Chemical Engineering Journal 101 (2004) 3–9

Chemical Engineering Journal

www.elsevier.com/locate/cej

Micro-structured string-reactor for autothermal production of hydrogen

C. Horny, L. Kiwi-Minsker, A. Renken*

Swiss Federal Institute of Technology, EPFL-LGRC, CH-1015 Lausanne, Switzerland

Abstract

Novel micro-structured string-reactor designed as catalytically active wires placed in parallel into a tube was developed. The small diameter of the channels (∼100 μm) leads to a short radial diffusion time, a narrow residence time distribution (RTD), and a low pressure drop. This reactor was applied for the oxidative steam-reforming of methanol (OSRM) to produce hydrogen in autothermal mode for fuel cells. The heat generated during methanol oxidation at the reactor entrance is axially transferred to the reactor zone of the endothermic steam-reforming. The brass metal wires (Cu/Zn = 4/1) were used as precursors for the preparation of string-catalysts. The brass wires have high thermal conductivity (120 W/(m K)) and the chemical composition is similar to the active phase of the $Cu/ZnO/Al_2O_3$ traditional catalyst during the steam-reforming of methanol. Brass-based string catalysts are obtained by metal/aluminium alloy formation on the outer surface of wires followed by an acid treatment leaching out aluminium. This treatment leads to an increase of the specific surface area (SSA) due to the formation of porous outer layer on the wire surface. The porous outer layer has the morphology of Raney metals. The catalysts were first tested for the steam-reforming of methanol and showed high activity together with selectivities close to 100% towards hydrogen and carbon dioxide. Then, the optimized catalyst was tested during the methanol partial oxidation (POX) and during OSRM. Oxygen was observed to be totally converted via total oxidation and therefore, higher methanol conversion in the OSRM together with CO_2 selectivity of 99% and H_2 selectivity of 60% were obtained.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrogen production; Methanol; Steam-reforming; Brass wires; Micro-structured

1. Introduction

During the last decades, fuel cells have been recognized as an efficient and clean technology to produce energy for mobile applications. For safety reasons, hydrogen storage is not suitable. More attractive is the on-board production of hydrogen. There are several "primary fuels" as potential hydrogen sources for proton exchange membrane fuel cells used in automotive propulsion [1] as methane (natural gas), liquefied gas, gasoline, alcohols. Due to their high storage density, liquid fuels are most attractive for mobile application. Methanol is considered to be safer than the currently used petrol with respect to ignition temperature [2], and it can be produced from biological, i.e. renewable, sources. Of all considered reactions, steam-reforming (1) offers the highest attainable hydrogen concentration in the product gas (75%):

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2, \quad \Delta_r H^0 = 49\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

The reaction occurs at relatively low temperatures in the range of 200–300 °C. As a consequence, only a relative small amount of CO (<2%) is formed, which can be eliminated by preferential oxidation [3].

The endothermicity of the reaction, however, requires permanent external heating of the reformer which makes short start-up times and fast transient behavior difficult to achieve [4].

This problem is avoided during the exothermic partial oxidation (POX):

$$CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2, \quad \Delta_r H^0 \cong -192\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

However, the hydrogen content in the product gas is low (40% with air operation). Moreover, the high exothermicity of the reaction drastically lowers the efficiency of the process since waste heat is generated and temperature control of the reactor may be complicated. Oxidative steam-reforming of methanol (OSRM) first proposed by Huang and co-workers [5,6] is based on the combination of the exothermic oxidation and endothermic reforming in the same reactor. At 300 °C a formally athermic reaction results for the following composition of the reactant feed:

* Corresponding author. Tel.: +41-21-693-3181; fax: +41-21-693-3190.
E-mail address: albert.renken@epfl.ch (A. Renken).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.01.003

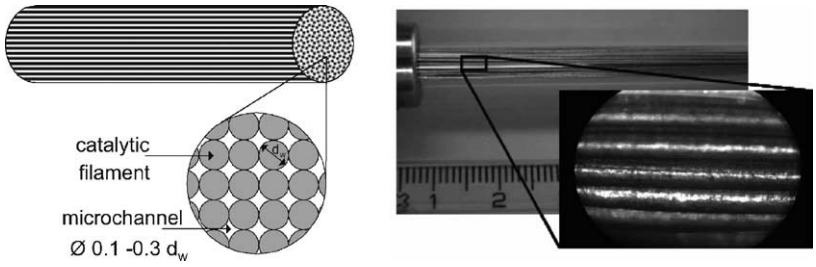

Fig. 1. Schematic presentation and photograph of the micro-structured string-reactor.

$$4CH_3OH + 3H_2O + 0.5O_2 \rightarrow 4CO_2 + 11H_2, \quad \Delta_r H^{573} \cong 0\,kJ\,mol^{-1} \tag{3}$$

Reactors for this process operate autothermally, i.e. does not require any external heating or cooling once heaving reached the reaction temperature. The maximum obtainable hydrogen content in the product gas is 73% with oxygen in the feed or 65% if air is used. For fast start-up or transient response the methanol/oxygen ratio can be varied as shown for the Hot-Spot® reformer [7,8].

Several groups studied the OSRM over copper/zinc/alumina catalysts and found optimum feed composition with oxygen to methanol and water to methanol ratios of 0.2–0.3 and 1.3–1.6, respectively [3,9,10]. The excess steam is mainly used to reduce the carbon monoxide content by the water-gas-shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta_r H^0 = -39\,kJ\,mol^{-1} \tag{4}$$

At temperatures above 300 °C, catalyst deactivation diminishes the reactor performance [11]. Therefore, the working temperature has to be carefully controlled, accounting for the catalyst lifetime.

2. Reactor concept

The main difficulty in carrying out the OSRM is due to much faster methanol oxidation compared to the reforming reaction. As a consequence, heat is generated mostly at the reactor entrance, whereas the heat consumption occurs in the middle and rear of the reactor. In conventional reactors with randomly packed beds and low axial and radial heat conductivity pronounced axial temperature profiles are developed. They are characterized by hot spots at the reactor entrance and a “cold spot” in the second part of the reactor [12]. The high temperatures may damage the catalyst and the low temperature diminishes the rate of the reforming reaction and leads to poor reactor performances.

Therefore, temperature control in the reactor is crucial.

Metal based catalysts with high thermal conductivity can help to integrate the exothermic combustion of methanol and the endothermic steam-reforming. The beneficial effect of improved heat transfer was demonstrated for the OSRM using either a conductive material [13], or the micro geometry of a monolith [14].

In the present study, we place the catalyst as thin metallic wires into tubular reactors with diameters in the millimeter range (Fig. 1). This design ensures laminar flow and narrow residence time distribution (RTD), low pressure drop through the catalytic bed [15,16].

The micro-structured reactor configuration presents hydrodynamics similar to those of multi-channel micro-reactors [16]. Brass wires with high heat conductivity (120 W/(m k)) are chosen for the micro-structured string-reactor as they contain the main elements (Cu and Zn) catalyzing the reforming/oxidation of methanol.

3. Experimental

3.1. Catalyst preparation

The material used as catalyst precursor was brass wires (Haver & Boecker, Goodfellow) with properties summarized in Table 1. The specific surface area (SSA) of the wires correspond to their geometric surface per volume and did not show any catalytic activity. To obtain metal wires with high SSA a thin metal/aluminium alloy is formed on the wire outer surface [17].

The aluminium is leached out either by acid (HCl 3.7%) or by basic (NaOH 10%) boiling solution resulting a thin porous layer with a morphology similar to that of Raney metals. The catalysts were calcined in air at 600 °C for 2 h, reduced in 10% H_2 in Ar at 250 °C during 2 h in the reactor, before the catalyst testing.

Table 1
Composition and specific surface area of the brass wire precursor and wire catalyst

	CuZn20	CuZn37
Composition of brass wires (wt.%)		
Cu	80	63
Zn	20	37
Diameter (mm)	0.25	0.33
SSA of brass wire (precursor) (m^2/g)	2×10^{-3}	1.35×10^{-3}
SSA of the catalyst (after acid treatment and calcination) (m^2/g)	54.2	29.6

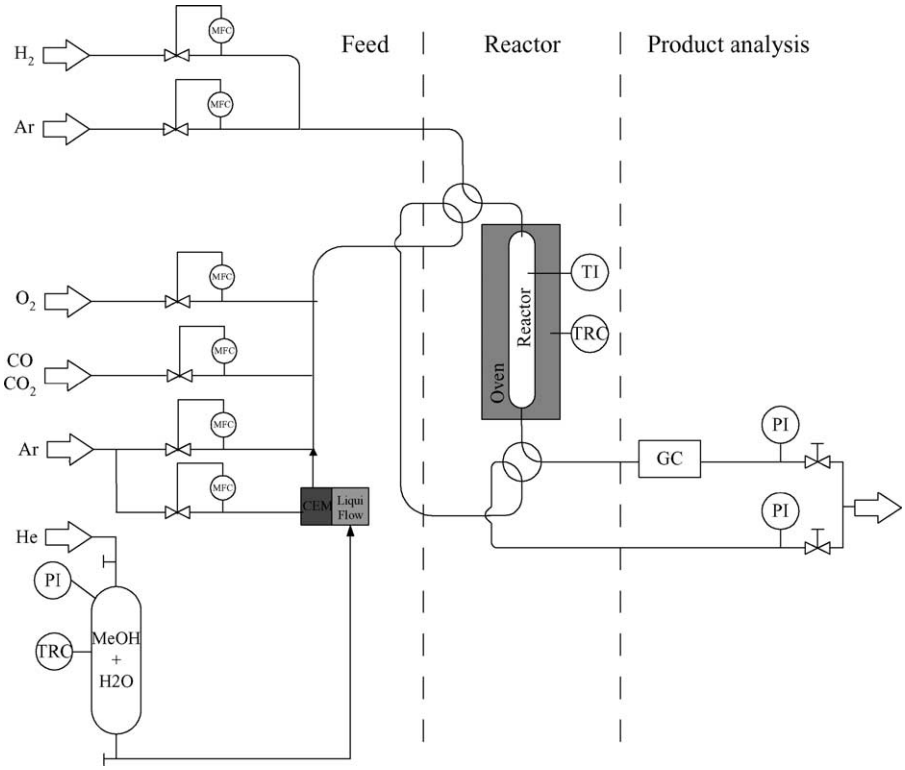

Fig. 2. Experimental set-up.

3.2. Catalyst characterization

The specific surface area of the samples was measured according to the Brunauer–Emmett–Teller (BET) method by nitrogen adsorption using a Sorptomatic 1990 (Carlo Erba) instrument. The content of copper, zinc and alumina was measured by atomic absorption spectroscopy (AAS), using a Shimadzu AA-6650 instrument.

3.3. Hydrodynamic measurements

A quartz tube with an internal diameter of 6 mm and different lengths were filled by metallic wires of 480 μm diameter. Residence time distribution experiments were performed by measuring the response to a step function (10 vol.% Ar in N_2) with a quadrupole mass spectrometer (QMS 400, Balzers, Liechtenstein). Gases were supplied through mass flow controllers (Bronkhorst High-Tech B.V.).

3.4. Catalyst testing

The catalytic activity of the wire catalysts are measured in the experimental set-up shown in Fig. 2. A tubular quartz reactor (9 mm i.d.) with a thermocouple in the middle of the catalytic bed was placed in a furnace. This design for catalyst testing was preferred to the set-up of Veser et al. [18] who used a single catalytic wire placed in the center of a silicon channel. Premixed water–methanol was fed to a vaporizer (Bronkhorst High-Tech B.V.) heated at 398 K with argon as carrier gas. Gas and liquid flows were adjusted by Bronkhorst mass flow controller. The whole installation was maintained at 423 K in order to avoid condensation in the tubing. The feed and product gases were analyzed by on-line gas chromatography with a thermal conductivity detector. The experimental conditions are listed in Table 2.

Table 2
Experimental conditions for catalytic activity measurements

Catalyst load (g)	1
Temperature (K)	473–573
Pressure (Pa)	1.32×10^5
Molar ratio H_2O/CH_3OH	1.2 (SR and OSRM)
Molar ratio O_2/CH_3OH	0.2–0.4 (POX), 0.3 (OSRM)
CH_3OH feed rate (mol/h)	0.022
H_2O feed rate (mol/h)	0.026
Total flow rate (mol/h)	0.25
Argon flow rate	Balance

4. Results and discussion

4.1. Residence time distribution

The parallel wires (strings) placed in the tube, form micro-channels with flow hydrodynamics similar to multi-channel micro-reactors. The equivalent diameter (d_{eq}) of the channels for gas flow between the strings depend on the diameter of the wires (d_w) and their geometric arrangement [16]: $0.1\, d_w < d_{eq} < 0.3 d_w$.

The flow system described has a hydraulic diameter in the order of 102 μm thus ensuring laminar flow. At a first glance, the parabolic laminar flow profile should result in a vast residence time distribution. But, Taylor and Aris showed that radial diffusion can compensate the broadening of the parabolic flow profile [19]. For circular tubes, the axial dispersion coefficient, D_{ax}, is given by

$$D_{ax} = D + \frac{u^2 d_c^2}{192 D} \quad (5)$$

where D is the molecular diffusion coefficient, u the average linear flow velocity, d_c the channel diameter.

Due to the small diameters of the micro-channels, the radial diffusion time is small compared to the mean residence time in the reactor and axial dispersion can be efficiently suppressed [20,21].

The RTD is characterized by the mean residence time, $\bar{t}$, and the variance around the mean value, σ^2, or in dimensionless form

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} \quad (6)$$

For the dispersion model, the Bodenstein number, $Bo = uL/D_{ax}$ characterizes the distribution of the residence time in a tubular reactor. D_{ax} is the axial dispersion coefficient, representing the spreading process [19].

Response curves $F(t)$ to concentration steps were measured at different flow rates and for two different reactor length. The dimensionless residence time distributions $E(\theta)$ is obtained by derivation of $F(t)$ and are shown in Fig. 3. For the 10 cm reactor, *Bo*-numbers from 53 to 72 were obtained depending on the flow rate. As expected, the dispersion decreases with increasing reactor length. The Bodenstein number was found to be in the range of $Bo = 200$ for the 20 cm reactor at $Q = 18.8\,cm^3/min$.

The experimental results confirm that the micro-structured string-reactor has characteristics close to an ideal plug flow tubular reactor.

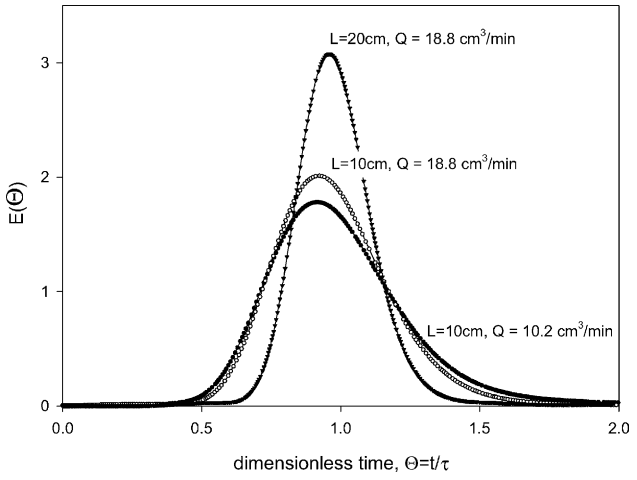

Fig. 3. RTD dependence on flow rate and reactor length.

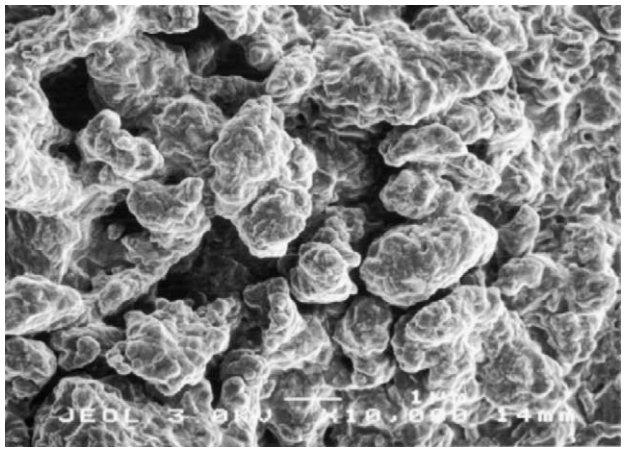

Fig. 4. SEM image of the surface of the string catalyst after calcination.

4.2. Catalyst characterization

The specific surface areas of the prepared catalysts are summarized in Table 1. The results show that the treatment leads to a tremendous increase of the specific surface area of four orders of magnitude compared to the geometric SSA of the wires. The surface morphology of the wires after acid treatment and calcination is shown in Fig. 4. The high SSA is provided by the surface porosity clearly seen by SEM. The catalysts prepared have a total BET surface area between 15 and 48 m^2/g. These values are close to those reported in the literature for traditional granulated catalysts [10,22–24].

In contrast to basic leaching, the composition of the catalyst changes significantly with time at the acid treatment (see Table 3). The leaching leads to a mass loss of about

Table 3
Composition of the wire catalyst after different treatment

	Catalyst compositions (%)		
	Cu	Zn	Al
CuZn20			
Initial composition	76.2	16.6	7.2
Basic			
20 min	81.6	12.6	5.8
30 min	80.8	13.0	6.3
Acid			
20 min	77.2	18.1	3.5
30 min	79.6	17.3	3.1
CuZn37			
Initial composition	61.5	35	3.5
Basic			
20 min	71.4	27.3	1.3
30 min	71.4	27.2	1.4
Acid			
20 min	68.9	30.9	0.4
30 min	72.1	27.8	0.1

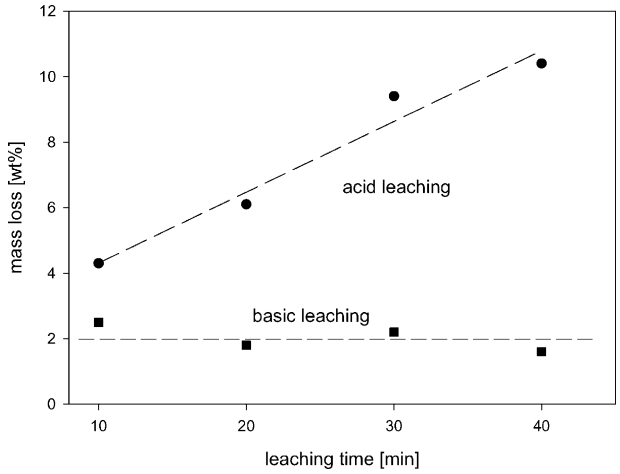

Fig. 5. Mass loss as function of leaching time.

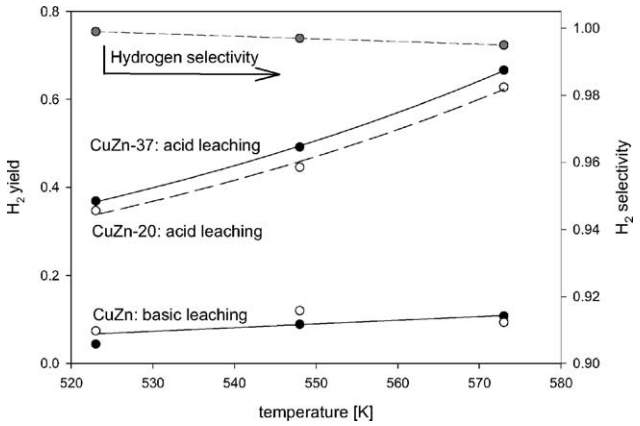

Fig. 6. Steam-reforming in a tubular reactor. Hydrogen yield and selectivity as function of temperature.

10 wt.% when using HCl for 30 min, and only 2–3 wt.% for NaOH treatment (Fig. 5) with mainly zinc and aluminium dissolved. The copper content was found to remain constant as generally observed for leaching during the preparation of Raney copper [25,26]. It was also reported for the treatment of brass in sulphuric acid that only zinc was dissolved [27].

During acid treatment mainly aluminium is removed whereas its content remains at a relatively high level under basic conditions. As a consequence, the copper to zinc ratio is higher after the basic leaching and independent of the leaching time. The results confirm observations of Devred et al. [28] who studied the influence of leaching parameters on the formation of active phases during the preparation of Raney metals.

4.3. Catalytic activity measurements

4.3.1. Steam-reforming

Steam-reforming was carried out over two brass-based catalysts CuZn20 and CuZn37 leached either in HCl or in NaOH. Moreover, a sample without aluminium incorporation was tested and was found to be totally inactive independently of the reaction temperature. Hence, aluminium oxide is necessary in the active phase of the catalysts. Fig. 6 shows hydrogen yields for different catalysts. An acid leaching leads to a much higher activity than a basic one. Moreover, catalysts treated in NaOH show rapid deactivation with time, as illustrated in Fig. 7. The deactivation is enhanced at higher temperatures. Fig. 8 shows the influence of time of acid treatment on activity at temperatures of 540 and 560 K. It is seen that the highest activity was reached after 20 min of HCl treatment. Thus, the latter treatment was applied for the CuZn37 catalyst preparation to study partial oxidation and oxidative steam-reforming of methanol (OSRM).

4.3.2. Partial oxidation of methanol

CuZn37 treated 20 min by HCl was tested during partial oxidation of methanol and results are presented in

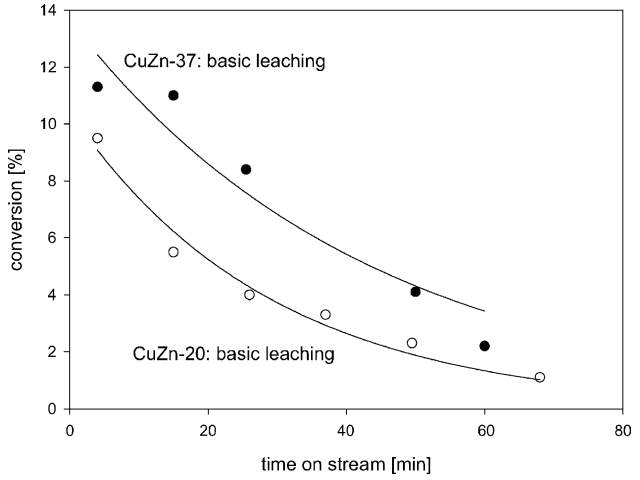

Fig. 7. Steam-reforming in a tubular reactor. Deactivation kinetics.

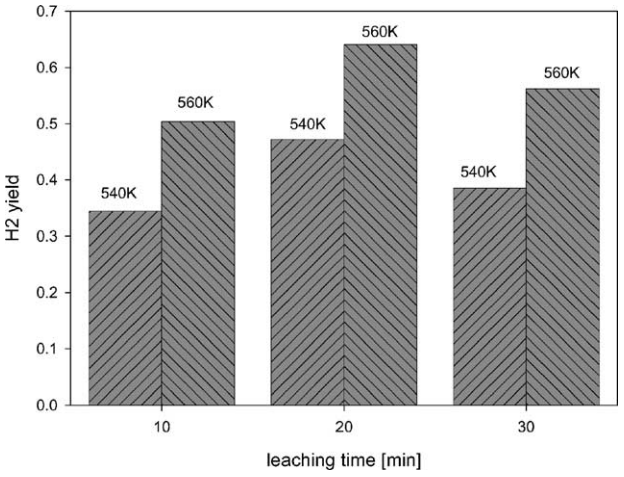

Fig. 8. Steam-reforming in a tubular reactor. Influence of leaching time on catalyst activity.

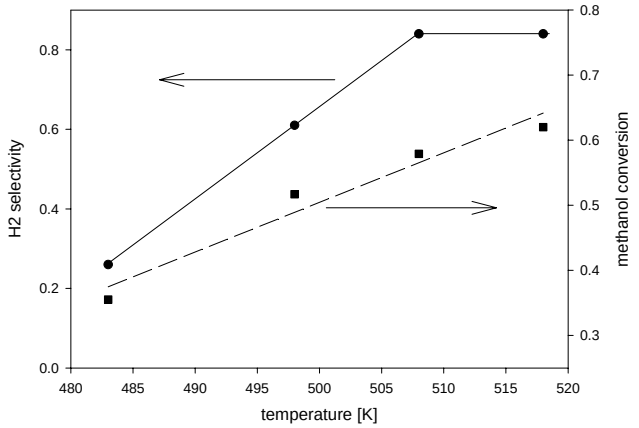

Fig. 9. Partial oxidation of methanol. Methanol conversion and H_2 selectivity as function of temperature.

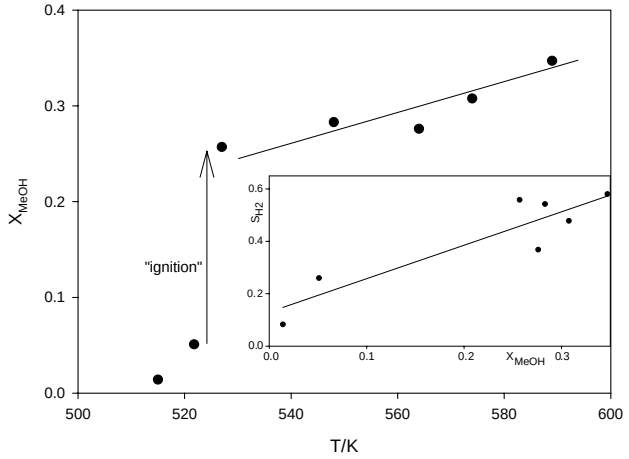

Fig. 10. Oxidative steam-reforming of methanol. Methanol conversion as function of temperature. H_2 selectivity vs. methanol conversion.

Fig. 9 and in Table 4. Table 4 summarizes the influence of the oxygen content in the feed. The results indicate that both, the methanol conversion and product selectivity are strongly dependent on the oxygen concentration in the gas phase. Methanol conversion and CO_2 selectivity increase with the oxygen to methanol ratio, whereas the H_2 selectivity decreases, indicating a contribution of total oxidation of methanol, carbon monoxide and hydrogen.

Temperature increases hydrogen selectivity and water production due to the increased conversion of methanol. That suggests that oxygen is first converted via total oxidation of methanol, followed by methanol reforming with the water produced as reported previously [3,9,24].

4.3.3. Oxidative steam-reforming of methanol

CuZn37 treated for 20 min in HCl was tested for OSRM. Methanol conversion increases with temperature up to 5% until ignition occurs at about 250 °C (see Fig. 10). In the low conversion domain with oxygen conversion up to 25% hydrogen selectivity is low (≤5%). From the observed H_2 to CO_2 ratio of ≤0.1 in the product gas, it can be concluded that the methanol conversion occurs mainly via TOX. After the ignition oxygen is completely consumed and an important hydrogen production is observed resulting in H_2 selectivities of ca. 60% at methanol conversion of 35%. The experimental results can be explained by the different oxidation state of the catalyst [29,30]: At low oxygen conversion the catalyst remains in an oxidative state, and the main reaction is the total oxidation. At high oxygen conversion, the catalyst away from the reactor entrance becomes reduced and hydrogen production through the steam-reforming becomes important. The CO_2 selectivity was found to be higher than 98% in the temperature range studied.

Table 4
Effect of oxygen to methanol ratios (0.2 and 0.4) on methanol partial oxidation over CuZn37 catalyst

Temperature (K)	Methanol conversion (%)		H_2 selectivity (%)	
	0.2	0.4	0.2	0.4
483	29.5	35.5	24.9	22.5
498	49.7	51.7	53.9	48.0

5. Conclusions

A novel micro-structured reactor based on catalytically active wires was developed. The micro-channels formed by parallel placed strings have an equivalent diameter in the range of 0.1 mm. This ensures laminar flow and short radial diffusion times. Residence time distribution measurements confirm the nearly plug-flow behavior of the micro-structured string-reactor. Bodenstein-numbers are found to be in the range of $50 < Bo < 200$ depending on flow rate and reactor length.

Brass wires with diameters of 0.25–0.4 mm were used as precursor for the development of string catalysts active in steam-reforming, partial oxidation and oxidative steam-reforming of methanol. The activity of the string catalyst depends on the composition of the brass wire and the treatment of the aluminium alloy formed at the outer surface of the wire. It turned out that an acid treatment for ca 20 min leads to the highest activity. In the OSRM the optimized catalyst showed high selectivity for CO_2 (≥98%) and reached 60% H_2 selectivity at methanol conversions of 35%.

Acknowledgements

The authors gratefully acknowledge the financial support of the Swiss National Science Foundation and the Max-Buchner-Forschungsstiftung.

References

[1] L.F. Brown, A comparative study of fuels for on-board hydrogen production for fuel cell-powered automobiles, Int. J. Hydrogen Energy 26 (2001) 381–397.

[2] K.A. Adamson, P. Pearson, Hydrogen and methanol: a comparison of safety, economics efficiencies and emissions, J. Power Sources 86 (2000) 548–555.

[3] K. Geissler, E. Newson, F. Vogel, T.B. Truong, P. Hottinger, A. Wokaun, Autothermal methanol reforming for hydrogen production in fuel cell applications, Phys. Chem. Chem. Phys. 3 (2001) 289–293.

[4] B. Höhlein, M. Boe, J. Bøgild-Hansen, P. Bröckerhoff, G. Colsman, B. Emonts, R. Menzer, E. Riedel, Hydrogen from methanol for fuel cells in mobile systems: development of a compact reformer, J. Power Sources 61 (1996) 143–147.

[5] T.J. Huang, S.W. Wang, Hydrogen production via partial oxidation of methanol over copper-zinc catalyst, Appl. Catal. 24 (1986) 289–297.

[6] T.J. Huang, S.L. Chren, Kinetics of partial oxidation of methanol over a copper-zinc catalyst, Appl. Catal. 40 (1988) 43–52.

[7] J. Jenkins, E. shutt, The hot spot reactor, Platinum Metals Rev. 33 (1989) 118–127.

[8] N. Edwards, S.R. Ellis, J.C. Frost, S.E. Golunski, A.N.J.V. Keulen, N.G. Lindewald, J.G. Reinkingh, On-board hydrogen generation for transport applications: the hot spot methanol processor, J. Power Sources 71 (1998) 123–1238.

[9] J. Agrell, H. Birgersson, M. Boutonnet, Steam reforming of methanol over a $Cu/ZnO/Al_2O_3$ catalyst: a kinetic analysis and strategies for suppression of CO formation, J. Power Sources 106 (2002) 249–257.

[10] S. Velu, K. Suzuki, M.P. Kapoor, F. Ohashi, T. Osaki, Selective production of hydrogen for fuel cells via oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts, Appl. Catal. A: Gen. 213 (2001) 47–63.

[11] P. Reuse, A. Renken, Hydrogen production for fuel cell application in an autothermal micro-channel reactor, Chem. Eng. J., 2004, in press.

[12] K. Geissler, Wasserstoffgewinnung aus Methanol für PEM-Brennstoffzellen, Swiss Federal Institute of Technology EPF-Lausanne No. 2442, 2002.

[13] M. Schuessler, O. Lamla, T. Stefanovski, C. Klein, D. Megede, Autothermalreforming of methanol in an isothermal reactor, Chem. Eng. Technol. 24 (2001) 1141–1145.

[14] B. Lindström, J. Agrell, L.J. Pettersson, Combined methanol reforming for hydrogen generation over monolithic catalysts, Chem. Eng. J. 93 (2003) 91–101.

[15] O. Wolfrath, Développement de réacteurs microstructurés pour la conversion du propane en produits valorisés, Thèse, EPFL, 2001.

[16] L. Kiwi-Minsker, O. Wolfrath, A. Renken, Membrane reactor microstructured by filamentous catalyst, Chem. Eng. Sci. 57 (2002) 4947–4953.

[17] L. Kiwi-Minsker, Novel structured materials for structured catalytic reactors, CHIMIA 56 (4) (2002) 159–163.

[18] G. Veser, G. Friedrich, M. Freygang, R. Zengerle, A simple and flexible micro-reactor for investigations of heterogeneous catalytic gas phase reactions, Reaction Kinetics and the Development of Catalytic Processes, 1999, pp. 237–245.

[19] M. Baerns, H. Hofmann, A. Renken, Chemische Reaktionstechnik, in: M. Baerns, F. Fetting, H. Hofmann, W. Keim, U. Onken (Eds.), Lehrbuch der Technischen Chemie, vol. Bd. 1, third ed., Georg Thieme Verlag, Stuttgart, New York, 1999, 444 pp. (215 figures; 41 tables).

[20] A. Rouge, B. Spoetzl, K. Gebauer, R. Schenk, A. Renken, Microchannel reactors for fast periodic operation: the catalytic dehydration of isopropanol, Chem. Eng. Sci. 56 (2001) 1419–1427.

[21] J.M. Commenge, A. Rouge, A. Renken, J.P. Corriou, M. Matlosz, Dispersion dans un microréacteur multitubulaire: etude expérimentale et modélisation, Récents Progrésen Génie des Procédés 15 (2001) 329–336.

[22] J.R. Mellor, N.J. Coville, A.C. Sofianos, R.G. Copperthwaite, I. Preparation, Raney copper catalysis for the water-gas-shift reaction. I. Preparation, activity and stability, Appl. Catal. A: Gen. 164 (1997) 171–183.

[23] J. Agrell, K. Hasselbo, K. Jansson, S.G. Jaras, M. Boutonnet, Production of hydrogen by partial oxidation of methanol over Cu/ZnO catalysts prepared by microemulsion technique, Appl. Catal. A: Gen. 211 (2001) 239–250.

[24] S. Murcia-Mascaros, R.M. Navarro, L. Gomez-saneiro, U. Constantino, M. Nocchetti, J.L.G. Fierro, Oxidative methanol reforming reactions on Cu-Zn-Al catalysts derivedfrom hydrotalcite-like precursors, J. Catal. 198 (2001) 338–347.

[25] A.J. Bridgewater, M.S. Wainwright, D.J. Young, J.P. Orchard, Methanol synthesis over Raney copper zinc catalysts. III. Optimization of alloy composition and catalyst preparation, Appl. Catal. 7 (1983) 369–382.

[26] H.E. Curry-Hyde, M.S. Wainwright, D.J. Young, Improvements to Raney copper methanol synthesis catalysts through zinc impregnation. I. Electron microprobe analysis, Appl. Catal. 77 (1991) 75–88.

[27] L. Burzynska, Comparison of the spontaneous and anodic processes during dissolution of brass, Corrosion Sci. 43 (2001) 1053–1069.

[28] F. Devred, B.W. Hoffer, W.G. Sloof, P.J. Kooyman, A.D. van Langeveld, H.W. Zandbergen, The genesis of the acative phase in Raney type catalysts: the role of leaching parameters, Appl. Catal. A: Gen. 244 (2003) 291–300.

[29] T.L. Reitz, S. Ahmed, M. Krumpelt, R. Kumar, H.H. Kung, Characterization of CuO/ZnO under oxidizing conditions for the oxidative methanol reforming reaction, J. Mol. Catal. A: Chem. 162 (2000) 275–285.

[30] T.L. Reitz, S. Ahmed, M. Krumpelt, R. Kumar, H.H. Kung, Methanol reforming over CuO/ZnO under oxidizing conditions, Stud. Surf. Sci. Catal. 130 (2000) 3645–3650.