# Post-plasma catalytic oxidative $CO_2$ reforming of methane over Ni-based catalysts

Kai Li [a,b], Jing-Lin Liu [a,b], Xiao-Song Li [a,b], Xiao-Bing Zhu [a,b,*], Ai-Min Zhu [a,b,*]

[a] Center for Hydrogen Energy and Liquid Fuels, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China
[b] Laboratory of Plasma Physical Chemistry, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China

## ARTICLE INFO

## ABSTRACT

To seek an efficient route for syngas production from oxidative $CO_2$ reforming of methane (OCRM) via post-plasma catalytic technique, three routes were compared using spark-shade plasma (input power = 106 W, with F1 of 1.36 SLM at $CH_4$:$O_2$:$CO_2$ = 1:0.6:0.7) and Ni/$CeO_2$/$Al_2O_3$ catalyst (catalyst temperature = 800 °C, with or without F2 of 0.52 SLM $CH_4$). Compared with Route 1 (plasma only, F1 only), $X_{O_2}$, $X_{CH_4}$, $C_{H_2+CO}$ and $H_2$/CO ratio of Route 2 (plasma + catalyst, F1 only) increased to 100%, 99%, 76% and 1.2, respectively; but $X_{CO_2}$ kept at about 35%, which was close to the thermodynamic-equilibrium values. In Route 3 (plasma + catalyst, F1 + F2), $X_{CO_2}$ increased dramatically to 67%, $C_{H_2+CO}$ and $H_2$/CO ratio further increased to 86% and 1.5, respectively, though $X_{CH_4}$ decreased to 77%. Both $S_{CO}$ and $S_{H_2}$ arrived at nearly 100%. Assuming that the plasma could supply the heat energy for the subsequent catalytic reaction at 800 °C, syngas energy cost as low as 0.5 eV/molecule and energy efficiency as high as 91% were achieved.

## 1. Introduction

Dry reforming of methane (DRM) via simultaneous conversion of $CH_4$ and $CO_2$ has been proposed to produce syngas ($H_2$ + CO) [1–5]. However, it is strongly endothermic and suffers from high energy cost. Combining the exothermal reaction of partial oxidation, via addition of oxygen, the energy cost of DRM can be lowered. Moreover, the presence of oxygen also inhibits coke formation. This process is referred to as oxidative $CO_2$ reforming of methane (OCRM).

Catalytic method is extensively employed for OCRM [6–10]. An alternative technique is non-thermal plasma, in which reactant molecules collided with energetic electrons to produce radicals via excitation and dissociation pathways, followed by radical reactions to form final products. Plasma technique has several merits, including compactness, feed flexibility, durability, and quick response. Recently, non-thermal plasma has been explored for OCRM [11–14]. Rueangjitt et al. [11] reported syngas energy cost of 13 eV/molecule with 81% of $CH_4$ conversion and 49% of $CO_2$ conversion using multi-stage gliding arc discharge at $CH_4$:$O_2$:$CO_2$

molar ratio of 1:0.3:0.4. Hwang et al. [12] reported syngas energy cost of 4.7 eV/molecule with 54% of $CH_4$ conversion and 27% of $CO_2$ conversion using arc-jet plasma at $CH_4$:$O_2$:$CO_2$ molar ratio of 1:0.4:1. In our previous work using a spark plasma reactor [14], syngas energy cost of 3.4 eV/molecule with 69% of $CH_4$ conversion and 52% of $CO_2$ conversion at $CH_4$:$O_2$:$CO_2$ molar ratio of 1:0.2:0.7 was reported. Obviously, high energy cost is the major obstacle to plasma technique. We have designed and reported a unique spark-shade plasma reactor with low energy cost to produce high-concentration syngas [15–17]. On the other hand, the combination of plasma with catalyst is a feasible and effective approach to reduce the energy cost [18–22]. Rafiq et al. [18] combined gliding arc discharge with Ni-based catalyst and reported syngas energy cost of 0.7 eV/molecule with 86% of $CH_4$ conversion and 4% of $CO_2$ conversion at $CH_4$:$O_2$:$CO_2$ molar ratio of 1:0.7:0.7. In this paper, in order to further reduce the syngas energy cost and increase methane and $CO_2$ conversions, the spark-shade plasma followed by Ni-based catalyst was employed to seek an efficient route for syngas production from oxidative $CO_2$ reforming of methane.

## 2. Experimental

### 2.1. Plasma and catalytic reactors

The spark-shade plasma reactor is the same as that in our previous paper [15]. A stainless steel rod of 6-mm diameter coaxial

* Corresponding author at: Laboratory of Plasma Physical Chemistry, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China.
Tel.: +86 411 84706094; fax: +86 411 84706094.
E-mail addresses: xzhu@dlut.edu.cn (X.-B. Zhu), amzhu@dlut.edu.cn, amzhu2009@gmail.com (A.-M. Zhu).

with a quartz tube was used as the high-voltage electrode. A stainless steel rod of 3-mm diameter, rotated around the axis of the quartz tube in a radius of 10 mm at a speed of 400 r/min, was employed as the ground electrode. The axial distance between the two electrodes was fixed at 17 mm. The plasma was powered by a 95 kHz AC high-voltage (0–30 kV) power supply (CTP-2000K, Nanjing Suman electronics Co., China). Following the plasma reactor, a quartz tube of I.D. 17 mm packed with $Ni/CeO_2/Al_2O_3$ catalyst was used as a catalytic reactor and heated by an oven. The experiment was performed at 1 bar. The flow rates were controlled by mass flow controllers.

Three routes were conducted for oxidative $CO_2$ reforming of methane in this study, as shown in Fig. 1. In Route 1, only spark-shade plasma was employed; in Route 2, $Ni/CeO_2/Al_2O_3$ catalyst followed the spark-shade plasma; in Route 3, besides the same feeding of F1 as Route 1 and 2, another feeding of F2 was introduced behind the plasma. The others were the same as those in Route 2. Route 3 was designed to raise further $CO_2$ conversion via introducing more $CH_4$ and to avoid the coke issue of plasma reactor in the presence of high-concentration $CH_4$. The feeding F1 was a flow rate of 1.36 SLM (Standard Liter per Minute) with a $CH_4:O_2:CO_2$ molar ratio of 1:0.6:0.7; the feeding F2 was pure $CH_4$ of 0.52 SLM. As a result, the total flow rate of Route 3 was 1.88 SLM and its $CH_4:O_2:CO_2$ molar ratio was 1:0.3:0.4.

## 2.2. Catalyst preparation and characterization

$Ni/CeO_2/Al_2O_3$ catalyst was prepared by sequential wetness impregnation method. $CeO_2/Al_2O_3$ was prepared by impregnation of γ-$Al_2O_3$ pellets (particle size: Φ1–2.5 mm) with $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution, followed by drying at 110 °C for 6 h and calcination in air at 500 °C for 6 h. $CeO_2/Al_2O_3$ was incipiently impregnated overnight at room temperature with $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution, followed by drying at 110 °C for 6 h and calcination in air at 500 °C for 6 h. The prepared catalyst had Ni of 11 wt.% and Ce of 8 wt.%, which was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV, Perkin Elmer).

In Route 2 and 3, $Ni/CeO_2/Al_2O_3$ catalysts of 6 g were packed into the catalytic reactor and reduced with 5 vol.% $H_2/N_2$ flow of 0.2 SLM for 1 h at 850 °C prior to the reaction test.

X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (D/MAX-2400, Rigaku) using a Cu Kα radiation at 40 kV and 100 mA in the $2\theta$ range from 20° to 80°. The Brunauer-E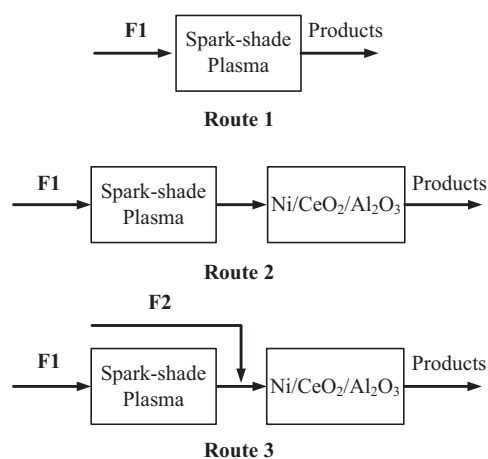mmett-Teller (BET) surface area was determined from N$_2$ adsorption–desorption isotherms measured with a surface area analyzer (NOVA2200, Quantachrome) at −196 °C. Prior to the measurement, the samples were degassed under vacuum at 200 °C for 5 h. The catalyst after reduction was observed by a transmission electron microscopy (TEM, TECNAI Spirit).

## 2.3. Analytical methods

Two gas chromatographs (Agilent 1790 T and Agilent 6890N) were employed to analyze online gaseous products. Nitrogen was used as an internal standard gas to quantify gaseous $O_2$, $CH_4$, $CO_2$, CO, $C_2H_2$, $C_2H_4$ and $C_2H_6$, and helium was used to quantify $H_2$. The detailed analysis of gaseous products was described in our previous papers [14,23].

Definitions of conversion, conversion rate, carbon-based (C-based) and hydrogen-based (H-based) selectivity, carbon and hydrogen balance are consistent with those in our previous papers [14], and briefly stated as follows:

Conversions of $O_2$ ($X_{O_2}$), $CH_4$ ($X_{CH_4}$), $CO_2$ ($X_{CO_2}$) and total-carbon ($X_{TC}$) are:

$$X_{O_2} = \left(1 - \frac{F_{N_2}}{F_{O_2}^{in}} \cdot \frac{C_{O_2}^{out}}{C_{N_2}^{out}}\right) \times 100\% \tag{E1}$$

$$X_{CH_4} = \left(1 - \frac{F_{N_2}}{F_{CH_4}^{in}} \cdot \frac{C_{CH_4}^{out}}{C_{N_2}^{out}}\right) \times 100\% \tag{E2}$$

$$X_{CO_2} = \left(1 - \frac{F_{N_2}}{F_{CO_2}^{in}} \cdot \frac{C_{CO_2}^{out}}{C_{N_2}^{out}}\right) \times 100\% \tag{E3}$$

$$X_{TC} = \frac{F_{CH_4}^{in} \cdot X_{CH_4} + F_{CO_2}^{in} \cdot X_{CO_2}}{F_{CH_4}^{in} + F_{CO_2}^{in}} \times 100\% \tag{E4}$$

where $F_{O_2}^{in}$, $F_{CH_4}^{in}$, $F_{CO_2}^{in}$ and $F_{N_2}$ denote the flow rates of $O_2$, $CH_4$ and $CO_2$ fed into the reactor, and internal standard $N_2$ gas, respectively. $C_{O_2}^{out}$, $C_{CH_4}^{out}$, $C_{CO_2}^{out}$ and $C_{N_2}^{out}$ represent the concentration of $O_2$, $CH_4$, $CO_2$ and $N_2$ in the effluent gas, respectively.

Conversion rates of $O_2$ ($r_{O_2}$), $CH_4$ ($r_{CH_4}$) and $CO_2$ ($r_{CO_2}$) are:

$$r_{O_2} = F_{O_2}^{in} \cdot X_{O_2} \tag{E5}$$

$$r_{CH_4} = F_{CH_4}^{in} \cdot X_{CH_4} \tag{E6}$$

$$r_{CO_2} = F_{CO_2}^{in} \cdot X_{CO_2} \tag{E7}$$

C-based selectivities of CO ($S_{CO}$) and $C_2$ hydrocarbons ($C_2H_2 + C_2H_4 + C_2H_6$, $S_{C_2}$) and carbon balance ($B_C$) are:

$$S_{CO} = \left(\frac{F_{N_2}}{F_{CH_4}^{in} \cdot X_{CH_4} + F_{CO_2}^{in} \cdot X_{CO_2}} \cdot \frac{C_{CO}^{out}}{C_{N_2}^{out}}\right) \times 100\% \tag{E8}$$

$$S_{C_2} = \left(\frac{2 \cdot F_{N_2}}{F_{CH_4}^{in} \cdot X_{CH_4} + F_{CO_2}^{in} \cdot X_{CO_2}} \cdot \frac{C_{C_2}^{out}}{C_{N_2}^{out}}\right) \times 100\% \tag{E9}$$

$$B_C = S_{CO} + S_{C_2} \tag{E10}$$

where $C_{CO}^{out}$ and $C_{C_2}^{out}$ represent the concentrations of CO and $C_2$ hydrocarbons in the effluent gas, respectively.

H-based selectivities of $H_2$ ($S_{H_2}$), $H_2O$ ($S_{H_2O}^H$) and $C_2$ hydrocarbons ($S_{C_2}^H$) and hydrogen balance ($B_H$) are:

$$S_{H_2} = \frac{0.5 \cdot F_{He}}{F_{CH_4}^{in} \cdot X_{CH_4}} \cdot \frac{C_{H_2}^{out}}{C_{He}^{out}} \times 100\% \tag{E11}$$



**Fig. 1.** Three routes for oxidative $CO_2$ reforming of methane. F1 = 1.36 SLM ($CH_4:O_2:CO_2$ = 1:0.6:0.7); F2 = 0.52 SLM ($CH_4$).