Catalysis Today 146 (2009) 132–140

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Nanocomposite catalysts for internal steam reforming of methane and biofuels in solid oxide fuel cells: Design and performance

Vladislav Sadykov [a,*], Natalia Mezentseva [a], Galina Alikina [a], Rimma Bunina [a], Vladimir Pelipenko [a], Anton Lukashevich [a], Sergei Tikhov [a], Vladimir Usoltsev [a], Zakhar Vostrikov [a], Oleg Bobrenok [b], Alevtina Smirnova [c], Julian Ross [d], Oleg Smorygo [e], Bert Rietveld [f]

[a] Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia
[b] Institute of Thermal Physics, Novosibirsk, 630090, Russia
[c] Connecticut Global Fuel Cell Center, UConn, Storrs, CT, USA
[d] Centre of Environmental Research, University of Limerick, Limerick, Ireland
[e] Powder Metallurgy Institute, Minsk, 220005, Belarus
[f] Energy Research Center of the Netherlands, Petten, The Netherlands

ARTICLE INFO

Article history:
Available online 29 March 2009

Keywords:
Composites
Ni–YSZ (ScCeSZ)
Doped ceria–zirconia oxides
Complex chromites
Ru
Pt
Pd
Steam reforming
CH_4
Ethanol
Acetone

ABSTRACT

Nanocomposite catalysts comprised Ni particles embedded into the complex oxide matrix comprised Y- or Sc-stabilized zirconia (YSZ, ScCeSZ) combined with doped ceria–zirconia oxides or La–Pr–Mn–Cr–O perovskite and promoted by Pt, Pd or Ru were synthesized via different routes (impregnation of YSZ or NiO/YSZ composites with different precursors, one-pot Pechini procedure). Both composition and preparation procedure determining degree of interaction between components of composites were found to strongly affect performance of nanocomposites in steam reforming of methane at short contact times as well as their stability to coking in stoichiometric feeds. Temperature-programmed reduction of composites by CH_4 followed by temperature-programmed oxidation by H_2O revealed more efficient dissociation of CH_4 on promoted composites yielding loose surface CH_x species more easily removed by water as compared with unpromoted composites. Best active components highly active and stable to coking were supported as thin layers on different substrates (Ni/YSZ anode platelets, refractory dense/porous metal alloys, cermet or corundum monolithic carriers). These structured catalysts demonstrated high efficiency and stability in the reactions of steam reforming of methane and oxygenates (ethanol, acetone) in pilot-scale reactors.

1. Introduction

Design of catalytic materials for internal steam reforming of methane in the intermediate temperature solid oxide fuel cells (IT SOFC) able to efficiently operate in feeds with a small (if any) excess of steam without coking represents important but demanding problem [1]. State-of-the-art $Ni/Y_2O_3–ZrO_2$ (Ni/YSZ) cermet anodes of solid oxide fuel cells have excellent catalytic properties and stability in the oxidation of hydrogen fuel at SOFC operation conditions [2]. However, the lack of a hydrogen infrastructure and the unsolved hydrogen storage problem have initiated the research aimed at direct utilization of natural gas, which represents one of the key aspects of SOFC technology. Internal steam reforming (SR) is the most promising concept in using the natural gas as a fuel [3,4]. In this case, the reaction takes place directly in the anode compartment, allowing within a stack a better management of heat produced by the exothermic electrochemical oxidation and consumed by the endothermic reforming reaction. For solid oxide fuel cells, an attractive option is direct internal reforming of bio-fuels on catalytically active anodes [5]. Unfortunately, with the Ni/YSZ cermet, coking occurs leading to the deterioration of anode performance [2,4]. Ni/YSZ cermet anodes can be used in hydrocarbons or oxygenates reforming only if the excess steam is present to suppress the carbon deposition. In this case, the overall electrical efficiency of the cell decreases due to the energy consumption for the excess water evaporation [3,4]. Hence, development of robust anode materials with a high and stable catalytic activity in the internal steam reforming of hydrocarbons/oxygenates in feeds with a small excess of steam is vital for design of SOFC.

The most promising approach to design of inexpensive catalytic materials possessing a high activity and coking stability in CH_4

* Corresponding author at: Boreskov Institute of Catalysis, Heterogeneous Catalysis, pr. Lavrentieva, 5, Novosibirsk, 630090, Russia. Tel.: +7 383 330 87 63; fax: +7 383 330 80 56.
E-mail address: sadykov@catalysis.ru (V. Sadykov).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.02.035

steam reforming in the middle-temperature range is to promote traditional cermets such as Ni/YSZ- or Ni/Sc–Ce-stabilized zirconia (Ni/ScCeSZ) by fluorite-like (doped ceria–zirconia) or perovskite-like (mixed chromates–manganites) oxides along with small (~1 wt.%) amounts of precious metals (Pt, Pd, Ru) [6–10]. In these systems, Ni and/or precious metals are responsible for activation of CH_4 molecules, while oxide components provide activation of water molecules and transfer of hydroxyls and/or hydroxocarbonate/oxygen species to the metal particles–oxide interface where they interact with activated C–H–O species producing syngas [6,7].

This paper summarizes experimental results on the catalytic properties of composite materials in methane SR in regard of the nature and content of a precious metal, a type of the oxide additive, the nature of doped zirconia electrolyte and the method of promoted composites preparation presented in part in earlier publications [8–11]. Detailed structural studies revealing pronounced interaction between the components of composites controlling their catalytic properties and reactivity were also reported earlier [8–11] and will be here referred to only in the extent required for explanation of the specific features of these systems performance. CH_4 temperature-programmed reduction (TPR) experiments followed by H_2O temperature-programmed oxidation (TPO) were used here for the first time to elucidate effects of interaction between the components of composites on the ability of surface sites to efficiently dissociate CH_4 molecules without forming dense graphite-like layers or whiskers and catalyze oxidation of surface polymerized CH_x species into syngas.

The best compositions supported as porous strongly adhering layers on anode platelets, nonporous (Crofer interconnects) or porous (Ni–Al foam) alloy substrates, corundum or cermet monolithic substrates [12] were tested in the reactions of methane and oxygenates (ethanol, acetone) steam reforming in pilot-scale installations.

2. Experimental

Catalysts prepared and studied in this work were based upon next types of composites:

(1) Composite **I** (specific surface area 11 m^2/g) comprised 60 wt.% NiO + 40 wt.% YSZ was prepared by mixing and ball milling of industrial sources as described elsewhere [8,9]. This composite was promoted by supporting 10 wt.% of fluorite-like ($Ce_{0.5}Zr_{0.5}O_{2-x}$, $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_2$, $La_{0.3}Ce_{0.35}Zr_{0.35}O_2$) or perovskite-like ($La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3$) oxides by impregnation with water solutions of corresponding polyester citric acid–ethylene glycol precursors followed by drying and calcination in air at 700 °C for 4 h.

(2) Composite **II** (specific surface area 23 m^2/g) comprised 10 wt.% $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3$ + 55 wt.% NiO + 35 wt.% ScCeSZ was prepared using powdered $Sc_{0.1}Ce_{0.01}Zr_{0.89}O_{2-y}$ electrolyte synthesized by co-precipitation as described elsewhere [13]. ScCeSZ powder was first dispersed in the water solution of Ni nitrate and polyester citric acid–ethylene glycol polymeric precursor of perovskite following so-called one-pot synthesis routine [10]. After evaporation, formed solid residue was decomposed in air at 500 °C and then calcined at 700 °C for 4 h.

(3) Composite **III** (specific surface area 9 m^2/g) comprised 60 wt.% NiO + 40 wt.% YSZ was prepared by impregnation of powdered $Y_{0.08}Zr_{0.92}O_{2-y}$ (Russian source) with Ni nitrate solution followed by drying overnight in air at 90 °C with subsequent calcination at 800 °C. After regrinding, the composite **III** was loaded with 10 wt.% fluorite-like oxides ($Pr_xCe_yZr_zO_2$, $La_qPr_{x-}Ce_yZr_zO_2$, $Sm_qPr_xCe_yZr_zO_2$, where $y = 0.35, 0.05$; $z = 0.35, 0.25, 0.2$; $x = 0.15–0.3$; $q = 0.15$) by impregnation with respective mixed nitrates solutions followed by drying and calcination at 800 °C [10].

(4) Composite **IV** (specific surface area 28 m^2/g) comprised 10 wt.% $Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2$ + 55 wt.% NiO + 35 wt.% YSZ (Russian source) was prepared by the one-pot Pechini procedure similar to that used for preparation of composite **II**.

Pt, Pd or Ru (0.3–1.4 wt.%) were supported on composites **I–III** by the incipient wetness impregnation with $PdCl_2$, H_2PtCl_6 or $RuCl_3$ solutions followed by drying and calcinations at 800 °C for 2 h.

For supporting thin layers of nanocomposites, NiO/YSZ green anode plates (manufactured and supplied by FRZ Jülich, Germany, or ECN, Netherlands, covered on one side by catalytically inactive dense YSZ layer), Crofer interconnects and NiAl foam substrates were used. Open-cell nickel foams were manufactured by the nickel electroplating of the polyurethane foam samples (thickness 5 mm, the cell density 60 ppi) followed by sintering in the dissociated ammonia atmosphere at 1100 °C for 1 h. The foam samples were then deformed by a uniaxial compression to 1 mm thickness modifying the cell morphology and decreasing porosity from 95.5% to 60–80%. Deformed foams were subjected to the pack aluminizing and then annealed at 1000 °C for 1 h under air to form a thin α-alumina layer over the foam cell walls for a better adhesion of catalytic layers.

Crofer interconnect substrates were precovered by a dense corundum sublayer through the blast dusting procedure [11,14].

Characteristics of thin-wall honeycomb monolithic corundum substrates or microchannel Cr–Al composite substrates used for supporting nanocomposite active components were described in details elsewhere [12,15,16].

Composite powders comprised 10 wt.% complex oxide promoter +55 wt.% NiO + 35 wt.% YSZ (Russian source) synthesized via one-pot Pechini route (vide supra) were ultrasonically dispersed in isopropyl alcohol with addition of polyvinyl butyral as a binder to make a slurry. Thin layers of composites were supported on substrates using these slurries and slip casting or painting procedures followed by drying and calcination at 1100 °C after each supporting step until loading of 4–7 wt.% was achieved. Ru or Pt (loading in the range of 0.5–1.0 wt.% as related to the weight of composite) was supported by the incipient wetness impregnation followed by drying and calcination under air at 800 °C.

SEM images of Ni–Al foam and composite layers on substrates were made with a JSM-6460 LV (Jeol) microscope.

Experiments for temperature-programmed reduction of samples by CH_4 (1% CH_4 in He feed) and their subsequent temperature-programmed oxidation by H_2O (1% H_2O in He feed) were carried out in flow installations equipped with quartz reactors, GC and PEM-2M gas analyzers under the temperature ramp of 5°/min up to 880 °C with the isothermal plateau at 880 °C for 70 min [9–11]. After CH_4 TPR run, samples were rapidly cooled in the flow of He to room temperature, then He stream was switched to 1% H_2O in He flow and the temperature ramp was repeated.

The steady-state activity of catalysts (0.25–0.5 mm fraction of powdered samples or platelets with a typical size 1 cm × 2 cm) in CH_4 SR was estimated in He- or Ar-diluted feeds with CH_4 concentration up to 20% and steam/methane ratio 1–3 using specially designed flow quartz reactors. The contact time was varied in the range of 10–70 ms. GC and PEM-2M gas analyzers were used for analysis of reagents and products [9–11]. Before reaction, samples were pretreated in O_2 at 500 °C for 1 h. Typically, experiments were started at 750 °C to reduce samples *in situ* by stoichiometric CH_4/H_2O feed with subsequent cycling of temperature in the studied range and keeping a sample at least 1 h at each temperature to obtain reproducible steady-state results.

Catalytic performance of monolithic catalysts with nanocomposite active components in the reactions of steam/autothermal