates that all the materials are porous and the N2 isotherms of all powders are of type IV, typical of a mesoporous sample. The XRD analysis shows the diffraction peak of Ce0.5Zr0.5O2 mixed oxide between 20 29.1°, 34° and 48.5°. The Ce0.5Zr0.5O2 mixed oxide possesses even grain size and stable crystalline structure, and its specific surface areas are 230.69, 120.55 and 53.53 m2/g after calcination at 973, 1073 and 1173 K for 2 h, respectively.

In recent years, CeO2 and materials containing CeO2 received much attention. Some studies found that the storing and releasing oxygen ability and high temperature resistance were greatly improved in Ce0.5Zr0.5O2 mixed oxide compared to CeO2 alone1-5. ZrO2 is an excellent catalyst support6-8. CeO2 has a structure of fluorite and is an efficient assisting catalyst due to its high ability of storing and releasing oxygen. The redox reaction of Ce4+/Ce3+ also plays a role of chemical regulator in air-to-fuel ratio. In Ce0.5Zr0.5O2 mixed oxide, some of Ce cations in the original lattice were replaced by Zr cations because the radius of Zr cation is smaller than that of Ce cation. The lattice contraction of CeO2 face-centered cubic structure led to micro-straining of its crystallinity and defectiveness of the face-centered cubic. As a result, flowing rate of oxygen anion in the fluorite lattice was largely enhanced, and the high ability of storing and releasing oxygen increased the activity of catalyst9. By comparison, single CeO2 would be self-sintered at high temperature (>1023 K) and led to decrease at catalytic activity. The Zr addition stabilized the cubic fluorite structure and improved anti-sintering ability of the assisting catalyst at high temperature10,11. In addition, different molar ratios of Ce/Zr could make the Ce0.5Zr0.5O2 mixed oxide to possess different structures. At a molar ratio of 0.5, Zr increased the defect space and oxygen flowing rate to the largest extent and CeZr1.5O2 had the highest catalytic activity12-15.

The high specific surface area of Ce0.5Zr1.5O2 mixed oxide could increase thermal stability of its carrier and assistant and benefit to the loading and dispersion of active constituents on the carrier, and would play an important role in the catalytic reactions of automotive exhaust (CO+O2, NO+CO).

Experimental

Synthesis of Ce0.5Zr0.5O2 mixed oxide
Zr(NO3)4·5H2O and Ce(NO3)3·6H2O were dissolved in distilled water, and then mixed with a cation surfactant, hexadecyl trimethyl ammonium bromide, to obtain a yellow solution. The mixture was slowly added, with stirring, into an ammonia water (125 ml of 25% ammonia + 125 ml water, pH=9.5) in a 600 ml beaker until the formation of a precipitant first showing slightly purple, then yellow colour. The mixture was continuously stirred for 1.5 h, followed by the oil bath at 363K for 5 days. The ageing product was filtered, and washed first with hot water and then with acetone. After being dried for 24 h, the lay-up product was put into a muffle furnace to calcine at 923 K for 2 h (β = 10 K/min).

Characterization of Ce0.5Zr0.5O2 mixed oxide
The BET parameters—The BET specific surface area, pore volume and pore size distributions of samples were obtained from the adsorption and desorption isotherms of nitrogen at 77 K by a Coulter OMNISORB-100 instrument. Surface area was measured following the BET procedures, and pore size distribution using the Full-Sorb model. Total pore volume was measured at P/P0 = 0.981.
FT-IR—The samples were mixed with KBr and ground to the size of micrometer. After pressing, the FT-IR spectrum was determined by a Nicolet 560 E.S.P magma IR spectrograph.

TG-DTA—The determination was made by a DTATG 7 thermal analyzer (PE, America) under the conditions of around 10mg sample, O₂ atmosphere, rates of temperature increment at 10, 20 and 30 K/min respectively.

H₂-TPR—A sample of 5–10 mg was activated in an O₂ stream at 773 K for 0.5 h. After it was cooled to 303 K, H₂-TPR was conducted by gas chromatography using a thermal conductivity detector. The reduction gas was a mixture of 5% H₂ and 95% N₂. Both H₂ and N₂ were purified using a 401 deoxidiser and silica gel. The flow rate of the H₂/N₂ mixture was 18 ml/min (p= 20 K/min).

XRD—X-ray diffraction (XRD) data were obtained at 298 K using a horizontal Rigaku B/Max IIIB powder diffractometer with CuKα radiation and a power of 40×30 mA. The diffraction angle was 20°, and the wavelength of the source used was CuKα = 1.540598 Å.

SEM—Scanning electron microscopy (SEM) was carried out using a X-570 microscope (Japan) at an accelerating voltage of 20 kV.

Results and discussion

Effect of surfactant

The Ce₀.₅Zr₀.₅O₂ mixed oxide was formed by the reaction of cation surfactant and hydrate of the mixed oxide in a basic medium and had a high specific-surface-area. The surfactant can form a double electro-layer on the particle surfaces, reduce the surface free energy, and restrain the particles from agglomeration. In our study, the solutions of surfactant and Ce/Zr were well mixed and stirred thoroughly during precipitation. As a result, particles of the Ce₀.₅Zr₀.₅O₂ mixed oxide were separated from each other, which restrained the formation of crystal grains and hindered the sintering of particles at calcination. When the surfactant was added into the porous materials, it would reduce the interfacial energy and the surface tension of water. It could also prevent contraction and subsidence of the reticulate structure when dried and calcined and help to maintain high specific surface area.

The amount of surfactant added was critical for the formation of high specific surface area of Ce₀.₅Zr₀.₅O₂ mixed oxide (Table 1). The specific surface area reached maximal at 70% amount of surfactant and decreased dramatically at either more or less amount of surfactant added.

After being washed with water and acetone repeatedly, the hydrate still contained a large amount of alkyl amine. As shown in the FT-IR measurements [Fig. 1 line (a)], the samples had special absorptive peaks at the wavenumbers of 2800-2900 cm⁻¹ and 1600 cm⁻¹ after being dried at 353 K. The stretches and curves of these peaks matched with the carbon-hydrogen bond absorptive peak of the surfactant, indicating that surfactant existed on the dried samples despite being washed repeatedly. After the samples were calcined at 923 K for 2 h, the peaks around the wavenumbers of 2800-2900 cm⁻¹ and 1600 cm⁻¹ disappeared, indicating that the surfactant was cleared up and no carbon or nitrogen atom remained on the surface of the Ce₀.₅Zr₀.₅O₂ mixed oxide [Fig. 1 line (b)].

Effect of medium pH

The specific surface area of Ce₀.₅Zr₀.₅O₂ mixed oxide was quite small at the medium pH 7.5 and reached a maximal value of 279.69 m²/g at pH 9.5, but decreased when the medium pH was above 9.5 (Fig. 2a).

In the process of crystallization, the medium pH of the mother solution was highly important. A co-precipitation occurred at pH>8 and the existence of the surfactant. The cation altered between H⁺ and the surfactant. Within a certain scale, an increase of OH⁻ concentration caused the equilibrium to react towards the right direction so that the process of crystallization hastened. On the other hand, lack of alkalinity would slow down the reaction and thus crystallization was incomplete and samples were impure.

The hydrate of Zr could mix with the cation surfactant effectively at any medium pH above the equipotential point. The equipotential point of Zr hydrate (6.70) was close to that of Ce hydrate (6.75), and therefore the convertible positions existed widely on

<table>
<thead>
<tr>
<th>Sample No</th>
<th>pH</th>
<th>Ageing time (h)</th>
<th>Surfactant (%)</th>
<th>Specific surface area (m²/g)</th>
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<tr>
<td>1</td>
<td>9.5</td>
<td>120</td>
<td>40</td>
<td>186.27</td>
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<tr>
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<td>9.5</td>
<td>120</td>
<td>60</td>
<td>219.54</td>
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<tr>
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<td>9.5</td>
<td>120</td>
<td>70</td>
<td>279.69</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
<td>120</td>
<td>80</td>
<td>193.69</td>
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<tr>
<td>5</td>
<td>9.5</td>
<td>120</td>
<td>100</td>
<td>180.54</td>
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Fig. 1—FT-IR pattern of CeO₂/ZrO₂ mixed oxide dried at 353K and at 923K (a) dried at 353K; (b) dried at 923K.

Fig. 2—Effect of synthesis conditions on the specific surface area of CeO₂/ZrO₂ mixed oxide (a) Medium pH, (b) Ageing time, (c) Calcinating temperature.
the surface where the hydrates could be replaced. At low pH, the binding ability of surfactant was weak due to shortage of exchangeable hydroxyl group on the surface and porous structure.

Effect of ageing time

After the sample was aged at 363 K for 24 h, the specific surface area of Ce0.5Zr0.5O2 mixed oxide was 93.8 m²/g (Fig. 2, b). The specific surface areas were 172.95 m²/g for 48 h, 189.45 m²/g for 72 h, and 279.69 m²/g for 120 h, but would remain largely unchanged with further increase in the ageing time.

Structure feature and N₂ adsorption

In order to examine the effects of calcining temperature on specific surface area and porous structure, N₂ adsorption-desorption of samples pretreated at different temperatures were measured. As shown in Fig. 2(c), the specific surface area of Ce0.5Zr0.5O2 mixed oxide decreased from 279.69 m²/g to 53.53 m²/g as the calcining temperature increased. This was because high temperature intensified calcinations and caused particle aggregation. The results of N₂ adsorption-desorption indicated all materials were porous. The isotherms were of Type IV with an obvious hysteretic ring, i.e. typical of a meso-porous and more-porous sample. In addition, pore size distribution of the samples was related to calcining temperature. It was between micro-pores and meso-pores at 923 K, was micro-porous but slightly leaned to meso-porous at 1073 K and mainly meso-porous at 1173 K, i.e. with increase in calcining temperature, micro-pores in the mixed oxide decreased while meso-pores increased. In the mean time, the pore size distribution became more narrowly ranged. The sample calcined at 1173 K had a pore radius of around 30-40nm, and was a typical meso-porous material.

The adsorption volume of the sample calcined at 923 K was higher than those treated at 1073 K and 1173 K. While total pore volume of the sample decreased with increase in calcining temperature, the average pore radius increased (Table 2). All these were due to the sintering of Ce0.5Zr0.5O2 mixed oxide or solid solution particles after calcined at high temperature, which caused aggregation of the mixed oxide and reduction of the micro-pores. As a result, some micro-pores were converted to meso-pores, and the pore volume and the specific surface area decreased.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Calcining temperature (K)</th>
<th>Specific surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore radius (nm)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>923</td>
<td>279.69</td>
<td>4.90×10⁻¹</td>
<td>7.01</td>
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<tr>
<td>2</td>
<td>973</td>
<td>230.69</td>
<td>4.11×10⁻¹</td>
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<td>3</td>
<td>1073</td>
<td>120.55</td>
<td>2.49×10⁻¹</td>
<td>8.28</td>
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<tr>
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<td>1173</td>
<td>53.53</td>
<td>1.44×10⁻¹</td>
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</table>

H₂-TPR profiles

The TPR profiles of CeO₂, ZrO₂ and Ce0.5Zr0.5O2 mixed oxide showed that ZrO₂ was not easy for reduction and CeO₂ had two small peaks due to the reductions of surface oxygen at 703 K and bulk oxygen at 843 K. By comparison, the Ce0.5Zr0.5O2 mixed oxide had a much bigger reduction peak at 803 K, indicating that the reducive ability of Ce0.5Zr0.5O2 mixed oxide was greater than CeO₂ or ZrO₂ alone.

XRD patterns

The XRD patterns of Ce0.5Zr0.5O2 mixed oxide at 923, 973, 1073 and 1173 K for 2 h are recorded. The diffraction peak of Ce0.5Zr0.5O2 mixed oxide appeared between 20 29.1°, 34° and 48.5° and sharply become much narrower after being calcined at 1173 K for 2 h.

SEM photographs

As can be seen in Fig. 3, the crystalline of Ce0.5Zr0.5O2 mixed oxide did not change after calcination at 923, 973 and 1073 K for 2 h, but enlarged slightly after calcination at 1173 K for 2 h. This may suggest that the Ce0.5Zr0.5O2 mixed oxide prepared by means of co-precipitation possessed even grain size and stable crystalline structure.

TG-DTA curves

The TG-DTA curve of the sample dried at 363 K for 24 h was obtained. During the measurement, the rate of temperature increment was 10 K/min. There were two obvious phenomena of weightlessness in the TG curve and two heat absorption peaks in the corresponding DTA curve. The first heat absorption peak was the desorption of the adsorbed water and acetone at 373 K and a weightless ratio of 7.34%, and the second peak was probably the decomposition peak of the surfactant at 773 K. The results matched with that of the FT-IR, indicating that the remaining surfactants on the Ce0.5Zr0.5O2 mixed oxide were removed after being calcined at 723 K.
Fig. 3—SEM photographs of Ce₀.₅Zr₀.₅O₂ calcined at (a) 923, (b) 973, (c) 1073 and (d) 1173 K for 2h

There was no weightlessness after calcination at 1073 K and all the surfactants were cleared up. The same conclusion can also be derived from the FT-IR curve of the sample calcined at 923 K, which did not show the absorptive peak of surfactant.

To conclude: (i) A high specific surface area Ce₀.₅Zr₀.₅O₂ mixed oxide was prepared by means of co-precipitant method and the specific surface area was largely affected by the amount of surfactant added, medium pH, ageing time and calcining temperature; (ii) the specific surface area of Ce₀.₅Zr₀.₅O₂ mixed oxide was up to 179.69 m²/g when the amount of surfactant added was 70%, medium pH 9.5, ageing time of 120 h and calcined at 923 K. The specific surface area was only 53.53 m²/g after calcination at 1173 K for 2 h; (iii) the adsorption-desorption isotherms of Ce₀.₅Zr₀.₅O₂ mixed oxide were of type IV, typical of a meso-porous sample; (iv) the Ce₀.₅Zr₀.₅O₂ mixed oxide had greater reductive ability than CeO₂ or ZrO₂ alone and (v) the Ce₀.₅Zr₀.₅O₂ mixed oxide prepared by means of co-precipitation possessed even crystalline size and stable structure.

References