



Strontium ferrite as a three-way catalyst component

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ABSTRACT

Ni-containing SrFeO_{3-δ}/Al₂O₃ and Ce_{0.5}Zr_{0.5}O_{2-δ}/Al₂O₃ catalysts were prepared and deposited onto surfaces of porous alumina oxide foams. The measured oxygen storage capacity values are 1448 and 1275 μmol-O/g for SrFeO_{3-δ} and Ce_{0.5}Zr_{0.5}O_{2-δ} powder, respectively (about 55% and 75% of their theoretical values). The experimental reactor using exhaust gas of a gasoline engine was assembled. Decrease of CO and other harmful components in case of Ni/SrFeO_{3-δ}/Al₂O₃ coating is comparable to that of Ni/Ce_{0.5}Zr_{0.5}O_{2-δ}/Al₂O₃ layer. After reactor conditions (700 °C during 15–20 min), microstructure of both catalysts remains unchanged. Strontium ferrite maintained an orthorhombic brownmillerite-type crystal structure, whereas nickel was detected in both metallic and oxide forms.

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Introduction

Non-stoichiometric oxides of metals with variable oxidation state that allow reversible oxygen incorporation/loss, are employed for automotive pollution control [1,2], catalytic reforming of hydrocarbons [3] and steam [4], carbon monoxide [5] and diesel soot [6], simultaneously utilizing excessive thermal energy in power plants and other industrial processes [4]. Due to a remarkable ability of ceria-zirconia solid solutions to store and release oxygen, these oxides are employed in car exhaust three-way catalysts (TWC) [1]. TWC converts un-burnt hydrocarbons, carbon monoxide and nitrogen oxides into CO₂, H₂O and N₂. Increasingly stringent emission regulations convey critical importance to development of sustainable TWC [2]. Also, these oxygen storage materials may enable efficient CO₂ capture and generate syngas through chemical-looping reactions [7]. Typical TWC composition now consists of noble metals or their alloys (as a rule Rh/Pt or Pd), ceria-zirconia (usually Ce_{0.5}Zr_{0.5}O_{2-δ}) and aluminum oxide, which ensures dispersion of two former components and also prevents their aggregation and deactivation of the catalyst [1].

However, described catalyst composition includes expensive components, such as ceria, zirconia and noble metals. Cerium-containing substances are produced by extremely limited number of countries which makes the market unstable and dependent on these suppliers. Rh, Pt and Pd are expensive and their substitution

by other components is of great practical importance. That is why the development of alternative materials showing a reasonable catalytic activity, but at lower price, are being intensively pursued nowadays [2,5–7]. Catalytic properties of metallic nickel are well-known [8]. A potential candidate to replace ceria-zirconia can be found in SrFeO_{3-δ}-based oxides family where significant oxygen content variations are measured [9]. Un-doped strontium ferrite undergoes a cubic perovskite ↔ orthorhombic brownmillerite phase transition when δ → 0.5 [10]. This ordering/disordering process may be beneficial for facilitated oxygen uptake/loss and consequently for exhaust gases treatment.

Experimental

Ce_{0.5}Zr_{0.5}O_{2-δ} and SrFeO_{3-δ} powders were prepared via sol-gel and glycine-nitrate processes, respectively. To produce a catalyst suspension, Ce_{0.5}Zr_{0.5}O_{2-δ} or SrFeO_{3-δ} powder was mixed with Ni and Al₂O₃ powders in ethanol using Retsch PM200 high energy planetary ball mill (200 RPM, 5 h). Ni/Ce_{0.5}Zr_{0.5}O_{2-δ} (or SrFeO_{3-δ})/Al₂O₃ weight ratio was 5/45/50 and ethanol amount was equal to the total powder weight. Commercial alumina porous foams (20 mm diameter, 8.5 mm height, 10 PPI, 85% porosity) from Pyrotec Engineering Materials Ltd. (Spain) were used as catalyst supports. To prepare catalyst coatings, these foams were immersed for a moment into a catalyst suspension, dried at room temperature and annealed at 1000 °C (for Ce_{0.5}Zr_{0.5}O_{2-δ}) and 750 °C (for SrFeO_{3-δ}) during 1 h in flowing 10% H₂ / 90% N₂ mixture. Also, for the sake of comparison, catalyst-free suspension (containing only

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Al₂O₃ powder and ethanol) was prepared and annealed onto alumina supports in the same conditions. All annealed coatings showed good adhesion to the supports, presented no cracking and were resistant towards scratching.

The X-ray diffraction (XRD) patterns were collected at room temperature employing a PANalytical X'Pert MPD PRO diffractometer (Ni-filtered Cu K α radiation) over a 2 θ range of 10–80°. The morphology of the powders and ceramics was studied by scanning electron microscopy (SEM) using a Hitachi SU-70 UHR Schottky Analytical FE-SEM coupled with a SDD-Bruker Quantax 400 EDS detector. The oxygen storage capacity (OSC) was measured in a Netzsch STA 449 F3 Jupiter thermogravimetric analyzer. The catalytic studies were conducted using a furnace-heated quartz tube (inner diameter of 20 mm), equipped with a thermocouple, and exhaust gases of a 4-stroke gasoline engine. For each composition (with or without catalyst), this quartz tube was loaded with 20 coated supports. Gas-solid contact time was about 0.65 s. The gas composition was measured by Gasetm CX4000 FTIR (CO measuring range 0–10,000 ppm) and SICK GMS810 (CO measuring range 0–35% vol.) gas analyzers. The catalyst tests were performed at 700 °C within CO concentration range of 0–7000 ppm.

Results and discussion

XRD patterns of Ce_{0.5}Zr_{0.5}O_{2- δ} and SrFeO_{3- δ} powders, annealed at 1000 °C for 5 h in air, consist of peaks corresponding to single-phase cubic fluorite- and perovskite-type crystal structures, respectively (Fig. 1A and B). Afterwards, to assess chemical stability of these materials in reducing conditions, Ce_{0.5}Zr_{0.5}O_{2- δ} and SrFeO_{3- δ} powders were kept at 750 °C for 1 h in flowing 10% H₂ / 90% N₂ mixture. Their XRD analysis showed that fluorite phase of Ce_{0.5}Zr_{0.5}O_{2- δ} remains unchanged, while strontium ferrite transformed into single-phase orthorhombic brownmillerite-type oxide (Fig. 1C). Following oxidation at 1000 °C for 1 h in air of this reduced strontium ferrite structure led to a restitution of single cubic perovskite-type phase.

Clearly, in such oxidizing/reducing cycles of Ce_{0.5}Zr_{0.5}O_{2- δ} oxygen uptake/loss results in increasing/decreasing of cerium oxidation state without significant phase transformation. In the case of SrFeO_{3- δ} , however, in addition to iron oxidation state decrease/increase, cubic perovskite-type oxide reversibly transforms into orthorhombic brownmillerite-type one upon reaching some critical concentration of oxygen vacancies. The amount of oxygen moving into/from oxide powder was measured at 750 °C in a continuous flow of alternating air and 10% H₂ / 90% N₂ mixture (50 ml/min). The determined average OSC values are 1275 and 1448 μ mol-O/g for Ce_{0.5}Zr_{0.5}O_{2- δ} and SrFeO_{3- δ} , respectively (about 2.0 and 2.3% weight oscillation). Corresponding theoretical values (when all cerium or iron cations switch between 4+ and 3+ oxidation states) are 1693 and 2611 μ mol-O/g. These measured OSC are comparable to earlier reported 1054–1506 μ mol-O/g for Ce_{0.5}Zr_{0.5}O_{2- δ} [1] and 1400 μ mol-O/g for La_{1-x}Sr_xFeO_{3- δ} [7], respectively.

SEM micrographs (Fig. 2A and B) and EDS maps (Fig. 2C and D) show that Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} /Al₂O₃ and Ni/SrFeO_{3- δ} /Al₂O₃ powders are composed of larger (1–2 μ m) Ce_{0.5}Zr_{0.5}O_{2- δ} or SrFeO_{3- δ} grains and smaller (200–400 nm) Al₂O₃ particles. Nickel detection is rather difficult, though sporadically possible, due to its low content. Both coatings, annealed at 750 °C for 1 h in flowing 10% H₂ / 90% N₂ mixture, are 20–30 μ m thick, quite dense and well-attached to the alumina supports (Fig. 2E and F). Fig. 2G and 2H (with higher magnification) confirm that Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} /Al₂O₃ and Ni/SrFeO_{3- δ} /Al₂O₃ layers are sintered and dense. Their grain size is notably more homogeneous compared to corresponding powders (Fig. 2A and 2B). Also, EDS analysis showed almost uniform distribution of the elements.

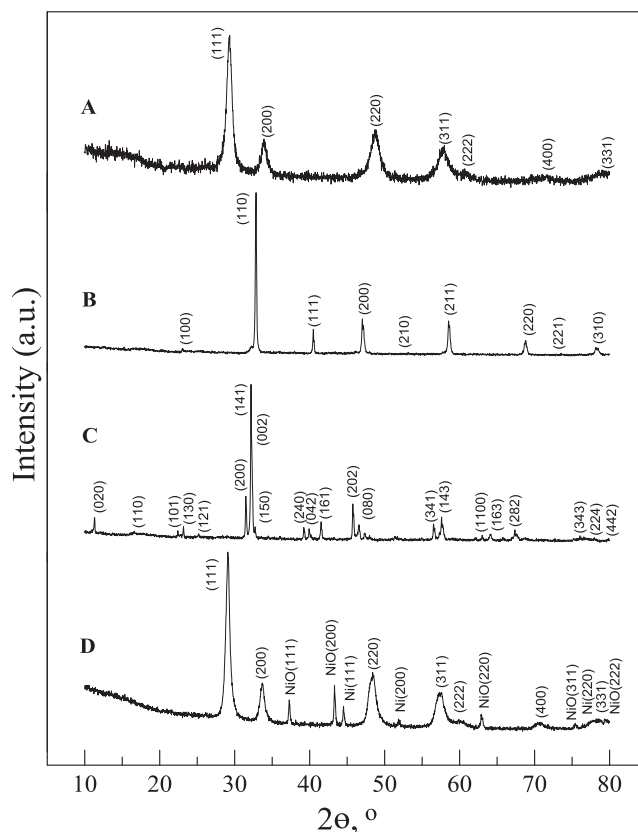


Fig. 1. XRD patterns of Ce_{0.5}Zr_{0.5}O_{2- δ} annealed at 1000 °C for 5 h in air (A), SrFeO_{3- δ} annealed at 1000 °C for 5 h in air (B) and at 750 °C for 1 h in 10% H₂ / 90% N₂ (C), Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} after reactor (D).

Raw exhaust of employed 4-stroke gasoline engine contains 8.0, 9.5, 0.2, 0.1% vol. of CO₂, CO, CH₄ and C₂H₄ (measurements made after quartz tube at 700 °C filled with 20 alumina foams coated with catalyst-free layer), along with other gases. Since SICK GMS810 gas analyzer only detects these four components, and CO concentration needed to be lowered down to the measuring range of Gasetm CX4000 FTIR gas analyzer, a valve-controlled portion of the raw exhaust was diluted with air (4 l/min) and directed to the same reactor quartz tube. At these conditions, CO concentration was stable at about 0.7% vol., or 7000 ppm (Fig. 3). Then the catalyst-free alumina foams were replaced with Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} /Al₂O₃ coated ones. This resulted in an abruptly lower concentration of CO and other harmful gases (Table 1). The time needed to replace alumina supports and attain working temperature corresponds in Fig. 3 to the curve segments close to zero, as gas analyzer measuring cell (for its protection) switched to atmospheric air at these periods.

Then Ni/SrFeO_{3- δ} /Al₂O₃ coated alumina foams were inserted. The concentrations of carbon monoxide and other components were similar, though little lower, than for Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} /Al₂O₃ catalyst (Table 1). The Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} and Ni/SrFeO_{3- δ} powders, as well as coated alumina supports, were annealed at the same reactor conditions. Powder XRD patterns show the presence of fluorite- and brownmillerite-type crystal structures (like in Fig. 1A and C) with nickel oxide and metallic nickel (XRD pattern of Ni/Ce_{0.5}Zr_{0.5}O_{2- δ} powder after reactor is given in Fig. 1D). SEM studies of both catalyst-coated alumina foams indicated that catalyst surfaces did not suffer any visible change due to reactor conditions.

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