Reaction study of auto thermal steam reforming of methanol to hydrogen using a novel nano CuZnAl-catalyst

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Abstract

A novel nano CuZnAl-spinel catalyst has been successfully synthesized and tested for autothermal steam reforming of methanol to produce onboard hydrogen for fuel cell applications. The catalyst performance has been studied using three crucial operating parameters, namely, the methanol space velocity, molar ratios of water/methanol and oxygen/methanol. The effects of these parameters have been investigated in terms of methanol conversion and hydrogen production rate. The optimal hydrogen production rate of about 575 mmol kg^{-1} s^{-1} has been achieved at 300 °C in this study.
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Keywords: Operating parameters; CuZnAl-catalyst; Hydrogen production; Fuel cell
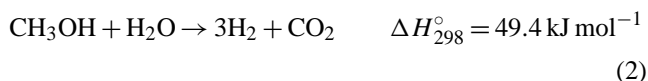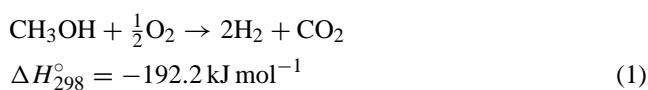
1. Introduction

Sustainable energy is of increasing concern worldwide. The rapid growth of global climate changes along with fear of energy supply shortage is creating a large consensus about the potential benefits of a hydrogen economy coming from renewable energy sources [1]. Besides, the increasingly stringent legislation [2] for controlling emissions from internal combustion engines to a point where alternative power sources for vehicles are necessary. Hydrogen fuel cell seems to be a promising solution to these global environmental and energy problems as using hydrogen in fuel cells produces useful energy at high efficiencies and generates only heat and water as emissions [3].

The development of fuel cell powered by hydrogen is well established, but it is not matched by the progress in establishing an infrastructure for the distribution and supply of hydrogen. This marks the paramount issue faced by hydrogen fuel cell. Therefore, in the short to medium term, onboard catalytic generation of hydrogen from liquid or liquefied fuels can provide the answer [4].
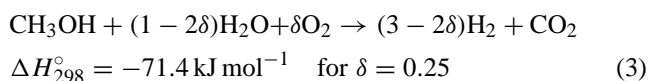
Methanol has been recommended as the best source for hydrogen fuel among the high energy density liquid fuels [5,6]. The main advantages offered by methanol are [4,7–10]:

- It contains such a high H/C ratio that it has a lower propensity for soot formation than other hydrocarbons.
- Its boiling point is relatively low.
- It can be obtained from renewable sources.
- It can be stored easily.

Most fuel-processing technologies reported in the literature so far has been based solely on either (1) partial oxidation [5,9,11–14], or (2) steam reforming [5,14–18] as shown below:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow 2H_2 + CO_2$$
$$\Delta H^{\circ}_{298} = -192.2 \, \text{kJ mol}^{-1} \tag{1}$$

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \qquad \Delta H^{\circ}_{298} = 49.4 \, \text{kJ mol}^{-1} \tag{2}$$

However, an ideal fuel-processor should combine the advantages of both the above reaction routes. This is because steam reforming produces higher concentrations of hydrogen without proportionally consuming the same amount of methanol, while partial oxidation offers compactness, fast start-up, and rapid responses [4]. Therefore, an integrated autothermal reaction based on the oxidative steam reforming of methanol [5,19–21] is the most favourable practical route for onboard hydrogen production as shown below:

$$CH_3OH + (1 - 2\delta)H_2O + \delta O_2 \rightarrow (3 - 2\delta)H_2 + CO_2$$
$$\Delta H^{\circ}_{298} = -71.4 \, \text{kJ mol}^{-1} \quad \text{for } \delta = 0.25 \tag{3}$$

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This paper reports the reaction study of autothermal oxidative steam reforming of methanol using novel nano-size CuZnAl-spinel structure catalyst prepared by hydrothermal approach.

2. Experimental

2.1. Catalytic testing

Catalyst performance was studied in a stainless steel tubular packed-bed micro reactor (3.5 mm i.d.). No activation procedure is required for the catalyst prior to reaction. 0.5 g of catalyst was sandwiched between quartz wool. The micro reactor was placed in an electrically heated furnace, which was controlled by a temperature controller through a thermocouple allocated at the center of the furnace. A separate thermocouple was used to monitor the temperature of the catalyst bed. This double arrangement aimed to ensure an accuracy of $\pm 1\,^{\circ}$C for the catalyst bed.

A premixed of methanol and water was fed into a vaporizer before entering the reactor, by means of a syringe pump (CEMS Marketing Pte. Ltd.). A helium stream of 40 ml min^{-1} served as carrier gas for the liquid mixture. Purified oxygen was supplied right in front of the catalyst bed to prevent homogeneous oxidation reactions. All pipelines were maintained at 150 $^{\circ}$C by means of heating tapes,

to avoid liquid condensation. Fig. 1 shows the schematic diagram of the system for oxidative steam reforming of methanol.

2.2. Product analysis

The compositions from the outlet reactor were analyzed on-line using a gas chromatograph equipped with a thermal conductivity detector (GC-TCD by HP, Series 6890). Three columns: Porapak Q, GC 200 and molecular sieve were connected in series to analyze the products. The catalytic activity was evaluated at reaction temperature of 300 $^{\circ}$C under atmospheric pressure.

3. Results and discussion

The catalytic performance on the oxidative steam reforming of methanol depends greatly on the methanol space velocity, and the molar ratios of both the H_2O/CH_3OH and H_2O/CH_3OH. It has been reported that the variations of these operating parameters may induce side reactions, hence influencing the overall catalytic performance. These side reactions may include water-gas shift reaction (reaction 4) [22–24], reversed water-gas shift reaction (reaction 5) [25], methanation reaction (reaction 6) [14] or oxidation of reaction products either CO (reaction 7) or H_2 (reaction 8).
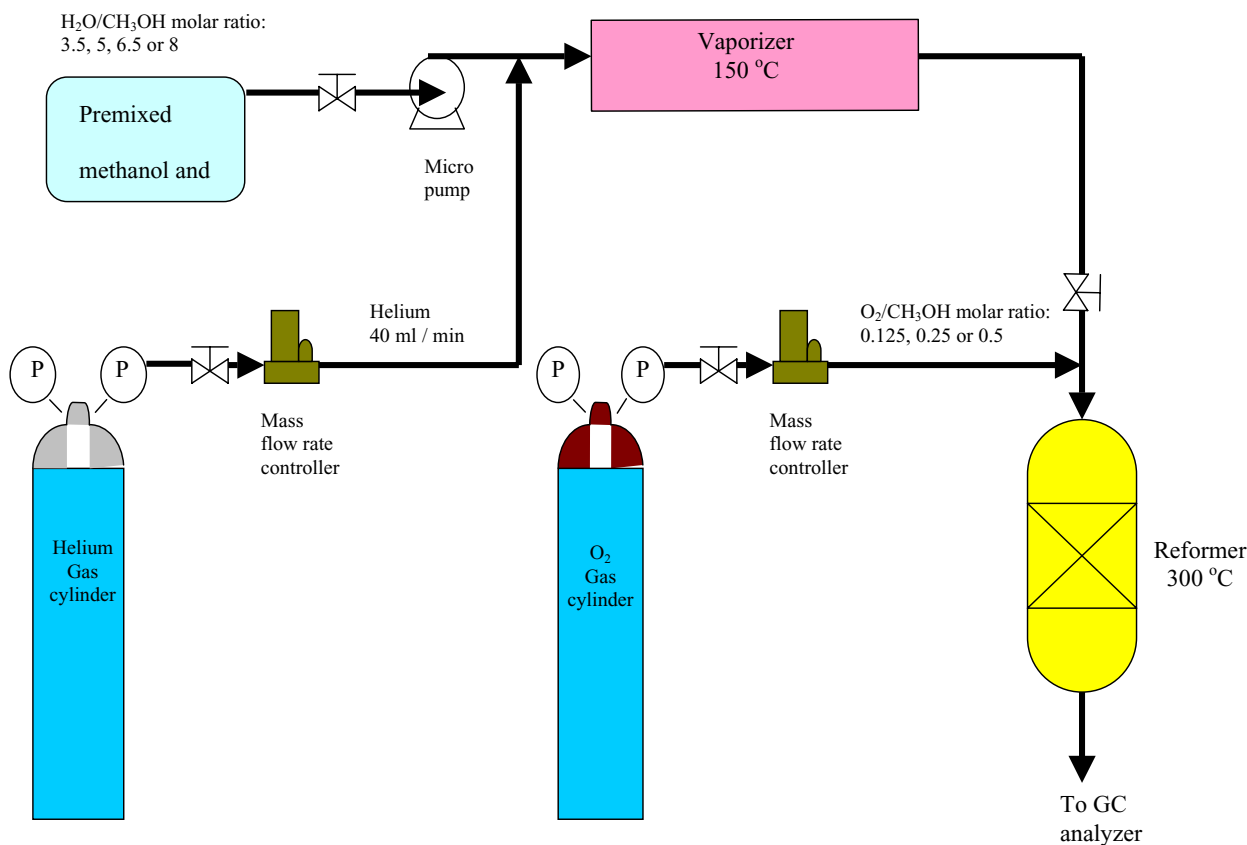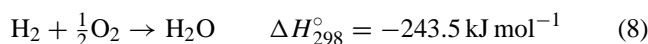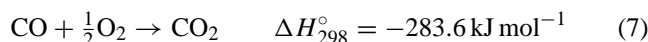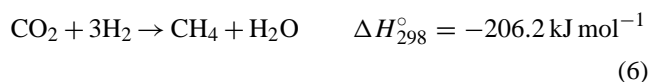

Fig. 1. Schematic diagram of the system for oxidative steam reforming of methanol.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^\circ_{298} = -41.2\,\text{kJ mol}^{-1} \tag{4}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^\circ_{298} = 41.2\,\text{kJ mol}^{-1} \tag{5}$$

$$CO_2 + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H^\circ_{298} = -206.2\,\text{kJ mol}^{-1} \tag{6}$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad \Delta H^\circ_{298} = -283.6\,\text{kJ mol}^{-1} \tag{7}$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H^\circ_{298} = -243.5\,\text{kJ mol}^{-1} \tag{8}$$
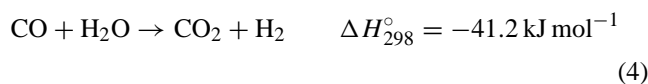
In the absence of both water and oxygen, the methanol decomposition reaction (reaction 9) has been reported to take place [5,13,26,27].

$$CH_3OH \Leftrightarrow 2H_2 + CO \qquad \Delta H^\circ_{298} = 92.0\,\text{kJ mol}^{-1} \tag{9}$$

The effects of three operating parameters (methanol space velocity, molar ratios of water/methanol and oxygen/methanol) on the methanol conversion and hydrogen production rate are shown below.

3.1. Effect of methanol space velocity

Fig. 2 shows the effect of methanol space velocity (WHSV) over the catalytic performance of the novel CuZnAl catalyst. The range of methanol space velocity studied is from 0.09 to 0.77 mol g-cat^{-1} h^{-1}. The methanol conversion is observed to be inversely proportional to the WHSV. The maximum methanol conversion of about 40 mol% was achieved at 0.09 mol g-cat^{-1} h^{-1} of methanol WHSV. On the other hand, the hydrogen production rate is directly proportional to the methanol space velocity. As shown

in Fig. 2, the highest hydrogen production rate achieved is about 97 mmol kg-cat^{-1} s^{-1}, which corresponds to a methanol conversion of 24 mol%. Methanol space velocity of 0.38 mol h^{-1} g^{-1} has been selected based on the results shown in Fig. 2. This methanol space velocity is then used to evaluate the effect of molar ratios of either H$_2$O/CH$_3$OH or O$_2$/CH$_3$OH, on the catalytic performance of the oxidative steam reforming of methanol over the novel CuZnAl-catalyst.

3.2. Effect of H$_2$O/CH$_3$OH molar ratio

As shown in Fig. 3, both the methanol conversion and hydrogen production rate increase with increasing H$_2$O/CH$_3$OH molar ratio. However, the incremental rates of methanol conversion and hydrogen rate for a molar ratio of H$_2$O/CH$_3$OH from 6.5 to 8 are lower compared to the ones from 3.5 to 6.5. The trends indicate that any further increase in H$_2$O/CH$_3$OH molar ratio would not result in higher methanol conversion or in greater hydrogen production rate. Therefore, the H$_2$O/CH$_3$OH molar ratio of 6.5 has been selected to evaluate the effect of O$_2$/CH$_3$OH molar ratio.

3.3. Effect of O$_2$/CH$_3$OH molar ratio

O$_2$/CH$_3$OH molar ratios at 0.125, 0.25 and 0.5 have been selected in this part of the study. Fig. 4 shows that methanol conversion increases with increasing O$_2$/CH$_3$OH molar ratio. For the lowest O$_2$/CH$_3$OH molar ratio of 0.125, the methanol conversion is about 73 mol%, while for the highest O$_2$/CH$_3$OH molar ratio of 0.5, the methanol conversion is about 92 mol%. It can also be observed in Fig. 4 that the hydrogen production rate increases with decreasing O$_2$/CH$_3$OH molar ratio. The optimal hydrogen produc-
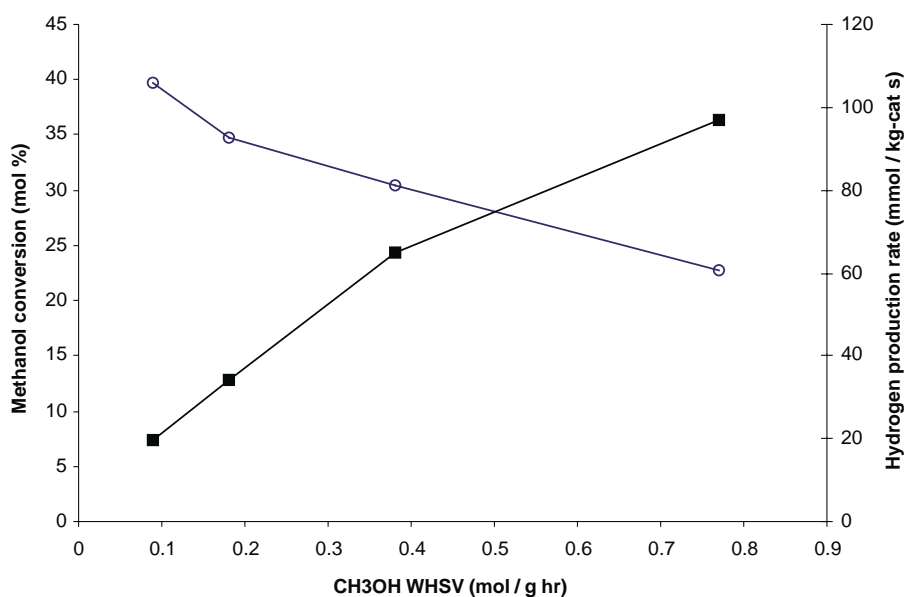

Fig. 2. Effect of CH$_3$OH space velocity (WHSV) on catalytic performance of the novel CuZnAl-catalyst: (○) methanol conversion and (■) hydrogen production rate. Reaction temperature = 300 °C.
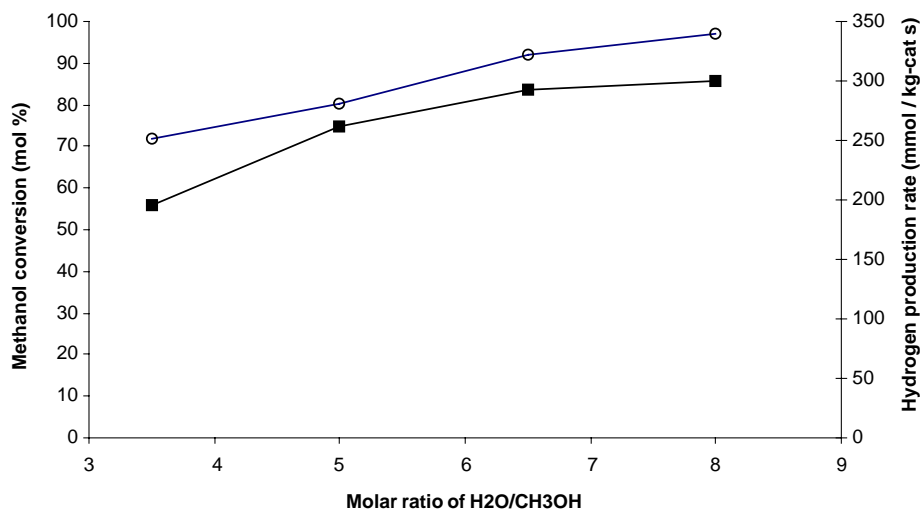
Fig. 3. Effect of molar ratio of H_2O/CH_3OH on catalytic performance of the novel CuZnAl-catalyst: (○) methanol conversion and (■) hydrogen production rate; WHSV = 0.38 mol g-cat^{-1} h^{-1}. Reaction temperature = 300 °C.
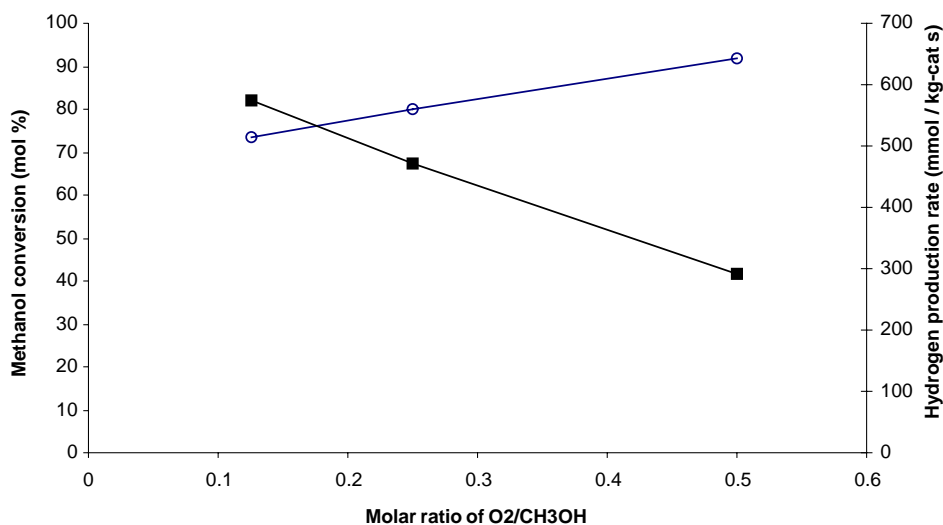

Fig. 4. Effect of molar ratio of O_2/CH_3OH on catalytic performance of the novel CuZnAl-catalyst: (○) methanol conversion and (■) hydrogen production rate; WHSV = 0.38 mol g-cat^{-1} h^{-1}, H_2O/CH_3OH = 6.5. Reaction temperature = 300 °C.

tion rate achieved in the present study is about 575 mmol kg-cat^{-1} s^{-1} with O_2/CH_3OH molar ratio of 0.125.

3.4. Comparison with the conventional CuZnAl catalyst

The catalytic performance of this novel CuZnAl-catalyst is compared with those of the conventional CuZnAl-catalyst prepared by impregnation method. Table 1 shows that novel nano-size catalyst is about 10% more efficient than the conventional one in term of hydrogen production rate. Furthermore, it is also noticed that no CO formation can be detected—within the limit of our GC—when the novel catalyst is used, whereas 0.16 mol% of CO was detected with the conventional one. Since it is known that CO can poison

Table 1
Comparison of the catalytic performance of the novel CuZnAl-catalyst prepared by hydrothermal approach with the conventional CuZnAl-catalyst prepared by impregnation approach

	New CuZnAl-catalyst	Conventional CuZnAl-catalyst
H_2 production rate (mmol kg^{-1} s^{-1})	575	518
Methanol conversion (mol%)	73	87
CO concentration (mol%)	None detected	0.16

WHSV = 0.38 mol g-cat^{-1} h^{-1}, H_2O/CH_3OH = 6.5, O_2/CH_3OH = 0.125, reaction temperature = 300 °C.

the Pt electrode and hence despite slightly lower methanol conversion, the overall catalytic performance of our novel CuZnAl-catalyst is superior than those of the conventional catalyst.

4. Conclusions

The novel nano-sized CuZnAl-spinel structure catalyst has been successfully tested on the catalytic performance of oxidative steam reforming of methanol. Three operating parameters are highly correlated to the catalytic performance; these include methanol space velocity, and the molar ratios of both the H_2O/CH_3OH and O_2/CH_3OH. Suitable operating parameters are selected to achieve the highest catalytic performance in terms of methanol conversion and hydrogen production rate. The optimum methanol space velocity is found to be $0.38 \, mol \, g\text{-cat}^{-1} \, h^{-1}$, while the optimum molar ratios of the H_2O/CH_3OH and O_2/CH_3OH are 6.5 and 0.125, respectively. Under such conditions, hydrogen production rate of about $575 \, mmol \, kg\text{-cat}^{-1} \, s^{-1}$ and methanol conversion of about 73 mol% is achieved at the reaction temperature of 300 °C. No CO formation is detected on the novel catalyst.

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