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Catalytic production of hydrogen from methanol

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Abstract

Catalytic production of hydrogen by steam reforming of methanol is an attractive option for use in decentralised production of clean electrical energy from fuel cells. Methanol fuelled solid polymer fuel cell (SPFC) systems are promising candidates for stationary and mobile applications such as passenger cars. Present methanol reformers are usually of the packed bed type which suffer from problems such as the occurrence of hot and cold spots and the slow response at start-up and during transients. These disadvantages are due to the slow heat transfer in the packed bed. Metal-supported catalyst systems that integrate the endothermic methanol steam reforming with the exothermic combustion of methanol or hydrogen containing gas from the fuel cell offer good heat transfer characteristics which are beneficial for the dynamical response at start-up and during transients. For methanol steam reforming, the concept of a washcoated heat exchanger showed better performance as compared to washcoated foam and packed beds. This is attributed to the good heat transfer characteristics of the heat exchanger. More than 600 l/h of hydrogen can be generated at methanol conversions higher than 95%. By proper temperature control, 450 h of continuous operation has been achieved with a washcoated reactor at an average methanol conversion >90%.

Keywords: Methanol; Hydrogen production; Catalytic steam reforming; Catalytic washcoat; Foam; Heat exchanger

1. Introduction

Currently, much attention is focused on fuel cells as a clean and efficient source of electrical power for both mobile and stationary applications [1]. Fuel cells need hydrogen or hydrogen-rich feed gas as fuel. Several proven technologies such as steam reforming, autothermal reforming, partial oxidation and water gas shift can be used to extract hydrogen from fuels like gasoline, diesel, LPG, methane, ethanol and methanol [2]. These fuel-processing technologies typically yield a gaseous product containing hydrogen and carbon dioxide. This hydrogen-rich gas can be fed to a fuel cell that generates electrical power by the electrochemical conversion of hydrogen with oxygen from the air. The only exhaust of this process is water vapour and carbon dioxide. Especially for mobile applications, methanol has been identified as a suitable (transportable) fuel that can be easily processed — on board — to hydrogen-rich gas for the solid polymer fuel cell (SPFC), the main candidate for transport applications [3]. Present methanol reformers are usually fixed-bed catalytic reactors [4] that suffer from a number of inherent problems. Hot and cold spots are commonly encountered in the catalyst bed that results in poor performance [5,6]. This type of reactor typically has poor response to transients. Similarly, they require a prolonged time to reach working temperature from cold start-up.

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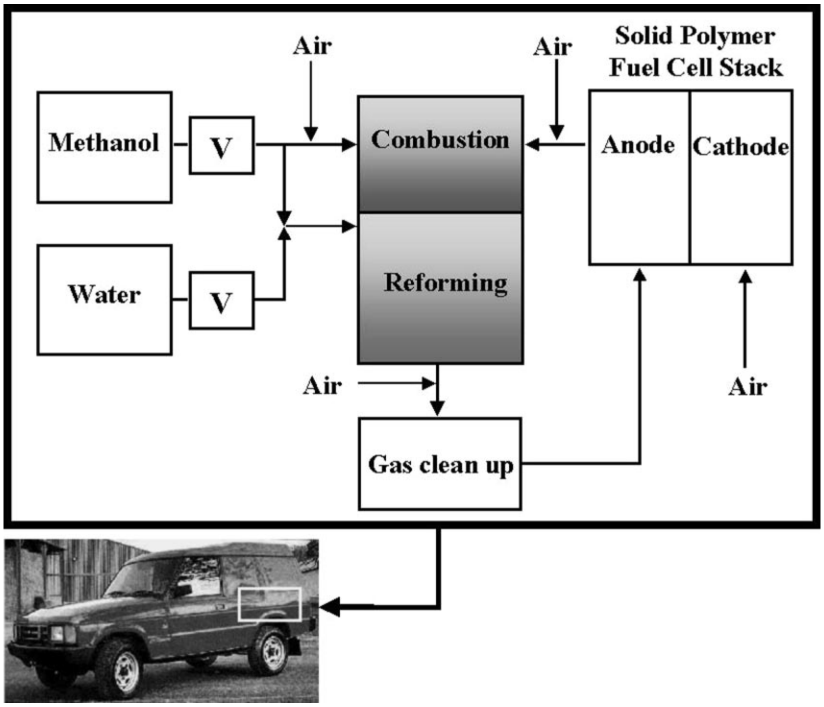

Fig. 1. The concept of the integrated reformer/combustor.

Fig. 1 illustrates the concept of a metal-supported catalytic system that integrates the endothermic methanol steam reforming with the exothermic combustion of methanol or hydrogen containing gas from the fuel cell ensuring good heat transfer characteristics which are beneficial for the dynamical response at start-up and during transients [7]. Typical overall energy efficiencies range from 32 to 35% for an optimised system including feed generation, integrated reformer/combustor, gas clean-up and fuel cell [9].

The feed for the reformer/combustor system consists of vaporised methanol and water. Part of the methanol vapour and/or hydrogen from the fuel cell anode off-gas is mixed with air and catalytically combusted in the combustion section of the system to generate the heat for the steam reforming of methanol in the reforming section. The hot flue gas from the combustor can be used to heat up water and methanol.

Steam reforming	Combustion
Endothermic reaction which consumes heat	Exothermic reaction which generates heat
Methanol + steam ⇒ hydrogen + carbon dioxide	Methanol + air ⇒ carbon dioxide + water
$CH_3OH + H_2O \Rightarrow 3H_2 + CO_2$	$2CH_3OH + 3O_2 \Rightarrow 2CO_2 + 4H_2O$
	Hydrogen + air ⇒ water
	$2H_2 + O_2 \Rightarrow 2H_2O$

The catalytic steam reforming of methanol yields a reformate with a composition of 75 vol.% H_2 and 25 vol.% CO_2. The gas also contains some residual methanol and a small amount of carbon monoxide (CO), typically up to 1 vol.%. SPFCs are extremely sensitive to CO which — even in low concentrations (0.01 vol.%) — rapidly deteriorates the fuel cell's performance. Therefore, removal of CO from the reformate gas is mandatory. The gas clean-up stage downstream the integrated reformer/combustor consists of a reactor for catalytic preferential oxidation (PROX) of CO. It should be noted that in order to maximise the efficiency of the CO-PROX reactor and to minimise reversible losses of the fuel cell performance, residual amounts of methanol should be kept as low as possible (typically below 5000 ppm [8]). This paper describes some results obtained with metal-supported catalyst systems for steam reforming of methanol.

2. Experimental

Methanol steam reforming has been studied with a commercial copper-based reforming catalyst. The material was used either as a fixed-bed of 3 mm pellets, as a sieve fraction thereof or incorporated into a washcoat on several specific aluminium substrates such as foams, corrugated foils and heat exchangers. The cylindrical foams are 10 cm in length, 5 cm in diameter and contain 20–25 cells per inch. The heat exchangers are of the plate-fin type with two approximately 0.23 l compartments for reforming and combustion. The catalyst structures that have been used are illustrated in Fig. 2 that presents a photograph of reforming catalyst pellets, typical coated foam, and a heat exchanger. One compartment of the heat exchanger contains a coating of the reforming catalyst, whereas the other compartment was used to supply the heat for the reforming reaction by flushing through a thermal fluid. Alternatively, this compartment can be coated with combustion catalyst (e.g. alumina-supported platinum) to generate heat by catalytic combustion of — part of — the methanol feed and/or hydrogen from the fuel cell anode off-gas with air. Integrated operation of the reformer/combustor is possible by balancing combustion with reforming at the desired temperature level for the reforming reaction.

To study the steam conversion of methanol with larger amounts of catalyst (50–150 g) or specific catalytic structures, a fully automated bench-scale test rig (mini-flow) has been used. This test rig consists of a section for generation of reactor feed gas mixture,

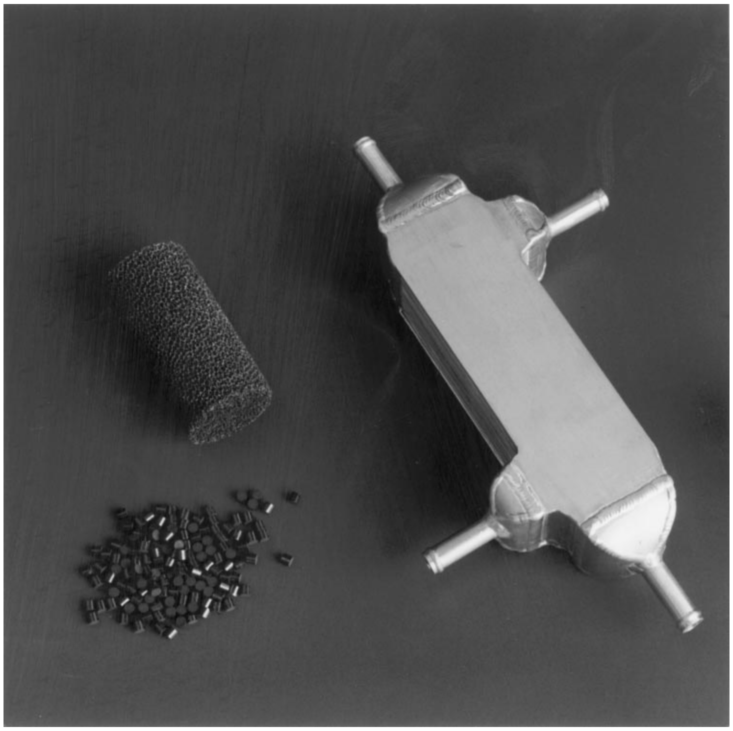

Fig. 2. Catalyst structures: commercial pellets, coated aluminium foam and aluminium heat exchanger.

Table 1
General test conditions in the mini-flow test rig for methanol reforming

Catalyst	Commercial copper based
Packed bed	74 g catalyst pellets or catalyst sieve fraction
Foam	17 g washcoat
Heat exchanger	18 g washcoat
Reactor feed flowrate	3.5–14 l/min at standard temperature and pressure (STP)
Hourly space velocity	3000 h^{-1} (fixed-bed), 1000 h^{-1} (foam), 1000–4000 h^{-1} (heat exchanger)
Reactor feed composition	15–36 vol.% CH_3OH, 30–54 vol.% H_2O, balance N_2
Steam/methanol molar ratio	1.5–2
System pressure	1.3–1.5 bar (a)
Temperature range activity measurements	130–300°C

a reactor section, gas chromatographic and infra-red analysis of gaseous products, off-gas handling equipment and PC-based automation hardware. The reactor section features a tubular reactor for testing foams and packed beds of catalyst pellets and a provision for testing heat exchangers.

The gas-phase reformation of methanol has been studied in the mini-flow test rig mainly to determine catalyst activity and catalyst stability as a function of catalyst structure (i.e. pellets, coated foam and coated heat exchanger). Table 1 presents the general test conditions for reforming that have been adopted for the catalytic measurements in the mini-flow test rig. The hourly space velocity is based on the reactor feed flow rate in l/h under standard conditions (STP (25°C, 1 atm)) divided by the internal volume of the reactor system.

3. Results and discussion

The reforming catalyst has been used for the preparation of the washcoat suspension. After having developed the proper composition of the washcoat suspension, the technique was scaled up to coat aluminium foam cylinders, corrugated aluminium foils and aluminium heat exchangers. Typical thickness of the coating layer was 5–10 μm.

Fig. 3 compares the methanol reforming activity of the investigated catalytic structures. When moving from pure catalyst pellets via coated foam to the coated heat exchanger, the overall performance clearly improves. The packed bed consisted of 74 g catalyst pellets, while the structured reactors only contained 17–18 g of catalyst. Maximum CO concentrations of 2000–3000 ppm were detected at high methanol conversions. In the three reactor systems, large differences have been observed in the temperature difference

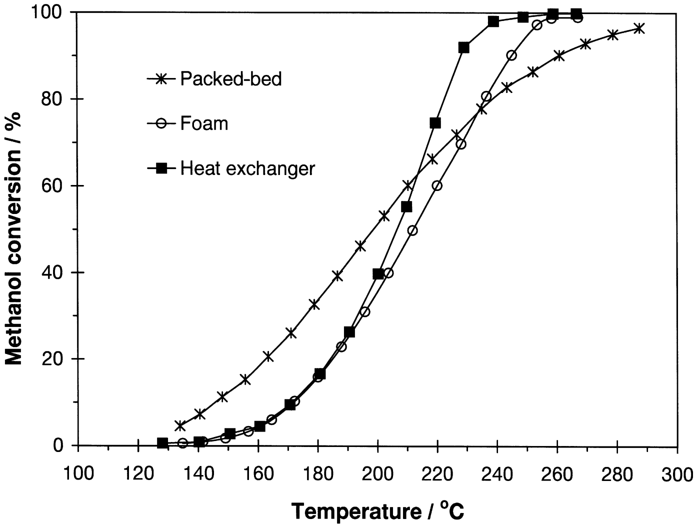

Fig. 3. Comparison of activity results for different catalytic structures in methanol steam reforming.

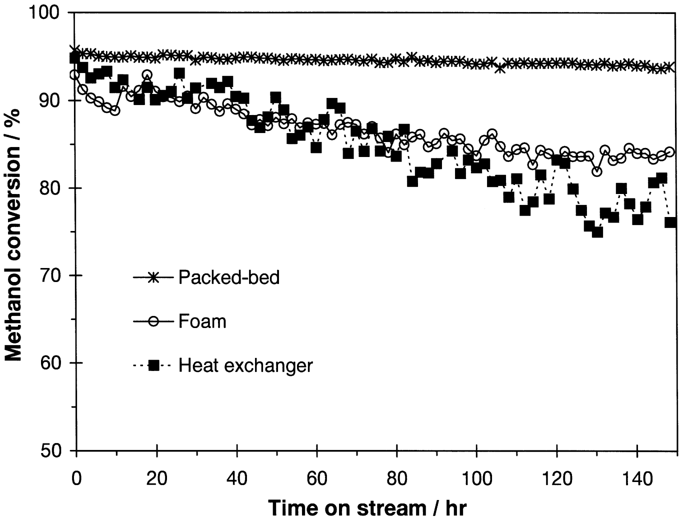

Fig. 4. Comparison of deactivation results for different catalytic structures in methanol steam reforming.

between the gas inlet and gas outlet temperatures at high methanol conversions (>95%) due to the endothermic steam reforming reaction. This can be ascribed to heat transfer limitations that are more pronounced in the packed bed of catalyst pellets than in the washcoated structures. The small temperature difference for the heat exchanger is inherent to its isothermal operation, with a thermal fluid supplying the heat for the reforming reaction.

Next to a high activity, long-term stability is important for further developments. In Fig. 4, the loss of methanol conversion is plotted as a function of time during continuous operation under standard conditions. The coated structures deactivate at a higher rate than the pure catalyst pellets, probably due to the low amount of catalytic material in the aluminium structures (17–18 g) when compared to the packed bed of pellets (74 g). Table 2 summarises the main results of the activity and stability measurements for the investigated catalytic structures.

The effect of a relatively high deactivation rate of the washcoated structures can be counteracted by the application of a higher load of washcoat in combination with the operation of the catalytic system at higher temperatures. The latter has been demonstrated for coated foam in a 450 h test run under standard conditions. The gas inlet temperature at the beginning of the test was adjusted to 235°C.

After each period of 150 h, the gas inlet temperature was increased by 10°C. Results are presented in Fig. 5 from which it is obvious that small temperature adjustments cause significant conversion increases. In addition, it seems that the deactivation tendency decreases at higher temperatures. This shows that in order to

Table 2
Main results for packed bed, coated aluminium foam and coated aluminium heat exchanger catalytic structures

Catalytic structure	Packed bed	Foam	Heat exchanger
Catalyst weight	74 g	17 g	18 g
Catalyst shape	1.2–2 mm particles	Washcoat	Washcoat
Reactor shape	Tubular reactor	Cylinder	Box
Reactor volume	0.077 l	0.2 l	0.23 l
Temperature of 95% methanol conversion	280°C	250°C	230°C
Temperature difference (gas outlet−gas inlet)	80–90°C	5–10°C	<2°C
Decrease in methanol conversion after 150 h	1.5%	10%	15%

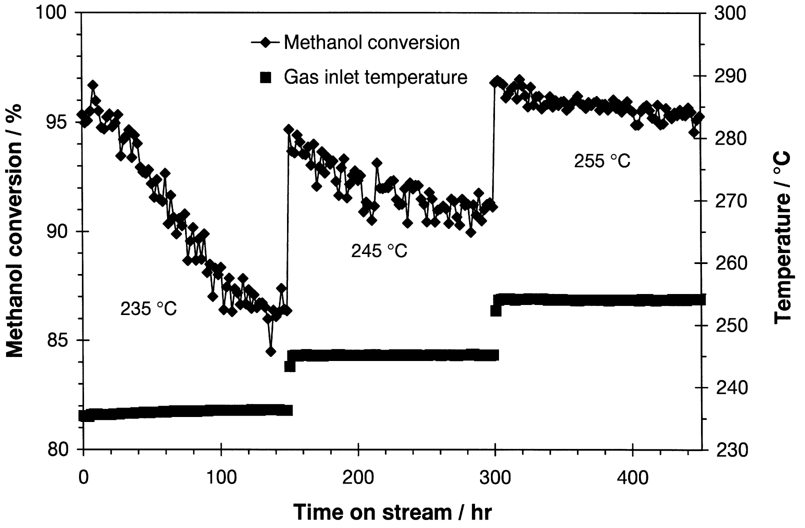

Fig. 5. Deactivation of coated aluminium foam in methanol steam reforming; effect of temperature.

maintain a high methanol conversion for at least 450 h, small periodical temperature increments are sufficient (e.g. as a function of the amount of generated hydrogen).

The hydrogen production potential of the heat exchanger reactor is an important parameter to gain some insight into the possible size of a methanol steam reformer capable of producing enough hydrogen to feed an SPFC on board a passenger car. The amount of hydrogen that can be generated with the coated heat exchanger has been estimated as a function of space velocity at a fixed temperature and as a function of temperature at a fixed space velocity. The effect of the space velocity was investigated through a stepwise

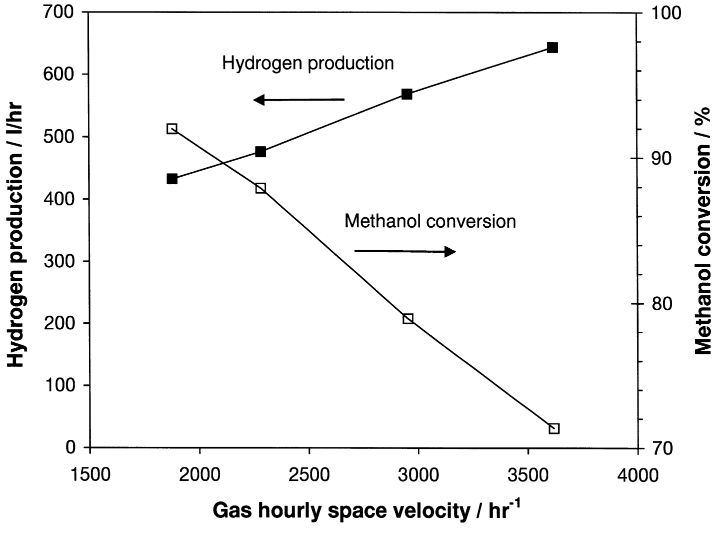

Fig. 6. Hydrogen production and methanol conversion at 265°C as a function of reactor feed space velocity for a coated heat exchanger.

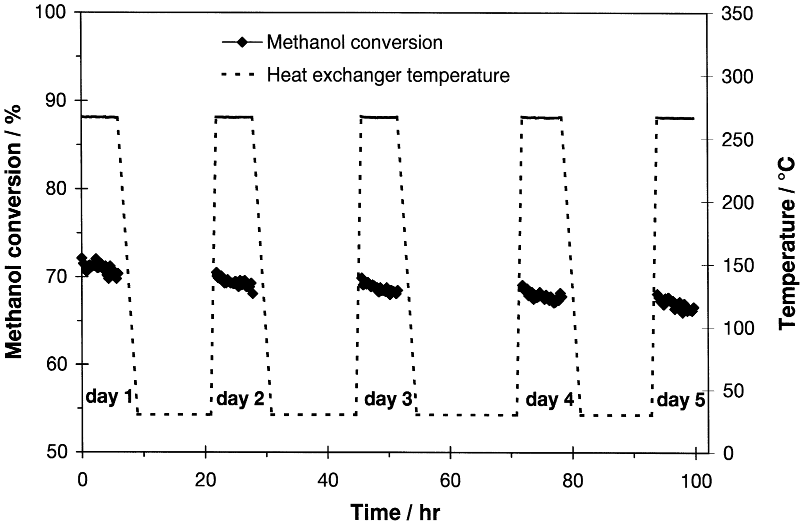

Fig. 7. Discontinuous deactivation measurement with a heat exchanger at 265°C, 1.5 bar (a) and 13.6 l/min (HSV=3600 h^{-1}, 37% methanol, 55% steam, balance nitrogen).

increase in flow rate of the steam/methanol feed at 265°C and a system pressure of 1.3–1.5 bar (absolute pressure). The reactor feed contained 54 vol.% steam, 36 vol.% methanol and balance nitrogen. At successive flow rates of 7, 8.6, 11 and 13.6 l/min (corresponding to an hourly space velocity range of 1900–3600 h^{-1}), methanol conversion was monitored for 1.25 h at each flow rate. Hydrogen production has been calculated from the methanol conversion and regularly confirmed by measuring the dry product gas flow rate. Fig. 6 shows that a maximum hydrogen production rate of about 650 l/h can be obtained at a space velocity of 3600 h^{-1} and a methanol conversion of 70%. A hydrogen production of 650 l/h roughly corresponds to 2 kW_{th} based on the lower heating value of hydrogen. The effect of higher heat exchanger temperatures on the methanol conversion and hydrogen production under conditions of high flow was subsequently investigated. It has been possible to generate >600 l/h hydrogen at high methanol conversion (>90%). At 320°C, the CO concentration level in the reformate had risen to 8000 ppm. Assuming a small passenger car of 20 kW_e, the observed maximum hydrogen production rate implies a minimal volume of approximately 6 l for the heat exchanger reactor reforming compartment.

To estimate the impact of repeated start-ups and shut-downs on the overall reactor performance, the effect of temperature cycling has been investigated for the heat exchanger by means of a discontinuous stability experiment at high flow conditions. At the beginning of each measurement day, the heat exchanger was rapidly heated up from room temperature to 265°C, after which the reactor feed was turned on. At the end of the day, the heating was turned off while replacing the steam/methanol/nitrogen reactor feed by nitrogen. During 5 days, the methanol conversion has been determined. Results are presented in Fig. 7. Obviously, the controlled temperature cycling of the heat exchanger is not particularly detrimental for its reforming performance, especially when taking into account the high flow conditions. The conversion results in Fig. 7 roughly correspond to a hydrogen production rate of 10 l/min.

4. Conclusions

Washcoat suspensions of commercial reforming catalysts can be applied successfully onto aluminium substrates such as foams and heat exchangers.

Among the investigated catalytic systems for methanol reforming, the aluminium heat exchanger shows the highest activity per gram of catalyst that can be ascribed to its good heat transfer characteristics. The hydrogen production potential corresponds to >600 l/h at high methanol conversions (>90%). Mainly due to the lower catalyst load, the coated aluminium structures deactivate at a higher rate than the packed bed of pure catalyst pellets. By proper temperature control, 450 h of continuous operation have been achieved for an aluminium foam at an average methanol conversion >90%.

Operating the heat exchanger under conditions of high flow and high temperature with periodic temperature cycling does not lead to excessive losses in activity over a period of 5 days. Deactivation rate is only marginally higher when compared to continuous operation.

Acknowledgements

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