Autothermal methanol reforming for hydrogen production in fuel cell applications

Konrad Geissler, Esmond Newson, Frederic Vogel, Thanh-Binh Truong, Peter Hottinger and Alexander Wokaun

Laboratory for Energy and Material Cycles, Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland. E-mail: konrad.geissler@psi.ch

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Fuel cell powered electric cars using on-board methanol reforming to produce a hydrogen-rich gas represent a low-emissions alternative to gasoline internal combustion engines (ICE). In order to exceed the well-to-wheel efficiencies of 17% for the gasoline ICE, high-efficiency fuel cells and methanol reformers must be developed. Catalytic autothermal reforming of methanol offers advantages over endothermic steam-reforming and exothermic partial oxidation. Microreactor testing of copper-containing catalysts was carried out in the temperature range between 250 and 330 °C showing nearly complete methanol conversion at 85% hydrogen yield. For the overall process a simplified model of the reaction network, consisting of the total oxidation of methanol, the reverse water-gas shift reaction, and the steam-reforming of methanol, is proposed. Individual kinetic measurements for the latter two reactions on a commercial Cu/ZnO/Al₂O₃ catalyst are presented.

1. Introduction

Hydrogen is considered to play an important role in future energy systems.¹ If produced from renewable sources, it is a clean and carbon-free energy vector which can be converted to electrical energy either by conventional combustion engines or by fuel cells, the latter not being limited in theoretical efficiency by the maximum Carnot efficiency. However, the idea of using fuel cell propulsion systems for mobile applications requires a safe and efficient means of hydrogen storage. Up to now, none of the physical or chemical storage options being considered as technically feasible has turned out to be the method of choice.² Among the liquid carriers under discussion, methanol offers a high energy density and the possibility of using similar infrastructure for distribution. It is considered to be safer than the currently used petrol³ with respect to ignition temperature and other factors and it can be produced from biological, i.e. renewable, sources as well as from natural gas.⁴ In order to serve as a hydrogen source, it must be converted by an on-board reforming process.

Even if the methanol for the above-mentioned process is produced from non-renewables (such as natural gas), the reformer-fuel cell combination is, due to its low emissions, a serious alternative to ICE if its full fuel cycle efficiency is higher or at least the same. System efficiency analyses can reveal whether this goal can be reached.

For the conversion of methanol to hydrogen different chemical reactions can be applied. The simplest option is the decomposition reaction (1)

$$CH_3OH \rightarrow CO + 2H_2; \quad \Delta_R H^\circ = +91 \text{ kJ mol}^{-1}$$
 (1)

yielding hydrogen and carbon monoxide. However, the high content of the latter in the product gas makes this reaction unsuitable for polymer electrolyte membrane (PEM) fuel cell applications. Probably the most widely used way of producing hydrogen from methanol is the endothermic steam-reforming reaction (2).

$$CH_{3}OH + H_{2}O \rightarrow CO_{2} + 3H_{2};$$

$$\Delta_{R}H^{\circ} = +49 \text{ kJ mol}^{-1}$$
(2)

Of all the considered reactions, it offers the highest maximum hydrogen content in the product gas (75%). In addition, since no gases need to be compressed in the feed, the reaction can easily be carried out at higher pressure, thus keeping membranes as an option for the successive gas clean-up step. The endothermicity of the reaction, however, requires permanent external heating of the steam-reforming reactor which makes short start-up times, as desired for mobile applications, and fast transient behaviour difficult to achieve.⁵⁻⁷

This problem is less severe if exothermic partial oxidation, reaction (3), is used.

CH₃OH +
$$\frac{1}{2}$$
O₂ → CO₂ + 2H₂;
 $\Delta_{\rm p}H^{\circ} = -192.3 \text{ kJ mol}^{-1}$ (3)

Due to the exothermicity of the reaction no external heating of a partial oxidation reactor is required and start-up times of less than 60 s for partial oxidation reactors are reported in the literature.⁸ However, in addition to the low maximum hydrogen content in the product gas (40% with air operation), the high exothermicity of the reaction is also the main drawback of this reaction. It drastically lowers the efficiency since waste heat is generated and temperature control of the reactor is complicated.

Autothermal reforming of methanol, reaction (4), an idea which was developed in the late 1980s by Johnson-Matthey,⁹ is a combination of reactions (2) and (3) having a net reaction enthalpy change of zero.

$$4 \text{ CH}_{3}\text{OH} + 3 \text{ H}_{2}\text{O} + \frac{1}{2}\text{ O}_{2} \rightarrow 4 \text{ CO}_{2} + 11 \text{ H}_{2};$$
$$\Delta_{\mathbf{p}}H^{573K} = 0 \tag{4}$$

As a consequence, a reactor for this process does not require external heating once having reached reaction temperature. Depending on temperature, slightly different stoichiometric ratios of the feed can be calculated. The maximum obtainable hydrogen content in the product gas is 65% using the stoichiometry at 300 $^{\circ}$ C. For faster start-up or transient response the

methanol/oxygen ratio in the feed can be varied which was shown in the compact Hot-Spot[®] reformer.¹⁰ As for partial oxidation, the main problem for scale-up of the autothermal reforming process is temperature control in the reactor. This is due to the strongly differing reaction rates of the exothermic oxygen conversion and the endothermic steam reforming reaction. In order to facilitate reactor design it is highly desirable to develop a complete kinetic model for the process.

2. Systems analysis

Current gasoline ICE technology reaches a full fuel cycle ("well-to-wheel") efficiency of about 17-18%.¹¹ This figure can be broken down into an overall vehicle ("tank-to-wheel") efficiency of 19-20% and a fuel efficiency ("well-to-tank") of 90%. Fuel efficiencies for methanol production from natural gas are in the range 67-71%. The overall vehicle efficiency for a methanol powered car must therefore reach at least 25-27% in order to equal the efficiency of the full gasoline ICE cycle. Steady-state system analyses, carried out at our institute, including an autothermal methanol reformer linked to a PEM fuel cell yielded overall vehicle efficiencies of 27-30% assuming anode rejected hydrogen of 17%. Höhlein¹¹ investigated other options for on-board methanol reforming and obtained overall vehicle efficiencies in the range 25-34%.

The efficiency cascade for on-board autothermal methanol reforming, starting with methanol and ending with the net electric power delivered to the motor, is represented graphically in Fig. 1. The values on the left represent the cumulative efficiency while those on the right represent the efficiencies of the individual sub-processes. Only 4% of the methanol's energy content is lost as heat during the reforming and gas clean-up process (preferential CO oxidation). Most of the losses occur in the fuel cell itself. Current fuel cell technology does not allow complete utilisation of hydrogen from the reformer if delivered to the anode as a gas mixture as compared to full utilisation of pure hydrogen stored on-board. Furthermore, only about 50% of the hydrogen converted in the fuel cell produces electricity. About 20% of the electric power generated by the fuel cell has to be used for driving auxiliary equipment (compressors, pumps) which reduces the net electricity available for the motor to 33% of the energy content in the methanol fed. Any improvements along the fuel processing chain will increase the overall efficiency. This analysis suggests that the fuel cell itself has the biggest potential for increasing the overall efficiency by increasing the hydrogen utilisation and reducing losses from hydrogen conversion to electricity.



Fig. 1 Calculated steady-state "tank-to-motor" efficiency for autothermal reforming of methanol and subsequent gas clean-up by preferential oxidation of CO. The values on the left represent the cumulative efficiency while the ones on the right represent the efficiencies of the individual sub-processes.

3. Experimental and results

3.1. Microreactor set-up

Microreactor experiments were carried out using an electrically heated tubular reactor (silica-coated stainless steel, inner diameter 4 mm), equipped with an inner tube (diameter 1.5 mm) containing a moveable thermocouple. The length of the isothermal zone of the reactor is 65 mm. Catalyst particle size was always 0.25 to 0.5 mm. Feed gases were 99.995% or higher purity, the used methanol was analytical grade $(\geq 99.8\%, Merck)$. All gas flows were controlled by electronic mass-flow controllers (Bronkhorst), the methanol-water mixture was dosed by a pump (RCT M16). Product gas analysis was carried out using a HP 5890 gas chromatograph equipped with both a thermal conductivity detector connected to a two-column switching system (HP Plot Q and HP Plot 5 A), and a flame ionisation detector connected to an Alltech AT 5 column. Additional measurements of the condensate water contents were done using a 737 KF coulometer (Metrohm). Activation of the catalyst at 400 °C consisted of a 1 h outgassing step under argon flow (30 ml min⁻¹) and a 1 h reduction with hydrogen (15 ml min⁻¹) with careful temperature control by slowly increasing the hydrogen content of the gas stream.

3.2. Results of catalyst testing

Three different commercial copper-containing catalysts were tested for their activity for the autothermal methanol reforming reaction. Catalyst A and B were of the formulation $CuO/ZnO/Al_2O_3$ whereas Catalyst C was a Cu/Al_2O_3 catalyst. Feed flows were adjusted according to the stoichiometry of reaction (4) with additional argon to model the nitrogen content of air.

Results are summarised in Table 1, showing that all three catalysts are active for the autothermal reforming of methanol, with catalyst A and B being more active and selective than catalyst C. Methanol conversions for these two catalysts reached almost 100% and hydrogen yields of 85% (corresponding to 90% lower heating value (LHV) efficiency) could be measured. Non-converted oxygen could never be detected in the product gas. While catalyst A showed almost no deactivation in terms of hydrogen production after 100 h, a slight activity loss of 9% was observed for catalyst B. Carbon monoxide concentrations in the range 0.3 to 3.5% were measured, with a strong dependence on temperature and space velocity. The extrapolated numbers for space–time yield of around 20 000 l_{H_2} (h $l_{REACTOR}$)⁻¹ can be correlated to a thermal power density of 60 kW_{th} per litre of catalyst.

3.3. Model of the reaction network

For further experiments, eventually aiming at the development of a kinetic model for the autothermal reforming of methanol, catalyst B was chosen. From the species being present in either the feed or the product gas, a system of at least 7 components and 8 possible reactions can be set up (see Fig. 2). The reaction scheme is strongly crosslinked since most of the species occur in more than one reaction and the products of one reaction might act as the reactant for other reactions. From these considerations it is highly desirable to simplify the reaction network.

It is known that all reactions incorporating molecular oxygen ((5), (6), (11) and (12); reaction numbers relating to Fig. 2) are fast and highly exothermic. On the contrary, the reverse water-gas shift reaction (10) is very slow and equilibrium limited. From measurements showing lower carbon monoxide concentrations than determined by equilibrium calculations it can be concluded that the steam-reforming reaction (9), being the major source of hydrogen in the system, is a single-step

Table 1 Catalyst screening results for the autothermal reforming of methanol

Furnace temperature /°C	$WHSV_{MeOH}/h^{-1 a}$	Hot-Spot/K	Conversion (%)	Yield H ₂ (%)	с _{со} (%)	с _{рме} (%)	H_2 -Production $/l_{H_2}$ (h $l_{REACTOR}$) ⁻¹
Commercial Ca	t A ^b						
280	6	2	99.9	84	2.7	n.d.	9700
	12	8	99.3	83	1.3	n.d.	19 500
	18	20	89	80	0.6	n.d.	27 800
250	18	25	70	61	0.3	n.d.	21 000
330	12	6	99.9	87	3.6	n.d.	20100
280 ^c	12	12	93	84	0.6	n.d.	19 400
Commercial Ca	t B ^d						
280	6	2	99.5	83	1.3	0.02	10900
	12	8	94	85	0.6	0.03	22 500
	18	21	82.5	58	0.4	0.16	23 000
250	18	25	70	40	0.3	0.1	15900
330	12	6	99.9	84	2	0.2	22100
280 ^c	12	11	91	78	0.5	0.1	20 500
Commercial Ca	t C ^e						
330	12	3	96	78	3.5	n.m.	11600
300	12	3	93	72	3.5	n.m.	10 600
	1			fantalant ban	162.4	6 Desetionstic	n shaala naint stran 100

^{*a*} WHSV: weight-hourly space velocity in mass methanol per time and mass of catalyst. ^{*b*} $m_{CAT} = 162.4$ mg. ^{*c*} Deactivation check-point after 100 h run time. n.d.: none detected, n.m.: not measured. ^{*d*} $m_{CAT} = 185.5$ mg. ^{*e*} $m_{CAT} = 100$ mg, l = 14 mm.

reaction, *i.e.* not a consecutive reaction consisting of methanol decomposition (7) and water-gas shift (10). The dimethyl ether (DME) formation (8) can be treated independently from the other reactions if DME is considered not to react further since the active sites for this reaction are unique (acidic sites of Al_2O_3). Additionally, it is assumed that the catalyst can be modified by cationic ion exchange or support composition, resulting in decreased or even zero DME formation activity.

Generally, the autothermal reactor can be divided into two parts. The first part with oxygen present in the gas has an exothermic overall reaction whereas the second part has an endothermic overall reaction. It is obvious that in the second part the steam-reforming reaction is mainly dominant. For the first part of the reactor two simplified models for the mechanism of oxygen consumption can be discussed: the pure partial oxidation (POX) case and the total oxidation (TOX) case. Both reactions can be combined with the steamreforming (SR) reaction to give the autothermal reforming (ATR) reaction. The coefficients are shown in Table 2.

In order to distinguish between the models, experimental conditions, *i.e.* temperature and space velocity, were chosen to ensure oxygen conversion less than 100%. From the observed hydrogen to carbon dioxide ratio close to zero in the product gas, as shown in Fig. 3, it can clearly be concluded that, in the presence of oxygen, the methanol conversion occurs mainly *via* the TOX reaction, the hydrogen being produced by subsequent steam reforming. This observation, made at 223–232 °C was verified later at a reactor temperature of 250 °C.

In comparison to this, it is reported for the reaction of water-free mixtures of methanol with oxygen over



Fig. 2 Considered reactions for the autothermal methanol reforming.



Fig. 3 H_2/CO_2 ratio in the product gas for different oxygen conversions. The lines show the expected H_2/CO_2 ratio for TOX $(n_{H_2}/n_{CO_2} = 0)$, POX $(n_{H_2}/n_{CO_2} = 2)$ and SR $(n_{H_2}/n_{CO_2} = 3)$. Conditions: 53 mg of Catalyst B; stoichiometric feed for ATR with 1.5 ml h⁻¹ methanol-water mixture; temperatures 222, 228 and 232 °C.

 Table 2
 Coefficients of linear combination for two models of autothermal reforming

		POX–SR	TOX–SR
SR POX TOX Σ: ATR	$\begin{array}{l} CH_{3}OH + H_{2}O \rightarrow CO_{2} + 3 H_{2} \\ CH_{3}OH + \frac{1}{2} O_{2} \rightarrow CO_{2} + 2 H_{2} \\ CH_{3}OH + \frac{3}{2} O_{2} \rightarrow CO_{2} + 2 H_{2}O \\ 4 CH_{3}OH + 3 H_{2}O + \frac{1}{2} O_{2} + 2 N_{2} \rightarrow 4 CO_{2} + 11H_{2} + 2 N_{2} \end{array}$	3 1 0	$3\frac{2}{3}$ 0 $\frac{1}{3}$

 Table 3
 Results of the kinetic measurements on Catalyst B

	RWGS	SR
T/K	513553	503548
m Catalyst/mg	511	197.5/77.6
$k^{(513 \text{ K})}$	4.38 × 10 ⁻⁸ mol (s g kPa) ⁻¹ (±5%)	1.52 × 10 ⁻⁵ mol (s g) ⁻¹ kPa ^{-0.4} (\pm 2%)
$E_A/\text{kJ mol}^{-1}$	123(±5%)	83(\pm 3.5%)

 $Cu/ZnO/Al_2O_3$ that hydrogen is produced from methanol at a maximum for substoichiometric oxygen to methanol ratios.¹² Further increase of the oxygen partial pressure to the stoichiometric value causes hydrogen production to decrease, probably because of surface oxidation of the catalyst. Reduction of the oxygen partial pressure could not recover the hydrogen production activity of the catalyst.

In order to answer the question, whether the small detected amount of hydrogen shown in Fig. 3 is produced by POX or SR, the experiment was repeated using the same conditions but exchanging H_2O in the feed by D_2O . The mass spectrum of the product gas clearly revealed that hydrogen production in the presence of oxygen is at least partially occurring via the SR reaction. However, the general non-existence of the POX reaction could not be concluded from this experiment. Nevertheless, it could be shown that the combination of the TOX and the SR reactions is an appropriate model for the methanol conversion by autothermal reforming of methanol. Considering the reverse water-gas shift reaction allows the carbon monoxide formation to be modelled.

3.4. Kinetic measurements

Based on the proposed simplified model for the autothermal reforming of methanol over catalyst B, kinetic measurements of methanol SR and the reverse water-gas shift (RWGS) reaction have been performed separately in the microreactor system with feed components being methanol-water for the SR reaction and hydrogen-carbon dioxide for the RWGS reaction. Other conditions and results of the measurements are listed in Table 3. For evaluation of the data obtained for both reactions the software package SIMUSOLV and a onedimensional plug-flow model were used. Possible equilibrium limitation was included by introducing temperaturedependent equilibrium terms.

The RWGS reaction was assumed to be first order in CO_2 as described in ref. 13. Due to the low pressure the number of



Fig. 4 Parity plot for methanol conversion in the SR reaction using the model described above. Good agreement between measured and fitted data is shown.

free sites was considered to be a constant. This leads to the following rate eqn. (13)

$$r_{\rm RWGS}(T) = k^{(513K)} \exp\left[\frac{E_{\rm A}}{R} \left(\frac{1}{T} \frac{1}{513K}\right)\right] \times p_{\rm CO_2} \left(1 - \frac{p_{\rm H_2O} p_{\rm CO}}{K_{\rm RWGS}^{\rm P}(T) p_{\rm CO_2} p_{\rm H_2}}\right)$$
(13)

The measured activation energy of 123 kJ mol⁻¹ for this reaction is higher than the literature value of 95 kJ mol^{-1,13}

For the SR reaction a simple power law fit was chosen since the Langmuir–Hinshelwood models described in ref. 14 and 15 consider the catalyst surface hydrogen concentration to always be in the equilibrium state, which means that those models cannot be applied for measurements with zero hydrogen concentration in the feed. Formal orders in methanol and water were determined to be 0.4 and 0. This is in good agreement with the formal orders described in ref. 16. The full rate equation is given in eqn. (14).

$$r_{\rm SR}(T) = k^{(513\rm K)} \exp\left[\frac{E_{\rm A}}{R} \left(\frac{1}{T} \frac{1}{513\rm K}\right)\right] \times p_{\rm MeOH}^{0.4} \left(1 - \frac{p_{\rm CO_2} p_{\rm H_2}^3}{K_{\rm SR}^{\rm P}(T) p_{\rm MeOH} p_{\rm H_2O}}\right)$$
(14)

The parity plot (Fig. 4) for the SR reaction shows that the model describes the measured data reasonably well.

Describing the TOX of methanol in the presence of water, being the third reaction considered in the model is more difficult. From preliminary results it can be suspected that the catalyst surface is changed in the presence of oxygen. The number and/or adsorption properties of the active Cu sites seem to be dependent on oxygen partial pressure. Furthermore, the high reaction enthalpy complicates isothermal measurements at elevated temperatures in the tubular reactor.

4. Conclusions

It has been shown that the autothermal reforming process of methanol is a promising option for hydrogen production. If used for non-stationary PEM fuel-cell-based propulsion, the system can at least compete with the 17% full fuel cycle efficiency of current state-of-the-art ICEs. Further optimisation of single process steps might even improve this figure, however, the clear benefit of first generation fuel cell vehicles will be in the field of emission reduction.

The microreactor results show that the reaction can be carried out over commercially available copper catalysts at temperatures around 300 °C, provided that deactivation is not significant. The observed high conversions and selectivities are very important for non-stationary reactor systems which, for reasons of simplicity, must work in the once-through operation mode. A closer look at the reaction network suggests that the total oxidation of methanol rather than the partial oxidation is the major oxygen-converting reaction. Yet, in contrast to the steam-reforming and reverse water-gas shift reaction, isothermal kinetic measurements of this reaction are difficult to perform under realistic conditions.

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