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Activation of methane and carbon dioxide in a dielectric-barrier discharge-plasma reactor to produce hydrocarbons—Influence of La_2O_3/γ-Al_2O_3 catalyst

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ABSTRACT

The activation of methane and carbon dioxide to produce hydrocarbons has been investigated in a dielectric barrier discharge (DBD) reactor. A high CH_4/CO_2 ratio is more selective for the production of C2 hydrocarbons, but the carbon balance is always far from 100% due to carbon deposition and formation of heavy molecules. An increase of the reaction temperature until 600 °C is more favorable for ethylene formation. The presence of glass or alumina balls in the plasma improves the stability of the plasma discharge leading to an increase of the CO_2 and CH_4 conversion. The use of the catalyst La_2O_3/γ-Al_2O_3 in the plasma zone, at 400 °C, modifies significantly the activation of carbon dioxide while it does not affect the activation of methane. This result can be attributed to the formation of surface oxycarbonate species responsible for the higher carbon monoxide selectivity.

1. Introduction

The use of methane, the main component of natural gas, is of particularly interest in the field of energy production due to its high availability.

Based on thermodynamic data, the production of hydrocarbons from methane requires high temperatures (>973 K), which makes the process little selective in C2 and expensive. The catalysts commonly used to synthesise hydrocarbons are basic catalysts within the temperature range of 923–1123 K [1–3]. Among 30 basic catalysts, Asami et al. showed that lanthanide oxide exhibited the best catalytic performances [4].

However there are needs for non-conventional systems to perform such reactions. One of the new approaches consists to perform the chemical activation of reactants by a plasma generated by an electric gas discharge. Indeed, non-thermal plasma, far from thermodynamic equilibrium, can initiate a series of plasma chemical processes such as ionization, dissociation and excitation, while the temperature of the reactants remains relatively low.

The successful use of plasma to produce hydrocarbons from methane and carbon dioxide has been demonstrated in the literature [5–8].

The combination of a catalyst with plasma has been reported for the direct conversion of methane and carbon dioxide to higher hydrocarbons. It is believed that the catalysts particles become electrically charged under the gas discharge. The combination of a DBD with heterogeneous catalysts could operate by an activation of the reactants in the discharge prior to the catalytic reaction [9]. Marques et al. showed that reactive species are formed from methane which can react with a catalyst (γ-alumina) placed after the discharge [10]. However a positive role of the combination of plasma with catalyst is not always obtained. Eliasson et al. showed that the presence of zeolithe in the plasma zone decreases the conversion of methane and carbon dioxide but increases significantly the light hydrocarbons selectivity [11]. The use of La_2O_3/γ-Al_2O_3 catalyst under a pulse corona plasma was reported by Zhang et al. [12]. The authors showed that the conversion of methane to C2 hydrocarbons was favored compared to a pure alumina catalyst in the plasma zone.

We report results in the transformation of methane and carbon dioxide to produce hydrocarbons using a DBD plasma reactor. The influence of the molar ratio CH_4/CO_2 and the reaction temperature was studied using plasma alone.

Since La_2O_3 is consider as one of the most efficient oxide catalysts for oxidative methane coupling, we decided to investigate the presence of La_2O_3 deposited over alumina balls in the plasma zone. The reaction was performed at temperatures from room temperature to 400 °C.

The use of balls is motivated by the complete filling of the plasma zone, while with powder only a catalytic bed can be used, the reaction in the homogeneous phase being preponderant in the last case.

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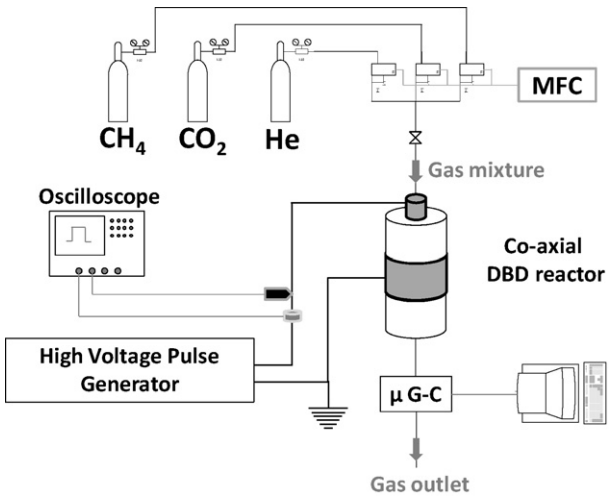

Fig. 1. Experimental set up.

2. Experimental

The reaction was performed by flowing a gas mixture of methane, carbon dioxide and helium in a alumina reactor (15 mm id) with a inner stainless steel electrode (3.2 mm o.d). The outer electrode is a copper tube wrapping the alumina tube (Fig. 1).

Plasma was generated by a monopolar pulsed electric generator (A2E Technologies). The voltage and current measurements were monitored with a digital oscilloscope (Lecroy CT3744, 500 MHz, 46510) through a high voltage probe (Lecroy, PPE 20 kV, 100 MHz) and a current probe (Stangenes Industrie 60 MHz).

A voltage of 18 kV and a frequency of 300 Hz were applied in this study, the rising front of the square pulsed generator being equal to 10^3 V ns^{-1}.

Recorded voltage and current waveforms are shown in Fig. 2. The discharge power was calculated from the time averaged product of discharge voltage and current.

The products were analysed by a four-way gas chromatograph (μGC Varian Quad CP-4900). A Poraplot Q, (10 m, 0.15 mm), a CP-Sil 5 CB (8 m, 0.15 mm), a CP-Wax 52 CB (4 m, 0.25 mm) and a molecular sieve 5 A (10 m, 0.32 mm) columns were used with TCD detectors to analyze on-line the different gases (H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, CH_3OH, CH_3OCH_3, and C_2H_5OH) within 3 min.

The alumina supported La_2O_3 catalyst was prepared using lanthanum nitrate as precursor and alumina balls supplied by AXENS (diameter 2 mm). The preparation was made by an incipient-wetness technique [13]: 15 g of γ-Al_2O_3 was impregnated with an aqueous solution of $La(NO_3)_3{\cdot}6H_2O$ at room temperature. Then the catalyst was dried at 150 °C for 10 h and calcined in air at 800 °C for 6 h. The resulting catalyst possessed a lanthana loading equal to 20 wt.%. A second impregnation was performed following the same procedure, the total loading was closed to 40 wt.%.

3. Results and discussion

3.1. Influence of the molar ratio CH_4/CO_2

The experiments were performed at a constant total flow rate (80 mL/min) and a constant helium content (82%) while the molar ratio CH_4/CO_2 was varied from 1 to 14. A voltage of 18 kV and a frequency of 300 Hz were applied. First of all we checked that the deposited power was not influenced by the gas composition, and due to the large excess of helium the input power was the same (40 W) whatever the ratio CH_4/CO_2. Fig. 3 shows that the carbon dioxide conversion is higher than the methane conversion when

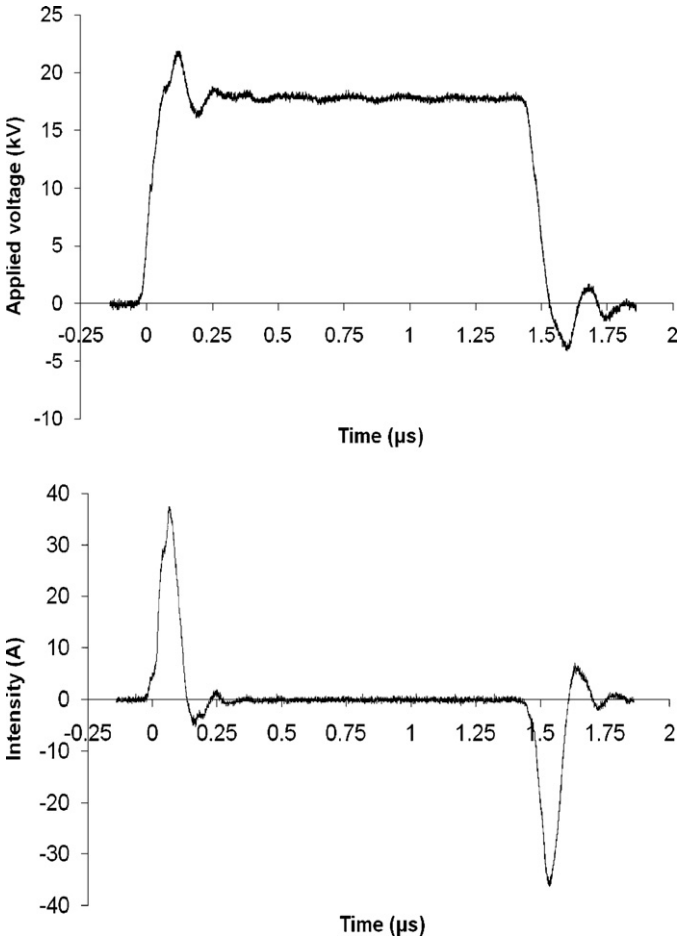

Fig. 2. Recorded voltage and current waveforms.

the ratio CH_4/CO_2 is higher than 4. The methane conversion is not strongly modified by the gas composition, the CH_4 conversion is closed to 25% in our experimental conditions. It is well admitted in the literature that, using non-thermal plasma systems, the reaction proceeds via excited species such as CH_x*, O*... which reacts to produce synthesis gas but also hydrocarbons [14–16]. The carbon balance, reported in Fig. 3 slightly decreases when the ratio CH_4/CO_2 increases, which shows that an excess of methane in the feed gas favors the formation of products not detected by the GC. Indeed in a previous study we showed that liquid products such as 2-methyl-2hexanol, 3-methyl-2-heptanone, 3-butyloctanol and 4-dodecene can be formed as soon as carbon dioxide is in excess

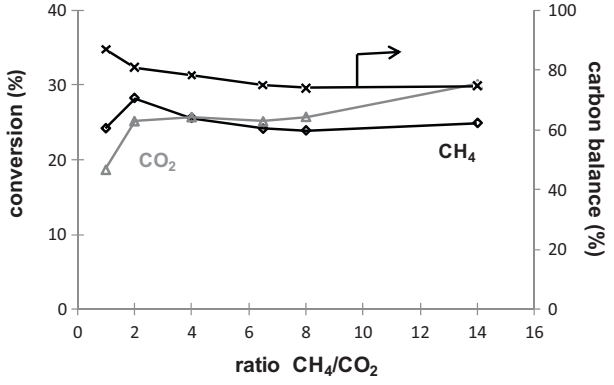

Fig. 3. CH_4 and CO_2 conversion as a function of the CH_4/CO_2 molar ratio. Room temperature, P = 40 W; total flow, 80 mL/min and He, 65 mL/min.

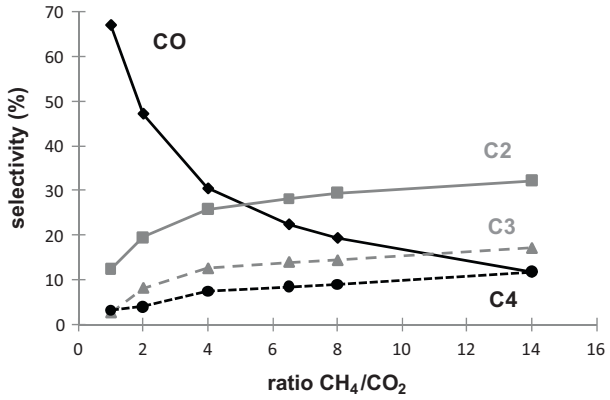

Fig. 4. Selectivity to products as a function of the CH_4/CO_2 molar ratio. Room temperature, $P = 40$ W; total flow, 80 mL/min and He, 65 mL/min.

[17]. Nevertheless a coke deposition cannot be excluded since the presence of a black solid, in the plasma zone, is observed after reaction.

The hydrocarbons selectivity is strongly dependent of the molar ratio CH_4/CO_2 as shown in Fig. 4. When a stoichiometric mixture of CH_4 and CO_2 is used, the production of synthesis gas is favored, the CO selectivity being equal to about 70%. The hydrocarbons selectivity from C2 to C4 is important when an excess of methane is used. Within C2 products, ethane is mostly formed its selectivity reaches 23% with a CH_4/CO_2 ratio equal to 6.5, whereas the C_2H_4 and C_2H_2 selectivity are lower than 3%. The production of hydrocarbons is accompanied by carbon deposition, mainly with high CH_4/CO_2 molar ratio (carbon balance = 75%).

The reactivity of methane in the presence of CO_2 can be explained not only by a direct activation of methane to produce methyl radicals but also by the interaction between active oxygen species, issued from CO_2, and methane according to Reactions (1) and (2) [15]:

$$CO_2 + e \rightarrow CO + O \quad (1)$$

$$CH_4 + O \rightarrow CH_3 + OH \quad (2)$$

The formation of hydrocarbons is favored when the amount of CH_4 is high because the probability for methyl radical recombination is maximum when the methane concentration in the gas phase is maximum too.

3.2. Influence of temperature

The influence of the reaction temperature was examined using the following gas mixture: CH_4/CO_2/He: 14/1/65 mL/min, while the temperature was varied from room T to 600 °C. The applied voltage was fixed at 18 kV and the frequency was equal to 300 Hz. Fig. 5 shows that the deposited power increases with increasing temperature which can be explained by the lower gas density at high temperature [18].

Fig. 6 shows a slight increase of methane conversion with the increase of temperature whereas the CO_2 conversion is not significantly modified. The carbon balance is always far from 100% whatever the operating temperature.

The product distribution changes significantly with temperature as shown in Fig. 7. Ethylene selectivity increases sharply with increasing temperature in the range 300–600 °C, while at the same time the ethane selectivity decreases significantly. These results can be explained by the dehydrogenation reaction of ethane favored at high temperature as shown by different studies [19,20]. However another reaction has been postulated to explain the formation of ethylene under DBD plasma [21]:

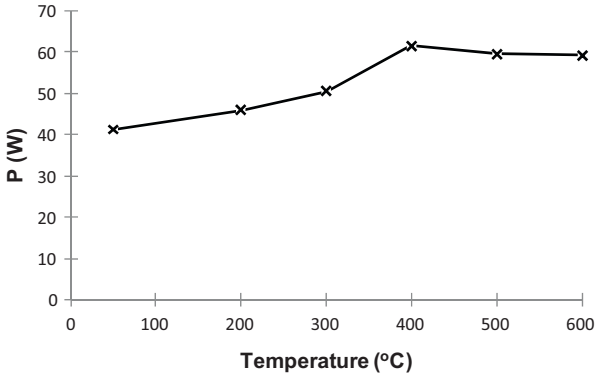

Fig. 5. Deposited power as a function of the reaction temperature. Voltage, 18 kV; frequency, 300 Hz and CH_4/CO_2/He, 14/1/65 mL/min.

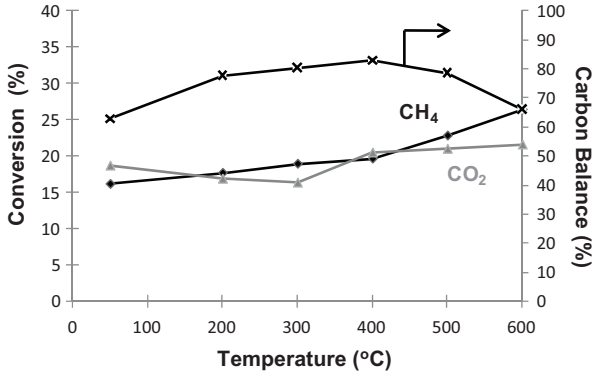

Fig. 6. CH_4 and CO_2 conversion as a function of the reaction temperature. Voltage, 18 kV; frequency, 300 Hz and CH_4/CO_2/He, 14/1/65 mL/min.

$$CH + CH_3 \rightarrow C_2H_4 \quad (3)$$

The CO selectivity slightly decreases until 300 °C and then increases which is in accordance with the works of Hammer et al. [22]. This result can be explained by the oxidation of the deposited carbon at high temperature leading to CO formation [23,24]. At temperature higher than 300 °C, the C3 and C4 hydrocarbons selectivity decreases significantly resulting from their cracking.

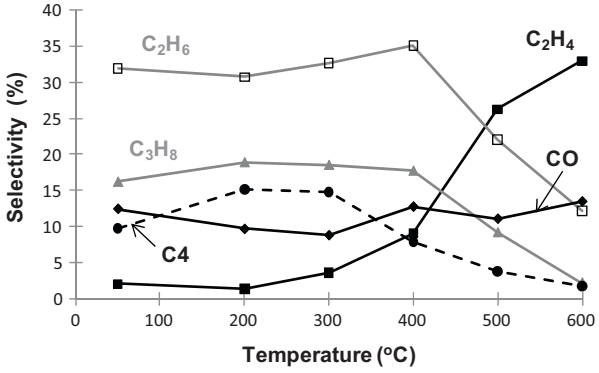

Fig. 7. Selectivity to products as a function of the reaction temperature. Open symbol: with glass balls and closed symbol: without glass balls. Voltage, 18 kV; frequency, 300 Hz and CH_4/CO_2/He, 14/1/65 mL/min.

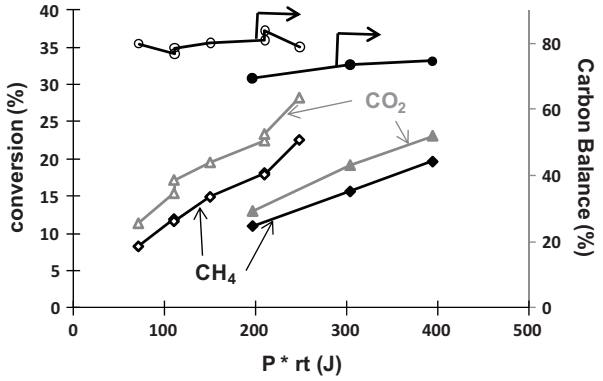

Fig. 8. CH_4 and CO_2 conversion with and without glass balls in the plasma zone. Open symbol: with glass balls and closed symbol: without glass balls. Voltage, 18 kV; frequency, 300 Hz and CH_4/CO_2/He, 14/1/65 mL/min.

3.3. Influence of the presence of glass and alumina balls in the plasma zone

It is known that the introduction of a solid in the plasma zone modify the discharge properties. Kraus et al. [25] explain that the presence of a ceramic foam in the plasma zone increase the efficiency of the discharge since it modifies the gap spacing leading to an increase of the breakdown field.

In our experimental conditions we investigated the influence of the presence of glass and alumina balls, with the same diameters, in the plasma zone. Since the introduction of balls in the plasma zone changes the residence time of the feed gases when the gas flow is not modified, we consider the joint effect of input power and residence time by using the product: $P \times$ rt (with P = input power in W, rt = residence time in second). As shown in Fig. 8 the presence of glass balls in the plasma zone increases methane and carbon dioxide conversion significantly. This result can be explained by a more stable DBD discharge as soon as the plasma zone is filled with a dielectric material such as glass balls [26].

The carbon balance is also increased in the presence of glass balls showing that carbon deposition is limited in these experimental conditions.

The products selectivity reported in Fig. 9 was not strongly modified by the introduction of glass balls in the plasma zone. However it is possible to notice that the C2 selectivity is slightly increased.

The introduction of alumina balls, instead of glass balls, in the plasma zone do not modify significantly the CH_4 and CO_2 conversion and the products selectivity. Indeed alumina is a support of catalyst and does not participate to the reaction between methane and carbon dioxide.

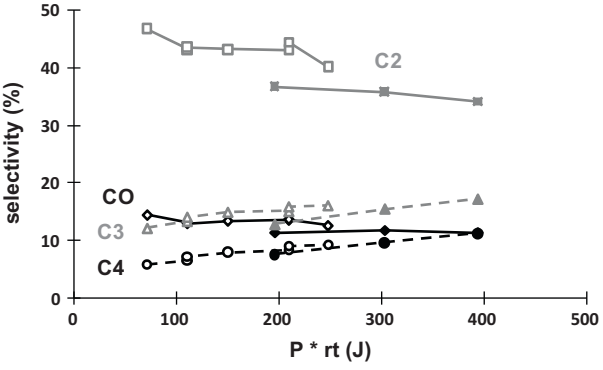

Fig. 9. Selectivity to products with and without glass balls in the plasma zone. Open symbol: with glass balls and closed symbol: without glass balls. Voltage, 18 kV; frequency, 300 Hz and CH_4/CO_2/He, 14/1/65 mL/min.

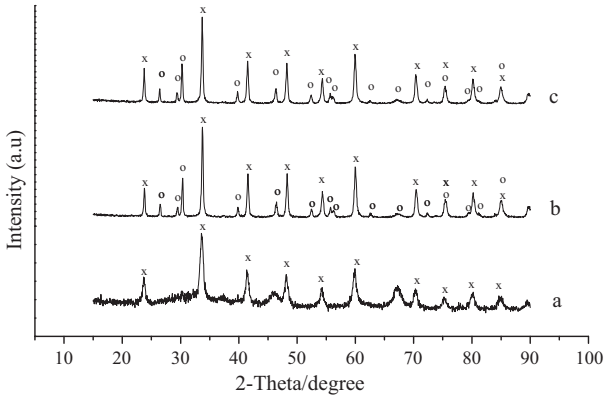

Fig. 10. XRD patterns of the catalyst balls: (a) after the first impregnation with lanthanum, (b) after the second impregnation with lanthanum and (c) after 2 h of reaction at 400 °C under plasma. x: $LaAlO_3$ and o: La_2O_3.

3.4. Influence of the presence of La_2O_3/Al_2O_3 balls in the plasma zone

3.4.1. X-ray diffraction characterization

The XRD patterns of the catalyst after the first, second impregnation with lanthanum and after reaction at 400 °C under discharge plasma, are shown in Fig. 10. Fig. 10a shows that the perovskite phase $LaAlO_3$ is present after calcination at 800 °C for the first impregnation of lanthanum on the alumina balls. This result is in accordance with the works of Boukha et al. [27] who showed the formation of the perovskite phase at a calcination temperature of 800 °C and above. A second impregnation of lanthanum leads to the formation of lanthanum oxide as shown in Fig. 10b. This result show that the first layer of $LaAlO_3$ obtained after calcination at 800 °C allow to avoid the diffusion of lanthanum into alumina during the calcination step after the second impregnation.

3.4.2. The plasma–catalyst association

The catalyst used to perform the plasma–catalyst reaction was the one obtained after two impregnation steps, showing the presence of lanthanum oxide.

The results obtained by combining non-thermal plasma and catalyst, at different temperatures, are gathered in Table 1. The deposited power increased from 45 W at room temperature until 53 W at 400 °C. It appears that, at room temperature, the presence of lanthanum oxide does not modify significantly the CH_4 and CO_2 conversion, the CO and hydrocarbons selectivity being approximately the same as those obtained with pure alumina balls.

When the temperature is increased from room temperature to 400 °C, the methane conversion remains stable while the CO_2 conversion is strongly increased. First of all, we checked that under La_2O_3/γ-Al_2O_3 balls without discharge plasma, no methane activation was possible until 400 °C, which results from the high stability of the CH_4 molecule. Concerning carbon dioxide, we observed that its amount at the exit of the reactor was not stable as soon as the temperature reached 200 °C, a low conversion of CO_2 was mea-

Table 1
CH_4 and CO_2 conversion, selectivity to products, carbon balance, deposited power as function of the temperature in the presence of La_2O_3/γ-Al_2O_3 balls in the plasma zone. Voltage: 18 kV, frequency: 300 Hz, CH_4/CO_2/He: 14/1/65 mL/min.

T (°C)	Conversion (%)			Selectivity (%)				CB (%)	P (W)
	CH_4	CO_2	CO	C_2	C_3	C_4	H_2		
Room (T)	19.5	23.3	10.7	42.9	12.4	5.6	16.6	72	45
200	20.9	32.0	9.2	41.2	15.0	8.7	16.6	74	52
400	21.4	56.1	24.8	39.5	11.7	5.3	19.5	81	53

sured followed by a CO_2 release. This result obtained in the absence of plasma discharge can be explained by the formation of carbonate species at the surface of the basic oxide La_2O_3. Indeed, it has been shown that oxycarbonate species can be formed at the surface of lanthanum oxide at low temperature, but those surface carbonate species are not stable and can released easily at 200 °C [28]. When the temperature reaches 400 °C, the amount of carbon dioxide consumed is increased but due to the instability of the lanthanum oxycarbonate, it is not possible to indicate a CO_2 conversion. However we can notice that the CO_2 consumption at 400 °C is accompanied by the production of a small amount of carbon monoxide while no methane was converted, showing that the activation of carbon dioxide proceeded via lanthanum carbonate species.

Under plasma discharges the activation of carbon dioxide is strongly enhanced when the temperature increased. The CO_2 conversion is closed to 32% at 200 °C and 56% at 400 °C. The higher activation of CO_2 leads to the production of a significant amount of synthesis gas (H_2 + CO), while the hydrocarbons selectivity is not strongly modified. We can notice also that an increase of temperature leads to a higher carbon balance, showing that the carbon deposition is limited at 400 °C.

The role of lanthanum carbonate species in the dry reforming of methane has been evidenced by different authors [29,30]. It is postulated that lanthanum oxide acts as an intermediate by storing CO_2 which is then released as carbon monoxide. It is also known that methane is only weakly adsorbs on La_2O_3, consequently the activation of methane is not enhanced by the presence of lanthanum oxide. In our experimental conditions, the carbon dioxide activation proceeds readily at 400 °C under plasma discharges which can be explained by the formation of surface lanthanum carbonate species while the activation of methane is the same whatever the reaction temperature and the presence or not of lanthanum oxide in the plasma zone.

The results show that the activation of methane proceeds only under the discharge plasma, the presence of the catalyst La_2O_3/γ-Al_2O_3 does not enhanced its activation. It modifies significantly the products selectivity due to the activation of CO_2 probably via the formation of surface lanthanum carbonate species an intermediate in the formation of carbon monoxide. The XRD spectra of the catalyst (Fig. 10c) after 2 h of reaction at 400 °C under non-thermal plasma show almost no difference with the fresh catalyst, however a surface modification of the solid, not visible by XRD, cannot be excluded.

4. Conclusion

We showed with this study that plasma is an effective tool to produce hydrocarbons from methane and carbon dioxide. An excess of methane ($CH_4/CO_2 = 14$) favors the production of C2 hydrocarbons while the formation of carbon monoxide is limited. However, the carbon balance never reaches 100% due to carbon deposition and the presence of heavy molecules formed during the reaction whatever the molar ratio CH_4/CO_2.

Ethane is mainly formed at room temperature while at 600 °C the ethylene production is strongly favored due to the dehydrogenation of ethane.

The use of a catalyst known for its activity in the oxidative coupling of methane was evaluated in association with non-thermal plasma. For that purpose, lanthanum oxide was deposited at the surface of alumina balls. We showed that a two-step impregnation method of lanthanum leads to the formation of lanthanum oxide besides the perovskite: $LaAlO_3$, after calcination at 800 °C.

At room temperature, the presence of the catalyst La_2O_3-$LaAlO_3$-γ-Al_2O_3 does not modify the CH_4 and CO_2 activation compared to glass balls placed in the plasma zone. At 200 °C, and particularly at 400 °C, the activation of carbon dioxide is significantly increased, in the presence of the catalyst, leading to a higher carbon monoxide selectivity, while the conversion of methane remains stable. This result shows that the non-thermal plasma discharges play an important role on the activation of carbon dioxide, most probably via the formation of oxycarbonate species at the surface of the catalyst.

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