

The effect of CO<sub>2</sub> feed rate on chemical reaction dynamics of dry reforming of CH<sub>4</sub>

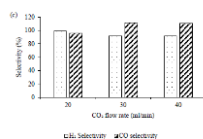
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## GRAPICAL ABSTRACT



## ABSTRACT

The threats of global warming to humanity is a pressing issue that receives tremendous attention, particularly after the 21st session of the Conference of the Parties (COP-21). In view of this, CO<sub>2</sub> reforming of CH<sub>4</sub> (dry reforming) was investigated in current study. The effect of CO<sub>2</sub> feed rate on dry reforming reaction catalysed by CoAl<sub>2</sub>O<sub>4</sub> was determined. The dry reforming reaction was evaluated based on CH<sub>4</sub> conversion and the rate of carbon deposition on catalyst. It was found that the feed rate of CO<sub>2</sub> had insignificant effect on CH<sub>4</sub> conversion. However, the increased of CO<sub>2</sub> feed rate was determined to be effective in mitigating the carbon deposition rate.

Keywords: carbon dioxide, methane, dry reforming, CoAl<sub>2</sub>O<sub>4</sub>, catalyst

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## 1. INTRODUCTION

High anthropogenic emission of greenhouse gases such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) into the atmosphere has largely contributed to the acceleration of global warming [1]. On account of that, research on CO<sub>2</sub> reforming of CH<sub>4</sub> (dry reforming) for the production of synthesis gas (hydrogen (H<sub>2</sub>) and carbon monoxide (CO)) (equation 1) has been viewed as a promising pathway to reduce the atmospheric concentrations of CO<sub>2</sub> and CH<sub>4</sub>.



Additionally, the syngas produced from dry reforming can be used as a raw material for the synthesis of a valuable liquid hydrocarbon through Fisher-Tropsch reaction [2]. However, despite the advantages of dry reforming, this process is yet to be industrialized due to the unwanted carbon deposition which leads to reactor plugging and catalyst deactivation. The carbon deposition occurs as a results of two side reactions in dry reforming process, i.e. CH<sub>4</sub> cracking (equation 2) and Boudouard reaction (equation 3) [1, 3].



In addressing the challenge to resolve the carbon deposition problem in dry reforming, many researchers were focusing on the development of new catalyst or modification of present catalyst by additional of doping materials or surface modifications [4-6]. However, the effect of process parameters such as gas feed rate and reaction temperature cannot be ruled out in influencing the chemical reaction dynamics of dry reforming. In this study, the effect of CO<sub>2</sub> feed rate was investigated. The dry reforming reaction was evaluated based on CH<sub>4</sub> conversion and rate of carbon

formation on CoAl<sub>2</sub>O<sub>4</sub> catalyst. The influence of side reactions on dry reforming caused by varying CO<sub>2</sub> feed rate was also discussed.

## 2. MATERIALS AND METHODS

## 2.1 Materials

All the chemical reagent used are of analytical grade. These chemicals include Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck, Malaysia), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck, Malaysia) and citric acid (Fisher, Malaysia). Deionized water was used during the synthesis of catalyst.

## 2.2 Catalyst preparation

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were used as the metal precursors and citric acid was used as chelating agent. CoAl<sub>2</sub>O<sub>4</sub> catalysts with Co:Al mole ratio of 1:2 were prepared using sol-gel method. Precisely, 0.05 mol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.10 mol of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.30 mol of citric acid were dissolved in 50 ml of deionized water. The molar ratio of metal ions to citric acid was 1:2. The mixture was stirred continuously and aged for 1 h followed by heating at 80 °C until it formed a xerogel. Then, the obtained gel was dried in an oven at 90 °C for 48 h. The dried gel was calcined at 500 °C with rate of 10 °C/min for 5 h, cooled to room temperature and finally grounded to powder form.

## 2.3 Catalyst characterizations

The surface structure of the CoAl<sub>2</sub>O<sub>4</sub> catalysts was characterized using transmission electron microscopy (TEM; Philips, model CM12) and field emission-scanning electron microscopy (FE-SEM; Supra-35VP). The N<sub>2</sub> adsorption/desorption analysis was performed at -196 °C with a

Micrometrics ASAP 2020 instrument. Structural analysis which included the chemical phases, and components of the catalysts were performed by X-ray diffraction (XRD), using a Siemens D5000 X-ray diffractometer with CuK $\alpha$  radiation operated at 40 kV and 40 mA in diffraction range ( $2\theta$ ) of  $20^\circ$  to  $90^\circ$  and a scanning rate of  $0.015^\circ/\text{s}$ . For the quantification of carbon deposited on catalyst after dry reforming reaction, thermogravimetric analysis (TGA) were conducted on the used catalyst using SDT Q600 TA-instrument.

## 2.4 Dry reforming of CH<sub>4</sub>

The dry reforming reaction experiments were conducted in a vertical stainless-steel reactor (ID: 12 mm and L: 400 mm), which was heated in a tubular furnace under atmospheric condition. A type-K thermocouple was fixed in the reactor to monitor the temperature of the gasses. In the experiment, 200 mg of synthesized catalyst was placed on top of quartz wool in the middle of the reactor. The reactant feed gas consists of CH<sub>4</sub> (99.99%, Air Product Co.) and CO<sub>2</sub> (99.99%, Air Product Co.) was controlled by two mass flow controllers (MKS, PR 4000). The product gas from the reactor was analyzed with an online gas chromatograph (GC, Agilent 7890N) equipped with a thermal conductivity detector (TCD). Argon was used as the carrier gas. The effect of different CO<sub>2</sub> feed rate (20, 30 and 40 ml/min) on CoAl<sub>2</sub>O<sub>4</sub> catalyst activity was examined at 750 °C for 8 h, with CH<sub>4</sub> flow rate of 20 ml/min under atmospheric pressure. Before undergoing dry reforming reaction, CoAl<sub>2</sub>O<sub>4</sub> catalyst were reduced at 750 °C for 3 hours.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of catalysts

SEM analysis was performed to examine the surface morphology of CoAl<sub>2</sub>O<sub>4</sub> catalysts. Fig. 1 (a) illustrates the CoAl<sub>2</sub>O<sub>4</sub> catalyst as irregular spongy agglomerates. Upon closer examination as shown in Fig 1 (b), we observed that the agglomerates were formed from fine particles. TEM micrograph illustrated in Fig. 2 reveals the nanostructure of the fine particles observed in SEM micrographs (Fig. 1 (a) and (b)).

The pore geometry of the CoAl<sub>2</sub>O<sub>4</sub> catalyst was analyzed by N<sub>2</sub> adsorption-desorption method. The N<sub>2</sub> adsorption-desorption isotherms of CoAl<sub>2</sub>O<sub>4</sub> are displayed in Fig. 3 The isotherms can be classified as type IV(a), indicating the adsorption-desorption behavior of typical conical and cylindrical mesopores with pore width exceeds a certain critical width [7]. Furthermore, the CoAl<sub>2</sub>O<sub>4</sub> catalyst exhibited hysteresis loop of type H1 at P/P<sub>0</sub> range of 0.7 -1.0, which is commonly found in uniform mesoporous materials [7].

Structural properties of the developed catalysts were investigated by XRD. Fig. 4 displays the XRD patterns of CoAl<sub>2</sub>O<sub>4</sub> catalysts. All the diffraction peaks were fitted perfectly with CoAl<sub>2</sub>O<sub>4</sub> (PDF 01-082-2252).

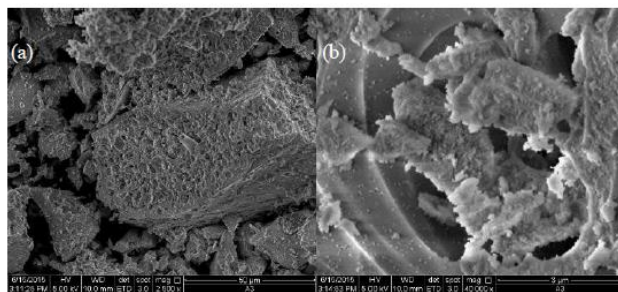


Fig. 1 (a) and (b) SEM micrographs of CoAl<sub>2</sub>O<sub>4</sub> catalyst

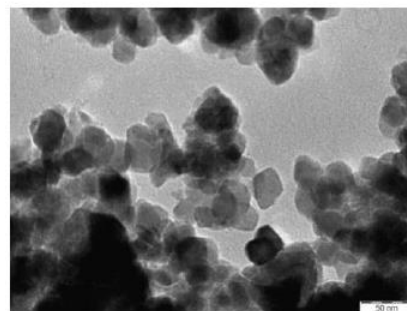


Fig. 2 TEM micrograph of CoAl<sub>2</sub>O<sub>4</sub> catalyst

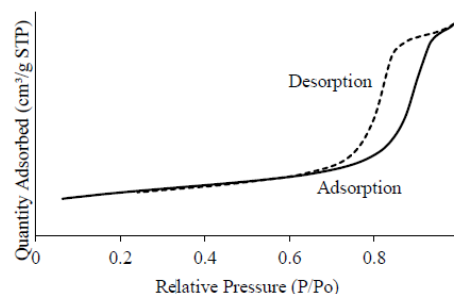


Fig. 3 Isotherm linear plot of CoAl<sub>2</sub>O<sub>4</sub> catalyst

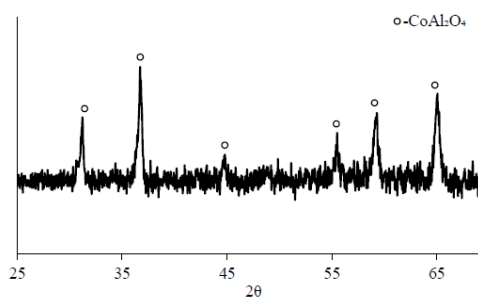
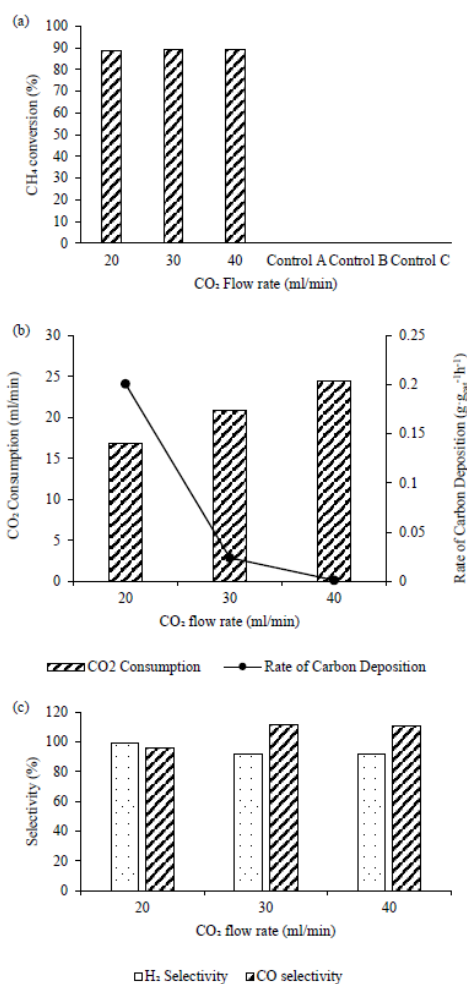


Fig. 4 XRD of CoAl<sub>2</sub>O<sub>4</sub> catalyst

### 3.2 Effect of CO<sub>2</sub> feed rate on Dry reforming of CH<sub>4</sub>

The investigation on the effect of CO<sub>2</sub> feed rate on the dry reforming of CH<sub>4</sub> and the rate of carbon deposition were conducted over the developed CoAl<sub>2</sub>O<sub>4</sub> catalyst under the reaction conditions mentioned in Section 2. To ensure the

products of reactions were stemmed from dry reforming of CH<sub>4</sub>, a series of control experiments (Control A, B, and C) were carried out under similar reaction environments with CO<sub>2</sub> feed rate = 20, 30, and 40 ml/min, respectively in the absence of CoAl<sub>2</sub>O<sub>4</sub> catalyst. The results of these control experiments as shown in Fig. 5. (a), suggested that CoAl<sub>2</sub>O<sub>4</sub> catalyst played indispensable roles in the reaction between CH<sub>4</sub> and CO<sub>2</sub>. Dry reforming reaction is unable to work without the presence of CoAl<sub>2</sub>O<sub>4</sub> catalyst.



**Fig. 5** (a) Conversion of CH<sub>4</sub> (b) CO<sub>2</sub> consumption of rate of carbon deposition (c) H<sub>2</sub> and CO selectivity against CO<sub>2</sub> feed rate.

Fig. 5 (a) shows the conversion of CH<sub>4</sub> on CoAl<sub>2</sub>O<sub>4</sub> catalyst under different CO<sub>2</sub> feed rate. Despite having different CO<sub>2</sub> feed rate, we observed that the amount of CH<sub>4</sub> converted stayed constant at around 89 % conversion for all the experiments with the presence of CoAl<sub>2</sub>O<sub>4</sub> catalyst. This degree of CH<sub>4</sub> conversion is similar to the simulated equilibrium conversion of CH<sub>4</sub> by Nikoo et al., 2011 [8] at the temperature of 750 °C. Thus, we concluded that the amount of CO<sub>2</sub> flow rate does not affect the dynamic equilibrium of dry reforming in term of CH<sub>4</sub> conversion.

On the other hand, the amount of CO<sub>2</sub> consumption is directly affected by the feed rate of CO<sub>2</sub>. As reflected in Fig. 5. (b), the higher the amount of CO<sub>2</sub> feed rate, the higher the amount of CO<sub>2</sub> consumed in dry reforming reaction. Based on equation 1, the ideal amount of CO<sub>2</sub> consumption in dry reforming reaction should be similar to the CH<sub>4</sub> consumption [9]. However, we observed the amount of CO<sub>2</sub> consumption recorded in the experiment where CO<sub>2</sub> flow rate = 20 ml/min is slightly lower than CH<sub>4</sub> consumption. It is hypothesized that the excess CH<sub>4</sub> consumption is due to CH<sub>4</sub> cracking reaction (equation 2) which resulted in the deposition of graphitized carbon on the catalysts [10]. The calculated carbon deposition rate on the catalyst in this set of reaction was 0.201 g<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>.

On the contrary, in the experiment where CO<sub>2</sub> flow rate = 30 and 40 ml/min, the amount of CO<sub>2</sub> consumption recorded was much higher than CH<sub>4</sub> consumed. The excess CO<sub>2</sub> consumption conversion was hypothesized to be converted into CO through reverse water gas shift (RWGS) reaction (equation 4) [11, 12]. The presence of RWGS reaction was further proven by examining the H<sub>2</sub> and CO selectivity shown in Fig. 5. (c). We observed that the H<sub>2</sub> selectivity of dry reforming experiment conducted at CO<sub>2</sub> feed rate = 30 and 40 ml/min was around 10 % lower than in the experiment conducted at CO<sub>2</sub> feed rate = 20 ml/min. Meanwhile, the selectivity of CO of dry reforming experiment conducted at higher CO<sub>2</sub> feed rate (30 and 40 ml/min) were around 10 % higher than that of experiment conducted at CO<sub>2</sub> feed rate = 20 ml/min. These observations pointed to the presence of RWGS reaction as this side reaction consumes the H<sub>2</sub> and CO<sub>2</sub> to produce CO and H<sub>2</sub>O. Accordingly, we deduced that around 10 % of the H<sub>2</sub> produced in the dry reforming reaction at CO<sub>2</sub> feed rate = 30 and 40 ml/min was consumed to produce additional 10 % of CO.



Fig. 5 (b) shows the rate of carbon deposition was significantly reduced with the increase of CO<sub>2</sub> feed rate. We observed that the carbon formation rate was decreased from 0.201, 0.024, to 0.001 g<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> when the CO<sub>2</sub> feed rate increase from 20, 30, to 40 ml/min. The reduction of carbon deposition rate was mostly due to increase of the carbon gasification rate through reverse Boudouard reaction (equation 3) initiated by the increase of CO<sub>2</sub> concentration.

#### 4. CONCLUSION

In summary, CoAl<sub>2</sub>O<sub>4</sub> is essential for the reaction of dry reforming while CO<sub>2</sub> feed rate greatly affects the reaction dynamics of the process. The experimental results revealed that the variation of CO<sub>2</sub> feed rate does not affect the conversion CH<sub>4</sub>. However, the rate of carbon formation was significantly reduced with the increase of CO<sub>2</sub> feed rate. These results provide insights into the mitigation of carbon

deposition and at the same time improving the efficiency utilizing CO<sub>2</sub> in dry reforming of CH<sub>4</sub>.

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