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Structured nanocomposite catalysts of biofuels transformation into syngas and hydrogen: Design and performance

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ABSTRACT

Main features of structured catalysts performance in bio-fuels reforming into syngas at lab-scale and pilot-scale levels using specially designed reactors and kinetic installations allowing to broadly tune the operational parameters are presented. Effects of the nature of nanocomposite active component comprised of Ru + Ni nanoparticles on bulk/alumina-supported perovskite or Mn–Cr–O spinel, type of substrate (Ni–Al alloy and SiC(Al₂O₃)/Al–Si–O foam substrates, FeChraloy microchannel plates or gauzes protected by thin corundum layer), type of fuel (natural gas, ethanol, acetone, ethyl acetate glycerol), feed composition and temperature on yield of syngas/byproducts and performance stability are considered. The best performance in real feeds with syngas yield approaching equilibrium at short contact times without any heat/mass transfer effects along with a high thermochemical stability were demonstrated for catalyst on heat-conducting microchannel substrate. Oxygen addition to the feed in optimized amounts allows to suppress coking and stabilize performance even for the case of such reactive fuel as glycerol only slightly affecting syngas yield.

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Introduction

Progress in sustainable and renewable energy field (including hydrogen production, synfuels synthesis, internal reforming in solid oxide fuel cells, etc.) requires design of efficient and inexpensive catalysts for transformation of natural gas/biogas/biofuels into syngas and hydrogen in the intermediate (600–800 °C) temperature range [1–3]. Due to a high reactivity of bio-fuel components (carboxylic acids, aldehydes, etc.), traditional catalysts based on Ni supported on refractory oxides (alumina, etc.) are rapidly deactivated by coke deposition. This problem is solved by using nanocomposite active components comprised of Ni alloy nanoparticles (carbon nucleation is prevented by dilution of the surface ensembles of Ni atoms) supported on complex oxides with perovskite-like (LnMeO_3 , Ln = La, Pr, Sm, etc.; Me = Mn, Ni, Fe, Cr, etc.) or fluorite-like (doped zirconia, ceria, ceria-zirconia, etc.) structures possessing a high lattice oxygen mobility and reactivity required to consume coke precursors [4–9]. However, for any wide-scale practical application the content of rather expensive rare-earth metals in the active component is to be decreased. One of the promising approaches is based upon loading rare-earth containing mixed oxides on the high surface area supports, such as alumina, MgAl_2O_4 etc. [10–12]. In this case, side reactions catalysed by the alumina sites (i.e., dehydration of ethanol producing ethylene) [10] can be minimized by alumina doping with basic promoters, such as Mg [11], etc. Another approach is based upon using transition metals (Mn, Cr, Fe, Ni, etc.) containing mixed oxides with spinel-like structure, which possess reasonably high oxygen mobility and reactivity and demonstrated promising performance in redox reactions, including fuels reforming into syngas [13,14]. Hence, further research in this direction could be promising for design of inexpensive catalysts of biofuels reforming. Three types of nanocomposite active components Ni–Ru/ $\text{La}_{0.8}\text{Pr}_{0.2}\text{Mn}_{0.2}\text{Cr}_{0.8}\text{O}_3/\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{2-\delta}$, $\text{LaNi}_{0.95}\text{Ru}_{0.05}\text{O}/\text{Mg}$ –alumina and Ni–Ru/ MnCr_2O_4 were studied in this work. The first active component was earlier demonstrated to provide required activity and performance stability in the reactions of methane and biofuels transformation into syngas, tested both as a fraction and porous layers supported on different substrates [5–7]. Comparison of catalytic properties of this nanocomposite with those of Ni–Ru/ MnCr_2O_4 containing the same type of Ru + Ni alloy nanoparticles supported on mixed spinel-type oxide is expected to clarify the question about possibility to provide a high and stable performance without rare-earth cations. Mg–alumina supported perovskite is studied here to check another possible approach to decrease the content of rare-earth cations in the active component without deteriorating performance by increasing specific surface area from $\sim 5 \text{ m}^2/\text{g}$ for bulk perovskites [7,9] to $\sim 100 \text{ m}^2/\text{g}$ for supported ones [10,12].

Structured catalysts with active components supported on ceramic honeycombs [6–8,15,16] and metallic substrates (Fechaloy foil and gauze honeycombs, foams and microchannel plates) [6,16–21] are well-known to have a lot of advantages providing an efficient heat and mass transfer within the reactor. Procedures of active components loading on these substrates are to be developed to provide required thermochemical stability of supported layers to thermal cycles and to

the corroding action of feeds containing biofuels and products of their partial oxidation (acids, etc.). Tailor-made design of structured catalysts must also take into account possibility of catalysis of side reactions by the exposed surface of substrates as well as occurrence of gas-phase reactions in the void space of the catalytic package.

This work presents results of research aimed at design of structured catalysts and elucidating main features of their performance in bio-fuels reforming at lab-scale and pilot-scale levels using specially designed reactors and installations allowing broad variation of the operational parameters [5–7,21]. A special attention is paid to new types of substrates comprised of open-cell foams with different composition (Ni–Al alloy, SiC/Al–Si–O, corundum/Al–Si–O) and porosity [18,22]. Dry reforming of methane (strongly endothermic reaction) and much less energy demanding steam/oxy-steam reforming of ethanol, acetone, ethyl acetate and glycerol are compared to elucidate the effect of supports thermal conductivity on their performance. Biofuels with different composition, functional groups and reactivity/coking ability were used to find operation conditions providing stable performance of developed catalysts with realistic feeds.

Experimental

Catalysts preparation

MnCr_2O_4 mixed oxide was prepared via polymerized ethylene glycol-citric acid polyester precursor (Pechini) route following earlier described procedures [5–7]. 2% Ru + 2% Ni were supported on oxide calcined at 500 °C under air by incipient wetness impregnation with mixed $\text{Ni}(\text{NO}_3)_2 + \text{RuCl}_3$ water solution followed by calcination at 700 °C for 2 h.

Nanocomposite containing 80% of manganite-chromite perovskite $\text{La}_{0.8}\text{Pr}_{0.2}\text{Mn}_{0.2}\text{Cr}_{0.8}\text{O}_3 + 10\% \text{ NiO} + 10\% \text{ YSZ}$ ($\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{2-\delta}$) was prepared by one-pot Pechini procedure and calcined at 700 °C under air [5–7]. Ru (2 wt.%) was supported on nanocomposite by incipient wetness impregnation with RuCl_3 water solution followed by drying and calcination at 800 °C in air.

10 wt.% $\text{LaNi}_{0.95}\text{Ru}_{0.05}\text{O}_3/\text{Mg}$ –alumina active component was prepared using as a source a high purity aluminium hydroxide “Disperal” (Sasol). After decomposition of hydroxide under air at 700 °C thus obtained γ -alumina was impregnated with Mg nitrate solution (loading 10 wt.% MgO) and calcined again at 700 °C for 2 h. 10 wt.% $\text{LaNi}_{0.95}\text{Ru}_{0.05}\text{O}_3$ was supported on Mg-modified alumina by incipient wetness impregnation with mixed inorganic salts solution followed by calcination under air at 700 °C.

Main characteristics of structured substrates are given in Table 1. Fechaloy microchannel plate substrates (provided by IMM, Germany) (Fig. 1) were protected by supporting a thin (ca. 5–10 microns) corundum sublayer by blast dusting technique [21]. As follows from Fig. 1, corundum layer is really uniform and dense to provide required protection, while its roughness is sufficient to ensure fixation of the porous layer of supported active component.

Open-cell nickel foams (Fig. 2) were manufactured by the nickel electroplating of the polyurethane foam samples

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