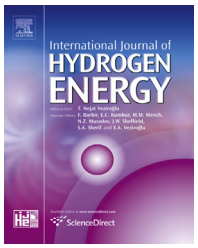
Available online at www.sciencedirect.com

ScienceDirect

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



Catalytic performance of structured packages coated with perovskite-based nanocomposite in the methane steam reforming reaction

Ludmilla N. Bobrova [a,*], *Vladislav A. Sadykov* [a,b], *Natalya V. Mezentseva* [a,b], *Vladimir V. Pelipenko* [a], *Nadezhda V. Vernikovskaya* [a,b], *Oleg P. Klenov* [a], *Oleg L. Smorygo* [c]

[a] *Boreskov Institute of Catalysis, 630090, Novosibirsk, Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090, Russia*
[c] *Powder Metallurgy Institute, Minsk, 220005, Belarus*

ARTICLE INFO

Article history:
Received 9 September 2015
Received in revised form
18 December 2015
Accepted 12 January 2016
Available online 6 February 2016

Keywords:
Methane
Steam reforming
Plate-type reactor
Ni + YSZ/YSZ anode half-cell
Ru + Ni-doped perovskite-based nanocomposite
CFD simulations

ABSTRACT

A conventional Ni + YSZ/YSZ anode half-cell (the Research Center Jülich) and the Ni + YSZ/YSZ planar half cell washcoated by a layer of the Ru + Ni-doped perovskite-based nanocomposite (Ru + Ni/LaPrMnCr/YSZ) were compared in terms of their activities and selectivities in the steam reforming of methane. The kinetic measurements were carried out in a laboratory scale plate-type reactor, and results were interpreted using computational models. A power-law kinetic model was verified against the experimental data, and parameters were estimated. Both numerical prediction and experimental testing indicate that the nanocomposite coated Ni + YSZ/YSZ plate shows much better catalytic performance under the middle-temperature operating conditions. CFD simulations show that for the high activity of thermally conductive catalytic plates, superior heat transfer performance is observed in the lab-scale reactor. The lab-scale data were successfully up-scaled for the case of steam reforming of natural gas on a structured catalyst at realistic operation conditions. Up to 700 °C, the pilot test data obtained with the structured catalyst comprised of three stacked parallel Ni–Al plates (50 × 50 × 1 mm) coated with perovskite-based nanocomposite correlate quite good with the 1-D plug-flow reactor model predictions assuming the proposed kinetics.

Introduction

One of the principal areas of modern green chemical and process engineering is the solid oxide fuel cells (SOFCs). Compared to the other fuel cell types, SOFCs are naturally fuel-flexible. The fuel flexibility is enabled by fuel reforming, i.e. the capability to convert different type of fuels from both renewable and fossil source to syngas containing hydrogen [1]. The reforming reactions in SOFC systems can be conducted both externally and internally. Generally, the reforming processes are faster than the anode H_2 and CO oxidation

* *Corresponding author*. Boreskov Institute of Catalysis 5, Pr. Ak. Lavrentieva, Novosibirsk, 630090, Russia. Tel.: +7 383 3269438.
E-mail address: lbobrova@catalysis.ru (L.N. Bobrova).

http://dx.doi.org/10.1016/j.ijhydene.2016.01.055

processes. This ability enables synthesis gas to be co-generated directly in the anode compartment and electrical power in a SOFC module by proper selection of the anode material [2–4]. Formation of H_2 and CO affects the charge-transfer chemistry, which in turn helps to drive the reforming reaction to completion by removing the hydrogen as it is formed within the fuel cell. Moreover, up to half of the heat produced by the exothermic oxidation reactions could be utilized by the endothermic reforming reaction. Such advantage of the hydrogen rich gas – fuel cells combination also drives recent developments in SOFC technology [5].

The nickel–yttria stabilized zirconia (Ni/YSZ) anodes are dominant in the SOFC application due to the excellent catalytic and electronic conducting properties of Ni and oxygen ions conducting phase of YSZ. The ceramic-metals composite known as cermet, such as the conventional Ni/YSZ anode, contains 40–50% of Ni by volume with the typical particle size of about 1 μm. Metallic nickel may serve as a catalyst for the steam reforming reaction on the anode. However, degradation in cell performance due to carbon formation has been reported to occur under direct internal reforming conditions [6]. Also, a conventional Ni-YSZ cermet anode is prone to deactivation over time due to the loss of activity and/or selectivity through the sintering of the active nickel phase in the presence of steam, hydrogen and methane.

Nowadays, recent advances in nanotechnology [6–10] have enabled the development of the robust anode materials, which is one of the main challenges of SOFC research. Nanocomposite materials exhibiting high mixed ionic and electronic conductivity as well as oxygen mobility can be used as anode materials [4,8,11,12] and catalysts in steam/auto-thermal internal reforming of gas and liquid fuels [13–16]. One way of enhancing the catalytic activity and stability of cermet Ni/YSZ materials in the direct reformation of CH_4 is their modification by promoters [10,13–18]. Supporting such nanocomposites on NiO/YSZ anode from the fuel side may also provide stable operation for an internal reforming SOFC [17,18].

In steam-methane reforming, the most efficient promoter for Ni/YSZ –based composite catalyst was proved [10] to be fluorite-like (doped ceria-zirconia) or perovskite-like (mixed chromates-manganites) oxides along with small (~1%) amounts of precious metals (Pt, Pd, Ru). Precious metal atoms incorporated into the surface layer of Ni particles provide sites for activating fuel molecules while decreasing the carbon nucleation probability, whereas the complex oxides of the support transfer oxygen species to active sites, hence, preventing their deactivation by coking.

Internal reforming can be achieved also through addition of a separate catalyst located in close proximity to the anode, either supporting catalytic layers on the Crofer interconnects or attaching to anode a plate of highly conducting Ni–Al alloy foam loaded with nanocomposite active component [10,15,19]. Thus, in the last case sufficient level of in-cell methane conversion was achieved in a planar SOFC in configuration Pt grid/LSC/20GCO/8YSZ/Ni-YSZ anode substrate/Ni–Al foam catalytic plate loaded with (Ru + Ni) LnMnCrO/Ni grid. Here platinum grid was used for cathode current collection, LSC is cathode La-Sr-cobaltite layer, 20GDC- $Ce_{0.8}Gd_{0.2}O_{2-y}$ interlayer between cathode and a thin layer of YSZ supported on a planar Ni-YSZ anode substrate. Nickel mesh as anode current collector was pressed to Ni–Al catalytic plate, so current was passed through it [10,15]. With a stream of $CH_4 + H_2O$ feed ($H_2O/CH_4 = 2$) or hymidified H_2, power density up to 350–850 mW/cm^2 in 600–800 °C range was achieved at internal steam reforming, which is promising for the practical application. At 600 °C and 700 mV the area specific resistance (ASR) was estimated to be 0.77 Ohm cm^2 without any contribution of the catalyst to R_{ohm}, which meets target of operation for intermediate temperature solid oxide fuel cells [10,15,19].

Over the past decade, it has been shown that steam reforming reaction can take place at a short gas residence time and is feasible in a catalytic plate reactor [10,13,20,21]. The plate-type catalytic reactor systems enable an effective dissipation of reaction heat by conductional heat transfer and a rapid response to load fluctuation. The feasibility of negligible pressure drops with minimal impact of diffusional limitations is aimed at exothermic or endothermic reactions, to take advantage of the improved heat transfer efficiency of the metallic plate-type reactor. The plate-type reformer is viewed as an innovation in the design of steam methane reformers for fuel cell systems [22]. Optimization of the overall performance characteristics of the process in a small-scale reformer including scale-up to practical applications deals with complex interaction of transport phenomena and chemical kinetics for specific catalyst formulations. The optimized operation strategy for SOFCs with the coupled reforming and electrochemical reactions could also be achieved based on fundamental knowledge of catalysis and simulations.

In this paper we address three different structured catalysts having the potential opportunity to be used in intermediate temperature SOFC systems: (a) Ni/YSZ cermet platelet covered by a thin layer of YSZ electrolyte (FZJ "standard" anode half-cell for reference); (b) the anode half-cell platelet coated on one side with Ru + Ni-doped perovskite-based nanocomposite (0.85% Ru + 5.3% wt.% of nanocomposite comprised of 50% $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3$ + 30%NiO + 20% YSZ), i.e., anode half cell promoted by supporting a porous layer of nanocomposite catalyst on the fuel side of anode half-cell; (c) Ru + Ni-doped perovskite-based nanocomposite on Ni–Al foam structure. Both system (b) and (c) were shown to have a potential to be applied for direct internal reforming [10,15]. The system (c) was already successfully tested in the direct internal reforming as was published in the joint paper with ECN (Petten, Holland) [10] in the frame of EC FP6 SOFC 600 Project. This was possible due to a high electronic conductivity of these alloy –supported structured catalysts, so just weakly pressing them to the anode side of the anode-supported planar SOFC (current collector was attached to this planar structured catalyst) allowed to provide a high power density along with a low area specific resistance when operating on the methane + steam mixture in the IT range [10,15,19]. A series of experiments was done in a laboratory scale plate-type reactor aiming to obtain information on kinetics of methane steam reforming reaction on the catalysts (a) and (b). The lab-scale data were up-scaled for the case of steam reforming of natural gas on a package of three stacked parallel Ni–Al foam (c) plates.