Plasma-catalytic dry reforming of CH$_4$ and CO$_2$: effect of different supported metal catalysts

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Abstract: Plasma-catalytic reforming of CH$_4$ and CO$_2$ over M/γ-Al$_2$O$_3$ catalysts (M = Ni, Co, Cu and Mn) has been carried out in a dielectric barrier discharge (DBD) reactor. The combination of plasma with the Ni and Mn based catalysts shows a synergistic effect and significantly enhances the conversion of CH$_4$ and energy efficiency of the process. However, the presence of any of these catalysts in the plasma did not show any synergy for CO$_2$ conversion.

Keywords: plasma-catalysis, dry reforming, dielectric barrier discharge, synthesis gas

1. Introduction

Catalytic dry reforming of methane and carbon dioxide has been regarded as a promising and attractive process which utilizes two abundant greenhouse gases as feedstock to produce value-added fuels and chemicals such as synthesis gas (syngas, H$_2$ and CO). In the past decades, significant efforts have been devoted to the design and development of novel catalysts to improve the conversion of CH$_4$ and CO$_2$ energy efficiently [1]. However, dry reforming of CH$_4$ and CO$_2$ using conventional catalytic methods still faces two major challenges that limit the use of this process on a commercial scale: firstly, high reaction temperature (>700 °C) is required to maintain reasonable conversions of reactants and yields of syngas since this is a very endothermic reaction and both reactants (CH$_4$ and CO$_2$) are very stable molecules, incurring a high energy cost; secondly, the formation of carbon deposition on the catalyst surface, causes rapid deactivation of catalysts, especially for non-noble metal catalysts [2].

Non-thermal plasma offers an attractive and promising alternative to thermal catalytic route for the conversion of CH$_4$ and CO$_2$ into value-added fuels and chemicals at atmospheric pressure and low temperatures [3]. Dry reforming of CH$_4$ and CO$_2$ for syngas production has been investigated using different plasma systems including dielectric barrier discharge (DBD) [4], gliding arc [5], corona discharge [6] and glow discharge [7]. However, the energy efficiency of the plasma process and selectivity towards target products are not satisfied in the absence of a catalyst. In addition to the production of syngas, noticeable amounts of C2-C4 and oxygenates were often produced [8].

The combination of non-thermal plasma and catalysis has been regarded as a promising and effective solution to overcome the drawback of plasma processes. Significant attention has been placed on the use of non-noble metal catalysts especially supported Ni and Co catalysts for thermal catalytic dry reforming of CH$_4$ and CO$_2$ due to their availability and low cost. Many of previous works have reported that both γ-Al$_2$O$_3$ supported Ni and Co catalysts show a considerable catalytic activity for dry reforming process, although Ni based catalysts showed a better activity than that of Co catalysts [9]. However, it was reported that Co/γ-Al$_2$O$_3$ catalyst had a better stability against temperature changes in thermal catalytic reactions [9]. The use of γ-Al$_2$O$_3$ supported Cu and Mn catalysts for catalytic dry reforming reactions at high temperatures has not been reported. Cu and Mn were usually used as an additive (e.g. promoter) to supported metal catalysts (e.g. Ni/γ-Al$_2$O$_3$) to suppress the deposition of carbon and to enhance catalyst stability [1]. In principle, those catalysts successfully demonstrated their activities in thermal catalytic dry reforming reactions are generally used as a starting point for plasma-catalytic dry reforming reaction. However, it is worth noting that catalysts showed poor activity in thermal catalytic reactions might work very well in plasma-catalytic processes. Up until now, only limited catalysts have been investigated in plasma-catalytic dry reforming processes, including Ni/γ-Al$_2$O$_3$ [2-3], Cu/γ-Al$_2$O$_3$ [3], Ni-Cu/γ-Al$_2$O$_3$ [3], Pd/γ-Al$_2$O$_3$ [8], Ag/γ-Al$_2$O$_3$ [8], La$_2$O$_3$/γ-Al$_2$O$_3$ [10] and zeolite [11]. The exploration of low cost and active catalysts is still not fully satisfied for plasma-catalytic reforming reaction. There are very limited works that evaluate the difference between two metal catalysts, while the plasma-catalytic dry reforming over different γ-Al$_2$O$_3$ supported non-noble metal catalysts (i.e. Ni, Co, Cu and Mn) has not been investigated and reported before. In addition, evaluating the effect of different metal phases on the performance of plasma-catalytic dry reforming process in terms of the conversion of reactants, the selectivity and yield of target products, as well as the energy efficiency of the plasma process, would enable us to get a better understanding of the synergistic effect resulted from the combination of plasma with different catalysts.

In this work, plasma-catalytic dry reforming of CH$_4$ and CO$_2$ over supported metal catalysts M/γ-Al$_2$O$_3$ (M = Ni, Co, Cu and Mn) has been investigated in a coaxial
DBD reactor at low temperatures. The influence of catalyst composition on the performance of the plasma reforming process has been evaluated in terms of the conversion of feed gases, the yield of major gas products, as well as the energy efficiency of the process.

2. Experimental

The experiments were carried out in a coaxial DBD reactor, as shown in Fig. 1. A stainless steel mesh (ground electrode) was wrapped over the outside of a quartz tube with an outer diameter of 22 mm and wall thickness of 1.5 mm, while a stainless steel rod with an outer diameter of 14 mm was placed in the centre of the quartz tube and used as a high voltage electrode. The length of the discharge region was 90 mm with a discharge gap of 2.5 mm. The DBD reactor was supplied by a high voltage AC power supply with a peak-to-peak voltage of 10 kV and a frequency of 50 Hz. The applied voltage was measured by a high voltage probe (Testec, HVP-15HF), while the current was recorded by a current monitor (Bergoz CT-E0.5). The voltage across the external capacitor (0.47 μF) was also measured. All the electrical signals were sampled by a four-channel digital oscilloscope (TDS2014). The Q-U Lissajous method was used to calculate the discharge power (P) of the DBD reactor.

10 wt.% M/γ-Al2O3 (M = Ni, Co, Cu, and Mn) catalysts were prepared by incipient wetness impregnation using nitrate salts (Alfa Aesar, 99.5%) as the metal precursor. The appropriate weight of support (γ-Al2O3) was added to the solution of nitrate salts. The slurry was continuously stirred at 80 °C for 4 h and then dried at 110 °C overnight, followed by calcination at 500 °C for 5 h. All the catalysts were pelletized and sieved to 20-40 meshes prior to plasma reaction. The reactant and reforming gas products were analyzed by a two-channel gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

3. Results and discussion

Fig. 2 shows the effect of γ-Al2O3 supported metal catalysts on the plasma dry reforming of CH4 and CO2. Compared to the plasma reforming reaction with no catalyst, the combination of plasma with the Ni/γ-Al2O3 and Mn/γ-Al2O3 catalysts significantly enhance the conversions of CH4 by 42% and 30%, respectively. However, the presence of the Co/γ-Al2O3 and Cu/γ-Al2O3 in the DBD reactor only improves CH4 conversion by 12% and 6%, respectively. The maximum CH4 conversion of 19.6% was achieved in the plasma-catalytic dry reforming over the Ni/γ-Al2O3 catalyst at a discharge power of 7.5 W and a gas flow rate of 50 ml min⁻¹. It is worth noting that the presence of these catalysts in the DBD reactor does not enhance CO2 conversion. This could be partly attributed to the enhanced water gas shift (WGS) reaction at low temperatures.

In this work, the temperature near the catalyst bed in the plasma reactor was below 150 °C. Since the theoretical conversions of CH4 and CO2 at thermodynamic equilibrium are less than 1% at a temperature of 300 °C [2]. We would expect that the dry reforming reaction at
150 °C has a very poor performance without plasma. These results show that the conversions of methane are significantly enhanced through the combination of plasma with the Ni/γ-Al₂O₃ or Mn/γ-Al₂O₃ catalysts, which is much higher than the sum of the reforming reaction using plasma-alone and catalysis alone, indicating a synergy of plasma-catalysis for CH₄ conversion. However, placing the Co and Cu based catalysts in the DBD reactor does not show a synergistic effect of plasma-catalysis. Furthermore, there is no synergy of plasma-catalysis obtained for the conversion of CO₂.

The combination of DBD with catalysts enhances the yields of CO and H₂. The Ni/γ-Al₂O₃ catalyst shows the best catalytic activity, followed by the Co/γ-Al₂O₃, Cu/γ-Al₂O₃ and Mn/γ-Al₂O₃. The presence of the Ni/γ-Al₂O₃ catalyst in the plasma process significantly increases the yield of CO and H₂ by 42% and 20%, respectively, compared to the plasma reaction in the absence of a catalyst.

Fig. 3. Energy efficiency of the plasma dry reforming process using different catalysts (CO₂/CH₄ = 1:1, total flow 50 ml min⁻¹, discharge power 7.5 W)

Fig. 3 shows that the energy efficiency of the plasma reforming reaction is 0.60 mmol/kJ without catalyst. Note that the combination of the plasma with catalysts cannot always enhance the energy efficiency of the plasma reforming process. Introducing the Ni/γ-Al₂O₃ and Mn/γ-Al₂O₃ catalysts into the discharge gap is found to improve the overall energy efficiency of the conversion by 20% and 17%, respectively, while packing the Cu and Co catalysts into the DBD reactor slightly decreases the energy efficiency of the plasma process. The maximum energy efficiency for the conversion of CH₄ and CO₂ (0.72 mmol/kJ) is achieved at a discharge power of 7.5 W and a total flow rate of 50 ml min⁻¹ when the Ni/γ-Al₂O₃ catalyst is placed in the plasma.

4. Conclusions

Combining plasma with the Ni/γ-Al₂O₃ and Mn/γ-Al₂O₃ catalysts significantly enhances the conversion of CH₄ and shows a synergistic effect of plasma-catalysis for CH₄ conversion. However, the presence of these catalysts in the plasma does not enhance the conversion of CO₂. In addition, packing these catalysts into the discharge gap enhances the yields of CO and H₂. The results show that these supported metal catalysts have different effects on the reaction performance of the plasma dry reforming process.

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6. References