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RESEARCH PAPER

Intergrowth Effects in CeO_2-γ-Al_2O_3 Mixed Oxides

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Abstract: An improved amorphous citric precursor method was used to synthesize Ce-Al-O mixed oxides. The samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, ^{27}Al magic angle spinning nuclear magnetic resonance, N_2 adsorption, and oxygen storage capacity (OSC) measurement. There was a strong intergrowth interaction between CeO_2 and γ-Al_2O_3 oxide crystallites during the synthesis, which influenced the microstructure and crystal growth of the two coexisting oxides and resulted in a high hydrothermal stability for γ-Al_2O_3. The OSC per unit mass of the Ce-Al-O system was 2–3 times higher than that of a single phase CeO_2 with a nanocrystalline structure even after hydrothermal treatment at a high temperature. With a mechanical mixture, this improved OSC was not observed because there was no oxide crystallite intergrowth.

Key words: ceria; alumina; biphasic intergrowth; strong interaction; lattice strain; hydrothermal stability; oxygen storage capacity

Cerium oxides (CeO_2) are widely used as oxygen storage materials in three-way catalysts (TWC) for automobile exhaust purification. Since the early 1980s, CeO_2/Al_2O_3 mixed oxides have been investigated, and the effects of the Al_2O_3 support on the performance of CeO_2 discussed [1–7]. In these investigations, the CeO_2/Al_2O_3 catalysts were prepared by impregnation, in which a CeO_2 phase was formed on the surface of the Al_2O_3 support. They coexisted, but there was no biphasic intergrowth. To induce biphasic intergrowth in the CeO_2-Al_2O_3 system, Djuricic et al. [8] and Sasikala et al. [9] prepared nano-composite materials of CeO_2 and Al_2O_3 using sol-gel and co-precipitation methods. The samples reported by Djuricic et al. [8] showed a third phase, namely, $CeAlO_3$, even at 573 K. The samples reported by Sasikala et al. [9] did not show this third phase, but they performed their study by ^{27}Al magic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR). A detailed investigation on the biphasic intergrowth of nano-CeO_2-Al_2O_3 mixed oxides (Ce-Al-O) as OSC materials has not yet been reported.

In our previous work, we studied biphasic intergrowth zeolites [10], $CuCrO_2/CuCr_2O_4$ composite oxides [11,12], and nanoscale spinel electrode materials [13,14]. Here we report biphasic intergrowth effects in nano-Ce-Al-O mixed oxides prepared by an improved amorphous citric precursor (IACP) method. The effects of the preparation method on the structure and properties are discussed.

1 Experimental

1.1 Sample preparation

Ce-Al-O mixed oxides with different Ce:Al molar ratios (9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9) were prepared by the IACP method. In a typical synthesis, 2.0 mol/L of both $Ce(NO_3)_3\cdot 6H_2O$ (AR, Beijing Chemical Reagent Plant, China) and $Al(NO_3)_3\cdot 9H_2O$ (AR, Beijing Chemical Reagent Plant, China) were dissolved in deionized water. Mixed solutions with different Ce:Al molar ratios were prepared by mixing the above solutions. Citric acid (AR) was added to the solution until the molar ratio of citric acid to the total amount of metal ions was 1:2. After the citric acid was dissolved, the solutions were stirred overnight. Carbon black (Cabot VXC-72 with specific surface area of 254 m^2/g) was added to soak up the solution. The solution-soaked carbon black was dried at 373 K, grounded into a fine powder, decomposed at 533 K, and calcined at 973 K under air flow for 3 h. These products are referred to as fresh samples. The mixed oxides of Ce-Al-O were yellow. For comparison purposes, a mechanical mixture of

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CeO_2 and γ-Al_2O_3 with a Ce/Al molar ratio of 1:1 was prepared by mixing CeO_2 and γ-Al_2O_3, which is referred to as CeO_2-γ-Al_2O_3.

The steam-aged samples were prepared by treating the oxides with 90% steam and 10% air for 12 h at 1 061 K.

1.2 Characterization

Powder X-ray diffraction (XRD) data were collected at room temperature on a Rigaku D/max-rA diffractometer with Cu K_α radiation and a graphite monochromator. The measurement conditions were 40 kV and 120 mA. Step scans were taken over the range of 2θ = 25°–80° in steps of 0.02°. The intensities for each point were collected for 2 s for phase identification and lattice parameter calculation. The data used to determine the average grain sizes and strain of CeO_2 samples were taken over the range of 2θ from 37° to 52° in steps of 0.01° and 10 s/step.

The lattice parameters were obtained by Fullproful 2000 [15,16]. The peak at 2θ of 47.3°, which corresponded to the (220) reflection of CeO_2, was nearly symmetric and fitted a Voigt lineshape well [17]. This diffraction peak was selected to determine the average crystalline sizes ($\overline{D}_{110}$) and the root-mean square strain $<\varepsilon_{110}^2>^{1/2}$ [17]. A well-crystallized CeO_2 sample was used as standard to calibrate the instrumental broadening contribution.

^{27}Al MAS NMR experiments were carried out at 9.4 T on a Varian Infinity plus-400 spectrometer equipped with a Chemagnetic double-resonance 4-mm probe. The samples were packed into a ZrO_2 NMR rotor (4 mm o.d.) with a Kel-F end cap. The resonance frequency was 104.26 MHz for ^{27}Al. The excitation pulse length was adjusted to $\pi/12$, and the pulse duration was 0.5 s for ^{27}Al single-pulse experiments. The ^{27}Al chemical shift was referenced to a 0.1 mol/L $Al(NO_3)_3$ solution. The MAS spinning speed was 11 kHz.

BET specific surface area was measured by nitrogen adsorption at 77.3 K on a Micromeritics ASAP 2010 analyzer after outgassing the samples under vacuum at 623 K. The specific surface area was calculated from the desorption branch of the isotherm using the BET formula.

X-ray photoelectron spectroscopy (XPS) data were collected on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K_α radiation (15 mA, 15 kV). The irradiated area was 2 mm × 1 mm. The detection depth was 2–5 nm. To compensate for surface charge effects, binding energies (BE) were calibrated by setting the measured BE of C 1*s* to 284.8 eV. The surface composition was obtained according to a literature method [18].

1.3 OSC determination

The oxygen storage capacity (OSC) was measured using a quartz fixed-bed microreactor [1]. The temperature used was 973 K. The effluents were analyzed by a GC-7890T gas chromatograph (Shanghai Tianmei Instrument Co. Ltd., China). The powder samples were pressed into tablets under 2 MPa, crushed into small pieces, and sieved. The samples (10–20 mg, 40–60 mesh) were mixed with 20 mg of quartz (40–60 mesh). The mixture was charged into a U-shaped quartz reactor (6.0 mm i.d.) with a sieve plate. The bed temperature was maintained within ±0.5 K. The amount of sample was chosen so that the CO remaining was in the range of 40%–60% of the CO content in the control experiment. A 2 ml mixture of 5.29% O_2-94.71% He gas was injected into the reactor five times at intervals of 2 min to fully oxidize the sample. Subsequently, 5 ml reducing gas (5.0% CO-95.0% He) was introduced into the reactor and the integrated area of the remaining CO was recorded. The above oxidation and reduction cycle was repeated five times and the results were averaged. The OSC (μmol/g) was calculated by averaging results using

$$\mathrm{OSC} = (1 - S_\mathrm{R}/S_\mathrm{B})\times M_\mathrm{B}/W$$

where S_R is the integrated area of remaining CO (μV·s), S_B is the integrated area of CO in the blank analysis (μV·s), M_B is the amount of CO in the blank analysis (μmol), and W is the sample mass (g).

2 Results and discussion

2.1 XRD

Figure 1 shows the XRD profiles of the fresh samples with various Ce:Al ratios and the mechanically mixed sample CeO_2-γ-Al_2O_3. For the fresh samples (Ce:Al molar ratio from 9:1 to 1:9), only CeO_2 (fluorite structure) peaks appeared (JCPDS 34-0394). These peaks were broadened as the Al_2O_3

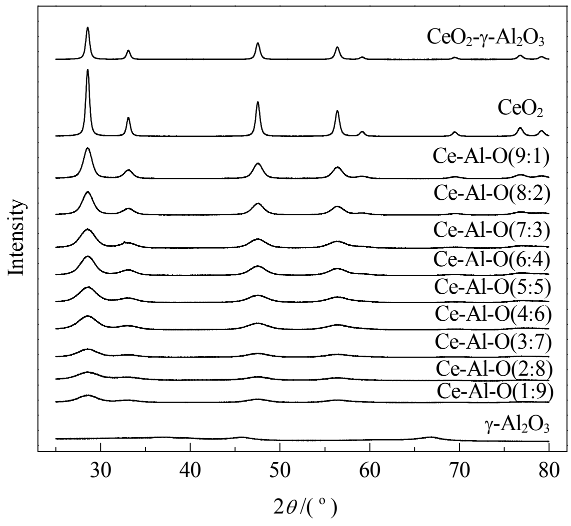

Fig. 1. XRD patterns of the Ce-Al-O samples prepared at different Ce:Al molar ratios and the mechanical mixture of CeO_2 and γ-Al_2O_3 (CeO_2-γ-Al_2O_3).

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