# Study on Aluminum Plates Coated with a Zirconia-sol and Catalyst Mixture for Methanol Steam-reforming in a Rectangular Reactor

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A reformer needs to be compact and to respond quickly to load fluctuations. To improve the heat transfer characteristics in a reactor with a desired catalyst loading, a rectangular reactor equipped with aluminum plates was designed for methanol steam-reforming and its performance was investigated. The aluminum plates were coated with a zirconia-sol and catalyst mixture. The coated plates exhibited a good adherence with the substrate over the course of reaction if the coated catalysts were below $0.0109 g/cm^2$. As expected, the rectangular rector exhibited excellent heat-transfer capability as compared to a traditional tubular reactor.

## 1. Introduction

Catalytic production of hydrogen by steam reforming of methanol is an attractive option for use in the decentralized production of clean electrical energy from fuel cells. Methanol fuelled solid polymer fuel cell systems are promising candidates for stationary and mobile applications as in passenger cars. Thus, steam reforming of methanol has been extensively studied to produce hydrogen for proton-exchange membrane fuel cells (PEMFCs). In hydrogen production by steam reforming of methanol or other hydrocarbons, the reactions involve a relatively large amount of endothermic reaction energy, thus requiring a reduction of the thermal time constant for an efficient supply of heat energy. Accordingly, the reformer needs to be compact and to respond quickly to load fluctuations. Present methanol reformers are usually of the packed-bed type, which poses 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 a packed-bed reactor. The plate reactor systems could be adopted to achieve an efficient transfer of thermal energy by conductional heat transfer, a rapid response to fluctuating loads by a lower pressure loss, and a downsizing of the reactor dimensions. The heat-transfer capability of the coated catalyst (commercial $Cu/ZnO/Al_2O_3$ catalyst, MDC-3) plates in a rectangular reactor was examined in this work. Kinetic behaviors collected in the experiments were to be compared with that predicted by the trademark kinetic model proposed by Peppley et al. (1999).

## 2. Experimental

### 2.1 Rectangular Reactor Design

The schematic diagram of the designed rectangular reactor including the cover plate and the catalyst plate is shown in Figure 1. Its spatial plot is depicted in Figure 2. Water and methanol are fed into the reactor from the left corner port. The product stream leaves the reactor from the right corner port. The flow pattern is guided by the weir deposited along the reactor. A total volume of 26 cm$^3$ in the reactor is available.
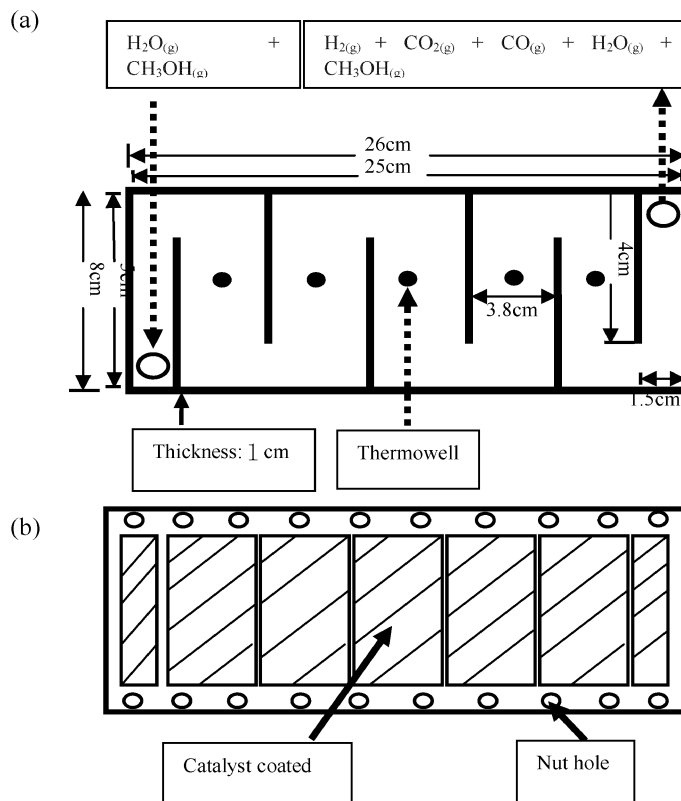


Figure 1. Schematic diagram of the rectangular reactor: (a) cover plate; (b) catalyst plate.

### 2.2 Catalyst coating

A commercial copper-containing reforming catalyst (MDC-3) from Süd-Chemie (approximately 45 wt.% Cu) was used for the methanol reforming reaction. In order to coat the catalyst, a zirconia sol solution was used Lim et al. (2005). Zirconia is a ceramic material that has superior adhesive properties to other ceramics in high-temperature combustion reactions. 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 (<10μm) was mixed
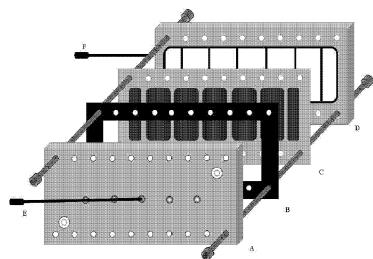
*Figure 2. Spatial diagram of the rectangular reactor: (A) cover plate; (B) packing; (C) catalyst plate; (D) fixing frame; (E) and (F) thermocouple.*

with 0.07 g of zirconiasol to give a 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 1ml isopropyl alcohol to 200 μl of zirconia-sol solution (material A). The zirconia-sol solution was ball-milled 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, 1ml diluted zirconiasol solution (material B), and 1ml isopropyl alcohol before being ball-milled 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 with the same method and dried at 70 °C for 6 h. The process was repeated to give the desired weight of the catalyst and the assembly was then calcined at 400 °C for 2 h. The coated catalyst weight for the catalyst plate (110 cm$^2$) was 0.2-1.2 g . When the catalyst loading was in excess of 1.2g, the cracking phenomenon of the coated catalysts over the plate was observed; therefore, the maximum catalyst loading adopted was 1.2g over the aluminium plate (110 cm$^2$).

## 2.3 Methanol Steam Reforming

A reforming reaction takes place between methanol and water to produce hydrogen, carbon dioxide and carbon monoxide. The three major reactions for the methanol-steam reforming, described by Peppley et al. (1999), are (a) Methanol-steam reforming reaction (MSR), (b) Methanol decomposition reaction (MD), and (c) Water-gas shift reaction (WGS). Measurements of the methanol–steam reforming reaction were performed at atmospheric pressure in the rectangular reactor as shown in the schematic diagram of the experimental apparatus (Fig. 1). A commercial CuO/ZnO/Al$_2$O$_3$ catalyst from Süd-Chemie (approximately 45 wt.% Cu) was used in all experiments. The reactor was placed in a furnace system (HTF55322A, LINDBERG/BLUE) in which the temperature of the reactor was regulated by the PID control of the heaters located in the furnace. The reactants, water, and methanol (purity = 99.8%) were introduced into the reactor at a molar ratio of 1. Prior to the activity measurements, the catalyst plate was activated at 250 °C in the reaction mixture. At the end of the catalyst reduction, the desired feed rates were applied to the reactor. Product analysis began with the separation of water and methanol from the rest of the product stream. The separation was achieved by passing the exhaust gases through the cold traps, and non-condensed product gases (CO, CO$_2$, and H$_2$) were separated from the unreacted water and methanol. The dry effluent gases were analyzed using a 15 ft. × 1/8 in. stainless steel (2.1 mm ID)

60/80 Carboxen -1000 column in a China GC 8900V equipped with a thermal conductivity detector. Helium was used as carrier gas. Though this column could detect the components $H_2$, CO, $CO_2$, $O_2$, $N_2$, $CH_4$, ethylene, and ethane, only the peaks of $H_2$, CO, $CO_2$, and $CH_4$ were found in the analysis. To determine the gas composition in the product, the calibration curves were built for $H_2$, CO, and $CO_2$ on the basis of the gas standards.

To carry out the designed experiments that followed, the mass balance around the reactor was first examined by comparing the estimated and measured methanol and water molar flow rates leaving the condenser in six experiments, in which the reacting temperature was kept at 250℃. The metering pump was calibrated by weighting the collected condensate from the condenser in due time while the reactor was packed with aluminum beads (inert) to simulate the actual catalyst packing condition. The reactor was operated at 250℃, and the condenser was kept at -5℃~0℃(the operating temperature was chosen to prevent the mixture of methanol and water from freezing and plugging the condenser).

### 2.4 Reference Kinetic Model

The experimental data in this study were compared with the packed-bed reactor (PBR) simulation on the basis of the kinetic model proposed by Peppley et al. (1999). Such a comparison may reveal the differences between the experimental results and the reference kinetic performance of steam reforming of methanol over a $Cu/ZnO/Al_2O_3$ catalyst.

## 3. Results and Discussion

### 3.1 Heat Transfer Performance of the Rectangular Reactor

Figure 3 gives the experimental results for the inside and outside temperature measurements of the catalyst plate (0.58-1.2g catalysts/110cm$^2$) of the rectangular reactor. Nitrogen gas flow passed through the plate catalyst. The temperature of the reactor was regulated by the PID control of the heaters located in the furnace. A maximum temperature difference $(T_o-T_i)$ of about 4℃ was achieved ($T_o$ and $T_i$ are the outside and inside temperatures across the catalyst plate). This was the expected result based on a plate catalyst design in which the thermal resistance was mainly attributed to the aluminium plate adopted for coating the catalysts.

### 3.2 Kinetic Performance of the Plate Catalyst in the Rectangular Reactor

The kinetic performance indices methanol conversion ($X_m$), hydrogen yield ($Y_{H_2}$), and selectivity of CO ($S_{CO}$) are defined as:

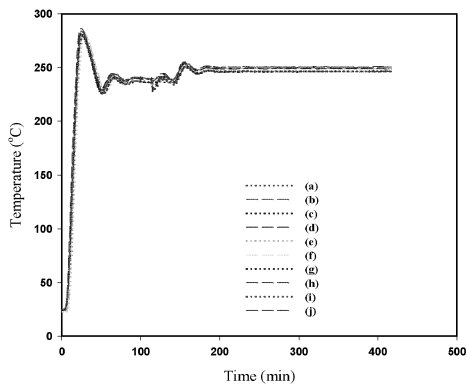$$X_m = 100\left(1 - \frac{F_{CH_3OH}}{F^0_{CH_3OH}}\right) \tag{1}$$

*Figure 3. Inside and outside temperature time profiles of the catalyst plate in the rectangular reactor with different catalyst loadings. (a)-$T_i$, (b)-$T_o$ ($w_c$=0.58g ); (c)-$T_i$, (d)-$T_o$ ($w_c$=0.58g ); (e)-$T_i$, (f)-$T_o$ ($w_c$=1.002g ); (g)-$T_i$, (h)-$T_o$ ($w_c$=1.2g ); (i)-$T_i$, (j)-$T_o$ ($w_c$=1.2g ).*

$$Y_{H_2} = 100 \left( \frac{F_{H_2}}{2F_{CH_3OH}^0 + F_{H_2O}^0} \right) \qquad (2)$$

$$S_{CO} = 100 \left( \frac{F_{CO}}{F_{CO} + F_{CO_2}} \right) \qquad (3)$$

The corresponding kinetic behavior (conversion of methanol, yield of hydrogen, and selectivity of CO) are shown in Figs 4-6, respectively. As shown in Figure 4, the conversion of methanol rises with the increase of $W_C / F_{CH_3OH}^0$. The simulated data based on the model of Peppley et al. (1999) seems to be a maximal conversion achievable. The performance of each catalyst plate is inferior to that predicted by the simulated data. The space between the cover plate and catalyst plate may impose mass transfer resistance, especially in case of the minimal coated catalyst plates (0.58g/110cm$^2$). For the performance of CO selectivity, one can observe that the simulated data for packed catalysts achieve a minimal selectivity of CO. The catalyst plates (1.0 and 1.2g over a 110cm$^2$ plate) present a similar performance of CO selectivity as shown in Figure 5. For hydrogen yield, the catalyst plate (1.2g over a 110cm$^2$ plate) exhibits a performance close to that of the simulated packed catalysts as shown in Figure 6.

## 4. Conclusions

The rectangular reactor equipped with the plate catalyst manifests an excellent heat-transfer characteristic. A maximum of 0.0109g/cm$^2$ catalysts can be coated on the catalyst plate. Compared with the ideal packed catalysts reactor simulation based on the model of Peppley et al. (1999), the plate catalyst (1.2g/110cm$^2$) performs equally well in turns of the methanol conversion, hydrogen yield, and selectivity of CO.

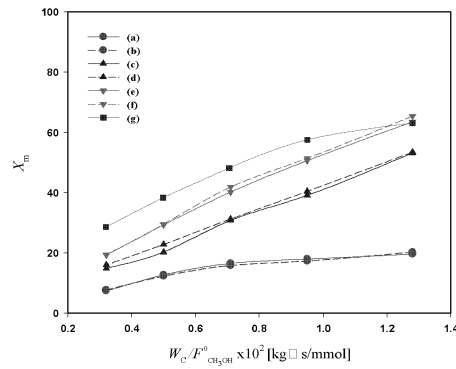*Figure 4. Methanol conversion as a function of $W_C / F^0_{CH_3OH}$ ratio for different catalyst loadings. (a), (b): 0.58g; (c), (d): 1.002g; (e), (f): 1.2g; (g): simulated data (left).*

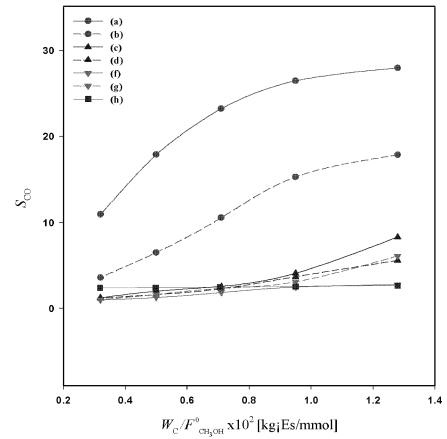*Figure 5. CO selectivity as a function of $W_C / F^0_{CH_3OH}$ ratio for different catalyst loadings. (a), (b): 0.58g; (c), (d): 1.002g; (e), (f): 1.2g; (g): simulated data (right).*



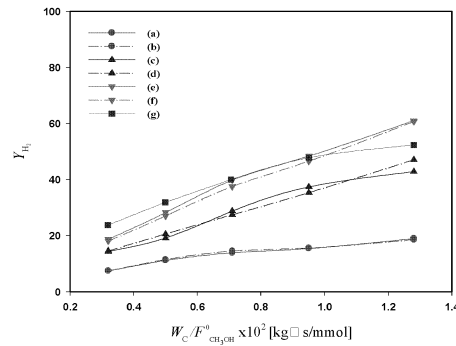*Figure 6. Hydrogen yield as a function of $W_C / F^0_{CH_3OH}$ ratio for different catalyst loadings. (a), (b): 0.58g; (c), (d): 1.002g; (e), (f): 1.2g; (g): simulated data.*

## References

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Peppley B. A., Amphlett J. C., Kearns L. M., Mann R. F., 1999, Methanol-steam reforming on Cu/ZnO/Al$_2$O$_3$ catalysts. Part 2. A comprehensive kinetic model, Appl. Catal. A: Gen., 79, 31-49.