Preparation and Characterization of Polymer Gel-Improved Cerium-Zirconium Solid Solutions (Postprint)

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Abstract

Using Ce(NO3)4・6H2O and Zr(NO3)4・5H2O with different molar ratios as solid solution precursors, polymer gel-modified cerium-zirconium solid solutions were prepared by adding appropriate amounts of acrylamide (C3H5NO), N,N' -methylenebisacrylamide (C7H10N2O2), and ammonium persulfate ((NH4)2S2O8) as polymer gel agents, and the influence of Ce/Zr ratio on the properties of the cerium-zirconium solid solutions was investigated. The results indicate that the three-dimensional polymerization network formed by the monomer and cross-linking agent disperses the powder particles of the solid solution, and a porous structure is formed after calcination of the polymer; the synergistic effect of these two factors promotes the formation of porous nanocrystalline cerium-zirconium solid solutions. When the mass ratio of C3H5NO to C7H10N2O2 is 5:1, the concentration of mixed solutes is 0.04 mol/L, and appropriate heat treatment is applied, cerium-zirconium solid solutions with particle sizes of 10–20 nm can be obtained. X-ray diffraction results show that when the Ce/Zr molar ratio is 3:7–5:5, the solid solution exhibits a tetragonal phase structure; when the Ce/Zr molar ratio increases to 6:4–7:3, the solid solution exhibits a cubic phase structure; the lattice constant decreases with increasing Zr4+ content. N2 adsorption-desorption experimental results indicate that when the Ce/Zr molar ratio is 6:4, the solid solution possesses excellent specific surface area and pore structure parameters: specific surface area of 120.5 m2・g-1; pore size reaching 8.12 nm; pore volume as high as 0.22 cm3/g. Scanning electron microscopy observation results show that the cerium-zirconium solid solution exhibits a honeycomb-like porous structure.

Characterization of Ceria-Zirconia Solid Solution Powders Synthesized with Polymer-Network Gel Additives

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Abstract: Ceria-zirconia solid solution powders were prepared using $Ce(NO_3)_4 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ at various molar ratios as precursor materials, with C_3H_5NO, $C_7H_{10}N_2O_2$, and $(NH_4)_2S_2O_8$ added as polymer-network gel agents. The influence of the polymer-network gel on the preparation process and the effect of Ce/Zr ratio on the properties of the resulting powders were investigated. The results demonstrate that the polymer additives facilitate both the separation of ceria-zirconia solid solution particulates through formation of a three-dimensional polymer network and the creation of nanoporous structures through polymer burnout during subsequent calcination. The synergistic effect of these two mechanisms promotes the formation of porous nanoscale ceria-zirconia solid solutions. Powders with particle sizes of 10–20 nm were obtained when the mass ratio of C_3H_5NO to $C_7H_{10}N_2O_2$ was 5:1, the mixed solute concentration was 0.04 mol/L, and an appropriate heat treatment process was employed. X-ray diffraction analysis revealed that solid solutions with Ce/Zr molar ratios of 3:7–5:5 exhibited a tetragonal structure, while those with ratios of 6:4–7:3 displayed a cubic structure; the lattice constant decreased with increasing Zr^{4+} content. N_2 adsorption-desorption measurements showed that the solid solution with a Ce/Zr molar ratio of 6:4 possessed excellent textural properties: a specific surface area of $120.5\ m^2 \cdot g^{-1}$, pore diameter of 8.12 nm, and pore volume of $0.22\ cm^3/g$. Scanning electron microscopy observations confirmed the formation of an alveolate-like porous network structure.

Keywords: organic polymer materials, ceria-zirconia solid solution, polymer-network gel, Ce/Zr ratio, specific surface area

Introduction

The rapid development of the automotive industry and growing environmental awareness demand automotive exhaust catalysts with enhanced catalytic performance and stability to meet increasingly stringent emission standards.

Three-way catalysts (TWCs) represent the most widely used automotive exhaust treatment systems, simultaneously facilitating the oxidation of CO and hydrocarbons (HC) and the reduction of NO . Ceria-zirconia solid solutions prepared from CeO_2 and ZrO_2 have attracted considerable research attention as promising promoter materials due to their high oxygen storage capacity, oxygen release capability, thermal stability, and co-catalytic activity. The promotional mechanism relies on the reversible Ce^{3+}/Ce^{4+} redox reaction, which enables oxygen storage and release. However, pure CeO_2 suffers from poor thermal stability and limited reducibility at low temperatures, necessitating the formation of $CexZr_1$ xO_2 solid solutions with Zr^{4+}. This coupling not only improves the bulk characteristics of CeO_2 but also enhances oxygen storage/release capacity, thermal stability, and co-catalytic performance by leveraging ZrO_2' s excellent ion exchange properties, redox behavior, and surface-enriched oxygen vacancies.

Despite these advantages, ceria-zirconia solid solutions typically exhibit relatively low specific surface areas. Numerous studies have focused on optimizing preparation methods to enhance surface area and structural properties. Liu et al. prepared $Ce_{0}\cdot_{5}Zr_{0}\cdot_{5}O_2$ solid solutions via co-precipitation using cost-effective $ZrOCl_2$ and $ZrO(NO_3)_3$ precursors, achieving a specific surface area of 76 $m^2 \cdot g^{-1}$ when $ZrO(NO_3)_3$ was employed. Wang et al. synthesized $CexZr_1$ xO_2 solid solutions with various Ce/Zr ratios using co-precipitation, obtaining specific surface areas of 51.39–63.86 $m^2 \cdot g^{-1}$ and good oxygen storage capacity, though with slight particle agglomeration. Qi et al. prepared $CexZr_1$ xO_2 solid solutions with different compositions using a urea-based hydrothermal method, reporting specific surface areas of 133.1 and 21.1 $m^2 \cdot g^{-1}$ after calcination at 550°C for 4 h and 900°C for 6 h, respectively, with grape-like particle morphology. While these process modifications facilitate solid solution formation and improve surface area, the relatively low values (around 70 $m^2 \cdot g^{-1}$) and dramatic reduction after high-temperature sintering (from 133 to 21 $m^2 \cdot g^{-1}$) result in significant performance degradation for exhaust catalysis.

To develop a simpler preparation route that yields higher specific surface area without compromising it through high-temperature calcination, this study employs $Ce(NO_3)_4 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ as precursor materials with C_3H_5NO, $C_7H_{10}N_2O_2$, and $(NH_4)_2S_2O_8$ as polymer-network gel agents. The preparation process of polymer-network gel-modified ceria-zirconia solid solutions and the influence of Ce/Zr ratio on material properties were systematically investigated.

Experimental Methods

1.1 Preparation of Ceria-Zirconia Solid Solution Powders A series of aqueous solutions containing cerium nitrate and zirconium nitrate were prepared with Ce/Zr molar ratios of 7:3 (CZ73), 6:4 (CZ64), 5:5 (CZ55), 4:6 (CZ46), and 3:7 (CZ37). C_3H_5NO and $C_7H_{10}N_2O_2$ were added to the solutions under continuous stirring, and the mixtures were placed in an 80°C water bath. A small amount of $(NH_4)_2S_2O_8$ was subsequently added to form uniform, stable gels. The gels were dried at 90°C for 12 h to obtain xerogels, which were then subjected to controlled heat treatment to remove the polymer and yield the final ceria-zirconia solid solutions.

1.2 Characterization The particle size and morphology of powders obtained from different gel formulations were examined using a HITACHI SU8010 scanning electron microscope at an operating voltage of 15 kV. Thermal analysis of the xerogels was performed using a NETZSCH STA449F3-0684-M simultaneous thermal analyzer with Al_2O_3 powder as reference, a heating rate of 5°C/min, in an air atmosphere. Phase composition was analyzed using a Bruker Axs D2 X-ray diffractometer at room temperature with Cu Kα radiation (40 kV, 30 mA), a step size of 0.02°, and a scanning range of 10°–60°. Specific surface area and pore structure were determined using a MICROMERITICS ASAP 2020 automated gas adsorption system.

Results and Discussion

2.1 Optimization of Powder Preparation To obtain ceria-zirconia solid solutions with minimal particle size, the effects of monomer-to-crosslinker ratio and mixed solute concentration on gel formation and particle size were investigated, as summarized in and .

As shown in , a uniform and stable gel with the smallest particle size (10–20 nm) was achieved at a monomer-to-crosslinker mass ratio of 5:1. Deviations from this ratio resulted in increased particle size and gel instability. The polymerization reaction between monomers and crosslinkers, catalyzed by the initiator, forms a three-dimensional polymer network that yields the gel structure. Excessive or insufficient polymerization adversely affects network uniformity, consequently altering particle size. Therefore, the optimal monomer-to-crosslinker ratio was determined to be 5:1.

demonstrates that a light blue, stable gel with particle sizes of 10–20 nm was obtained at a mixed solute concentration of 0.04 mol/L. At concentrations below 0.04 mol/L, the ceria-zirconia particles were uniformly dispersed within the gel network, resulting in small particle sizes (10–20 nm). However, at concentrations exceeding 0.04 mol/L, limited network dispersion capacity led to slight particle agglomeration and increased particle size. Thus, a solute concentration of 0.04 mol/L was selected to achieve the desired small particle size.

The heat treatment protocol significantly influences the final powder morphology and properties. Thermogravimetric and differential thermal analysis (TG-DTA) of the polymer-derived gel is presented in [Figure 1: see original paper]. The DTA curve exhibits four exothermic peaks at 257°C, 276°C, 305°C, and 607°C. The substantial mass loss (>70%) in the TG curve between 200°C and 350°C corresponds to decomposition of the three polymer components represented by the first three exothermic peaks. Above 400°C, the DTA curve shows a gradual upward trend with a broad exothermic peak at 607°C, while the TG curve remains nearly flat, indicating further crystallization of nanoparticles. Consequently, the optimal heat treatment process was established in three stages: (1) room temperature to 200°C for water evaporation at 5-10°C/min; (2) 200-310°C for controlled polymer decomposition at 2-5°C/min to ensure complete burnout; and (3) 310-800°C at 5-10°C/min to achieve high powder purity and crystallinity.

The polymer-network gel method leverages free radical polymerization of monomers and the bifunctional effect of crosslinkers with two activated double bonds to rapidly form three-dimensional networks that inhibit mass transfer during calcination. This approach yields solid solutions with small, uniformly distributed particles under simple, rapid synthesis conditions. However, improper parameter selection can significantly affect particle size and morphology, producing detrimental effects. Based on this analysis, the optimal experimental parameters for preparing ceria-zirconia powders via polymer-network gel were determined as: (1) monomer-to-crosslinker ratio of 5:1; (2) mixed solute concentration of 0.04 mol/L; and (3) heat treatment protocol of room temperature-200°C (5-10°C/min), 200-310°C (2-5°C/min), and 310-800°C (5-10°C/min).

2.2.1 XRD Analysis The X-ray diffraction patterns of ceria-zirconia solid solutions synthesized via polymer-network gel are shown in [Figure 2: see original paper]. The method successfully produced thermally stable solid solutions with uniform structures. At Ce/Zr ratios of 3:7-5:5, the materials exhibited a tetragonal structure (reference: JCPDS 17-923 for tetragonal ZrO_2). When the Ce/Zr ratio increased to 6:4-7:3, the materials displayed a cubic structure (reference: JCPDS 34-0394 for cubic CeO_2). Since cubic phases generally exhibit superior co-catalytic activity compared to tetragonal phases, compositions with higher Ce/Zr ratios are preferred. The sharp diffraction peaks indicate good crystallinity of the synthesized nanoscale powders.

presents the positions of four major diffraction peaks and corresponding lattice constants for different compositions. As Zr^{4+} content increases, the main diffraction peaks shift to higher angles, approaching the pattern of pure ZrO_2 (JCPDS 17-0923). This shift occurs because Zr^{4+} (ionic radius 0.079 nm) substitutes for Ce^{4+} (ionic radius 0.092 nm) in the solid solution, causing progressive lattice contraction and decreasing lattice constants.

2.2.2 Specific Surface Area and Pore Structure The influence of Ce/Zr ratio on specific surface area and pore structure is summarized in . Specific surface area is a critical parameter for automotive exhaust co-catalytic performance, with higher values promoting catalytic activity. For spherical crystallites, the theoretical specific surface area can be calculated using Scal = 3000/(rd), where r is the crystallite radius (nm) derived from XRD peak broadening (r = D/2), and d is material density (g/cm^3) calculated from d = MZ/VN (M = molar mass of formula unit, Z = number of formula units per unit cell, V = unit cell volume, N = Avogadro' s number). The calculated Scal values of approximately 100 m$^2 \cdot$ g^{-1} are close to the experimentally measured BET surface areas (SBET). The slight discrepancy arises from the assumption of isolated spherical particles, whereas actual powders experience particle aggregation and pore collapse during heat treatment, reducing surface area.

The data in reveal that surface area, pore size, and pore volume vary with Ce/Zr ratio. The composition with a 6:4 ratio exhibited the largest pore size (8.12 nm) and pore volume (0.22 cm^3/g), along with the maximum measured specific surface area of 120.5 m$^2 \cdot$ g^{-1}. Compared with conventional preparation methods, the polymer-network gel approach effectively prevents interparticle aggregation and promotes pore formation, acting as a pore-forming agent that enhances specific surface area and pore structure.

2.2.3 Powder Morphology [Figure 3: see original paper] shows SEM images of the high-surface-area ceria-zirconia solid solution (Ce/Zr = 6:4) after calcination at 800°C for 2 h in air. The material exhibits a porous, honeycomb-like network structure. During synthesis, cerium and zirconium ions were chelated into the polymer resin network, which upon calcination transformed into oxide powders. The incorporated polymer created a cellular porous architecture that significantly reduced interfacial tension and pore collapse, yielding high porosity. Although minor blocky residues were observed (trace ash from polymer combustion), they did not adversely affect co-catalytic performance. The measured specific surface area was 120.5 m$^2 \cdot$ g^{-1} with a pore diameter of 8.12 nm and pore volume of 0.22 cm^3/g. [Figure 3b: see original paper] reveals that the honeycomb structure consists of uniformly distributed, well-dispersed nanoparticles with regular spherical or near-spherical morphology, measuring 10–20 nm in size.

The data in and [Figure 3: see original paper] indicate that calculated surface areas exceed measured values, while calculated crystallite sizes are smaller than actual particle sizes. This discrepancy suggests the presence of lattice strain, which creates a distribution of interplanar spacings around the average value, causing additional XRD peak broadening and resulting in underestimated crystallite sizes.

Conclusion

The polymer-network gel method enables homogeneous mixing of reactants at the molecular or ionic level through three-dimensional polymerization networks. This simple, industrially scalable approach facilitates synthesis of porous oxide solid solutions. Using the optimized polymer-network gel method, the optimal parameters for preparing ceria-zirconia solid solutions were established as:

monomer-to-crosslinker ratio of 5:1; mixed solute concentration of 0.04 mol/L; and heat treatment protocol of room temperature-200°C (5-10°C/min), 200-310°C (2-5°C/min), and 310-800°C (5-10°C). The resulting materials exhibited single-phase cubic or tetragonal structures with lattice constants decreasing as Zr^{4+} content increased. The powders showed narrow size distributions of 10-20 nm and excellent textural properties: specific surface areas of 83-120 $m^2 \cdot g^{-1}$, pore diameters of 5.32-8.12 nm, and pore volumes of 0.14-0.22 cm^3/g.

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