

# Nonthermal plasma-assisted catalytic methanation of CO and CO<sub>2</sub> over nickel-loaded alumina

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## Abstract

Nonthermal dielectric barrier discharge plasma was applied for the heterogeneously catalyzed methanation of CO and CO<sub>2</sub> over alumina-supported catalysts at 180–320°C and atmospheric pressure. The characteristics of methane synthesis under plasma discharge conditions were investigated with several catalysts, including Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The results obtained with Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts indicated that either gas-phase reactions or photocatalysis induced by the plasma as well as the adsorption of carbon oxides on Al<sub>2</sub>O<sub>3</sub> hardly contribute to the methanation of CO and CO<sub>2</sub>. On the other hand, nickel-loaded catalysts like Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> were found to be considerably affected by the plasma, resulting in enhanced methanation rate. It is believed that the nonthermal plasma created in the catalytic reactor can accelerate the rate-determining step by dissociating carbon-oxygen bonds of carbon oxides adsorbed on the active sites of the catalysts.

*Keywords:* CO, CO<sub>2</sub>, catalytic methanation, nonthermal plasma.

## 1 Introduction

Methanation ('the hydrogenation of CO') have been investigated extensively, not only for the production of synthetic natural gas (SNG) from synthesis gas, but also as a gas purification process in chemical plants where CO acts as a catalyst poison. The same catalysts used for CO methanation are also active for carbon dioxide (CO<sub>2</sub>) that is closely related to the global warming. Hence CO<sub>2</sub> may also



be an attractive gas in methanation study in terms of recycling of disposed material into fuel as one of the possibilities [1].

Methane synthesis from CO and CO<sub>2</sub> proceeds over various supported metal catalysts. Although methanation catalysts consisting of a noble metal such as ruthenium, rhodium or platinum have also been developed [2], the most common catalyst for methane synthesis is based upon nickel supported on alumina. Nickel is cheap and easily accessible, but one disadvantage of nickel-based catalysts may be that relatively high temperatures are needed to maintain the catalytic activity for methane synthesis. The catalysts can chemically be modified with support materials and additives so that they have enhanced low temperature activity. Alternatively, the catalytic activity can be improved by physical means such as nonthermal plasma. According to recent studies reported in the literature, nonthermal plasma created by dielectric barrier discharge (DBD), glow discharge or pulsed corona discharge often facilitates catalytic reactions such as oxidation of organic compounds, decomposition of fluorinated carbons or reforming of hydrocarbons. In a similar manner, nonthermal plasma can also promote the catalytic conversion of CO/CO<sub>2</sub> into methane. The methanation of CO over Ni/alumina was previously studied [3], which showed that the plasma significantly increased the catalytic activity, especially at lower temperatures and pressures.

The present work is aiming at providing a CO/CO<sub>2</sub> methanation process enhanced by nonthermal plasma. The plasma-catalytic methanation of CO<sub>2</sub> was not dealt with in the previous study [3]. In this work, the methanation was carried out in a DBD reactor packed with catalyst pellets. Four different catalysts, i.e., Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, were used to examine comparatively the effect of the plasma on the methanation of CO and CO<sub>2</sub>.

## 2 Experimental

The nickel-loaded catalysts were prepared with alumina (Al<sub>2</sub>O<sub>3</sub>) ball (Sigma-Aldrich Co) and nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Acros Organics), on which the nickel content was varied by the concentration of aqueous nickel nitrate solution. Alumina ball used as the catalyst support was crushed in a mortar, sieved to a size of 1-2 mm. TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (TiO<sub>2</sub> content: 10wt%) was prepared by adding aqueous TiO<sub>2</sub> suspension to the alumina particles prepared as above. After drying in an oven at 110°C overnight, calcination was carried out at 550°C for six hours. The TiO<sub>2</sub> used in the present investigation was in the form of anatase phase, which was purchased from Sigma-Aldrich Co. The Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> have the BET specific surface areas of 195.7 and 9.7 m<sup>2</sup>/g. As well known, the anatase form of TiO<sub>2</sub> is a photocatalyst under ultraviolet (UV) light. Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was made by incipient wetness impregnation method with aqueous nickel nitrate solution. After impregnation, it was dried overnight to drive off water, and calcined at 550°C for six hours in air atmosphere. Finally, the catalyst previously calcined was reduced by flowing hydrogen at 550°C for six hours. Ni-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was also prepared by impregnating TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with aqueous

nickel nitrate solution, which was dried, calcined and reduced in the same way as mentioned above. The BET specific surface areas of  $\text{TiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Ni}/\text{Al}_2\text{O}_3$  and  $\text{Ni-TiO}_2/\text{Al}_2\text{O}_3$  prepared were measured to be 168.8, 138.5 and 116.4  $\text{m}^2/\text{g}$ , respectively.

Fig. 1 shows the schematic diagram of the experimental apparatus for methane synthesis. The catalyst-packed bed reactor referred to as plasma reactor, described in Fig. 2, was made of a quartz tube (inner diameter: 15 mm; thickness: 1.5 mm) and a 6.4-mm-concentric stainless-steel rod acting as the discharging electrode. An aluminum foil used as the ground electrode wrapped the outer surface of the quartz tube. The plasma reactor was packed with catalyst pellets whose apparent volume and mass were 17  $\text{cm}^3$  and 13.6 g, respectively. The effective length of the plasma reactor was measured to be 110 mm. An alternating current (AC) high voltage (operating frequency: 1 kHz) in the range of 6–11 kV was applied to the stainless-steel rod to create nonthermal plasma in the catalyst-packed reactor. The feed gas was heated to desired temperatures with two heating tapes, one covering the mixing chamber and the other covering the plasma-catalytic reactor. The feed gas preheated in the gas mixing chamber was directed to the plasma-reactor where the methanation of  $\text{CO}/\text{CO}_2$  occurred.

The feed gas was prepared by mixing pure hydrogen and carbon monoxide or by mixing pure hydrogen and carbon dioxide via a set of mass flow controllers (MKS Instruments, Inc.). For the methanation of  $\text{CO}$ , the molar ratio of  $\text{H}_2$  to  $\text{CO}$

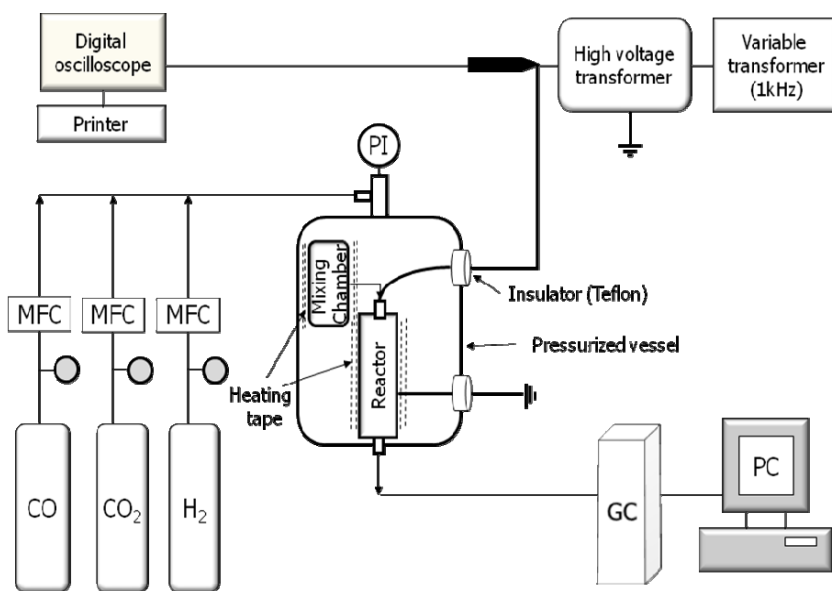


Figure 1: Schematic diagram of the experimental apparatus for methane synthesis.

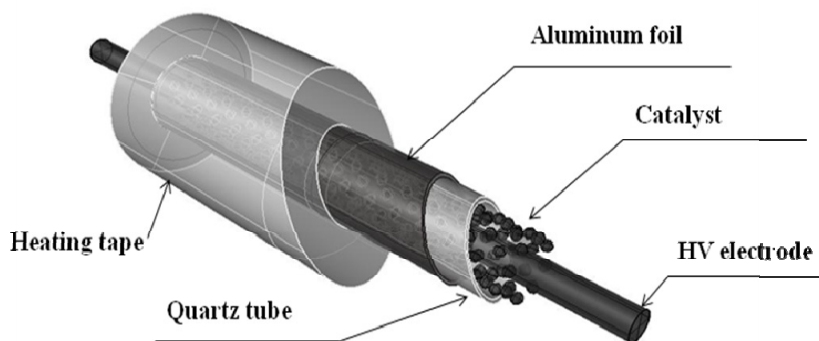


Figure 2: Schematic diagram of plasma-catalytic reactor.

in the feed gas was adjusted to 3. The methanation of  $\text{CO}_2$  was separately conducted with a  $\text{H}_2/\text{CO}_2$  molar ratio of 4. The flow rate of the feed gas was  $12,000 \text{ cm}^3 \text{ h}^{-1}$  for CO methanation, and  $15,000 \text{ cm}^3 \text{ h}^{-1}$  for  $\text{CO}_2$  methanation. The reacted gas coming out of the plasma-catalytic reactor was diluted with pure helium ( $500 \text{ cm}^3 \text{ min}^{-1}$ ), and then analyzed by a gas chromatograph (Varian Micro GC CP-4900) equipped with an analytical column (10 m Pora Plot Q Column), using high purity helium as carrier. The gas chromatograph was calibrated for concentrations of  $\text{H}_2$ , CO,  $\text{CO}_2$  and  $\text{CH}_4$  with their known concentrations. Methanation experiments were performed over the temperature range of  $200\sim 320^\circ\text{C}$  with an interval of  $20^\circ\text{C}$ . The voltage applied to the plasma reactor was measured with a 1,000:1 high voltage probe (P6015, Tektronix) and a digital oscilloscope (TDS 3032, Tektronix). The discharge power consumed in the plasma reactor was determined by using charge-voltage Lissajous figure.

### 3 Results and discussion

#### 3.1 Comparison between CO and $\text{CO}_2$ methanation over $\text{Ni}/\text{Al}_2\text{O}_3$

Fig. 3 shows the conversion efficiencies of CO and  $\text{CO}_2$  over  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst (Ni content: 10wt%), where the results obtained with and without the plasma were compared. The temperature was varied in the range of  $180\text{--}300^\circ\text{C}$ , while the voltage was fixed at 10.3 kV. When high voltage enough to induce electrical discharge is applied to the plasma reactor, active species such as energetic electrons, ultraviolet (UV) photons, radicals and excited molecules are formed through various reaction pathways [4]. Looking into generally accepted catalytic methanation mechanism, it is quite probable that all or some of these kinds of active species can enhance the catalytic reactions. In general, catalytic methanation proceeds via the adsorption of carbon oxides, followed by the hydrogenation of surface carbon resulting from the dissociation of the adsorbed carbon oxides. As can be seen, the conversion efficiencies of either CO or  $\text{CO}_2$  were largely enhanced in the presence of the plasma. Like other catalytic

reactions, the rate-determining step (RDS) in the methanation of CO and CO<sub>2</sub> is regarded as the dissociation of adsorbed carbon oxides molecules. In other words, the methanation rate mainly depends on the rate of the carbon-oxygen bond dissociation, not on the adsorption of carbon oxides or on the succeeding hydrogenation of surface carbon. In Fig. 3, the enhancement of the methanation arising from the generation of nonthermal plasma may be explained by the acceleration of the rate-determining step. The bond strengths for gaseous CO and CO<sub>2</sub> are 1,072 kJ mol<sup>-1</sup> (11 eV) and 782 kJ mol<sup>-1</sup> (8 eV), respectively, but they get weak when adsorbed on the catalyst surface. As a result, the energetic electrons generated by the plasma can easily break the carbon-oxygen bond of the adsorbed carbon oxides through direct electron impact, speeding up the rate-determining step. Meanwhile, with the catalyst alone, CO<sub>2</sub> exhibited higher methanation rate than CO at temperatures below 280°C, but at higher temperatures, it was reversed since the maximum conversion efficiency of CO<sub>2</sub> was limited to around 90%. The rate of CO<sub>2</sub> methanation under the plasma was also higher than that of CO at lower temperature region below 220°C. Even though the plasma was found to shift the optimal reaction temperature lower, it did not further increase the maximally attainable CO<sub>2</sub> conversion to above 90%.

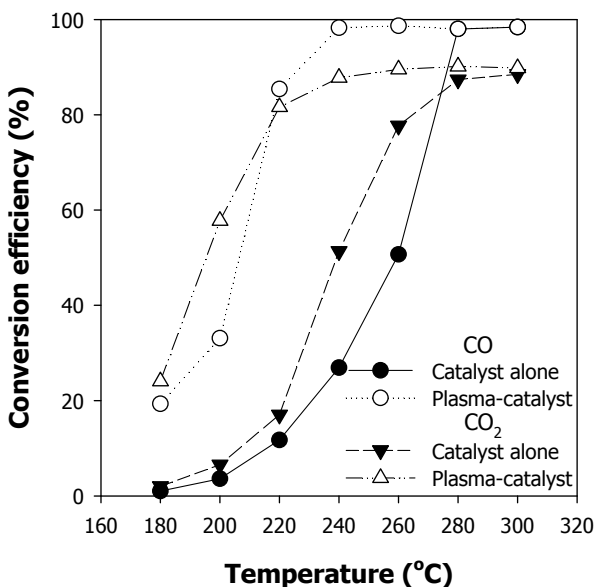


Figure 3: Conversion efficiencies of CO and CO<sub>2</sub> with and without nonthermal plasma (catalyst: Ni/Al<sub>2</sub>O<sub>3</sub>; voltage: 10.3 kV).

### 3.2 Comparison of CO and CO<sub>2</sub> methanation on different catalysts

Figures 4 and 5 show the conversion efficiencies of CO and CO<sub>2</sub> over four different catalysts over a temperature range of 180–320°C. When the plasma was

used, the applied voltage was controlled to 10.3 kV. As can be seen, there was no conversion of CO with either  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2/\text{Al}_2\text{O}_3$  catalyst, regardless of the plasma and the reaction temperature, which implies that UV photons and gas-phase reactions caused by nonthermal plasma do not directly contribute to the methanation. It should be noted that  $\text{TiO}_2$  photocatalyst in the anatase form whose band gap energy is about 3.2 eV can be activated by UV photons with wavelengths less than 390 nm. The electron-impact excitations of CO and  $\text{CO}_2$  emit UV light with various wavelengths [5, 6], but the photocatalytic effect on the methanation was negligible for the present catalysts. Different from the results obtained with  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , the plasma largely affected the conversion of CO and  $\text{CO}_2$  over Ni-loaded catalysts, i.e.,  $\text{Ni}/\text{Al}_2\text{O}_3$  and  $\text{Ni-TiO}_2/\text{Al}_2\text{O}_3$  catalyst. Compared to the catalyst alone, the temperature effect on the methanation became much greater when the plasma was generated in the reactor, displaying respective CO and  $\text{CO}_2$  conversion efficiencies of 98% and 90% at 240°C. Like the case of CO, the conversion of  $\text{CO}_2$  with  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2/\text{Al}_2\text{O}_3$  catalyst was not significant, and moreover, the  $\text{CO}_2$  converted was mostly reduced to CO, not to methane. Unexpectedly, the performance of  $\text{Ni-TiO}_2/\text{Al}_2\text{O}_3$  catalyst was found to be inferior to that of  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst for both CO and  $\text{CO}_2$ , which may be another evidence that the UV photons produced by the plasma did not contribute to the methanation. According to a previous study [7], noble metals supported on titania such as  $\text{Pt}/\text{TiO}_2$ ,  $\text{Rh}/\text{TiO}_2$  and  $\text{Ir}/\text{TiO}_2$  were reported to be effective for photo-induced dissociation of  $\text{CO}_2$ , conflicting with the present study conducted with nickel as the active metal. It is believed that the

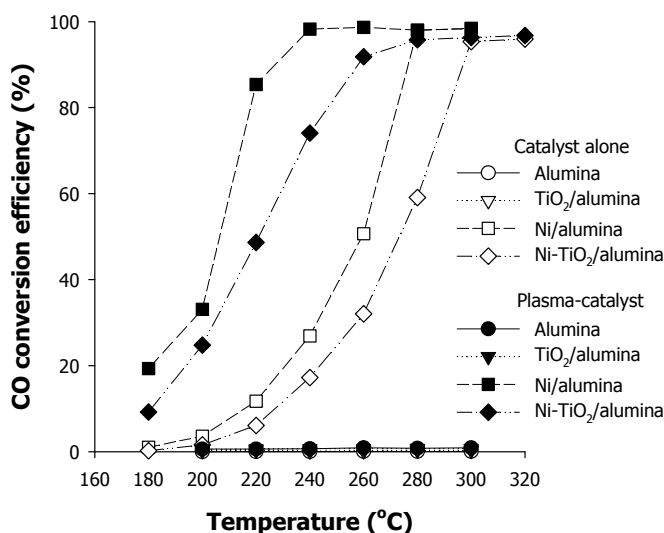


Figure 4: Conversion efficiencies of CO over different catalysts (10.3 kV).

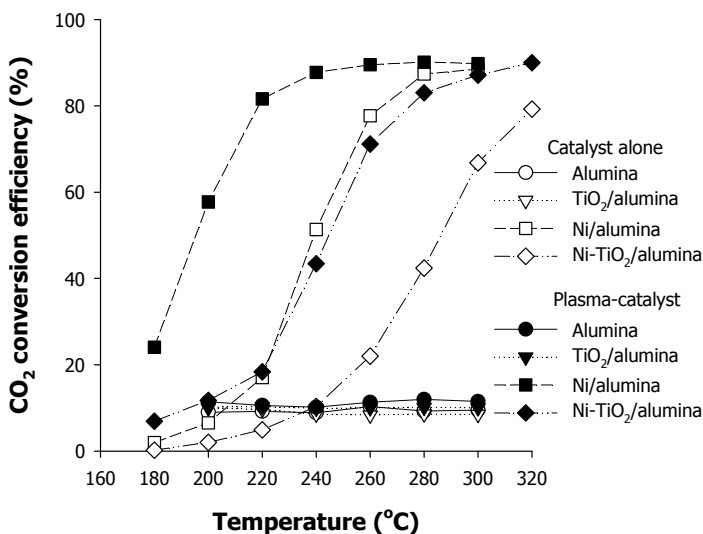


Figure 5: Conversion efficiencies of CO<sub>2</sub> over different catalysts (10.3 kV).

photocatalytic activity of TiO<sub>2</sub> is closely related to the nature of the active metal used. The lower performance of Ni-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> than Ni/Al<sub>2</sub>O<sub>3</sub> may also be attributed in part to its smaller BET specific surface area. As mentioned above, the BET specific surface areas of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> were 138.5 and 116.4 m<sup>2</sup>/g, respectively.

## 4 Conclusions

The conversions of CO and CO<sub>2</sub> into methane were investigated in the plasma-catalytic reactor packed with nickel-loaded catalysts. The plasma was found to be beneficial to the catalytic methanation of CO and CO<sub>2</sub> in that it shifted the optimal reaction temperature lower. The experimental data obtained by varying the catalyst composition have shown that the enhancement in the methanation rate by the plasma results from speeding up the rate-determining step, namely, the dissociation of the carbon-oxygen bond of the adsorbed carbon oxides, and the contributions of gas-phase reactions and photocatalysis caused by nonthermal plasma are insignificant. Both in the presence and absence of the plasma, CO<sub>2</sub> exhibited higher methanation rate than CO at lower temperatures, but it was reversed at higher temperatures due to the limitation of the maximally attainable CO<sub>2</sub> conversion efficiency.

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