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**CATALYSTS AND CATALYTIC PROCESSES FOR THE PRODUCTION OF HYDROGEN-RICH GAS FOR FUEL CELL FEEDING****S.D. Badmaev<sup>1,2</sup>, V.D. Belyaev<sup>1,2</sup>, M.V. Konishcheva<sup>1,2</sup>, A.V. Kulikov<sup>1,3</sup>, A.A. Pechenkin<sup>1,2</sup>, D.I. Potemkin<sup>1,2</sup>, V.N. Rogozhnikov<sup>1</sup>, P.V. Snytnikov<sup>1,2,3</sup>, V.A. Sobyenin<sup>1</sup>**

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**Abstract:** *The paper considers new approaches to the preparation of structured catalysts and peculiarities of the processes for the production of hydrogen-rich gas from hydrocarbons and dimethyl ether for fuel cell feeding applications. The results of the studies of structured catalyst for CO removal from reformat by selective methanation are presented.*

**Keywords:** *partial oxidation, dimethyl ether, structured catalyst, methane, liquefied petroleum gas, associated petroleum gas, preferential CO methanation*

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## 1. Introduction

In the most R&D works on fuel cell (FC) based electrochemical generators in the past 20-25 years, it was assumed that by the beginning of mass introduction of these devices, the fuel (hydrogen) supply infrastructure and logistics would already have been created, including sufficient network of refueling stations and hydrogen storage facilities. The expectations appeared overly optimistic. Even currently existing and actively developing natural gas (raw material for about 60% of global hydrogen production) infrastructure lags behind the mass needs. In this regard, the world research centers involved in the development of FC-based power units focus special attention on conventional widely available high energy density fuels, such as natural gas, liquefied petroleum gas, gasoline, aviation kerosene, diesel fuel, methanol, ethanol, dimethyl ether. Alternative fuels (ammonia, dimetoxymethane, formic acid, formaldehyde)

are considered as well. It should be noted that among currently available hydrogen storage solutions, hydrocarbon fuel has the highest content of hydrogen per unit volume [1].

Hydrocarbon fuels cannot be oxidized directly on the FC anode at low temperatures, while at higher temperatures they often cause electrode coking and FC damage. Therefore, the fuel is first converted to hydrogen-rich gas (or syngas) in a fuel processor, and the obtained hydrogen is then oxidized in FC [2]. Depending of FC type, hydrogen-rich gas with varying content of CO and CO<sub>2</sub> can be used as a fuel. Sulfur-containing compounds are detrimental for all types of fuel cells and must be removed from the fuel during production stage at the refinery or before feeding to fuel processor.

Hydrogen-rich gas can be produced by the processes of steam reforming (SR), partial oxidation (PO), or their combination - autothermal reforming (ATR) of fuel [3–10].

SR of hydrocarbons and oxygenated compounds at temperatures of 300 to 800°C in water excess (molar ratio  $H_2O/C = 1.1-3$ ) is the most effective process which provides the highest hydrogen yield. However, it requires a lot of heat for the reaction, water vaporization, steam heating, and needs water conditioning system. Therefore, SR is mainly suggested for use in stationary applications. Integration of endothermic and exothermic processes, which take place in the fuel processor and FC stack at the stages of hydrogen-rich gas production and utilization, facilitate the reaching of high efficiency of FC-based power units. The PO and ATR processes are intended mainly for portable and autonomous applications, for which the priority issues are compactness, water-independence and rare service. Syngas produced by fuel SR, PO and ATR can be used directly for solid-oxide fuel cells (SOFC) feeding.

For using in proton exchange membrane fuel cells (PEMFC), syngas must be deeply purified from CO. For this purpose, CO water gas shift (WGS) reaction is applied. Besides hydrogen, the outlet gas usually contains (vol.%) ~20 CO<sub>2</sub>, ~10 H<sub>2</sub>O and ~0.5–2 CO. It can be used for feeding high-temperature PEMFC (operating temperature 160-190 °C), but inappropriate for low-temperature PEMFC (80-120 °C) because CO is the anode poison. CO must be removed from the reformat to the level of <10 ppm. Currently, catalytic preferential (selective) methanation (PreMeth) of CO is considered as one of the most promising processes for deep purification of reformat from CO [11]. The process requires no additional reagents. The presence of CO<sub>2</sub>, water vapor and methane in the outlet gas has no negative effect on PEMFC operation. However, the best CO PreMeth performance is reached only in the presence of highly active and selective

catalysts. Otherwise, accompanying highly exothermic reaction of CO<sub>2</sub> methanation will cause considerable hydrogen losses, catalyst overheating and unstable operation of the fuel processor.

Being highly exothermic, the process of partial oxidation requires no external heating that allows minimization of auxiliary equipment to provide stable operation of the reformer. However, high thermal effect of the reaction implies strong requirements for the catalyst stability and thermal conductivity, and resistance to the active component sintering.

In our earlier works we suggested to use highly heat-resisting (up to 1350°C) FeCrAl alloy materials in a form of meshes and foams as a heat-conducting structural carrier of the catalysts for the reactions of complete and partial oxidation of gaseous hydrocarbons, and steam and autothermal reforming of diesel fuel [12–16]. The applied approach appeared universal and technologically advanced. It allowed manufacturing catalytic modules of various sizes and geometry for all steps of hydrogen-rich gas production in a fuel processor.

The present paper demonstrates the advantages of FeCrAl alloy wire mesh for the production of structured catalytic modules with high heat-conductivity, effective mass-transfer and high surface area. The processes of partial oxidation of natural gas (NG), liquefied petroleum gas (LPG), associated petroleum gas (APG) and dimethyl ether (DME) to synthesis gas over the same catalyst were performed to demonstrate the feasibility of multi-fuel concept which suggests the using of various fuels for FC-based power units feeding. The developed procedure was also adapted for the synthesis of structured catalysts for deep CO removal from hydrogen-rich gas mixtures.

## 2. Experimental part

### 2.1 Catalyst preparation and characterization

Composite oxide Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2-δ</sub> (CZ) with fluorite structure was purchased from Ecoalliance Ltd. (Russia). CZ was prepared by

direct precipitation described in detail elsewhere [17]. Solutions of Ce<sup>3+</sup> and ZrO<sup>2+</sup> nitrates were combined in fixed proportions resulting in concentrations of components totaling 0.1 g cm<sup>-3</sup>. The composite oxide was

precipitated from the solution by adding 25% aqueous ammonia dropwise under permanent stirring. The mixture was held at 100 °C and atmospheric pressure for 120 h. Thereafter, the precipitate was filtered and repulped in isopropanol. The resulting slurry was dried at 100 °C for 12 h and calcined at 500 °C for 2 h, and then at 800 °C for 1 h. The synthesized CZ material was crashed in an agate mortar, and the 0.2 - 0.5 mm fraction was separated for further catalyst synthesis. Properties of CZ are described in detail elsewhere [17]. CZ specific surface areas ( $S_{\text{BET}}$ ) was  $69 \text{ m}^2 \text{ g}^{-1}$ .

Supported Rh/CZ catalyst with metal loading of 1 wt.% was prepared by a sorption-hydrolytic deposition technique according to [18] and described in detail elsewhere [19]. The main idea of this technical approach is to form a solution of "metal complex + alkaline agent" which is metastable at the given conditions (temperature, concentrations) with respect to homogeneous metal hydroxide precipitation. This is due to the kinetic inertness of the metal complexes for ligand exchange [20]. As the support surface accelerates heterogeneous nucleation and growth of metal hydroxide particles [21], addition of support to the reagent mixture initiates hydrolysis which leads to uniform depositing of the metals over the support surface. For this purpose, a solution of  $\text{RhCl}_3$  was mixed with  $\text{Na}_2\text{CO}_3$  in a molar ratio of  $\text{Na}/\text{Cl} = 1$ . The mixture was then brought into contact with CZ support at 75 °C. After the end of the deposition procedure (i.e., when no reaction of the solution with  $\text{NaBH}_4$  was observed), the sample was thoroughly rinsed with hot water by decanting, dried and reduced in a hydrogen flow at 250 °C for 30 min.  $S_{\text{BET}}$  of the prepared catalyst was close to

that of the support. According to TEM analysis, the Rh particles in the catalyst existed on the support surface predominantly in a form of 1 - 2 nm clusters in good agreement with the CO chemisorption data. Prepared Rh/CZ catalyst was tested in DME partial oxidation.

FeCrAl alloy wire mesh (grid cell size is 0.5 mm, wire diameter is 0.25 mm) purchased from "NPO Souznichrom" Inc. (Russia) was used as a substrate for catalyst deposition. The main steps for the catalytic module preparation procedure were previously described in detail [16].

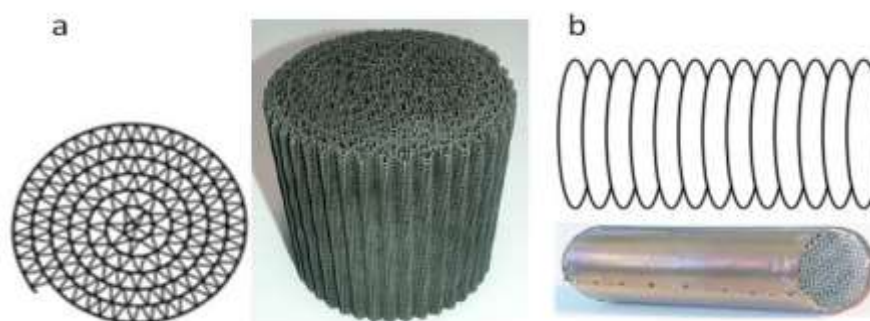
Honeycomb - type module consisting of corrugated and flat FeCrAl alloy wire meshes twisted in an Archimedes' spiral was coated by a  $\gamma\text{-Al}_2\text{O}_3$  protective layer based on preparation technique described in previous research [12]. Then the  $\gamma\text{-Al}_2\text{O}_3$  - coating was impregnated by a saturated solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  ( $\text{Ce}/\text{Zr} = 3$ ) during 7 sequential steps with intermediate thermal treatment at 800 °C for 5 min and final calcination at the same temperature for 0.5 h. Thus the  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-\delta}\text{-}\gamma\text{-Al}_2\text{O}_3/\text{FeCrAl}$  structured support was prepared. Finally, the catalytic module was synthesized by deposition of Rh onto structured support by the sorption-hydrolytic deposition technique described above. For simplicity, Rh/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-\delta}\text{-}\gamma\text{-Al}_2\text{O}_3/\text{FeCrAl}$  wire mesh catalyst (further labeled as Rh/CZ-Al/FCA) was tested in partial oxidation of NG, LPG, their mixture modeling APG, and DME. Figure 1a presents the final design of the honeycomb-type composite catalytic module (the size of channel cross - section is *ca.*  $1.7 \text{ mm}^2$ ). Specification of the catalytic module used in the PO experiments is presented in Table 1.

**Table 1.** Specifications of catalytic modules used in the PO and PreMeth experiments

Module abbreviation	Module dimensions, mm		Composition, wt.%					Total weight, g
	diameter	length	Rh	Ni	$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-\delta}$	$\text{CeO}_2$	$\gamma\text{-Al}_2\text{O}_3$	
Rh/CZ-Al/FCA	42	54	0.24	-	6.3		5.5	84.3
Ni/Ce-Al/FCA	8	17	-	1.1		10.0	6.0	0.87

For PreMeth CO catalyst preparation the procedure of depositing the active component on a structured support was adapted. Sandwich-type FeCrAl alloy wire mesh support (Figure 1b) with a  $\eta$ -Al<sub>2</sub>O<sub>3</sub> protective coating were impregnated with an aqueous solution of Ce(NO<sub>2</sub>)<sub>3</sub> and calcined at 400 °C to produce the CeO<sub>2</sub> film on the support surface. This procedure was repeated several times until the CeO<sub>2</sub> amount reached ~10 wt% of the support weight. The CeO<sub>2</sub>/FCA catalytic module were then

impregnated with an aqueous solution of nickel salts (molar ratio of Ni(NO<sub>3</sub>)<sub>2</sub>:NiCl<sub>2</sub>=4, calculated Ni loading of 10 wt% with regards to CeO<sub>2</sub>), dried at 110 °C for 2 h and reduced in a flow of 5 vol% H<sub>2</sub>/He at 400 °C for 2 h. Then the catalytic module was cooled down to room temperature in He flow and taken out to the ambient atmosphere. The active component (Ni, Cl and CeO<sub>2</sub>) loading in the structured catalyst (further denoted as Ni/Ce-Al/FCA) was ~11 wt% with respect to FCA (See Table 1).



**Fig. 1.** Images of Rh/CZ-Al/FCA catalytic module twisted in an Archimedes' spiral (a) and Ni/Ce-Al/FCA sandwich - type catalytic module (b).

Previously, the as-prepared and used Rh supported over composite ceria – zirconia - alumina FeCrAl alloy wire mesh catalysts (synthesized by the same preparation protocol as described above for the Rh/CZ-Al/FCA honeycomb catalytic module) [13,15,16] and Ni/Ce-Al/FCA sandwich-type catalytic modules [22,23] were characterized by several techniques. It was shown by transmission electron microscopy (TEM) study that the rhodium in the catalysts uniformly distributed over the ceria - zirconia surface. The sizes of Rh clusters were 1 - 2 nm. Several 3 - 4 nm particles were observed as well. In general, these results agreed well with the CO chemisorption data. According to scanning electron microscopy (SEM) study, a layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> consisted of columnar or needle -shaped crystals (5 - 10  $\mu$ m thick, up to 50  $\mu$ m long) evenly covering the surface of FeCrAl alloy wire mesh. The thickness of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> coating was 30 - 50  $\mu$ m. After supporting Rh/Zr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2- $\delta$</sub>  over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, the surface microstructure has modified. The surface of the crystals became rougher, while

the thickness of the final layer remained the same (30 - 50  $\mu$ m). Concentrations of the Rh, Ce, Zr, Al, and O elements throughout all areas studied by energy-dispersive X-ray analysis were similar that proves uniform distribution of Rh and Zr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2- $\delta$</sub>  over the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystals, in good agreement with TEM data.

The microstructure of the mesh surface also changed substantially after deposition of CeO<sub>2</sub> and Ni over the alumina layer. It was shown [22], that the surface was covered by a continuous layer of small (ca. 1-10  $\mu$ m) agglomerates of particles. The thickness of this layer was about 90  $\mu$ m. EDX analysis showed that the surface layer of Ni/Ce-Al/FCA contains Ce, Ni, Cl, O and a small amount of Al. The concentrations of these elements in all areas were similar, indicating a uniform distribution of Ni, CeO<sub>2</sub> and Cl over the alumina layer on FeCrAl alloy wires. The TEM data were in line with SEM data and confirmed that the surface structure of the Ni/Ce/FCA catalyst was similar to that of the powdered chlorinated nickel ceria catalysts

studied in detail in [24].

Thus, the different parts of the Rh/CZ-Al/FCA and Ni/Ce-Al/FCA composite catalysts have their own functionality. Metal wire mesh structure provides high heat conductivity and mechanical strength for the whole module. Alumina intermediate layer in the form of columnar or needle-shaped crystals chemically bonded with the FeCrAl alloy substrate prevents its degradation in the reaction environment. At the same time, such structure provides elasticity of the catalytic coating and preserves secondary  $Ce_{1-x}Zr_xO_{2-\delta}$  layer with Rh or  $CeO_2$  layer with Ni particles in the dispersed state.

The carbon formation in the Rh/CZ pellets and Rh/CZ-Al/FCA catalytic module during catalytic activity experiments was quantified by temperature programmed oxidation (TPO) using a quartz fixed bed flow reactor. The gas mixture of 8 vol.%  $O_2$  in He was supplied at a rate of 6  $L \cdot h^{-1}$ . The temperature was increased from 20 to 600  $^{\circ}C$  continuously at a rate of 10  $^{\circ}C \cdot min^{-1}$ . A mass-spectrometer QMC - 200 (Stanford Research Systems, USA) was used for online measurement of the outlet  $CO_2$  concentration.

## 2.2. PO activity measurements

DME partial oxidation was carried out in a U-shaped quartz reactor (i.d. 4 mm, wall thickness  $\sim 1$  mm) at 1 atm in the temperature range of 500-700 $^{\circ}C$ . Rh/CZ catalyst pellets with volume of 0.5  $cm^3$  ( $\approx 0.5$  g) was placed in

the reactor. All empty space in the reactor before and after catalyst bed was filled by quartz pellets of the catalyst-size fraction ( $\approx 0.5$  mm) to prevent the homogeneous oxidation of DME, which, as shown by separate experiments, takes place in the gas phase under the studied reaction conditions.

Experiments were performed in the mixture  $DME:O_2:N_2 = 30:15:55$  vol.% at gas hourly space velocity (GHSV) of 10,000  $h^{-1}$ . The temperature was controlled by K - type thermocouple in the middle of the catalyst bed. Prior experiments, the catalyst was reduced at 550  $^{\circ}C$  in 10 vol.%  $H_2$  in the  $N_2$  flow during 0.5 hour.

The inlet and outlet concentrations of gas mixtures were measured online (with an accuracy of  $\pm 2$  rel.%) using a gas chromatograph Chromos GC - 1000 (Chromos, Russia). It had Porapak T and molecular sieves CaA columns and thermal-conductivity (TCD) detector. The main reaction products were  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$  and  $H_2O$ . Formaldehyde, methanol and  $C_2$  hydrocarbons were observed in trace amounts (less than 200 ppm). The carbon balance was controlled with an accuracy of  $\pm 3$  rel.%.

The catalyst performance in the DME partial oxidation was characterized by the outlet concentrations of the main reaction products, DME ( $X_{DME}$ ) and  $O_2$  ( $X_{O_2}$ ) conversion, which were calculated by the following equations:

$$X_{DME}(\%) = \frac{C_{DME}^0 - C_{DME} \times \frac{C_{N_2}^0}{C_{N_2}}}{C_{DME}^0} \times 100 \quad (1)$$

$$X_{O_2}(\%) = \frac{C_{O_2}^0 - C_{O_2} \times \frac{C_{N_2}^0}{C_{N_2}}}{C_{O_2}^0} \times 100 \quad (2)$$

Rh/CZ-Al/FCA catalytic module was tested in a stainless steel fuel reformer under

atmospheric pressure, GHSV of 40,000-50,000  $h^{-1}$  and the following feed gas compositions:

- NG PO, vol.%: 59,6  $N_2$ , 16,0  $O_2$ , 21,8  $CH_4$ , 1,4  $C_2H_6$ , 0,5  $C_3H_8$ , 0,6 Ar.
- LPG PO, vol.%: 70,3  $N_2$ , 18,9  $O_2$ , 8,1  $C_3H_8$ , 1,9  $C_4H_{10}$ , 0,6 Ar.
- APG PO, vol.%: 63,3  $N_2$ , 17,0  $O_2$ , 11,5  $CH_4$ , 0,6  $C_2H_6$ , 5,4  $C_3H_8$ , 1,3  $C_4H_{10}$  0,8 Ar.
- DME PO, vol.%: 57,3  $N_2$ , 15,4  $O_2$ , 26,5  $(CH_3)_2O$ , 0,7 Ar

The temperature was controlled by K - type thermocouples at the inlet and outlet of the catalytic module. Prior experiments, the catalyst was reduced at 700 °C in 5 vol.% H<sub>2</sub> in the N<sub>2</sub> flow.

The inlet and outlet concentrations of gas mixtures were measured online (with an accuracy of ± 2 rel.%) using a gas chromatograph Chromos GC – 1000 (Chromos, Russia). It had Porapak Q and molecular sieves CaA columns and flame ionization (FID) and thermal-conductivity (TCD) detectors. A moisture trap was used for water removal from the gas mixture before analysis. During the experiments, the carbon balance was controlled with an accuracy of ± 3 rel.%. N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> concentrations were monitored and compared with the equilibrium values, which were calculated using the HSC Chemistry 7.0 software by minimization of the Gibbs free energy of the system.

### 2.3 PreMeth CO activity measurements

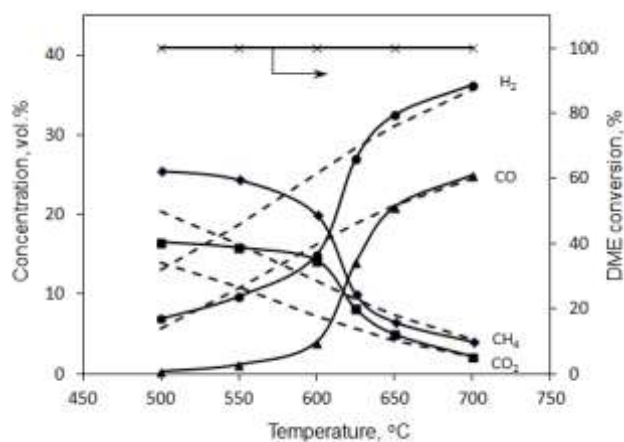
Preferential methanation of CO in the presence of CO<sub>2</sub> was carried out in a U-shaped quartz reactor (i.d. 8 mm, wall thickness ~1 mm) at 1 atm. The sandwich -type Ni/Ce-Al/FCA catalytic module was placed in the reactor. Quartz-wool filters were placed before and after the catalyst. The temperature was measured by a K-type thermocouple (diameter 0.1 mm) placed approximately in the middle of

the catalyst bed. Catalytic experiments were performed using a hydrogen-rich gas mixture of the following composition (vol%): 1.0 CO, 65 H<sub>2</sub>, 10 H<sub>2</sub>O, 20 CO<sub>2</sub> with He as balance gas, and at GHSV of 29,000 cm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> with regard to the weight of the deposited Ni(Cl)/CeO<sub>2</sub> layer. Initially, the catalyst was heated to 170°C in a He gas flow, and then reduced in the reaction mixture at 400°C for 1 h; after that the temperature was decreased and the experiment was started. The experiment was repeated in several cycles of increased/decreased temperatures. Catalytic characteristics of Ni/Ce/FCA were reproduced in several cycles. The total duration of the tests was ca. 100 h. The inlet and outlet concentrations were determined using a Chromos GC-1000 chromatograph (Chromos, Russia) equipped with a methanation reactor unit and flame-ionization detector. Methane was the main reaction product. The detection limit of CO and CO<sub>2</sub> was 1 ppm. The catalyst performance was characterized by the outlet concentrations of CO, CH<sub>4</sub> ([CO]<sub>out</sub> and [CH<sub>4</sub>]<sub>out</sub>) and CO selectivity (S<sub>CO</sub>), which was calculated by the following equation:

$$S_{CO}(\%) = \frac{F_{CO}^{in} - F_{CO}^{out}}{F_{CH_4}^{out}} \cdot 100, \quad (3)$$

where  $F_{CO}^{in}$  - the inlet molar flow rate of CO;

$F_{CO}^{out}$  and  $F_{CH_4}^{out}$  - the outlet molar flow rate of CO and CH<sub>4</sub>.

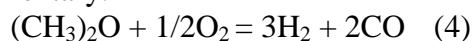


**Fig. 2.** Effect of temperature on DME conversion and H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> concentrations in DME partial oxidation over Rh/CZ catalyst. Points and solid lines – experimental data, dashed lines – equilibrium concentrations.

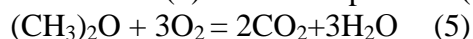
## 2. Results and discussion

As Fig. 2 shows, DME conversion on Rh/CZ catalyst reached 100% in the whole studied temperature interval 500-700°C. It is seen that the outlet concentrations of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> attained respective equilibrium values at temperatures above 630°C. The catalyst demonstrated stable operation and, as proved by TPO experiments, high coking-resistance.

At temperatures below 600°C, the outlet concentrations of DME PO reaction products deviated from the equilibrium values. The gross reaction of partial oxidation of DME, which is described by equation (4), is not elementary:

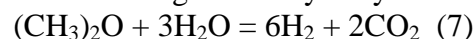


In the frontal part of the catalyst most likely dominate the reactions of DME complete oxidation (5) and decomposition (6):

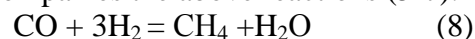


The reaction of DME SR (7) can be

realized further along the catalyst layer:



Low concentration of CO and high concentration of CH<sub>4</sub> in the outlet gas allow suggestion that the reaction of CO methanation (8) accompanies the above reactions (5-7):



Combination of all these reactions seems to explain adequately the observed deviation of the outlet product concentrations from respective equilibrium values at temperatures below 600 °C (Fig. 2).

Structured Rh/CZ-Al/FCA catalyst showed excellent catalytic performance in DME PO as well. As Table 2 shows, DME conversion was 100% even at GHSV = 45,000 h<sup>-1</sup>, which 4.5-times exceeded respective value in experiments with catalyst pellets. The structured catalyst syngas (H<sub>2</sub> + CO) productivity was more than 3 m<sup>3</sup>/h. This value is sufficient for a 3 kW<sub>e</sub> SOFC feeding.

**Table 2.** Inlet conditions and experimental results of NG, LPG, APG and DME partial oxidation with Rh/CZ-Al/FCA catalytic module.

Reaction conditions	Type of fuel						
	NG		LPG		APG		DME
GHSV, h <sup>-1</sup>	40.000	50.000	40.000	50.000	40.000	50.000	45.000
T <sub>inlet</sub> , °C	800	800	950	960	860	870	840
NG flow rate, L/min	11.8	14.7	-	-	6.1	7.6	-
LPG flow rate, L/min	-	-	4.9	6.1	3.3	4.1	-
DME flow rate, L/min	-	-	-	-	-	-	15
Air flow rate, L/min	38.1	47.6	44.9	56.2	40.5	50.6	41.5
Fuel conversion, %	99	98	99	99	99	99	100
Syngas productivity*, m <sup>3</sup> /h	2.5	3.3	2.6	3.1	2.6	3.1	3.2
Outlet gas mixture composition (dry basis), vol%							
H <sub>2</sub>	32.7	32.9	27.2	26.1	31.1	30.6	33.4
O <sub>2</sub>	0	0	0	0	0	0	0
N <sub>2</sub>	43.9	43.8	47.6	49.1	45.2	45.6	34.8
CO	16.1	15.9	19.2	19.4	16.9	17.1	22.7
CO <sub>2</sub>	2.7	2.8	2	1.9	1.9	2.1	3.6
CH <sub>4</sub>	2.2	2.4	0.03	0.07	1.2	1.4	1.6

\*Calculated on H<sub>2</sub> + CO

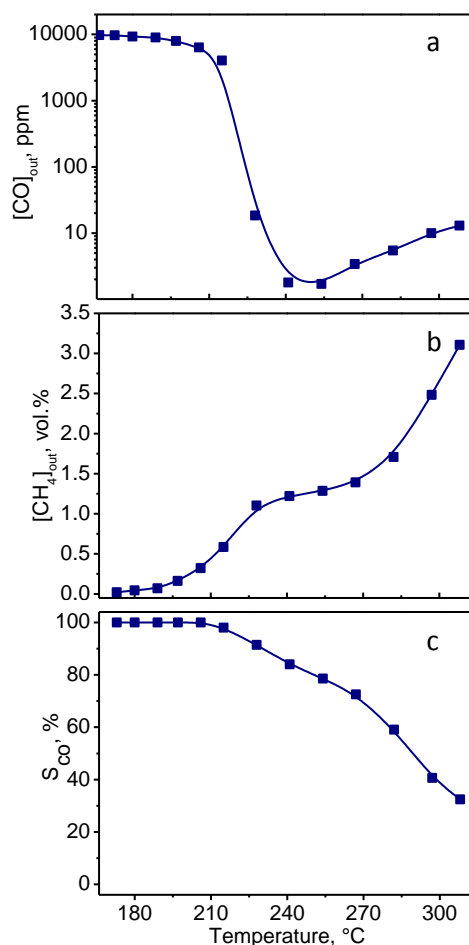
In our earlier work [16], partial oxidation of NG and LPG was performed using structured Rh/CZ-Al/FCA catalytic module of

a smaller size (2.5-time smaller than in this work). It was shown that at temperatures 820 (NG PO) and 950 °C (LPG PO) at the surface

of the catalyst module inlet the measured  $H_2$ , CO,  $CO_2$ ,  $CH_4$ , and  $N_2$  concentrations were constant and still closed to equilibrium values at GHSV up to 100,000 and 80,000  $h^{-1}$ , respectively. The concentrations of ethane and propane slightly increased from trace amount to 0.02-0.05 vol.% with increasing space velocity. The reformat gas contained high concentrations of  $H_2$  and CO and, thus, can be used for SOFC feeding. The maximum observed syngas ( $CO + H_2$ ) productivity per catalyst volume was  $\sim 60 \text{ m}^3 L_{\text{cat}}^{-1} h^{-1}$  (STP). These results showed high performance of composite catalyst, which was achieved, most likely, due to the high heat conductivity of the FeCrAl alloy support. The difference between the hottest and coldest parts of the catalytic module did not exceed 140 °C. Good thermal properties of the catalyst helped to minimize the possibility of local hot spot formation,

catalyst overheating, sintering of the active catalytic phase, and thus prevented catalyst deactivation.

The data presented in Table 2 prove that the experiments with Rh/CZ-Al/FCA catalytic module agree with the previous results. Partial oxidation of NG, LPG, and surrogate APG provided complete conversion of the initial fuel with both GHSV values of 40,000 and 50,000  $h^{-1}$ . The outlet product concentrations were close to the equilibrium ones. According to our calculations, the structured catalyst provided more than 3  $\text{m}^3/h$  syngas ( $H_2+CO$ ) productivity for all the studied fuels under similar reaction conditions that makes it highly promising for using in a multi-fuel reformer. The TPO experiment with the used Rh/CZ-Al/FCA composite catalyst revealed no carbon formation during NG, LPG and APG PO.



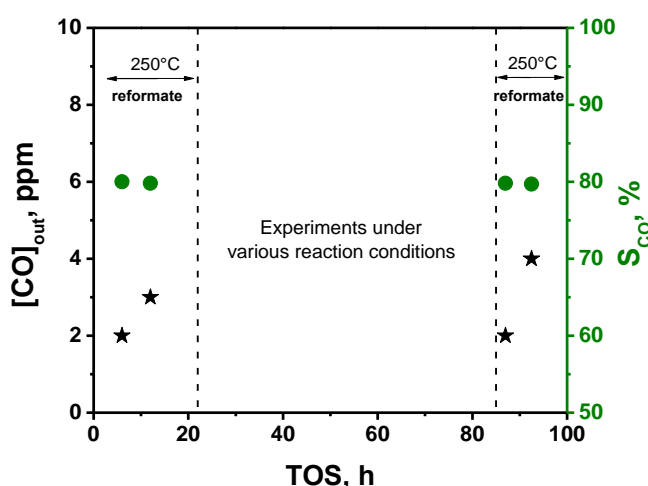
**Fig. 3.** The temperature dependence of the outlet concentration of CO (a),  $CH_4$  (b) and CO selectivity (c) for the preferential CO methanation over Ni/Ce-Al/FCA.



Fig. 3 illustrates the performance of Ni/Ce-Al/FCA catalyst in PreMeth CO reaction. It is seen that the catalyst provided the outlet CO concentration below 10 ppm at high selectivity (Fig. 3 a,c). The presence of  $\eta$ -Al<sub>2</sub>O<sub>3</sub> had no negative effect on the Ni/Ce-Al/FCA catalyst performance as we shown earlier [25] by comparison with Ni/CeO<sub>2</sub> catalyst pellets. Alumina acted as a structural promoter for the deposited Ni/CeO<sub>2</sub> layer. At temperatures below 280 °C, the reaction of CO<sub>2</sub> methanation was suppressed (Fig.3b), as

demonstrated by the plateau of the temperature dependencies of the outlet CH<sub>4</sub> concentration.

As the temperature exceeded 280 °C, the contribution of CO<sub>2</sub> methanation became obvious. As shown in our earlier works [22,26,27], chlorine species CeOCl on the surface of the nickel-ceria catalysts inhibited the CO<sub>2</sub> methanation reaction. The structured Ni/Ce-Al/FCA provided CO cleanup to a level of <10 ppm in the reformat gas containing 20 vol.% CO<sub>2</sub> in the temperature interval of 230-270 °C with a selectivity  $S_{CO} > 70\%$ .



**Fig. 4.** CO outlet concentration (★) and selectivity (●) as a function of time on stream in preferential CO methanation over Ni/Ce-Al/FCA at 250°C.

Structured Ni/Ce-Al/FCA catalyst was stable under PreMeth CO conditions. It is seen (Fig. 4) that during the first 13 h Ni/Ce-Al/FCA provided deep CO removal ( $[CO]_{out} < 10$  ppm) at  $S_{CO} \approx 80\%$ . During the next ~60 h the catalyst was tested under varying conditions (CO content, temperature, space velocity). Then the experiment was returned to initial conditions in order to check the catalyst

stability. Clearly, even after 80 h on-stream Ni/Ce-Al/FCA demonstrated stable reproducible characteristics:  $[CO]_{out} \leq 10$  ppm at  $S_{CO} \approx 80\%$ . No damage or losses of the catalyst layer were identified after *ca.* 100 h of catalytic testing, indicating a reasonably good adhesion of the catalytic coating onto the FeCrAl alloy wire mesh.

### 3. Conclusions

Honeycomb Rh/CZ-Al/FCA wire mesh composite catalytic module was designed and manufactured. It demonstrated stable operation and excellent catalytic performance in multifuel partial oxidation

reformer with natural gas, liquefied petroleum gas, associated petroleum gas and dimethyl ether. It provided equilibrium product distribution at GHSV 40,000-50,000 h<sup>-1</sup>. The

syngas (CO + H<sub>2</sub>) productivity was sufficient to feed a 3 kW<sub>e</sub> solid oxide fuel cell.

A structured Ni/Ce-Al/FCA wire mesh catalyst was developed for the reaction of preferential CO methanation in the presence of CO<sub>2</sub>. In a hydrogen-rich gas mixture of the

composition (vol.%): 1.0 CO, 65 H<sub>2</sub>, 10 H<sub>2</sub>O, 20 CO<sub>2</sub>, He - balance, GHSV = 29,000 cm<sup>3</sup>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>, the catalyst reduced the CO concentration to a level of <10 ppm in the temperature interval of 230-270°C with a selectivity >70%.

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**КАТАЛИЗАТОРЫ И КАТАЛИТИЧЕСКИЕ ПРОЦЕССЫ ДЛЯ ПОЛУЧЕНИЯ ВОДОРОДСОДЕРЖАЩЕГО ГАЗА ДЛЯ ПИТАНИЯ ТОПЛИВНЫХ ЭЛЕМЕНТОВ**

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*В работе обсуждаются новые подходы по приготовлению структурированных катализаторов и особенности проведения процессов получения водородсодержащего газа из углеводов и диметилового эфира для питания топливных элементов различных типов. Также представлены результаты исследования структурированного катализатора очистки реформата от СО на примере избирательного метанирования монооксида углерода.*

**Ключевые слова:** *парциальное окисление, диметиловый эфир, структурированный катализатор, метан, сжиженный нефтяной газ, попутный нефтяной газ, избирательное метанирование СО*

**YANACAQ ELEMENTLƏRİNDƏ İSTİFADƏ OLUNAN HİDROGEN TƏRKİBLİ QAZIN ALINMASI ÜÇÜN KATALİZATORLAR VƏ KATALİTİK PROSESLƏR**

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*Müxtəlif növ yanacaq elementləri üçün karbohidrogenlərdən və dimetil efirindən hidrogen tərkibli qazın alınması üçün strukturlaşdırılmış katalizatorların hazırlanmasının yeni üsulları müzakirə olunur. Eləcə də riformatın karbon monooksiddən təmizlənməsi üçün strukturlaşdırılmış katalizatorlar carbon monooksidin metanlaşma reaksiyasında öyrənilib.*

**Açar sözlər:** *yanacaq elementləri, dimetil efiri, strukturlaşdırılmış katalizatorlar, metan, karbon monooksidi*