



Catalytic coatings on steel for low-temperature propane prereforming to solid oxide fuel cell (SOFC) application

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ARTICLE INFO

Article history:

Received 4 February 2009

Accepted 23 April 2009

Available online 12 May 2009

Keywords:

Coating

Colloid

PEG

Steam reforming

Fuel processing

ABSTRACT

Catalyst layers (4–20 μm) of rhodium (1 wt%) supported on alumina, titania, and ceria–zirconia ($\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$) were coated on stainless-steel corrugated sheets by dip-coating in very stable colloidal dispersions of nanoparticles in water. Catalytic performances were studied for low-temperature (≤ 500 °C) steam reforming of propane at a steam to carbon ratio equal to 3 and low contact time (≈ 0.01 s). The best catalytic activity for propane steam reforming was observed for titania and ceria–zirconia supports for which propane conversion started at 250 °C and was more than three times better at 350 °C than conversion measured on alumina catalyst. For all catalysts a first-order kinetics was found with respect to propane at 500 °C. Addition of PEG 2000 in titania and ceria–zirconia sols eliminated the film cracking observed without additive with these supports. Besides, the PEG addition strongly expanded the porosity of the layers, so that full catalytic efficiency was maintained when the thickness of the ceria–zirconia and titania films was increased.

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1. Introduction

Solid oxide fuel cells (SOFC), due to their high working temperature, have some internal reforming ability. However, it has been shown that direct use of hydrocarbons higher than CH_4 to feed a nickel-based anode caused carbon deposition (coke) followed by a catalyst deactivation [1]. Thus, feeding a SOFC with common fuels (natural gas, gasoline, etc.) will require a prereforming unit in order to convert hydrocarbons in a mixture of smaller molecules such as H_2 , CH_4 , CO , and CO_2 , compatible with the nickel anode catalyst of a medium-temperature SOFC [2]. The conversion of hydrocarbon fuels into hydrogen-rich mixtures can be carried out by several reaction processes, including steam reforming, partial oxidation, and autothermal reforming [3]. But only the steam-reforming process can reach hydrogen concentrations above 75% in the dry product gas [4], leading to the best FC efficiency [5]. However, because the steam-reforming reaction is strongly endothermic, heat transfer restrictions will lead to a temperature drop at the reaction site. This will lower reaction rate but will also increase the risk for carbon deposition blocking the active sites.

Enhanced heat and mass transfer can be obtained by using metallic structured reactors. These devices are built by stacking metallic plates incorporating narrow parallel channels coated with

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a thin layer of catalyst [6–8]. Furthermore, this reactor design allows thermal coupling between endothermic and exothermic reactions in integrated heat exchangers/reactors [9]. Thus, the energy content of the anodic off gas, mainly unconverted hydrogen from the fuel cell stack, can be recovered in order to supply heat for the endothermic steam-reforming reaction, boosting the overall system efficiency.

Improving heat and mass transfer increases the effective activity and more active catalysts, for example, based on precious metals, can be employed. The most efficient metals for steam reforming of methane on alumina-stabilized magnesia-supported catalysts were reported to be rhodium and ruthenium [10]. Though some authors [11] have found that platinum was actually the best catalyst whatever the support, many other studies have confirmed the high activity of rhodium. With more active catalysts the reaction temperature can be lowered so that less thermally stable oxide supports, like titania, for example, can be used and the reactors can be made of standard stainless steels (less expensive). In most of the studies reported on steam reforming in structured reactors the full conversion of hydrocarbon is reached only from 700 °C. Such a temperature is incompatible with a long-term stability of standard steels.

In this paper we report our work on rhodium catalytic coatings for low-temperature (≤ 500 °C) steam reforming of propane. These catalysts were synthesized by sol–gel routes and coated on corrugated stainless-steel sheets by dip-coating. This kind of substrate, used to build heat exchangers, could be interesting for large-scale production of low-cost structured reactors.

2. Materials and methods

2.1. Sol synthesis

Boehmite sols, precursors of alumina xerogels, were synthesized according to the process originally reported by Yoldas [12–14]. A large excess ($H_2O/Al \approx 100$) of hot (85 °C) distilled water was quickly poured in aluminum tri-sec-butoxide, $Al(OC_4H_9)_3$ under vigorous stirring. After 15 min the hydroxide precipitate was peptized by adding 0.07 mol of nitric acid per mole of alkoxide and stirring at 85 °C until a clear sol was obtained (≈ 24 h). At this stage the pH of the sol was 5.0 ± 0.5 . After peptization, the sol was concentrated by heating at 85 °C until 2/3 of the solvent has evaporated.

$Ce_{0.5}Zr_{0.5}O_2$ sols were synthesized by a method based on that reported by Deshpande et al. [15]. The first step was the hydrolysis of the mixed precursors ($Ce(NO_3)_6(NH_4)_2$, and $ZrO(NO_3)_2 \cdot xH_2O$) by addition of an aqueous NH_3 solution up to pH >10. The precipitate was thoroughly washed and then it was peptized (by addition of 0.6 mol of nitric acid per mole of Ce + Zr) until a clear sol was obtained (≈ 48 h). At this stage the pH of the sol was 2.0 ± 0.5 . The peptization time can be shortened by sonication. The sols were then concentrated by ultrafiltration (using MWCO 2000 dialysis membranes).

Titania sols were prepared by hydrolysis of titanium alkoxide in a large excess of water. This method can give colloids of titania nanocrystallites dispersed in water [16,17]. The following procedure was optimized to produce very stable sols. Hot (80 °C) distilled water ($H_2O/Ti \approx 90$) was added quickly, under vigorous stirring, on titanium(IV) isopropoxide dissolved in isopropyl alcohol ($C_3H_8O/Ti = 3.5$). A white precipitate was obtained. After 5 min, a solution of nitric acid ($H^+/Ti = 0.2$) was added to the suspension and the mixture was kept for 16 h at 80 °C under stirring. The white suspension changed gradually to a translucent sol by peptization. At this stage the pH of the sol was 1.0 ± 0.5 . More concentrated sols were obtained by evaporation at the same temperature until the required concentration was reached.

For the three kinds of sol, the rhodium precursor ($RhCl_3 \cdot xH_2O$), dissolved in a minimum amount of water, was added, in suitable proportion, into the sol at the end of the peptization step. Then the sol was stirred at room temperature for 1 h. These sols remained stables (no precipitation) for more than 1 year.

2.2. Powder X-ray diffraction (PXRD)

The crystal structure was investigated by powder X-ray diffraction. Data were collected, at room temperature, on a Seifert 3003TT θ – θ diffractometer in Bragg–Brentano geometry, using filtered Cu $K\alpha$ radiation and a graphite secondary-beam monochromator. Diffraction intensities were measured by scanning from 20° to 80° (2θ) with a step size of 0.02° (2θ). Crystalline structures were refined using FullProf software [18]. The peak profiles were modeled by pseudo-Voigt functions. The refined FWHM (full-width at half-maximum) of the lines was used to compute, by the Scherrer's equation, the average crystallite size [19]. The instrumental broadening contribution was measured by using a highly crystalline rutile sample as standard.

2.3. Specific surface area, PSD, and density

The specific surface areas were computed from the adsorption isotherms, using the Brunauer–Emmett–Teller (BET) method [20]. Adsorbate was nitrogen for xerogels. Krypton was used for coatings which were done on both sides of a set of four small stainless-steel sheets (20 × 15 mm) because the sheets used in the steam-reform-

ing reactor were too large to fit in adsorption cells. Isotherms were recorded at 77 K, with a Micromeritics ASAP 2010M. The pore size distributions (PSD) were computed from nitrogen desorption isotherms by the NLDFT method [21] (with Quantachrome Autosorb-1 software using silica equilibrium transition kernel at 77 K, based on a cylindrical pore model).

Skeletal densities of powder were determined using a gas pycnometer (Micromeritics AccuPyc 1330) and working with helium. Each experimental value results from the average of 10 successive measurements on the same sample.

2.4. Thermal analyses

Simultaneous thermogravimetric (TG) and differential thermal (DT) analyses were carried out on a SETARAM TG-DTA 92 thermobalance using 20 mg of sample; α -alumina was taken as reference.

2.5. Electron microscopy

Transmission electron microscopy (TEM) analyses were done on a JEOL 2010. Samples were prepared by dipping a carbon-coated grid in a sol diluted 50 times in water. Then the grid was allowed to dry 48 h at room temperature. Scanning electron microscopy (SEM) analyses were done, with a JEOL JSM-6700F, on small pieces cut in coated substrates.

2.6. Coating of stainless-steel substrates

The corrugated-steel sheets used in this work were made by the Liebherr-Aerospace Company¹ for their heat exchangers. The steel grade was AISI 321 with a square-wave profile; the sheet thickness was 0.1 mm and the channel width was 1 mm.

In order to ensure an optimal adhesion between the layer and the substrate, the stainless-steel plates were immersed in an alkaline cleaner (TurcoTM 4181) at 75 °C for 30 min before the coating. Then they were rinsed with water in an ultrasonic bath. Finally they were dried and heated in air at 500 °C for 2 h. The catalyst layers were applied by dip-coating using a NIMA DC-mono dip-coater. The thickness of the coating was mainly controlled by the sol concentration, the withdrawal rate being kept constant at 10 mm/min. The amount of catalyst coated on the plates has been evaluated by weighting before and after the coating. From this value, the density and the porosity of the layer, an average thickness has been estimated by the equation

$$t = \frac{W}{\rho[1 - \varphi] S} \quad (1)$$

where t is the thickness in cm, W is the catalyst mass in g, ρ is the crystal density in g/cm^3 , φ the porosity, and S is the coating area in cm^2 .

2.7. Test rig for propane steam-reforming reaction

Propane and argon were dosed by mass flow controllers (Brooks 5850). The water was dosed by an HPLC pump (Knauer Wellchrom K1001) and injected in the propane-argon mixture preheated at 150 °C. Fig. 1 shows a picture of the open testing reactor containing one structured sheet (10 cm length, 5 cm wide, and 1 mm deep). The reactor was designed for containing more than one sheet but the results reported in this paper were obtained by using only one sheet. The free space was filled by nonstructured steel plates with the same dimensions. Thus, the structured sheet was tightly enclosed and the inlet stream was constrained to flow through

¹ http://www.liebherr.com/ae/en/default_ae.asp.

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