

# CATALYST COMBINATION STRATEGY FOR HYDROGEN PRODUCTION FROM METHANOL PARTIAL OXIDATION WITH SPRAYS

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## ABSTRACT

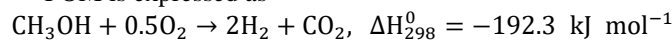
This study presents the hydrogen production from partial oxidation of methanol (POM) under sprays and dual-catalyst bed. In the experiment, two different catalysts of h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> and h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> with low Pt and Pd contents (0.2 wt%) are utilized. The effects of different preheating temperatures (100, 150, 200, 250, 300 °C), O<sub>2</sub>-to-methanol molar (O<sub>2</sub>/C) ratios (0.4-0.8), and Pt/Pd ratios (0:1, 1:2, 1:4, 1:9) on POM are also examined. The results show that a preheating temperature as low as at 100 °C can lead the Pd catalyst to trigger a POM reaction. Nevertheless, there is no significant effect on performance with increasing preheating temperature. Because of the autothermal property from the Pt catalyst during POM, it can be used to replace the preheating system in this study. The Pt catalyst is placed as the upper layer to provide heat for the Pd catalyst layer. The maximum H<sub>2</sub> yield (1.61 mol (mol methanol)<sup>-1</sup>) is observed at O<sub>2</sub>/C=0.6. In this study, reducing the amount of the Pt catalyst does not significantly affect POM performance. The methanol conversions are close to 100% and H<sub>2</sub> yield is from 1.55 to 1.57 mol (mol methanol)<sup>-1</sup>. Overall, POM can be triggered by preheated h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> or by a dual-catalyst bed (h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> and h-BN-Pt/Al<sub>2</sub>O<sub>3</sub>) without preheating to produce hydrogen. It is noteworthy that the POM performed by a dual-bed catalyst together with a small amount (3g) of Pt catalyst can achieve a similar CH<sub>3</sub>OH conversion and hydrogen production to that which use a full Pd catalyst with preheating.

**Keywords:** Partial oxidation of methanol (POM); Sprays; Dual-catalyst bed; Noble-metal catalyst; hydrogen production.

## 1. INTRODUCTION

Partial oxidation is an exothermic reaction, meaning that the reaction can be triggered without additional heating. When platinum-based (Pt-based) catalysts are used, partial oxidation of methanol (POM) can be cold started. Partial oxidation reactions have the advantage of requiring a shorter start-up time for reaction in the reactor.

POM is expressed as



To proceed with hydrogen production with higher flexibility, dual catalyst bed setups have been developed to enhance the H<sub>2</sub> yield from fuel processing. A dual-catalyst beds reactor (Pt/Al<sub>2</sub>O<sub>3</sub> and Ni-MgO) was also investigated for its use in partial oxidation and reforming of DME to produce hydrogen Zhang et al. [1]. They indicated that the H<sub>2</sub> yield was much higher through the dual-catalyst beds reactor than through the single catalyst bed process.

The reviewed literature suggests that both Pt-based and Pd-based catalysts can be applied in POM for hydrogen production. However, the difference between the two catalysts is that the Pt-based catalysts can trigger POM from a cold start, whereas the Pd-based catalysts cannot [2]. In other words, a preheating stage is required when the Pd-based catalysts are utilized for POM. However, the price of the former is higher than the latter. Based on the aforesaid information, a strategy of catalyst bed combining the two types of catalyst, namely, the dual-catalyst bed, is conducted. Moreover, the knowledge about the effects of preheating and different ratios of Pt/Pd in the dual-bed is absent, especially in a spray system. For this reason, a comprehensive study of

POM with sprays is carried out. POM triggered in an h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst bed is first investigated where the influence of preheating temperature of the catalyst bed on POM is evaluated. Then, the dual-catalyst bed with the addition of an h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at the top of the h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst is constructed. The h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, which can trigger POM at room temperature, is employed to provide heat for the h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst further driving POM. Accordingly, the preheating unit in the system is replaced by the Pt-based catalyst. On account the high cost of Pt compared to Pd, this study also aims to reduce the usage amount of h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for future economic applications.

## 2. MATERIALS AND METHODS

### 2.1 Reaction system

The overall experimental system was divided into four units: the feeding unit, the reaction unit, the gas treatment unit, and the gas analysis unit. The schematic of the experimental setup is presented in **Fig. 1**.

To ascertain the measurement quality, two electric flow rate controllers were calibrated by a flow rate meter (Gillan-Stander Flow Cell-P/N 800266-1). The GA was calibrated by nitrogen (99.9%) to establish a zero point, followed by a standard gas (CO: 29.98 vol%; CO<sub>2</sub>: 20.12 vol%; CH<sub>4</sub>: 11150 ppm; and N<sub>2</sub>: balance). For the GC equipped with a thermal conductivity detector (TCD) and an auto-sampling system (VICI, E310UWT-110), a calibration curve in terms of four gas mixtures of H<sub>2</sub> and N<sub>2</sub> (the H<sub>2</sub> concentrations were 10, 15, 20, and 25 vol%) was established to measure the H<sub>2</sub> concentration in the product gas

### 2.2 Experimental procedure

The experiments were divided into three parts: (1) using a single catalyst bed of h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> with preheating; (2) using a dual-catalyst bed with 50 wt% h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> and 50 wt% h-BN-Pd/Al<sub>2</sub>O<sub>3</sub>; and (3) using the dual-catalyst bed with different weight ratios of the catalysts. In the first part, the h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst bed was preheated to five different temperatures of 100, 150, 200, 250, and 300 °C. The oxygen-to-methanol molar (O<sub>2</sub>/C) ratio was 0.5 for the case of single h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst bed with preheating. In the second part with the dual-catalyst bed, the total amount of the catalysts for POM was fixed at 30 g, and five different O<sub>2</sub>/C ratios of 0.4, 0.5, 0.6, 0.7, and 0.8 were regarded. The flow rates of oxygen and methanol at the five O<sub>2</sub>/C ratios are listed in **Table 1**. In the third part, the total

amount of the catalysts was also fixed at 30 g. Four different catalyst ratios (Pt:Pd) of 1:0, 1:2, 1:4, and 1:9 were considered. In all experiments, a mixture of air and N<sub>2</sub> were used with a total flow rate of 5417 mL min<sup>-1</sup> and the methanol flow rate was controlled at 1 mL min<sup>-1</sup> (at room temperature).

The flow rate of the product gas was measured by the flow rate meter. Based on the flow rate and the CO, CO<sub>2</sub>, and CH<sub>4</sub> concentrations, methanol conversion is calculated by:

$$\text{CH}_3\text{OH conversion (\%)} = \left( \frac{\dot{n}_{\text{CO}_2, \text{out}} + \dot{n}_{\text{CO}, \text{out}} + \dot{n}_{\text{CH}_4, \text{out}}}{\dot{n}_{\text{CH}_3\text{OH}, \text{in}}} \right) \times 100 \quad (2)$$

where  $\dot{n}$  designates the molar flow rate (mol min<sup>-1</sup>), and the subscripts *in* and *out* represent the inflow and outflow, respectively. Meanwhile, the H<sub>2</sub> yield from POM is estimated from the molar flow rate of H<sub>2</sub> (mol min<sup>-1</sup>),  $\dot{n}_{\text{H}_2}$ , as the following:

$$\text{H}_2 \text{ yield (mol/mol CH}_3\text{OH)} = \left( \frac{\dot{n}_{\text{H}_2}}{\dot{n}_{\text{CH}_3\text{OH}}} \right) \quad (3)$$

### 2.3 Catalysts characterization

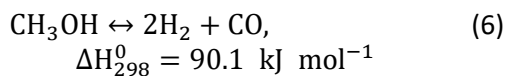
Catalysts play a pivotal role in methanol conversion and hydrogen production. Two commercial catalysts (Green Hydrotech Inc.) of h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> and h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> were utilized to elicit POM. The two catalysts were spherical in shape and had a diameter of 5 mm. X-ray diffraction (XRD, PANalytical X'Pert PRO), the peaks of Pd developed at 2θ= 45.88 and 67.26°, and those of Al<sub>2</sub>O<sub>3</sub> developed at 2θ=19.98, 37.34, 43.06, 45.88, and 67.26°. The peaks of Pt developed at 2θ= 37.28, 45.78, and 67.38°, while the peaks of Al<sub>2</sub>O<sub>3</sub> are exhibited at 2θ= 20.1, 37.28, 43.04, 45.78, and 67.38°. These angles are consistent with the observations of Huang et al. [3], Taṭa et al. [4], Banerjee et al. [5], and Sathish et al. [6].

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of preheating

H<sub>2</sub> yield and CH<sub>3</sub>OH conversion are two crucial indexes of the performance of POM. To figure out the performance of POM under various preheating temperatures, the profiles of H<sub>2</sub> yield and CH<sub>3</sub>OH conversion are plotted in **Fig. 2a**. The H<sub>2</sub> yield is in the range of 1.53-1.58 mol (mol methanol)<sup>-1</sup>, and the maximum H<sub>2</sub> yield, namely, 1.58 mol (mol methanol)<sup>-1</sup>, appears at the preheating temperature of 200 °C. In the five cases, the lowest CH<sub>3</sub>OH conversion is 86% at a preheating temperature of 150 °C. The reaction

temperature is the lowest and therefore the conversion of CH<sub>3</sub>OH is at minimum. When the preheating temperature is higher at 300 °C, the methanol drops on the catalyst bed could be directly decomposed. The methanol decomposition reaction is expressed as the following:



The highest CH<sub>3</sub>OH concentration was 94% achieved at the preheating temperature of 300°C. It is noteworthy to mention that when the h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst is preheated at 200 °C and 300 °C, the CH<sub>3</sub>OH conversion can be achieved at around 95%. Based on the results of H<sub>2</sub> yield, the best preheating temperature is at 200 °C.

### 3.2 Effect of O<sub>2</sub>/C ratio with dual-bed catalyst

CH<sub>3</sub>OH conversion and the H<sub>2</sub> yield are two crucial indexes to indicate the performance of POM, and their profiles at O<sub>2</sub>/C = 0.4-0.8 are presented in **Fig. 2b**. When the O<sub>2</sub>/C ratios are 0.4 and 0.5, the values of the CH<sub>3</sub>OH conversion are 53.9% and 76.9%, respectively. In contrast, the CH<sub>3</sub>OH conversion is almost 100% at O<sub>2</sub>/C = 0.6-0.8. The lower CH<sub>3</sub>OH conversion at O<sub>2</sub>/C = 0.4 and 0.5 is resulting from less oxygen supply for POM. On the other hand, the higher O<sub>2</sub>/C ratios render higher reaction temperatures and give rise to consuming more methanol, which is responsible for the high CH<sub>3</sub>OH conversion. As for the H<sub>2</sub> yield, it is in the range of 0.5-1.61 mol (mol methanol)<sup>-1</sup>, with the maximum H<sub>2</sub> yield of 1.61 mol (mol methanol)<sup>-1</sup> occurred at O<sub>2</sub>/C = 0.6. This shows that the Pd catalyst blended with 50wt% of Pt catalyst has a better performance in POM for H<sub>2</sub> production than Pd alone. In summary, O<sub>2</sub>/C = 0.6 is the best operating condition for POM with Pt and Pd catalysts.

### 3.3 Effect of Pt/Pd ratio with dual-bed catalyst

**Fig. 2c** shows the profiles of H<sub>2</sub> yield and CH<sub>3</sub>OH conversion with different Pt/Pd ratios. The H<sub>2</sub> yield ranges from 1.55 to 1.57 mol (mol methanol)<sup>-1</sup>. The highest H<sub>2</sub> yield (1.57 mol (mol methanol)<sup>-1</sup>) appears at a Pt/Pd ratio of 1:2. For these four cases, the CH<sub>3</sub>OH conversions are almost 100%. This means that the decrease of Pt amount does not affect the performance of POM reaction. Overall, it is feasible to use Pt catalyst instead of heating tape and reduce the amount of Pt to

carry out POM reaction when the reduction of Pt does not have significant effect towards the reaction. In other word, using 3 g of Pt catalyst is able to achieve the similar effect as the preheating of 27 g of Pd catalyst. Based on this observation, the amount of Pt catalyst can be reduced with blending Pd catalyst and the performance is almost the same. On the other words, it implies that the cost of catalyst is also reduced.

## 4. CONCLUSIONS

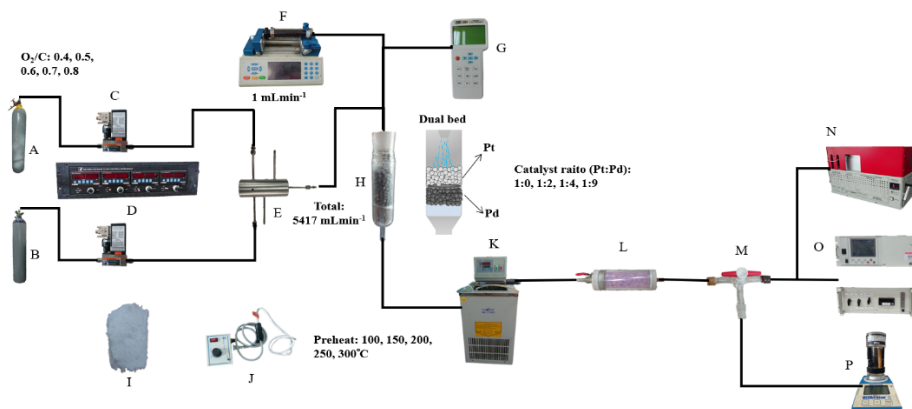
The results indicate that POM can be triggered by a preheated h-BN-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst or by a Pt/Pd dual-catalyst bed. The POM reaction reaches a steady state after 20 min by the preheated Pd catalyst. The preheated Pd catalyst at 200 °C shows the maximum H<sub>2</sub> yield of 1.58 mol (mol methanol)<sup>-1</sup> and a CH<sub>3</sub>OH conversion up to 94%. In addition, using the h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> in a dual-catalyst bed system with the Pd catalyst is a feasible option to replace the preheating system. In this case, the temperature of the h-BN-Pt/Al<sub>2</sub>O<sub>3</sub> layer was always higher than h-BN-Pd/Al<sub>2</sub>O<sub>3</sub>. The optimum O<sub>2</sub>/C ratio for maximizing CO production develops at 0.6 in that a higher O<sub>2</sub>/C ratio (≥0.7) leads to combustion mechanism favored over oxidation. Almost 100% CH<sub>3</sub>OH conversion is obtained when O<sub>2</sub>/C ratio ≥0.6. In the cases of different Pt/Pd ratios, it is worth mentioning that the CH<sub>4</sub> concentration decreases from 1610 ppm to 814 ppm with increasing the amount of Pd catalyst. The H<sub>2</sub> yield (1.55 to 1.57 mol (mol methanol)<sup>-1</sup>) and CH<sub>3</sub>OH conversion (close to 100%) are not affected by decreasing the amount of Pt used in the dual-bed. This implies that using a small amount of Pt catalyst (3 g) without preheating can achieve similar results with the full Pt catalyst cases with preheating except for temperature. Based on this observation, the preheating system for POM can be removed with adding only a small amount of Pt catalyst which in turn further reduces the cost of the system setup.

## ACKNOWLEDGEMENT

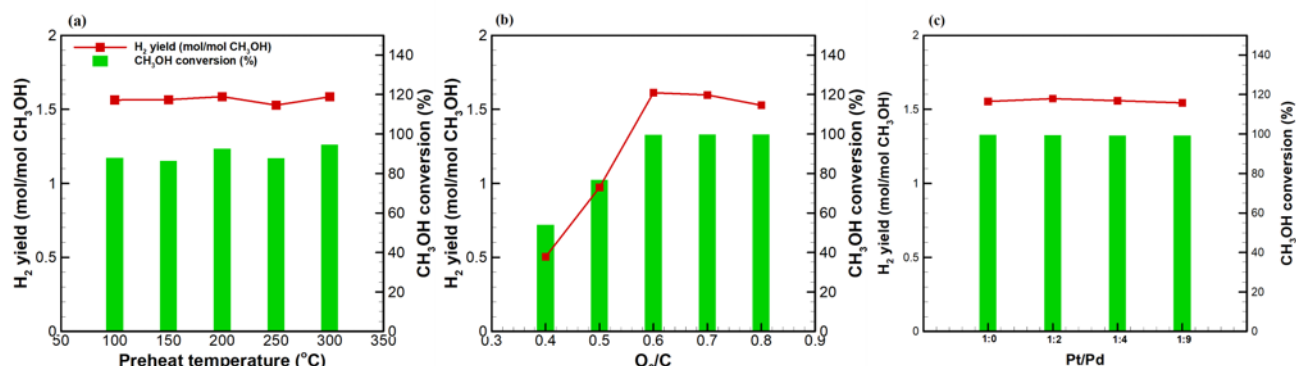
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**Table 1** Volumetric flow rates of feed gas, air, and N<sub>2</sub> (at room temperature).

O <sub>2</sub> /C	Feed gas (Air+N <sub>2</sub> ) (mL min <sup>-1</sup> )	Air (mL min <sup>-1</sup> )	N <sub>2</sub> (mL/min <sup>-1</sup> )
0.4	5417	1167	4250
0.5	5417	1458	3959
0.6	5417	1750	3667
0.7	5417	2042	3375
0.8	5417	2333	3084



**Fig. 1** A schematic view of the experimental system (A: N<sub>2</sub> cylinder; B: air cylinder; C: electric flow rate controller; D: controller readout; E: gas mixer; F: syringe pump; G: thermometer; H: reactor; I: refractory wool; J: heating tape; K: condenser; L: dryer; M: triage valves; N: gas chromatography; O: gas analyzer; P: flow rate meter).



**Fig. 2** Profiles of H<sub>2</sub> yield and CH<sub>3</sub>OH concentration at (a) different preheating temperatures, (b) different O<sub>2</sub>/C ratios and (c) different Pt/Pd ratios.

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