Structured catalysts of biofuels steam/autothermal reforming on functionally graded substrates based on carbon foam: design and performance

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Abstract: For structured catalysts of biofuels reforming new types of inexpensive functionally graded substrates with a high thermal conductivity and thermochemical stability comprised of amorphous carbon foams with protective Ni, Ni-Al and $NiAl_2O_4$/corundum layers were designed. Procedures for supporting nanocomposite active components (Ni+Ru)/$CaTiO_3$/10%Mg-Al_2O_3 and $PrNi_{0.95}Ru_{0.05}O_3$ /10%Mg-Al_2O_3 on these substrates providing uniform spatial distribution were elaborated. These structured catalysts have a high and stable performance in reactions of steam and autothermal reforming of biofuels (ethanol, ethyl acetate, etc) in real feeds without coking and thermochemical degradation.

Keywords: Biofuels reforming, foam substrates, structured catalysts.

1. Introduction

Transformation of biofuels into syngas and hydrogen is one of the most important task in the renewable energy field. Structured catalysts comprised of nanocomposite active components supported on heat-conducting substrates (Ni-Al foam, Fechraloy foil and gauze, etc) demonstrate a high performance in these reactions without any impact of heat and mass transfer along with a high stability to coking and corrosion by reaction feed [1, 2]. However, for their broad application, less expensive substrates are required. In this work substrates based on carbon foam with Ni/Ni-Al/$NiAl_2O_4$ /Al_2O_3 protective layers were designed and applied for preparation of structured catalysts of biofuels reforming into syngas.

2. Experimental

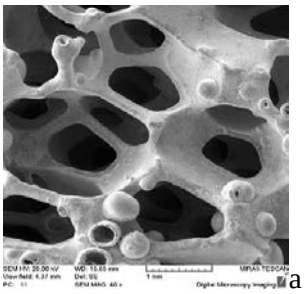
Vitreous carbon foam with the cell size of 30 ppi and thickness of 4 mm was prepared via replication of the polyurethane foam template with phenolic resin precursor followed by pyrolysis at 1100^{o}C in N_2 flow [3]. Nickel layer (thickness up to 100 μm) was then electrolytically deposited. This substrate was subjected to pack aluminizing as described in [4] for the creation of a protective nickel aluminide film (up to 10 μm). Finally, the substrate was subjected to hydro-thermal treatment at 200^{o}C for 48 h and, after drying, was calcined in air at 500^{o}C for 15 min. Their thermal conductivity was characterized as described in [3].

Nanocomposite active components were prepared using Mg-doped γ-Al_2O_3 [2]. For catalyst I 10wt.% $PrNi_{0.95}Ru_{0.05}O_3$ were loaded by wet impregnation with respective mixed salts solution, while for catalyst II 20wt.% $CaTiO_3$ were supported using ethylene glycol –citric acid precursor solution followed by calcination in air and then loading 5%Ni+1%Ru [2]. Active components (up to 10 wt.%) were supported on substrate platelets 19x10x5 mm^3 from suspensions in isopropanol with addition of polyvinyl butyral [1,2].

Catalytic platelets were tested in steam/autothermal reforming of ethanol and ethyl acetate in feeds with fuel content up to 30% and H_2O/fuel ratio 2-4 at 600-800 ^{o}C and contact times 50-150 ms using earlier described procedures [1,2]. Substrates and catalysts texture was studied by SEM with EDX (JSM 6460SV).

3. Results and discussion

Typical SEM images (Fig. 1) demonstrate a good adhesion of segregated $NiAl_2O_4$/corundum layer (thickness up to 3 μm) as well as supported catalytic layer after testing in EtOH SR. Thermal conductivity was up to 0.4 Wt/mK, which is sufficient for the good heat transfer. Any carbon deposition was not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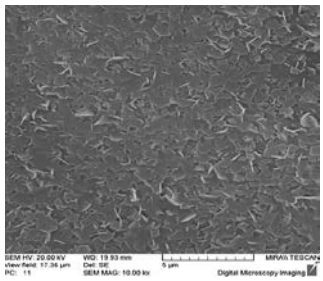
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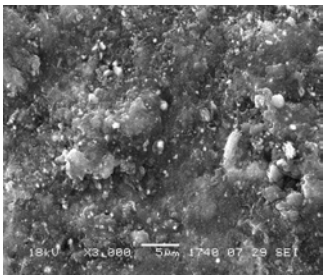
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Figure 1. SEM images of initial foam substrate with segregated protective oxide layer (a, b) and with supported layer of active component II after testing in steam reforming of ethanol (c) .

observed by SEM. For both types of supported active component in 10% C_2H_5OH+40% H_2O+N_2 feed at contact time 150 ms EtOH conversion at 650-800 ^oC varied in the range of 90-100% with H_2 content up to 37 %, which is close to characteristics of best catalysts on Ni-Al foam substrate [1, 2]. Main by-product was CH_4 with its content decreasing up to 4% at high temperatures. For more concentrated feed with a lower steam excess performance was also high and stable (Fig. 2).

In the oxi-dry reforming of ethyl acetate a high yield of syngas was obtained even at short contact time approaching equilibrium value at high temperatures (Fig. 3). In this reaction performance characteristics were also close to those observed for best catalysts on Ni-Al foam substrates [1,2].

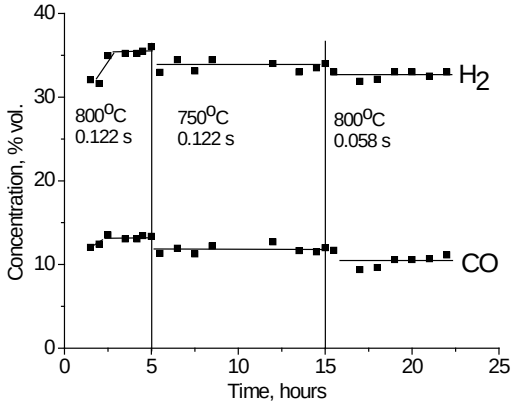

Figure 2. Variation of H_2 and CO content vs. time-on-stream in ESR at 750-800 ^oC . Feed 30% EtOH+60% H_2O +N_2, catalyst II

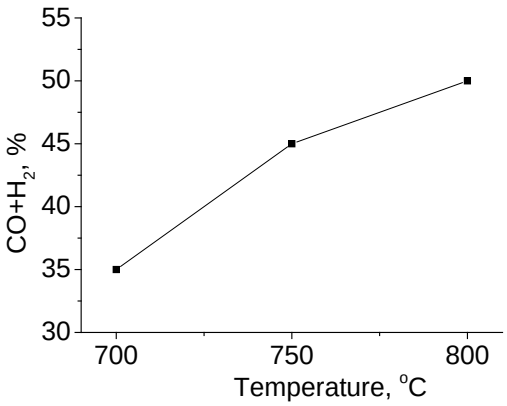

Figure 3. Temperature dependence of syngas content in ethyl acetate oxi-steam reforming on catalyst II. Feed 2.6%O_2+ 30% $C_4H_8O_2$ +60% H_2O +N_2, contact time 0.06 s

4. Conclusions

Novel types of functionally graded foam substrates based of amorphous carbon with protective layers of Ni-Al alloy and segregated $NiAl_2O_4$/corundum layer demonstrate a good thermal conductivity, compatibility with supported layers of nanocomposite active components of biofuels transformation into syngas along with required thermochemical stability in real operation conditions of biofuels reforming. Performance characteristics of these types of catalysts are close to those of the best catalysts on traditional Ni-Al foam substrates, which makes them promising for the practical application.

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