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Catalyst assisted by non-thermal plasma in dry reforming of methane at low temperature

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ABSTRACT

The transformation of methane and carbon dioxide into synthesis gas was performed by a plasma discharge coupled with a catalyst at room temperature and 300 °C. The combination of the catalyst with the discharge does not modify significantly the transformation of reactants at room temperature whereas at 300 °C, at which the catalyst alone (10% La₂O₃/alumina balls) is inactive, the CH₄ conversion increases almost by a factor of 3 in comparison with inert glass balls, the CO₂ conversion being only slightly increased. The synergy between plasma and catalyst is then clearly demonstrated at 300 °C whereas at room temperature the effect remains very low. It is proposed that the reaction between the oxygen species generated by CO₂ dissociation in gas phase (CO₂ splitting) replenish the surface oxygen species which have reacted with methane according to a Mars and Van Krevelen type mechanism. The catalyst surface modification under the plasma discharge was evidenced by Raman spectroscopy, a strong fluorescence effect being visible after reaction under plasma at 300 °C.

1. Introduction

Interest in carbon dioxide valorization to valuable chemical products is more and more increasing due to the awareness of the greenhouse effect. Among the possible technologies to valorize CO₂, the dry reforming of hydrocarbons by thermal catalysis has been largely studied although high temperatures are required to overcome the unfavorable thermodynamic limitation ($\Delta G > 0$ at $T > 700$ °C). As an alternative to conventional catalytic dry reforming reaction, non-thermal plasma appears as an interesting technology since highly energetic electrons generated by plasma are able to initiate the chemical processes at room temperature. Dielectric Barrier Discharge (DBD) plasma was used for many applications such as ozone production [1], VOC removal [2], surface treatment [3] and reforming reactions [4,5]. Direct CO₂ dissociation (CO₂ splitting) was also investigated either with pure CO₂ or diluted by Ar or He [6,7].

The reforming reaction of CH₄ by CO₂ to produce syngas using DBD plasma was the subject of many papers in various experimental conditions at different input power, total flow rate, CH₄/CO₂ ratio, and plasma reactor design [8–10].

The combination of a heterogeneous catalyst with the discharge has attracted attention from many researchers in order to increase conversions and selectivity to the target product [11]. In many applications the interaction between non-thermal plasma and catalysts may lead to

the development of processes not achievable using catalyst or plasma separately [12]. Two different strategies were used to perform reactions: the catalyst is placed either directly into the discharge zone (in-plasma) or downstream to the discharge (post plasma). The use of a catalyst into the discharge zone presents the advantage to allow a possible surface reaction of short lived species generated by the plasma on the active sites of the catalyst. However the presence of a solid into the plasma zone is not trivial since the physical properties of the plasma can be modified: the dielectric properties and homogeneity of the discharge [13]. Careful studies are therefore required before concluding on a possible synergy effect between the plasma discharge and a catalyst. For example, a comparison between an empty reactor and a reactor filled with a catalyst makes no sense since the residence time of the gas in the plasma zone is significantly reduced as soon as a solid is present in the discharge. The use of a catalyst into the discharge zone influences the plasma and the plasma influences also the catalyst: catalyst's structure can be modified (size of metal species, of pores...), leading to higher or lower catalytic activity [14]. The catalyst used in combination with plasma is usually in a powdered form and placed between the two electrodes. The influence of the particle size has been shown by Tu et al. [15]. Ceramic monoliths were also used as catalyst support, the size of the microporous channels affecting the formation of surface micro-discharges [16]. The beneficial effect of a catalyst in combination with non-thermal plasma is still controversial [17]. Most of the studies were

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performed at ambient temperature and atmospheric pressure. Jiang et al. [18] showed that the use of a zeolite A reduces CH₄ and CO₂ conversions but inhibits the formation of carbon black. Long et al. [19] and Pietruszka et al. [20] have found that the combination of a plasma jet with Ni/γ-Al₂O₃ increases both CH₄ and CO₂ conversion, which could be attributed to heating of the catalyst by the discharge. The use of La₂O₃/Al₂O₃ under pulse corona plasma was reported by Zhang et al. [21]. The authors showed a higher CO₂ conversion and a lower CH₄ conversion in the presence of lanthanum oxide compared to alumina alone, the reaction being performed at room temperature. In a hybrid system, with alumina based material inside the plasma zone, Sentek et al. [22] showed that temperatures in the range 120–290 °C did not affect the overall methane conversion but increased formation of ethane particularly when Pd catalyst was used.

Using Ni/Al₂O₃ catalyst, Kim et al. [23] observed a significant methane activation at temperature higher than 360 °C compared to DBD only. The authors speculate that vibrationally excited CH₄ species located on or near the catalytic site participate to the reaction favoring the C–H bond activation at high temperature.

According to the different studies reported until now, we consider that there is need to investigate the reaction of carbon dioxide reforming of methane by coupling non-thermal plasma and catalyst with a focus on the effect of temperature and evolution of conversions and selectivity with time on stream.

In the present study, lanthanum oxide was deposited on the surface of alumina balls. To our knowledge, the reaction in DBD plasma combined with alumina supported lanthanum oxide has only been previously investigated in a temperature range, close to room temperature, where this catalyst alone is not active. We have checked in a previous paper [24] that the thermal increase under the plasma discharge was not responsible for catalyst activation. In this current study, the reaction was performed at room temperature and 300 °C, over inert glass spheres and porous alumina spheres: with and without lanthanum oxide. Interactions between the plasma and the catalyst surface are discussed and a consistent mechanism is proposed.

2. Experimental

The reactor is a classical coaxial packed-bed type filled with balls (glass or alumina) of 1.8–2.0 mm diameter, which allows comparing in roughly the same plasma formation conditions, residence time (void in the plasma zone) the influence of the nature of the material on the plasma process.

The alumina balls (supplied by SASOL) consist of γ-Al₂O₃ with a specific surface area of 221 m² g⁻¹ and a porous volume of 0.52 cm³ g⁻¹.

The lanthanum oxide supported on alumina balls catalysts were prepared according to an incipient wetness method. The alumina balls support (30 g) was stirred in a solution (40 mL) containing from 11 to 44 wt% of La(NO₃)₃·6H₂O, in order to get from 5 to 20% of La₂O₃/Al₂O₃ after calcination. The impregnation was carried out under reduced pressure in a rotary evaporator during four hours. The balls were dried at 110 °C during twelve hours, and then calcined under air at 300 °C during 4 h. The textural properties are reported in Table 1. The specific surface area was 221 m² g⁻¹ for γ-Al₂O₃ balls decreasing to

Table 1
BET surface area, pore volume and average pore diameter of La₂O₃/γ-Al₂O₃ catalysts.

Catalyst	S BET (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
γ-Al ₂ O ₃	221	0.52	104
5%La ₂ O ₃ /Al ₂ O ₃	217	0.49	104
10%La ₂ O ₃ /Al ₂ O ₃	196	0.47	108
20%La ₂ O ₃ /Al ₂ O ₃	170	0.44	112

217, 196 and 170 m² g⁻¹ for 5, 10, and 20% La₂O₃/Al₂O₃ respectively. The average pore size increased slightly with the amount of La₂O₃ after the calcination step. This can be explained by blocking of small pores for the highest La₂O₃ loadings. The catalysts were characterized by Raman spectroscopy before and after reaction under plasma. Raman spectra were obtained at room temperature, using a Labram HR 800 UV confocal scanning spectrometer (Horiba Jobin Yvon) equipped with a Peltier-cooled charge-coupled device for detection. The Raman scattering was excited using a 514.52 nm excitation wavelength supplied by an external Ar⁺ laser through an Olympus high-stability BXFM confocal microscope. Patterns were recorded in the 50–1850 cm⁻¹ Raman shift range with a spectral resolution of 0.5 cm⁻¹. LabSPEC v. 5 software was used for data acquisition and processing.

The reactor tube (20 mm o.d, 15 mm i.d.) is made of α-alumina. The inner electrode is a stainless steel rod (6.2 mm o. d.) and the outer electrode is a copper foil (80 mm length) wrapped on the external reactor wall (Fig. 1).

The high voltage is applied to the inner electrode whereas the outer electrode is grounded.

The reaction was performed by flowing carbon dioxide and methane diluted by helium in the reactor.

The plasma discharges were generated using a AC high-voltage generator (Trek inc., 30/20A). The voltage and current measurements were monitored with a digital oscilloscope (Lecroy CT3744, 500 MHz, 46510) through two high voltage probe (Lecroy, PPE 20 kV, 100 MHz). The discharge power was calculated from the voltage-charge integration (Manley method). All the experiments were performed at a power of 8W adjusted by varying the voltage: 24 kV peak to peak at room temperature and 22 kV at 300 °C, at a constant frequency of 800 Hz. The product gases were analysed by a three-way gas chromatograph (µGC Varian Quad CP-4900). PoraPLOT Q, CP-Sil 5CB, and a-molecular sieve 5A columns were used with TCD detectors to analyze on-line within 3 min the gases: H₂, CO, CO₂, CH₄, C₂H₆, and C₂H₄.

All the experiments were performed three times after cleaning the inner electrode and changing the catalyst (when used), a margin error of ± 3% was calculated.

The conversion, selectivity, yields and energy efficiency were defined as:

Conversion (%) of CH₄ and CO₂ = 100 × mole of CH₄ (or CO₂) converted/mole of CH₄ (or CO₂) in the feed

The selectivity was calculated based on carbon atoms:

Selectivity to C_nH_y (%) = 100

$$\times \frac{n \times \text{mole of C}_n\text{H}_y}{(\text{mole of CH}_4 + \text{mole of CO}_2)\text{converted}}$$

Selectivity to CO (%) = 100 × $\frac{\text{mole of CO}}{(\text{mole of CH}_4 + \text{mole of CO}_2)\text{converted}}$

Selectivity to H₂(%) = 100 × $\frac{\text{mole of H}_2}{2 \times \text{mole of CH}_4 \text{ converted}}$

Yield in CO (%) = 100 × $\frac{\text{mole of CO}}{(\text{mole of CH}_4 + \text{mole of CO}_2)\text{introduced}}$

Yield in H₂(%) = 100 × $\frac{\text{mole of H}_2}{2 \times (\text{mole of CH}_4) \text{ introduced}}$

Carbon Balance: CB (%) = 100

$$\times \frac{\text{mole of CO} + \sum n \times \text{mole of C}_n\text{H}_y}{(\text{mole of CH}_4 + \text{mole of CO}_2) \text{ converted}}$$

Energy efficiency:

$$E_{\text{eff}}(\text{mmol/kJ}) = \frac{\text{mole of CH}_4 + \text{mole of CO}_2 \text{ converted (mmol/s)}}{\text{input power (kW)}}$$

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