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Biofuel steam reforming catalyst for fuel cell application

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ABSTRACT

Within the ongoing project, related to fuels and energy production from biomass, agricultural and other wastes, the technology based on SOFC stack and steam reforming is under development. The project aims to present an efficient technology for biogas reforming and continuous supply of reformate fuel to the working SOFC stack. The decision, concerning reforming unit and the stack separation, has been made after detailed analysis of advantages and disadvantages of internal reforming. The set of Ni-based catalysts was prepared and investigated for the external biogas steam reforming. To determine the optimal condition of the reforming process the effect of reaction temperature (RT–773 K) for steam to carbon (S/C) molar ratio of 2.5 in the feedstock was investigated. Conversions rates and H_2/CO ratios in the produced syngas were influenced by the feedstock composition and catalyst used. The increase in the catalyst activity can be attributed to the specific catalyst–promoter interactions such as the redox capacity of V_2O_5 and its influence on surface Ni-species.

1. Introduction

Growing concerns related to petroleum based fuels together with the environmental and health regulations indicate the necessity of the clean technology development for energy production using biofuels or the second generation of alternative fuels [1–6]. Fuel cells (FCs), especially hydrogen based, are considered to be attractive in modern applications for their high efficiency and ideally emission-free use, in contrast to conventional methods of producing electricity [7,8]. FCs are significantly more energy efficient than internal combustion engines [4,9]. Thus, power stations based on FCs are able to achieve a system efficiency of 70–80%, compared to 30–37% for combustion [10]. In the transport sector, polymer exchange membrane fuel cells (PEMFCs) or high-temperature fuel cells, in particular solid oxide fuel cells (SOFCs) achieve an efficiency of 40–50%, compared to internal combustion engines (IC) which have a present-day efficiency of 20–35% [10,11]. PEMFCs are compact, have high power density and can be operated at low temperatures. However, they suffer from electrode poisoning (anodic catalyst Pt, Pt–Ru) by carbon monoxide, if the concentration of carbon monoxide is above 20 ppm (v). It is difficult to completely eliminate CO after reforming and the water gas shift reaction, because CO is one of the reforming products. Thus for PEMFCs application, there is a need for CO removal from hydrogen-containing mixtures [11,12]. In the SOFCs case, CO can be treated as a fuel and moreover the reforming of small molecules can be below 100%, because working SOFCs can operate with small amount of unreformed/not complete reformed fuel [13–15]. SOFCs have the ability to operate at high temperatures in the range of 973–1273 K. The electrolyte of a SOFC is a solid, what makes it better than molten carbonate fuel cell, which also operates at high temperatures (923 K) and can tolerate impurities. SOFC has the ability to utilize variety of fuels: hydrogen, methane, syngas, biogas and products of SR which are mixtures of hydrogen, carbon monoxide, carbon dioxide, steam and methane [16]. Internal reforming improves heat balance and cools down FC. Endothermic SR compensates exothermic electrochemical reaction, but lowers electrical efficiency because of the dilution of fuel with steam. High amount of steam (steam to carbon ratio $\geq$2) is used in order to suppress carbon formation. Unfortunately, internal reforming might lead to damage of FC because of large temperature gradients across the electrode surface [17]. Effects described above limit the application of internal reforming.

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SR of biofuels, including second generation biofuels, is currently considered as a promising process for catalytic fuel production for FC on a small/medium scale [5,6,18]. Presently, most of primary fuels need to be converted into a hydrogen-rich gas over catalyst before entering SOFCs. Heat demands of a reformer are very often secured by hot exhaust gases from the stack or burner [10,17]. However, the study shows that the main problem of those systems concerns surface deactivation and catalytic activity loss with reaction time and during often start-up and shut-down operation [19]. The use of copper catalyst in reforming processes is limited because of their thermal deactivation. Spinel type catalytic materials, e.g. $CuFe_2O_4$ [20,21], or based on nickel supported on alumina e.g. Ni/Al_2O_3 or mixed oxide systems $(Ce–ZrO_2) + Ni/Al_2O_3$ [14] are considered as more stable and active in a proper temperature range. The advantage of nickel catalysts over other systems, including those based on precious metal, results from their high selectivity for H_2, thermostability, relatively simple preparation methods and lower price [22]. Moreover, Ni-catalysts can be made by various methods such as impregnation of defined supports or different co-precipitation techniques. These advantages are particularly evident in the case of high-temperature SR of various hydrocarbons for SOFC [23].

Although Ni-based catalysts are effectively used for reforming reactions, they deactivate with time on stream due to the metal sintering and the high rate of carbon formation [18,19,24]. Thermodynamic analysis of coking during hydrocarbon steam reforming shows the increase in coke formation in the temperature range of 673–873 K, irrespective of the S/C ratio [25]. Further increase in temperature above 873 K could inhibit coke formation. Currently, the development of catalysts presenting excellent resistance toward coking is one of the key issues related to effective hydrogen production from hydrocarbons via different reforming variants, i.e. dry, steam, internal, etc. [26]. Literature data show two possibilities of catalysts modification and increase catalyst resistance toward coking, i.e. (i) by increasing the catalyst support alkalinity (the coke precursor is formed directly on the support acidic centers), or (ii) by the catalyst surface doping with oxygen-rich compounds, which mechanism of action is based on surface oxidation of the deposit nuclei. An interesting option is to use certain metal oxides, including V_2O_5 which exhibits redox properties and may act as oxygen donor for coke oxidation [27–29].

In this work, commercial Ni-based catalyst was used as a reference sample and set of Ni–V catalysts have been prepared, using commercial alumina as a support. These catalysts have been characterized for their metal particle size, active site distribution, and metal textural properties. This work is a part of investigation aimed at the development of technology based on SOFC and efficient catalysts for syngas production by biogas steam reforming.

2. Experimental

2.1. SOFC performance study

All tests were carried out at the Institute of Power Engineering (IEN) using commercial SOFC stack. The stack consists of 60 electrolyte supported SOFC fuel cells (ES-SOFC). In Fig. 1 the pilot-stand scheme and reagents flow are presented. During the test start up the SOFC stack was fueled with 5% H_2 + 95% N_2. At temperature 1023 K the fuel composition was changed to reference fuel (Fuel I 40% H_2 + 60% N_2) and the reference test was performed. After completing reference run the simulated syngas (Fuel II 19% CO, 10% CO_2, 3% CH_4, 13% H_2, 54% N_2) and finally syngas (Fuel III) were provided to the stack at temperature 1023 K. The Fuel III composition was not worse than: 18.24% CO, 12.35% CO_2, 2.6% CH_4, 12.35% H_2, 54.46 N_2. The Fuel II gas mixtures were prepared from cylinder gases and controlled by mass flow controllers (Bronkhorst) and Fuel III was provided by working gasifier. For the experiment purpose 30 kW gasifier made by IEN was used. Beech and alder chips fueled the gasifier while air was gasifying medium.

2.2. Catalyst preparation

The series of a newly developed catalyst has been prepared by a multi-stage impregnation with nickel and vanadium salts. The porous Al_2O_3 ($A_{BET} = 2\,m^2/g$) in the form of 7-hole rings was used. In the first step, alumina support was double impregnated with an aqueous nickel (II) nitrate (V) solution ($Ni(NO_3)_2$, Stanlab). After each impregnation, materials were dried at 378 K for 12 h and calcined at 723 K for 4 h in order to decompose nickel nitrate. Next, the system was impregnated with vanadium salt solution in the way to obtain 0.5, 1 and 3 wt.% of V in the final catalyst. Afterwards the catalysts were dried at 393 K for 12 h and calcined at 773 K for 3 h. For the purpose of this work the final catalysts, obtained in industrial form, are denoted as 0.5V–Ni, 1V–Ni, 3V–Ni. The commercial Ni/Al_2O_3 catalyst (New Chemical), denoted as 19Ni WSP, was used as a reference sample.

All catalysts were characterized by Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS). The TEM images were taken with a Philips CM200 (200 kV) microscope equipped with an EDX (Energy Dispersive X-ray) detector on powder samples deposited onto a copper mesh grid coated with a carbon film. The XRD patterns were recorded with a Siemens D-501 goniometer equipped with a Johansson type monochromator with a Ge(1 1 1) crystal. Cu Kα radiation and a fixed power source (45 kV and 35 mA) were used. The XPS spectra were obtained by using a Physical Electronics 5700 spectrometer with a Mg K_α X-ray source and a hemispherical electron analyzer. The C 1s peak at 284.8 eV was

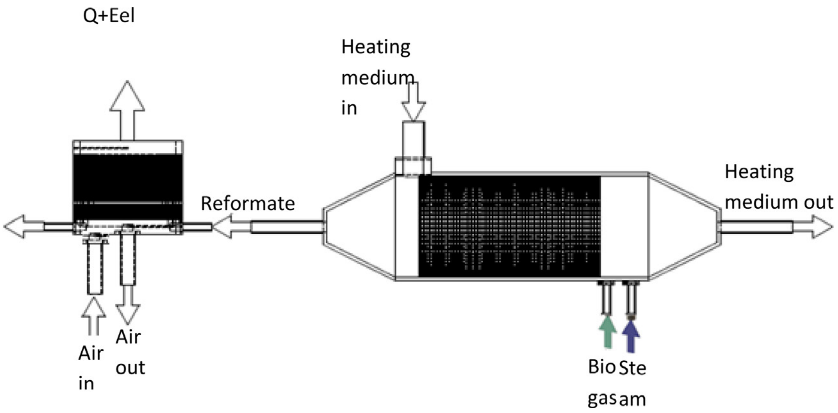

Fig. 1. Conceptual pilot-stand scheme.