Short communication

A plate-type reactor coated with zirconia-sol and catalyst mixture for methanol steam-reforming

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Abstract

A plate-type reactor with 10 channels is designed for methanol steam-reforming and its performance is investigated in the temperature range 210–290 °C. A catalyst coated with zirconia-sol solution in the channels of the reactor exhibits a good adherence with the substrate that is maintained even after reaction including fast feed flow rates at high temperature. Five plate-type reactors are stacked in order to test their performance for methanol steam-reforming. At 270 °C, hydrogen at $3.1\,l\,h^{-1}$ is obtained at a feed flow rate of $2.0\,g\,h^{-1}$, which corresponds to results for a conventional packed-bed reactor under various reaction conditions.
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1. Introduction

Large amounts of hydrogen are used for many industrial applications [1,2]. More recently, hydrogen has attracted interest as an energy carrier for fuel cells, especially in vehicle applications, due to its high efficiency and negligible pollution [3,4]. It is difficult, however, to store and handle hydrogen directly as an on-board fuel. On the other hand, fuels such as gasoline, ethanol, methane and methanol can be converted into hydrogen-rich gas. This can be achieved through various technologies such as steam-reforming, autothermal reforming, and partial oxidation that involve various unit components such as a reformer, a shift reactor and a selective oxidation reactor. Methanol is an attractive fuel because of its low reforming temperature and low content of sulfur compounds. The former attribute results in reduced heat losses, requires less insulation and simplifies thermal management of the integrated system. In addition, methanol offers much higher specific energy than either lithium batteries or stored hydrogen, which makes the fuel an attractive candidate for portable power systems.

It is important for the fuel reformer to be both small and lightweight for portable devices. Conventional reformer technology based on the packed-bed reactor has disadvantages in terms of size and weight. Therefore, there has been considerable interest in the development of microreactors with microchannels [5–11]. The microreactor exhibits reduced heat and mass transfer resistances and allows chemical reactions to proceed at much higher rates, which provides for increased efficiency.

Battelle [6–8] has developed micro-process technology for various devices including fuel vapourization, fuel processing, catalytic combustion, and partial oxidation. A microchannel methanol reformer of size ranging from 25 to $100\,W_e$ has been designed and tested. The system consists of a methanol reformer, a combustor, two vapourizers, and a heat exchanger. Other researchers [12] developed a methanol steam-reformer that consisted of stainless-steel plates with microchannels. The plate-type micro reformer had dimensions of $75\,mm \times 45\,mm \times 100\,mm$ and comprised of six plates with 40 channels each. The reformer used a Cu/ZnO

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catalyst and was operated at 150–270 °C. A sufficient amount of hydrogen for running a 50 W_e unit was obtained.

A plate-type methane reformer has also been patented [13]. The main unit included a combustor filled with a catalyst and a reforming reactor filled with another catalyst. A heat-conductive partition wall was sandwiched between the combustor and the reformer, and therefore effective heat transfer was achieved and the reformer was more compact than a conventional tubular reactor. On the other hand, Loffler et al. [14] developed a more compact plate reformer in which the catalyst was coated on the plate such that, the heat was transferred only through a solid.

In this study, a plate-type reactor with channels is developed and is evaluated for methanol steam-reforming. The reactor is designed such that the heat from the combustion reaction is used for the endothermic reforming reaction. The performance of the plate-type reactor is investigated at various operating conditions and compared with that of a packed-bed reactor. In addition, a technology for catalyst coating is presented in order to improve the adherence between the catalyst and the substrate.

2. Experimental

2.1. Plate-type reactor design

The plate-type reactor was manufactured from 304 stainless steel by an etching process. The size of the plate was 80 mm length, 35.5 mm width, and 1 mm thickness. The plate contains 10 channels of 45 mm length, 1 mm width, and 0.5 mm depth. As shown in Fig. 1, the reactant mixtures pass through an inlet A and are distributed over the plates, then pass over the parallel channels, and are finally collected in an outlet B. The inlet C and outlet D are included for the combustion reaction. After the catalyst was applied, five plates were stacked and tested for methanol steam-reforming. A stainless-steel gasket of 0.2 mm thickness was placed between each plate and the whole reactor was contained in a stainless-steel housing.

2.2. Catalyst coating

A commercial copper-containing reforming catalyst (ICI 33-5: CuO 50%, ZnO 33%, Al_2O_3 8%, BET surface area: $66 \, m^2 \, g^{-1}$) was used for the methanol reforming reaction. In order to coat the catalyst, a zirconia sol solution was used. Zirconia is a ceramic material that has superior adhesive properties than other ceramics in high-temperature combustion reactions [15]. The zirconia-sol acts as a binder and was prepared by adding HNO_3 (HNO_3:Zr = 1:2) to a zirconium isopropoxide isopropanol complex (Aldrich, 99%). 1.33 g of zirconia powder ($<10 \, \mu$m) was mixed with 0.07 g of zirconia-sol to give ratio of 95:5 and then 10 ml of isopropyl alcohol was added to obtain adequate viscosity (material A). Also, diluted zirconia-sol solution (material B) was prepared by adding 1 ml isopropyl alcohol to 200 μl of zirconia-sol solution (material A). The zirconia-sol solution was ball-milled
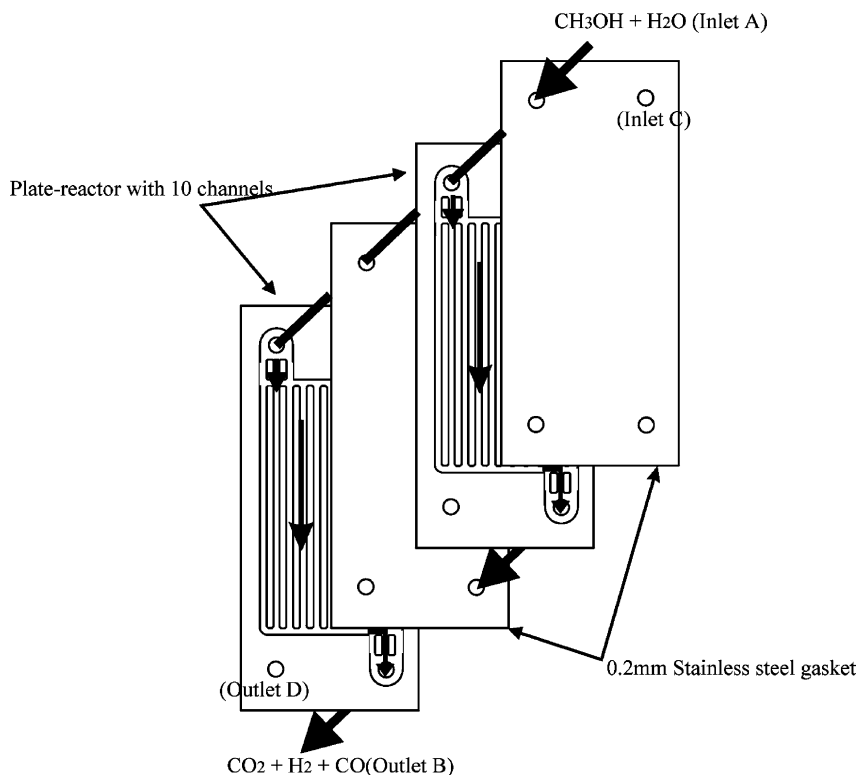

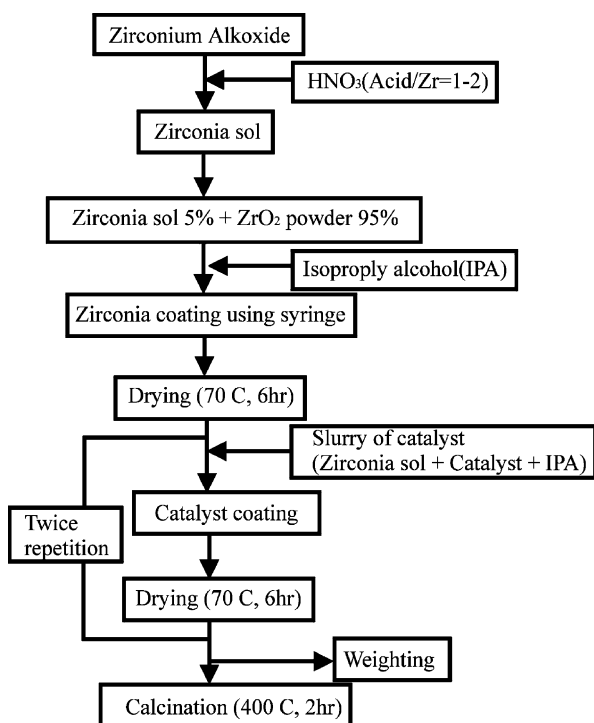Fig. 1. Schematic diagram of plate-reformer with fluid flow.

Fig. 2. Procedures for catalyst coating.

for 12 h. The catalyst slurry was prepared by adding the catalyst powder to the zirconia-sol solution. The catalyst slurry was obtained by mixing 0.2 g catalyst, 1 ml diluted zirconia-sol solution (material B) and 1 ml isopropyl alcohol and then ball-milling for 12 h. In order to enhance the adhesion between the catalyst and the stainless-steel substrate, a syringe was used to undercoat the zirconia-sol solution on the surface of the channels and the coating was then dried at 70 °C for 6 h. The catalyst slurry was coated on the preformed zirconia layer by same method and dried at 70 °C for 6 h. The process was repeated to give the desired weight of catalyst and the assembly was then calcined at 400 °C for 2 h. The coated catalyst weight was 0.025–0.027 g per plate reactor. The procedure of catalyst coating is shown in Fig. 2.

2.3. Methanol steam-reforming reaction

Five plates, each loaded with catalyst were stacked and integrated within a housing. The total weight of catalyst coated on the five plates was 0.135 g. A pre-mixture of methanol and water (1:1, 1:1.5 molar ratio) was introduced to the reactor using a syringe pump with carrier gas (helium) and vapourized through a feed line that was heated at 150 °C. The feed rate of liquid reactant mixtures was 0.01–0.1 ml per min.

The vapourized reactants were passed through the steam reformer, where they were converted to a hydrogen-rich stream with a small amount of CO. The steam-reforming reaction was performed in the temperature range 210–290 °C. The reactor was heated by electrical heating tape with a temperature controller, and the temperature was measured by a thermocouple placed inside housing. For steam-reforming, pre-reduction by hydrogen was not necessary before each run. The catalyst was activated in situ by treatment with the vapourized mixture (i.e., feed) at the reaction temperature.

The produced gas stream was directed through a cold-trap at 0 °C to remove liquid components, and then passed to an on-line gas chromatograph for analysis of H_2, CO and CO_2.

3. Results and discussion

3.1. Catalyst coating

The coated catalyst should strongly adhere to the metal substrate for long reaction times. Therefore, various coating methods have been tested for good adherence to the metal substrate. First, the general polymer binder was mixed with catalyst and then this slurry was coated on the channels of the plate reactor. A catalyst slurry was also prepared with only water, i.e., without binder. After calcination, the adherence was evaluated by the method described by Yasaki et al. [16], which is based on the measurement of the weight loss caused by exposure in an ultrasonic bath for 1 h. With such coating, serious weight losses were observed and the catalyst was separated from the substrate under blowing.

It is well known [15–17] that coating improves the adherence between the catalyst and the substrate. The zirconia layer formed after coating zirconia sol on the channels is shown in Fig. 3. The thickness of the layers increases with the concentration of the zirconia sol, and the latter is controlled with isopropyl alcohol. A thicker zirconia layer is more easily separated from substrate, as mentioned elsewhere [17]. Therefore, a dilute sol solution is preferable for good adherence of zirconia to the substrate, as shown in Fig. 3(b).

The catalyst slurry is composed of catalyst, zirconia sol solution and isopropyl alcohol. In order to obtain a thin layer catalyst, the slurry was diluted by isopropyl alcohol, and the catalyst coating was repeated twice to load a proper amount of catalyst on to the channels. With this procedure, a significant weight loss does not occur and visible separation of catalyst does not appear after exposure to ultrasonic treatment. In addition, the catalyst layer remains intact after reaction under the gas flow for a few days, as shown in Fig. 4.

3.2. Performance of microreactor in methanol steam-reforming reaction

A new methanol steam-reformer was designed and its performance was evaluated between 210 and 290 °C. The reactor was heated above 200 °C and then the reactant was introduced. The steam-reforming reaction took place when the surface of the catalyst was activated. The methanol conversion and hydrogen generation rate were investigated over a wide range of reaction temperature as shown in Fig. 5. Methanol starts to be converted above 200 °C and the con-
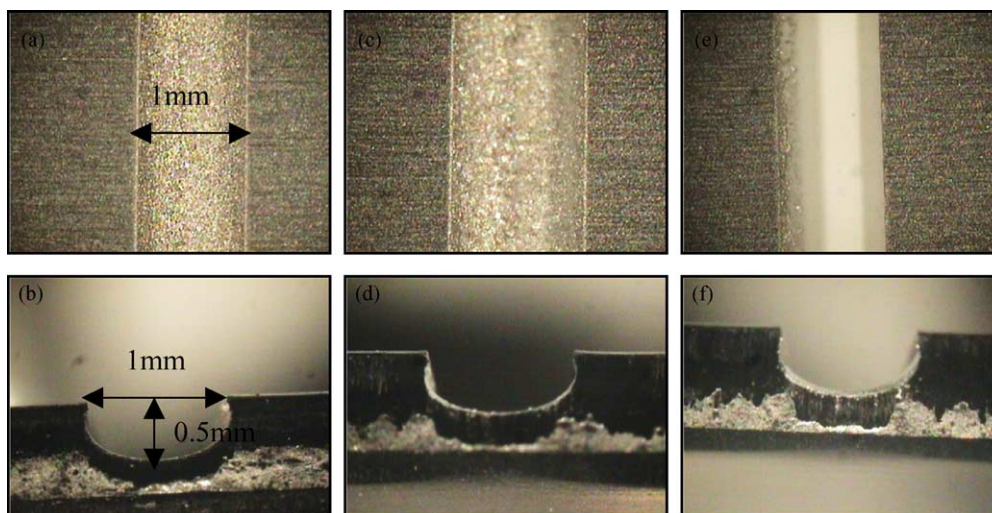
Fig. 3. Images of ZrO_2 layer on channels before catalyst coating: (a) before coating, top view; (b) before coating, cross-section view; (c) ZrO_2 material A, top view; (d) ZrO_2 material A, cross-section view; (e) ZrO_2 material B, top view; (f) ZrO_2 material B, cross-section view.

version is above 95% at 290 °C. A hydrogen generation rate of 2.6 l h^{-1} is observed at a constant liquid feed rate of 2.76 ml h^{-1}. The selectivity of hydrogen and carbon dioxide is high and a typical dry gas composition is 73–75% H_2, 24–26% CO_2, and 0.0–1.2% CO.

A low level of CO formation is achieved when only methanol is used as the fuel. The performance of cell in a PEMFC dramatically decreases in the presence of CO [18–20]. Therefore, a CO clean-up step such as the water-gas shift reaction and preferential oxidation of CO is required. A water-gas shift reactor will not, however, be required in a methanol steam-reformer and a CO clean-up system can be more simplified.

In methanol steam-reforming, CO_2 and H_2 are not formed from a consecutive reaction consisting of methanol decomposition followed by water-gas shift, but are formed from methanol in a single step as follows [20]:

$$2CH_3OH \leftrightarrow HCOOCH_3 + 2H_2 \tag{1}$$

$$HCOOCH_3 + H_2O \leftrightarrow HCOOH + CH_3OH \tag{2}$$

$$HCOOH \leftrightarrow CO_2 + H_2 \tag{3}$$

It can be seen from these proposed pathways that carbon monoxide can be formed only by a reverse water-gas shift reaction.
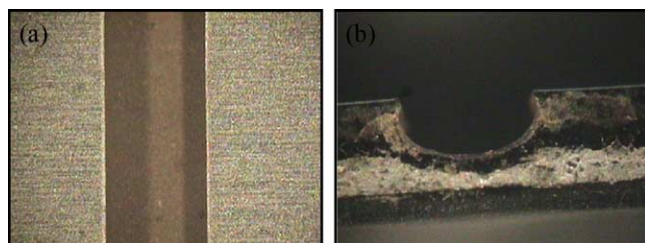

Fig. 4. Image of coated catalyst layer: (a) top view; (b) cross-section view.

In addition, the amount of CO formed is slightly increased from 0.8 to 1.2 on decreasing the water to methanol ratio from 1.5 to 1.0 at 290 °C. Agrell et al. [21] reported the influence of this ratio on CO formation in methanol steam-reforming. They observed that CO selectivity at 320 °C increased from 3 to 11% when the ratio was changed from 1.3 to 1.0. Therefore, excess water is used to reduce the formation of CO.

The methanol conversion and hydrogen generation rates are not affected when the amount of water is increased to 50% excess of H_2O above the stoichiometric ratio. This result is in good agreement with previous studies in packed-bed reactors [22–25].

In order to evaluate reformer performance under various reaction conditions, methanol steam-reforming was investigated at reactant flow rates between 0.01 and 0.07 ml min^{-1}; the results are given in Fig. 6. The hydrogen generation rate increases with feed flow rate, while methanol conversion decreases. A hydrogen flow of 3.1 l h^{-1} is obtained at 270 °C
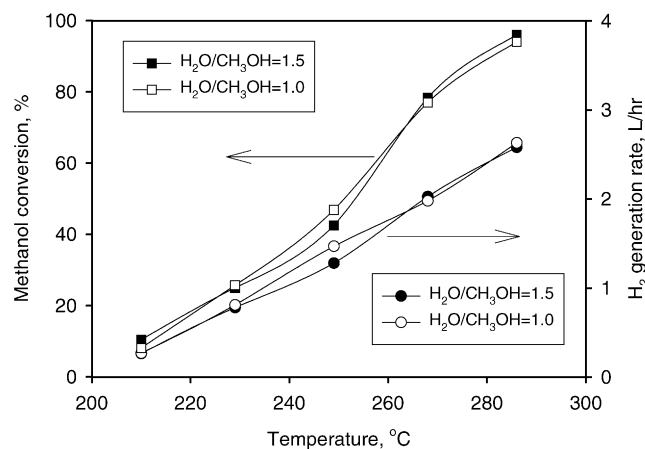

Fig. 5. Methanol conversion and H_2 generation rate as function of reaction temperature; liquid feed rate = 2.76 ml h^{-1}.
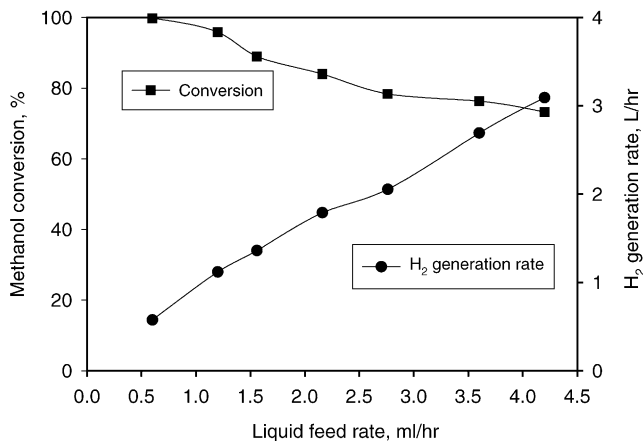
Fig. 6. Performance of plate-type reactor as function of feed rate; reaction temperature = 270 °C; $H_2O:CH_3OH$ molar ratio = 1.5.

with a feed flow rate of $4.2\,ml\,h^{-1}$ and methanol conversion is above 70%.

Seo et al. [10] developed a microchannel methanol reformer and reported that the generation rate of hydrogen was $5.6\,l\,h^{-1}$ for a liquid feed flow rate of $6\,ml\,h^{-1}$ at 260 °C and a steam to carbon ratio of 1.1. The methanol conversion was about 82–83%. By comparison, the five-plate reformer developed here has a lower capacity. The performance can be improved, however, if more plates are added and more catalyst is loaded into the channels.

Methanol steam-reforming has been investigated in a packed-bed reactor in order to confirm the catalyst activity in a stacked plate-type reactor as shown in Fig. 7. The same weight of coated catalyst was packed in quartz tube reactor and methanol steam-reforming was conducted under the same operating conditions. The reactivity for methanol steam-reforming in the plate-type reactor is similar to that for the conventional packed-bed reactor. This suggests that most of the catalyst coated in the channels of the plate-type
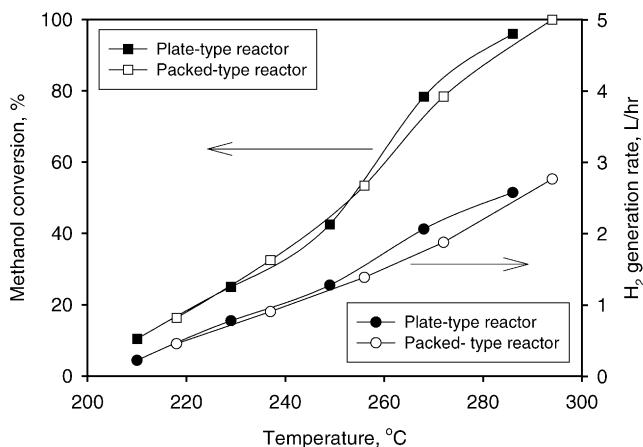

Fig. 7. Comparison of performance between plate-type reactor and packed-type reactor; liquid feed rate = $2.76\,ml\,h^{-1}$; $H_2O:CH_3OH$ molar ratio = 1.5.

reactor participates in methanol steam-reforming and that the reactor delivers a good performance.

4. Conclusions

A plate-type reactor with 10 channels has been designed for methanol steam-reforming and its performance is investigated over a temperature range between 210 and 290 °C. A new method for catalyst coating, which uses a zirconia sol solution, has been developed to enhance the adherence between the catalyst and the substrate. It is found that the optimum catalyst slurry consists of 0.2 g catalyst and 1 ml zirconia sol based on isopropyl alcohol. A hydrogen production rate of $3\,l\,h^{-1}$ is obtained at a feed flow rate of $4.2\,ml\,h^{-1}$ at 270 °C. The reactivity for methanol steam-reforming of the plate-type reactor corresponds to that obtained for a packed-bed reactor with the same catalyst.

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