Investigation of a methanol reformer concept considering the particular impact of dynamics and long-term stability for use in a fuel-cell-powered passenger car

R. Peters *, H.G. Düsterwald [1], B. Höhlein

Institute for Materials and Processes in Energy Systems IWV 3, Energy Process Engineering, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

A methanol reformer concept including a reformer, a catalytic burner, a gas cleaning unit, a PEMFC and an electric motor for use in fuel-cell-powered passenger cars was investigated. Special emphasis was placed on the dynamics and the long-term stability of the reformer. Experiments on a laboratory scale were performed in a methanol steam reformer consisting of four different reactor tubes, which were separately balanced. Due to the endothermy of the steam reforming reaction of methanol, a sharp drop in the reaction temperature of about 50 K occurs at the beginning of the catalyst bed. This agrees well with the high catalytic activity at the entrance of the catalyst bed. Forty-five percent of the methanol was converted within the first 10 cm of the catalyst bed where 12.6 g of the CuO/ZnO catalyst was located. Furthermore, CO formation during methanol steam reforming strongly depends on methanol conversion. Long-term measurements for more than 700 h show that the active reaction zone moved through the catalyst bed. Calculations, on the basis of these experiments, revealed that 63 g of reforming catalyst was necessary for mobile PEMFC applications, in this case for 400 W_{el} at a system efficiency of 42% and a theoretical specific hydrogen production of 5.2 $m_n^3/(h \ kg_{Cat})$. This amount of catalyst was assumed to maintain a hydrogen production of at least 80% of the original amount over an operating range of 3864 h. Cycled start-up and shut-down processes of the methanol steam reformer under nitrogen and hydrogen atmospheres did not harm the catalytic activity. The simulation of the breakdown of the heating system, in which a liquid water/methanol mixture was in close contact with the catalyst, did not reveal any deactivation of the catalytic activity. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Compact methanol reformer; Dynamic operation; Catalyst ageing; Fuel cell drive system

1. Introduction

The problem associated with road traffic in terms of reducing the quantity and improving the quality of emissions has led to a number of different approaches. Cars with drive systems based on polymer electrolyte membrane fuel cells (PEMFCs) offer considerable advantages with respect to energy efficiency as well as emissions. To avoid the difficulties of hydrogen storage, a system is useful that produces the hydrogen on board by reforming a liquid energy carrier. A fuel-cell drive system based on methanol as the liquid fuel is one attempt at solving these

problems [1–6]. The hydrogen generating system in Fig. 1 consists of a methanol reformer, a catalytic burner and a gas cleaning unit. It is combined with a PEMFC and an electric motor. This concept combines the components of an electric drive with the capability potential of a liquid energy carrier. The operating range is limited by the capacity of the tank, as in the case of internal combustion engines.

During operation, liquid methanol will be mixed with water coming from the cathode side of the fuel cell. A fuel pump delivers the methanol/water mixture to an evaporator where it is heated, evaporated and superheated. The vapour is then passed to a reformer. The endothermic steam reforming of methanol is catalysed by CuO/ZnO-type catalysts and can be performed in integral fixed-bed reactors. Within the reactor tubes the heterogeneously catalysed conversion to hydrogen, carbon dioxide and

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* Corresponding author. Tel.: +49-2461-61-4260; fax: +49-2461-61-8163; e-mail: ra.peters@fz-juelich.de
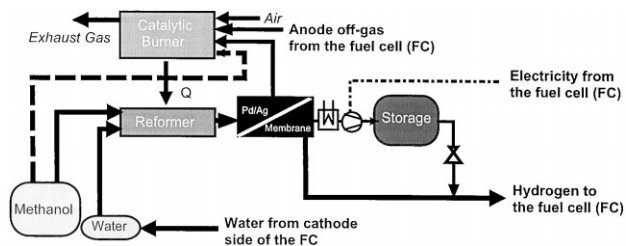[1] Present address: Adam Opel, ITEZ GAPC, D-65423 Rüsselsheim, Germany.

Fig. 1. Hydrogen production for a PEFC drive system.

carbon monoxide takes place according to the following equations [7]: Steam reforming of methanol:

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 \tag{1}$$

Methanol decomposition:

$$CH_3OH \rightleftharpoons CO + 2H_2 \tag{2}$$

Water–gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

The frequency of these reactions (Eqs. (1)–(3)) in different reaction zones will be discussed in Section 2.

The heat requirements of the reformer during operation are provided by the catalytic combustion of the exhaust gas of the anode side of the fuel cell, which contains unconverted amounts of hydrogen.

$$H_2 + 1/2O_2 \rightarrow H_2O \tag{4}$$

The reformer product gas has to be treated in a gas cleaning unit in order to adapt it to the fuel cell requirements. In the fuel cell drive proposed by Emonts et al. [8], a Pd membrane was adopted to separate hydrogen from the product gas. The residual gas, the so-called retentate, contains hydrogen, carbon monoxide, carbon dioxide, water and unconverted methanol. According to Eqs. (4)–(6),

the residual amounts of hydrogen, carbon monoxide and methanol are converted into carbon dioxide and water in the catalytic burner, which only releases emissions of less than $1/10$ of the ULEV-standard [8].

$$CO + 1/2O_2 \rightarrow CO_2 \tag{5}$$

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \tag{6}$$
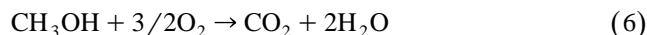
The difference in the enthalpy flow between the inlet of the catalytic burner and the tail pipe of the system is balanced with the heat requirements of the reformer, the pre- and superheater and the evaporator. The start-up phase of the system is performed by the combustion of methanol according to Eq. (6) until all the components have reached their operating temperature and full power. During the first few minutes of start-up the hydrogen required is supplied by the gas storage system. Furthermore, the gas storage system can deliver hydrogen during severe acceleration arising from the log of some components in the gas generation system. More details about the fuel cell drive system are given in Refs. [5–8].

In previous papers the general performance of a methanol steam-reforming reactor has been discussed [9] in terms of the gas cleaning system [5,10] and the whole fuel conditioning process [5,12]. Düsterwald et al. [13] examined the methanol steam-reformer performance as a function of catalyst bed length. The demands of the fuel cell drive on the dynamics of the reformer and its actual transient behaviour were discussed by Wiese et al. [14]. Aspects of catalyst ageing and its importance for the technical design of a methanol steam reformer in a fuel cell drive are treated here. Attention is focused on the methanol reformer, considering the particular impact of dynamics and long-term stability.
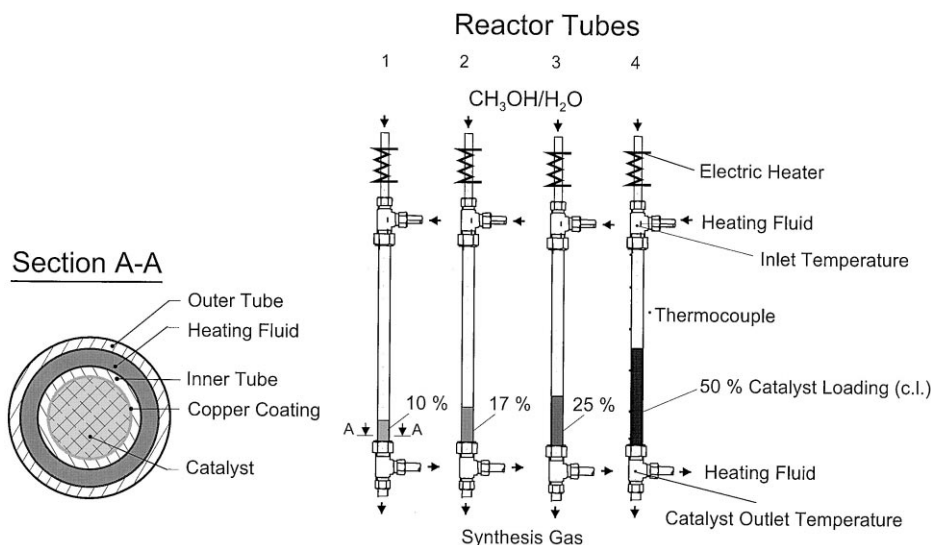

Fig. 2. The methanol steam reforming setup: integral fixed bed reactor tubes with different catalyst loadings (10%, 17%, 25% and 50%, catalyst: $CuO/ZnO/Al_2O_3$); cross-section of a reactor tube (Section A-A).

2. Experiments

2.1. Experimental set-up

The experiments were carried out in a methanol steam reformer consisting of four reactor tubes that were individually balanced (Fig. 2). In Fig. 2 the four reactor tubes and a cross-section of a reactor tube (Section A-A) are shown. Two stainless steel tubes were arranged concentrically in each reactor tube. The heat needed for the endothermic reaction is provided by condensing steam ($p_{H_2O} = 65$ bar, $T_{H_2O} = 280°C$) that flows in the gap between the tubes.

Before entering the reactor tube, the liquid methanol–water mixture of 1 mol CH_3OH/1.5 mol H_2O was fed from the storage tank into the evaporator by a piston membrane metering pump (LEWA metering pump type EK — horizontal with worm gear and flange motor). After evaporation, the mixture was superheated to a temperature of 260°C or 280°C. In order to avoid condensation, an electrical heating coil (Fig. 2) was installed at the front of the reactor inlet. The hydrogen-rich synthesis gas leaves the reactor tube and passes through a cooling system where water, unconverted methanol and byproducts are condensed and separated from the synthesis gas. The gaseous components H_2, CO_2, CO and, if present, CH_4 are analysed in a gas chromatograph (Hewlett Packard Series II 5890) equipped with a thermal conductivity detector. In order to observe the dynamic behaviour of the steam reformer, the gas composition of the wet product gas was determined on-line by a mass spectrometer (VG Analysis, MM 8-80) with time intervals of 25 s. In order to perform a mass balance of the methanol steam reformer, the following flow rates were measured: the flow rate of

the methanol/water mixture before entering the metering pump, the flow rate of dry reformate (gas meter Schlumberger type REMUS 4 G1,6, manual time measurement), after pressure control (Bronkhorst EL PRESS electronic pressure control), and the flow rate of dry reformate to the gas chromatograph analysis. The temperature was measured at the reactor tube inlet (T_{in}) and the catalyst bed outlet (T_{cat}). The pressure of the heating fluid (p_{steam}) was controlled and measured at the inlet (p_{in}) and after the outlet (p_{out}) of the reactor tube. More details concerning the construction of the reactor, the measurements and the evaluation of the results are given in Refs. [11,13].

The catalyst loadings of the four tubes were 10, 17, 25 and 50% of the reactor volume, so for a reactor length of 1 m the catalyst beds have a length of 10, 17, 25 and 50 cm, respectively.

Using such a design it is possible
1. to combine the data, that is, the temperatures at the end of the catalyst bed and composition of product gas, measured in each reactor tube and
2. to make a reconstruction of the process along the length of a completely filled methanol steam-reforming reactor on the basis of experimental data.

The interpretation of CO selectivity, methanol conversion and the catalyst temperature (T_{cat}) as a function of the length of one catalyst bed has been discussed in detail by Düsterwald et al. [13]. A brief summary is given in the Section 2.2.

2.2. Experiments

The experiments described below were performed to determine the catalyst activity depending on load, that is, the methanol conversion rate as a function of the theoreti-
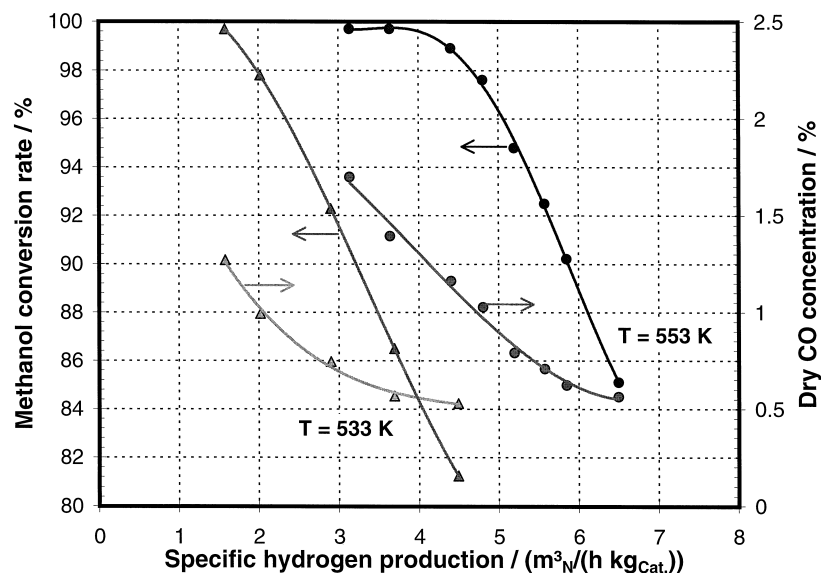

Fig. 3. Methanol steam reformer performance for two different temperatures (533 and 553 K) with a catalyst loading of 50%; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); operating pressure 3.8 bar.

cal specific hydrogen production. Fig. 3 shows a series of measurements at temperatures of 260 and 280°C using a catalyst bed with 31.5 g (25%) of catalyst at 3.8 bar. The catalyst used was a methanol-reforming catalyst in the form of pellets. Fig. 3 shows measurements of the methanol conversion rate as a function of hydrogen production. These values include the amount of hydrogen produced under standard conditions (1.013 bar, 273.15 K) per hour and per litre catalyst. It can be seen that the conversion rate is 100% for low inlet mixture loads, that is, low hydrogen production rates. At higher loads or hydrogen production rates, the methanol conversion rate decreases with increasing load. A possible operating point for a reformer may be 5.2 $m_n^3/(h\ kg_{cat})$, that is 6.2 $m_n^3/(h\ l_{cat})$, for a conversion rate of 95% at 280°C. Operating conditions with conversion rates below 95% are not of interest for operating a compact reformer. In comparison, the measurements by Colsman [10] for conversion rates of up to 95% at 280°C show 13 $m_n^3/(h\ l_{cat})$. It can also be seen that the hydrogen production rates increase about two-fold in a temperature interval from 260°C to 280°C at constant conversion rate.

In addition, Fig. 3 shows the CO content, dry state, in the reformer product gas as a function of hydrogen production rate for both temperatures, i.e., 260°C and 280°C. It can be seen that, starting from equilibrium, the CO content decreases with increasing hydrogen production rate. Due to the CO content in equilibrium, the CO contents reach a higher level with rising temperature. For a conversion rate of 95% and a hydrogen production rate of 5.2 $m_n^3/(h\ kg_{cat})$, a CO content of 0.8% CO at 280°C is shown for a bed filled with catalyst up to a length of 25 cm.

In order to understand and to control the dynamic behaviour of the reforming unit and the deactivation of the catalyst, it is necessary to analyse the processes within the catalyst bed of the fixed-bed reforming reactor. For this purpose, the reaction was performed in parallel in four partly filled reactors under almost identical reaction conditions of pressure, feed stream and composition, temperature of the heating fluid for more than 700 h. During the experiments the methanol/water mixture flow rate of 3.8 mol CH_3OH/h, 5.7 mol H_2O/h each tube was constant over the operation time of 700 h for all four reactor tubes. This results in identical gas velocities and reaction conditions in respective sectors of the catalyst bed.

The specific production of hydrogen under constant experimental conditions can be taken as a yardstick for catalyst activity. This activity was analysed with regard to operating time in the four reactor tubes within a period of 700 h (Fig. 4) [13]. The loss in activity with operating time was most pronounced in the first catalyst zone for 10% of the catalyst bed, whereas almost no deactivation was observed with the catalyst filling 50% of the reactor. High specific loads, that is 3.8 mol CH_3OH/h, contacting the 10% catalyst bed (reactor tube 1), should theoretically produce 22 $m_n^3\ H_{2,theor}/(kg_{cat}\ h)$. The specific hydrogen
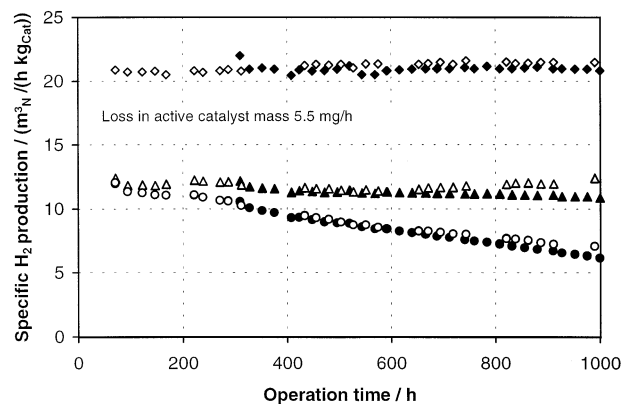

Fig. 4. Specific hydrogen production for two data series with catalyst loadings of 10% as a function of operation time; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); temperature of heating fluid 280°C; operating pressure 3.8 bar; methanol feed flow 3.8 mol/h for each tube. ◆ Theor. spec. H_2 production (VR4); ◇ Theor. spec. H_2 production (VR5); ▲ Corr. spec. H_2 production (VR4); △ Corr. spec. H_2 production (VR5); ● Spec. H_2 Production (VR4); ○ Spec. H_2 production (VR5).

production at the beginning of the experiment reached 10 $m_n^3\ H_2/(kg_{cat}\ h)$. This value decreased considerably over 700 h to 5.8 $m_n^3\ H_2/(kg_{cat}\ h)$.

The experiments were repeated to clarify, whether the observed ageing rates were reproducible. At the beginning of the new data file 5, the specific hydrogen production amounted to 12 $m_n^3\ H_2/(kg_{cat}\ h)$, i.e., 2 $m_n^3\ H_2/(kg_{cat}\ h)$ more than for data file 4. In order to understand catalyst behaviour during their operating time, for data file 4, experiments were performed to determine the pressure drop through the catalyst bed for different flows after the reduction process. Taking the time required for these measurements of 300 h into account, it was found that the hydrogen production rate, data file 4, corresponds to the data determined for data file 5. It was apparent that catalyst degradation started immediately after the reduction process.

Due to the practically linear decrease of activity with time, the negative slope of these curves can be interpreted as a deactivation rate. From these values a loss of active catalyst mass of 5.5 mg/h was estimated. This value was the same for all four tubes. The ageing can be understood assuming that an active zone moves through the catalyst bed. Recalculating the hydrogen production rate for a catalyst mass with regard to the observed ageing rate, a constant value of 12 $Nm^3/(kg_{cat}\ h)$ was found.

Following the experiments determining the ageing behaviour under stationary conditions [13], further measurements of catalyst activity were performed under more relevant dynamic conditions. A problem was caused by the stand-by operation of the reformer and the handling of the catalyst during this period. It was not expedient useful to heat the reformer during such periods, perhaps for several hours or over night. Therefore, it was important to clarify

how the catalyst performed under start-up and shut-down procedures. The conditions were chosen from mild at the beginning to severe at the end of the experiments:

(a) The first shut-down processes were performed at a constant temperature of 280°C (2 h) with a hydrogen purge of 100 l_n/h for 63 g catalyst in a volume of 58.5 ml, that is, a gas exchange of 33 times per minute. Afterwards, the reactor was cooled down. The reformer was operated for 26 h, shut down and purged with hydrogen, or nitrogen for 23 h. During the weekend, the catalyst was purged for 90 h. This procedure was repeated for several weeks, for example, 15 weeks for tube 4 with a 50% catalyst filling (63 g catalyst).

(b) As an alternative nitrogen was used for purging.

(c) In order to simulate a breakdown of the heating system, liquid methanol–water mixture was pumped into the reactor without being previously evaporated. Afterwards, the catalyst bed was purged with hydrogen.

Upon observing the gas composition during start–up after purging with hydrogen or nitrogen, a peak concentration of carbon monoxide was noted. During the shut-down of the reformer this effect was also found. More details about the behaviour of the catalyst during start-up are given by Düsterwald [11] and Wiese et al. [14]. Further measurements must be performed to clarify the basic reasons for these effects. A following paper will explain the catalyst behaviour.

The measurements described focus on the hydrogen production and long-term stability of the catalyst. Fig. 5 shows the methanol conversion rate for the four tubes as a function of operating time. The events described below occurred on different time scales for each tube due to their different histories. As can be seen, the methanol conversion decreases linearly with operating time up to 900 h. At 800 h an alert (event 1) led to purging with hydrogen. It is apparent that the performance of the catalyst was improved for three tubes, i.e., tubes 2–4 (17–50%). After 1200 h of
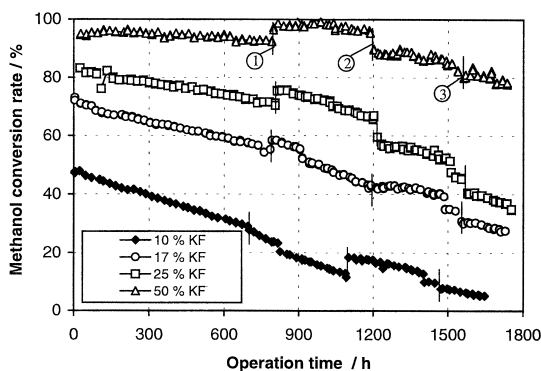

Fig. 5. Methanol conversion rate as a function of operating time; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); temperature of heating fluid 280°C; operating pressure 3.8 bar; methanol feed flow 3.8 mol/h for each tube; event 1: purging with hydrogen for 48 h; event 2: purging with nitrogen after an alert; event 3: starting with a modified stand-by mode.

operation, a second alert (event 2) with corresponding purging of the catalyst with nitrogen led to a decrease in conversion for tubes 3 and 4, while the performance of tube 1 (10%) was improved. This could be explained by poor distribution of nitrogen purging. Basic experiments performed by Idem and Bakhshi [15] show that catalyst performance depends on catalyst handling during synthesis and operation and also on purging rate and purging gases. A definite procedure to improve the catalyst performance by purging as well as an unequivocal explanation for the sudden loss in activity is not possible from the technical scale of these experiments. After event 2, the methanol conversion reached values, which followed the trend line given by the ageing rate determined during the experiments under stationary conditions. Between events 1 and 2, and in part, between events 2 and 3 up to 1300 h of hydrogen purging was applied. After 1300 h, the catalyst was purged with nitrogen. As is shown in Fig. 5, the catalyst degradation was constant.

A different mode for the four tubes was applied after 1560 h of stand-by operation (event 3). The catalyst was purged with 30 Nl/h hydrogen at an elevated pressure of 9.8 bar instead of 3.8 bar. After 1700 h the wet synthesis gas was entrapped in the tube without purging. Tube 1 was purged with hydrogen during standby, while the catalyst in tube 3 was expressed in an atmosphere of cold wet synthesis gas. Initially, the catalyst in tube 3 was trapped, then after 1700 h a methanol–water mixture was introduced into the tubes in order to simulate the worst case, i.e., a failure of the heating system. It is clear from Fig. 5 that the different procedures do not harm the catalyst and did not change its degradation behaviour. A more detailed discussion of the reasons for degradation is given by Düsterwald [11].

Fig. 6 shows the temperature in the reformer off-gas for the four tubes, as a function of operating time. It can be seen that the temperature for tube 1 (10%) dropped from 503 K at the beginning of the experiments, to 498 K after 700 h of operation. Between 700 and approximately 1080 h, the temperature increased to 518 K due to significant degradation of the catalyst. After event 2, the temperature returned to 503 K and subsequently increased to 528 K. The temperature drop corresponded to the increase in catalyst activity indicated in Fig. 5. The temperatures for reactor tubes 2–4 show almost a linear decrease as a function of operating time. The temperatures measured at the outlet of tube 4 before and after event 2 were not consistent with the methanol conversion shown in Fig. 5. The temperatures in tubes 2 and 3 correspond to the behaviour of methanol conversion.

At first sight, the dry CO concentration shows a different performance for each reactor tube as a function of operating time (Fig. 7). The CO production in tube 1 (10%) increased with increasing operating time, while tubes 2 and 3 showed a weak decrease. The CO concentration at the end of tube 4 dropped from 1% at the beginning
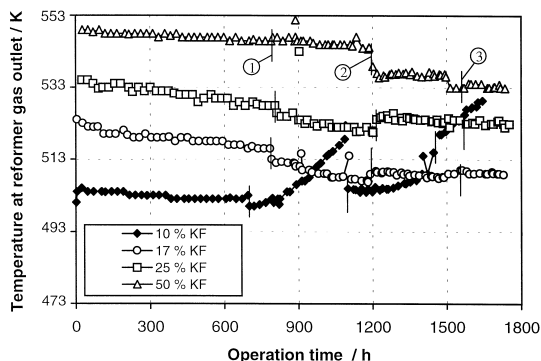
Fig. 6. Catalyst temperature at the reformer gas outlet as a function of operating time; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); temperature of heating fluid 280°C; operating pressure 3.8 bar; methanol feed flow 3.8 mol/h for each tube; event 1: purging with hydrogen for 48 h; event 2: purging with nitrogen after an alert; event 3: starting with a modified stand-by mode.

of the experiments to 0.4% at 1500 h. Between 800 and 1200 h, that is, between events 1 and 2, the CO concentration was higher than the extended trend line given by the data up to 700 h. At 800 h the CO concentration increased again up to 1% and decreased to 0.8% at 1200 h. After event 2 the CO concentration amounted to 0.5%, the value which would have been detained by extending the trend line from stationary operation between 0 and 700 h. The higher CO concentrations between 800 and 1200 h correspond to an improved catalytic activity, also shown in Fig. 5. Unfortunately, the higher activity was lost after event 2. At operating times of more than 1700 h, the CO concentration was higher, too.

It appears that the CO content in the dry reformate decreases with increasing weight hourly space velocity accompanied by decreasing methanol conversion. The higher the temperature of the heating fluid, the higher is

the CO selectivity and the methanol conversion in the product gas. The observed influence of weight hourly space velocity and temperature on CO selectivity and methanol conversion during methanol steam reforming could be understood in the following way. In Fig. 8 the selectivity for carbon monoxide (σ_{CO}) is shown as a function of the methanol conversion rate. Referring to the four reaction tubes, the selectivities calculated from all experimental data are depicted in Fig. 8. As can be seen, the formation of carbon monoxide from methanol is a direct function of the methanol conversion rate. This observation confirms the experimental results obtained by Amphlett et al. [16,17]. At high rates of methanol conversion, the selectivity increases more rapidly with increasing conversion than at lower rates. It appears that at higher methanol conversion rates, the reverse water–gas shift reaction produces CO. This means that the two equilibrium reactions (Eqs. (1) and (3)) compete with each other. The ageing of the catalyst is indicated by a decrease in the methanol conversion rate and a consequently lower selectivity. This behaviour can be observed for all tubes until catalyst degradation is extensive. In the case of long operating times and short catalyst beds, CO selectivity increases with decreasing methanol conversion rate.

In the following, the data are given as a function of the normalised catalyst bed length of a hypothetical total reforming reactor. In Fig. 9 the total conversion of methanol is depicted as a function of the catalyst bed length. It is evident that 50% of the methanol is converted within only 10% of the fresh catalyst. In the remaining part of the catalyst bed, the conversion increases and reaches an equilibrium value after 50% of the catalyst bed length. These data indicate that the degree of catalyst utilization depends on the relative position of the catalyst within the bed: high utilization is evident at the beginning and diminishes towards the end of the catalyst bed. This general picture does
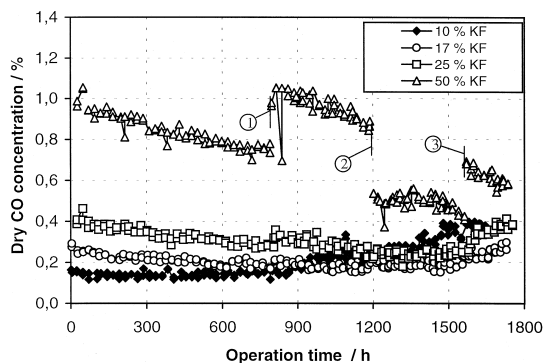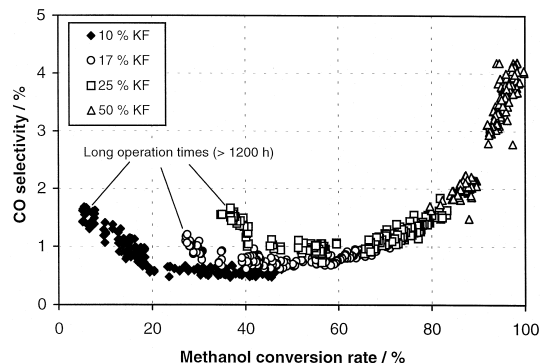

Fig. 7. Dry CO concentration as a function of operating time; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); temperature of heating fluid 280°C; operating pressure 3.8 bar; methanol feed flow 3.8 mol/h for each tube; event 1: purging with hydrogen for 48 h; event 2: purging with nitrogen after an alert; event 3: starting with a modified stand-by mode.

Fig. 8. CO selectivity as a function of methanol conversion rate; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); temperature of heating fluid 280°C; operating pressure 3.8 bar; methanol feed flow 3.8 mol/h for each tube; event 1: purging with hydrogen for 48 h; event 2: purging with nitrogen after an alert; event 3: starting with a modified stand-by mode.
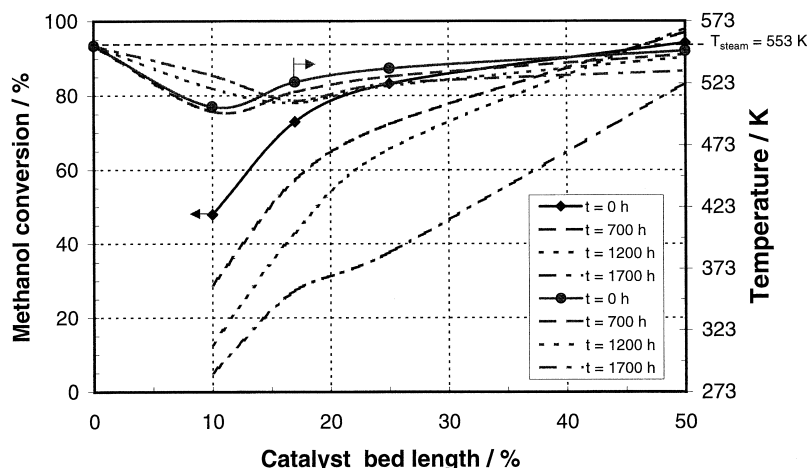
Fig. 9. Methanol conversion and temperature as function of catalyst bed length for four operating times; molar water/methanol ratio 1.5:1; mixture density 0.905 kg/l (25°C); temperature of heating fluid 280°C; operating pressure 3.8 bar; methanol feed flow 3.8 mol/h for each tube.

not change with a catalyst used for 700 h. The shape of the conversion curve up to 1200 h remains unchanged. However, with spent catalyst only 30% of the methanol is converted in the first 10% of the catalyst bed. This loss in initial efficiency is offset by a higher relative activity of the catalyst in the last section of the bed. Then at 50% of the catalyst bed, both conversion values, at 0 h and 700 h operation time, are equal to the equilibrium value. For 1200 h, the methanol conversion decreased further but the remaining part of the catalyst bed can compensate for this loss in activity. For 1700 h the active loss is considerable at the end of the bed, indicated by a decrease in methanol conversion from 98% to 80%. This behaviour may indicate a limitation of the endothermic reaction caused by heat transfer and additionally a degradation due to catalyst utilization. If the former argument is true, an axial temperature gradient would be expected within the catalyst bed.

Also, in Fig. 9, the temperature profiles along the catalyst bed are plotted for a catalyst at the beginning of the experiments, and after 700, 1200, and 1700 h of operation. Both curves show the same characteristics: under the given conditions a sharp drop in temperature of around 50 K occurs within the first 10% of the catalyst bed. In the consecutive catalyst zones the temperature increases continuously. Consequently, the temperature of the heating fluid is nearly reached at 50% along the length. The heat transfer from the heating fluid to the catalyst particles seems to be slower than the reaction rate. Therefore, the heat necessary for the strongly endothermic reaction cannot be sustained. Comparing the two curves, it becomes clear that a more gradual recovery of the temperature occurs with a catalyst used for 700 h. This agrees very well with the observation after 700 h of operation concerning the higher relative degree of methanol conversion further along the bed. For 1200 h, and for 1700 h, the reaction zone extends further along the catalyst bed. The

temperature drop is not so pronounced as at the beginning, that is the temperature profile becomes flatter. This corresponds to a lower integral methanol conversion.

As reported in literature by Amphlett et al. [18] and Düsterwald et al. [13] the chemical reactions according to Eqs. (1)–(3) occur in different reaction zones. Amphlett et al. [18] found that the methanol decomposition (Eq. (1)) takes place within approximately the first 4 cm of catalyst bed length. In the steam-reforming plant described, only the catalyst performance within the first 10 cm of catalyst bed length could be studied. Düsterwald et al. [13] showed for this configuration that the carbon monoxide concentration increases with increasing catalyst bed length. Also, in can be seen in Fig. 8, that CO-selectivity is a direct function of methanol conversion rate, for example, at high integral conversion rates the CO-selectivity is much higher than for lower methanol conversions. It can be asserted that CO is produced in a reaction zone located behind the steam reforming section, within the near half of the catalyst bed. Due to catalyst degradation, the reaction zone moves along the catalyst bed. With progressive operating time, the methanol steam reforming reaction takes place in parts of the catalyst bed where the reverse shift reaction was located previously. Consequently, the CO-concentration decreases with continuing catalyst degradation.

3. Conclusions

The results of these catalytic experiments show a sharp drop in the reaction temperature of about 50 K at the beginning of the catalyst bed. This is due to the endothermy of the steam reforming reaction of methanol. This finding agrees well with the observation that, at the

entrance of the catalyst bed, the activity is most pronounced. 45% of methanol is converted within the first 10 cm of the catalyst bed where 12.6 g of the CuO/ZnO catalyst is placed. Furthermore, CO formation during methanol steam reforming strongly depends on methanol conversion. The higher the methanol conversion the higher is the amount of CO produced.

Long-term measurements of more than 700 h show severe ageing of catalytic activity which can be explained by a loss of 3.5–6.5 mg of active catalyst per hour. Furthermore, these experiments show that the active reaction zone moves through the catalyst bed. Calculations on the basis of the long-term measurements reveal that the necessary amount of reforming catalyst for mobile PEMFC applications is 63 g. This is valid for a PEMFC system supplying 400 W_{el} at a system efficiency of 42% and a theoretical specific hydrogen production of 5.2 $m_n^3/(h \cdot kg_{Cat})$. This amount of catalyst is assumed to maintain a hydrogen production of at least 80% of the original hydrogen production at the beginning of operation for an operating range of 3864 h.

Cycled start-up and shut-down processes of the methanol steam reformer under nitrogen and hydrogen atmospheres do not harm the catalytic activity. The simulation of breakdown of the heating system, in which a liquid water/methanol mixture is in close contact with the catalyst, did not reveal any deactivation of the catalytic activity.

Acknowledgements

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