FUEL PROCESSING IN MICRO REACTOR FOR H_2 PRODUCTION WITH LOW CO CONCENTRATION

Slavko Amon[1], Danilo Vrtačnik[1], Drago Resnik[1], Matej Možek[1], Stanko Hočevar[2]*, Jurka Batista[2], Iztok Stegel[3]

[1]University of Ljubljana, Faculty of Electrical Engineering, Laboratory of Microsensor Structures and Electronics, Tržaška 25, SI-1000 Ljubljana, Slovenia
[2]National Institute of Chemistry, Laboratory of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
[3]Ministry of Defence, Dimičeva 15, SI-1000 Ljubljana, Slovenia
*Presenting Author: stanko.hocevar@ki.si

Abstract: A methanol fuel processor was built based on Si wafers micro channel and micro chamber structures for unit operations which were fully integrated into a single rugged device. The fuel processor encompasses fuel combustor, vaporizer, steam reformer, and selective CO oxidation. The influence of catalyst deposition method and its activation on the micro-channel fuel processing characteristics were studied. The concentration of CO in the dry gas below 50 ppm has been achieved.

Keywords: fuel processing, micro reactor, methanol reforming, selective CO oxidation

INTRODUCTION

In recent years micro fabrication technologies have been introduced in the field of chemical process engineering to realize micro channel reactors. These devices have an inherently large surface area-to-volume ratio, offering high heat and mass transfer rates.

Compact fuel cell systems that operate on liquid hydrocarbon fuels offer an efficient, lightweight alternative to batteries, thus, allowing for greater portability and longer effective use. The energy densities of liquid fuels, among them methanol, are at least an order of magnitude greater than that of the state-of-the-art lithium-ion batteries [1].

Technology for converting methanol into a hydrogen-rich supply for fuel cells is mainly based on steam reforming (SR). The reformed gases contain at complete methanol conversion about 50% H2, 20% CO2, 0.5-1% CO, 10% H2O. Such reformed gas is not clean enough fuel for proton exchange membrane fuel cells (PEMFC), where anode catalyst (Pt/C) will be poisoned by CO at levels higher than few tens of ppm.

Methods for CO removal include palladium diffusion membranes, methanation and selective catalytic oxidation. Among these methods CO selective catalytic oxidation, also known as preferential oxidation (PROX) of CO, is the most promising and practical method. It requires the use of catalyst with high activity and selectivity to maximize the levels of CO oxidation while minimizing the extent of hydrogen oxidation.

A methanol fuel processor was built based on Si wafers micro channel and micro chamber structures for unit operations which were fully integrated into a single rugged device. The fuel processor encompasses fuel combustor, vaporizer, steam reformer, and selective CO oxidation (Figure 1). The concentration of CO in the dry gas below 50 ppm has been achieved.

EXPERIMENTAL

Starting material were single-side mechanical polished silicon wafers of diameter 100 mm, thickness of 380 μm and (100) crystal orientation. AZ 9260 resist from Clariant, USA of thickness 6.5 μm was used for silicon etch mask. Mask pattern was transferred to oxide mask by standard photoresist photolithography, followed by wet etching of patterned oxide in buffered HF, and stripping of photoresist in plasma asher. In addition, each sample was etched for 15 s in diluted HF (1:100), immediately before RIE of micro channels. 1 mm holes, which were designed for in/out fluidic connections were etched in wafers. Micro channel chips were hermetically covered with Pyrex wafers by anodic bonding (Figure 2) [2].
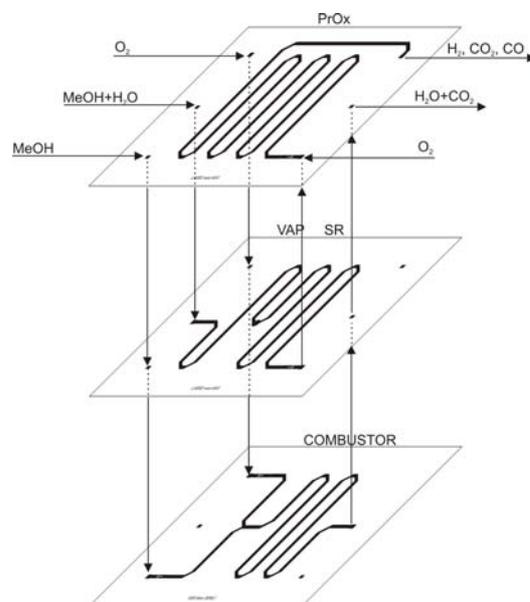

Fig. 1: Scheme of the integrated fuel processor

The catalysts used for methanol steam reforming were commercial $CuO-ZnO-Al_2O_3$ and synthesized 2 wt.%Pt/CeO_2.

Dry catalyst precursor of Pt (2 wt. %)/CeO_2 was prepared by method of wet impregnation of cerium oxide. Final suspension of catalyst precursor was obtained by mixing the dry catalyst precursor with previously prepared diluted sol-gel suspension of ZrO_2 with 2-propanol. In this case sol-gel suspension of ZrO_2 formed from nanoparticles serves as binder for dispersion of Pt (2 wt. %)/CeO_2 catalyst precursor and as adhesion promoter [3].

The catalysts for PrOX were $CuO-CeO_2$ co-precipitated. CuO (20 mol %)-CeO2 catalyst was prepared by co-precipitation from mixtures of cerium and copper aqueous nitrate solutions with ammonium hydroxide under vigorous mixing conditions in a precipitation reactor at high reaction temperature [4]. Addition of acetic acid to the reaction mixture (i.e. present during the precipitation reaction) enables to prepare stable dispersion of nano-sized grains of mixed oxide in aqueous media. The catalyst slurry was prepared by mixing catalyst (6.5 wt. %), sol-gel suspension of ZrO2 and 2-propanol. [4,5].
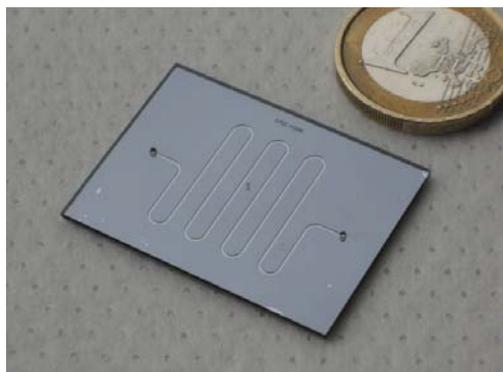

Fig. 2: Finished single channel micro-reactor chip.

The catalysts were deposited either in the closed channels or in the open channels. Figure 3 shows the scheme of catalyst precursor deposition by syringe pump into closed structures. Alcohol based sol-gel viscosity of the catalysts ink in order to increase the amount of coated catalyst in the micro channels.
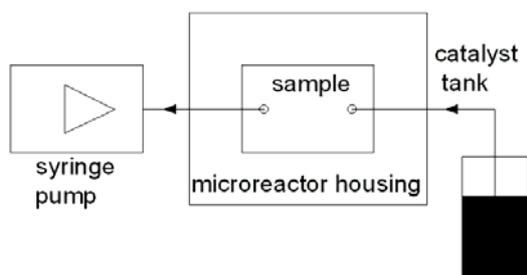

Fig. 3: Scheme of the system for deposition of catalyst precursor into the closed micro-channel reactor

Micro reactor housing for testing is shown on Fig. 4. The housing is made of stainless steel material. Tightening of fluidic connections between micro reactor housing and micro reactor chip is realized by gaskets which were fabricated of 1 mm thick flexible graphite material (Grafilit-SF 1.0). Outside fluidic connections are realized with stainless steel 1/16" tube fittings (Swagelok).

The catalysts activity and stability were tested at first separately in each of the catalyzed processes (steam reforming of methanol and preferential oxidation of CO present in a reformate gas mixture) with its own micro reactor design. Then, the two reactors were connected in order to obtain H_2–rich gas mixture with as low as possible CO concentration (Figure 5).
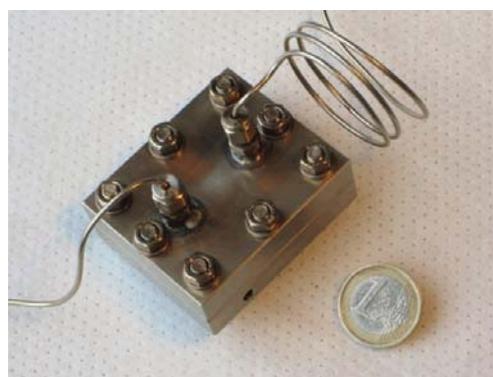

Fig. 4: Housing for testing of micro-reactor chip.

Gas flows of gas mixture and oxygen were regulated by mass flow controllers (MFC). Outlet from the micro reactor was connected to gas chromatograph (Micro GC 3000A, Agilent), equipped with thermal conductivity detectors and bubble meter (Supelco 2-0431, 25 ml) to measure on-line the composition of outlet gases and volumetric flow, respectively. Helium was used as carrier gas. Molecular sieve 5A PLOT column was used to separate CO, O_2 and H_2. PLOT U column was used to separate CO_2, CH_3OH and H_2O.
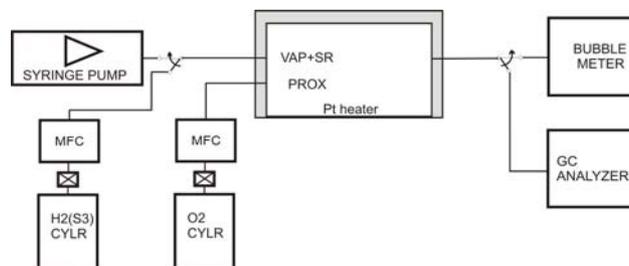

Fig. 5: Scheme of the fuel processor test system

RESULTS AND DISCUSSION

The steam reforming of methanol over 2.8 mg of Pt(2 wt.%)/CeO_2 catalyst loaded into 14 cm long micro channel having 400 μm width and 100 μm depth was performed first at the reaction temperatures from 200 ^{0}C to 300 ^{0}C with the inlet flow of liquid feed (H_2O:CH_3OH molar ratio = 1.7:1) at 0.13 cm^3/h. The outlet gas composition vs. reactor temperature is shown on Figure 6. A 100% methanol conversion is reached at 300 ^{0}C. At that reaction temperature the outlet gas composition (in mol.%) is 69.7% H_2, 13.5% CO_2, 14.0% H_2O, 2.7% CO.

The time-on-stream behavior of the micro reformer is shown on Figure 7. Up to 1040 minutes of operation the reactor temperature was 280 ^{0}C and from that point on 300 ^{0}C. One can observe a slight increase in H_2 concentration, CO_2 concentration and slight decrease in H_2O and CO concentration. At 300 ^{0}C the CH_4 concentration is zero.
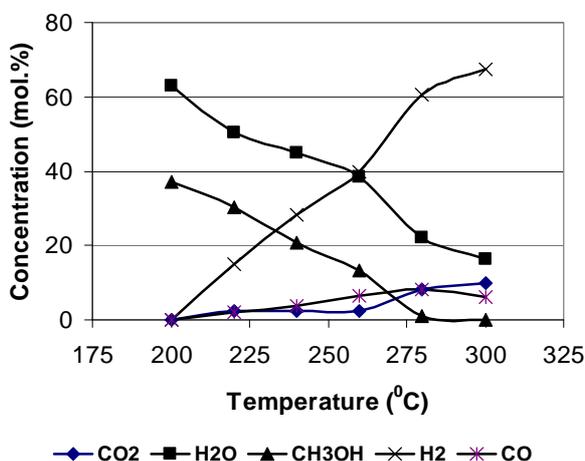

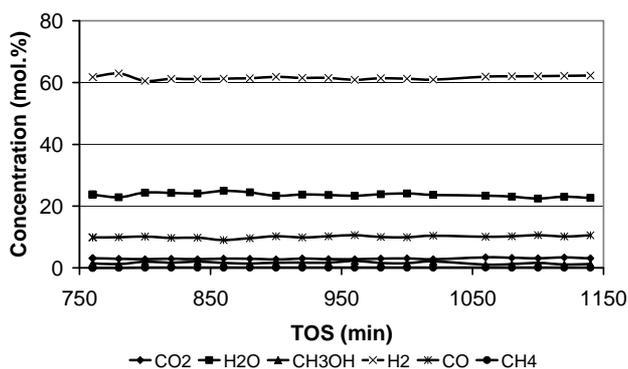Fig. 6: Steam reformer outlet gas composition vs. reactor temperature

Fig. 7: Steam reformer outlet gas composition vs. time-on-stream. Reaction conditions: H_2O:CH_3OH =1.7:1; T_{react} = 280-300 ^{0}C; Φ_{feed} = 0.13 cm^3/h

The methanol steam reforming over commercial CuO-ZnO-Al_2O_3 catalyst under the same reaction conditions results in similar conversion, however the outlet gas composition is different: 10 mol.% CO_2, less than 1 mol.% CO, 20 mol.% H_2O and a small concentration of CH_4.

When the PrOX micro reactor loaded with 9.3 mg of CuO(20 mol %)/CeO_2 coprecipitated catalyst and put on stream after the methanol reformer loaded with commercial CuO-ZnO-Al_2O_3 catalyst, the results were as shown on Figure 8.
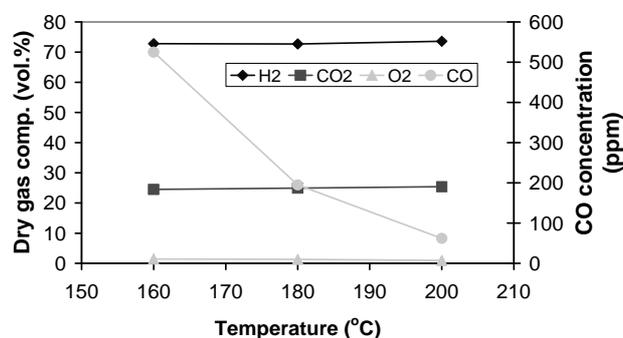

Fig. 8: Dry gas composition at the outlet from PrOX microreactor versus temperature

At gas inlet flows below 7 sccm and 0.16 sccm O_2 into PrOX micro reactor in direct connection with the methanol steam reforming micro reactor one can obtain CO concentration below 50 ppm in H_2-rich gas at the reaction temperature of 200 ^{0}C. The results on Figure 8 show that the selectivity of CO oxidation does not change with reaction temperature, which is specific characteristics of this PrOX catalyst in comparison with Pt or Au containing catalysts [6]. Such low concentration of CO in H_2 is suitable for use in low temperature PEM fuel cells.

CONCLUSION

The results obtained show that both types of catalysts are active for steam reforming of methanol and that CuO(20 mol %)/CeO_2 coprecipitated catalyst is capable of oxidizing selectively CO in the H_2-rich gas at the temperature as low as 150 ^{0}C. However, Pt (2wt.%)/CeO_2 catalyst was found to be active and stable in methanol steam reforming and could reach 100% methanol conversion at 300 ^{0}C. It has been shown that CuO(20 mol %)/CeO_2 mixed oxide catalyst is active and remarkably selective in CO oxidation in the temperature interval between 160 and 200 ^{0}C . In addition, the space velocity over this catalyst is high, above 100,000 h^{-1}. It has been shown also that concentration of CO in H_2-rich gas stream was reduced from 0.96% to below 50 ppm with selectivity in excess of 90 %.

In general, oxygen concentration added to H_2-rich feed gas should be close to stoichometric value required for the CO oxidation.

It was also shown that the presence of water in H_2-rich gas stream shifts the reaction temperature for 20 ^{0}C towards higher values. In this case, almost 100 % conversion of CO is obtained at 200 ^{0}C, and selectivity does not drop substantially.

REFERENCES

[1] Patil A S, Dubois T G, Sifer N, Bostic E, Gardner K, Quah M, Bolton C 2004 Portable fuel cell systems for America's army: technology transition to the field J. of Power Sources, 136 220-225

[2] Vrtačnik D, Resnik D, Aljančič U, Možek M, Penič S, Amon S 2008 RIE of deep silicon microchannels for microfluidic applications Proceedings MIDEM'08 (Fiesa, Slovenia, 17-19 September 2008) 93-98

[3] Wootsch A, Descorme C, Duprez D 2004 Preferential oxidation of carbon monoxide in the presence of hydrogen (PROX) over ceria-zirconia and alumina-supported Pt catalysts J. Catal. 225 259-266

[4] Avgouropoulos G, Ioannides T, Matralis H K, Batista J, Hočevar S 2001 CuO–CeO2 mixed oxide catalysts for the selective oxidation of carbon monoxide in excess hydrogen Catal. Lett. 73(1) 33-40

[5] Sedmak G, Hočevar S, Levec J 2003 Kinetics of selective CO oxidation in excess of H2 over the nanostructured Cu0.1Ce0.9O2−y catalyst J.Catal. 213 135–150

[6] Avgouropoulos G, Ioannides T, Papadopoulou C, Batista J, Hočevar S, Matralis H K 2002 A comparative study of Pt/γ-Al2O3, and CuO-CeO2 catalysts for the selective oxidation of carbon monoxide in excess hydrogen Catal. Today 75 157-167