Carbon dioxide reforming of methane using a non thermal plasma Effect of power supply on plasma-catalyst interaction

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Introduction

A lot of research has been done in catalytic reforming of methane with carbon dioxide. However, the major drawback of the reaction is the cost of the process which requires temperatures between 800 and 1000°C. In these fields, significant advantages are currently expected from non traditional approaches to catalysis. One of these new approaches consists to perform the chemical activation of reactants by a plasma generated by an electric gas discharge [1]. Non-thermal plasma is an effective tool to generate energetic electrons, which can initiate plasma chemical processes such as ionization, dissociation and excitation at room temperature.
The use of a catalyst in combination with a non-thermal plasma has been studied but the results published in the literature are often contradictory [2,3], most probably because of the important differences in the plama reactor configuration used (gas gap distance, deposited power range, nature of dielectric, electric source . AC, DC, microwave, pulse…).
In this context, the main objective of the present study was to investigate the interaction between gas discharges and a catalyst and to elucidate the role of the excited species.
It is known that the performances of a plasma process depend on many parameters such as temperature, contact time, nature of dilutant, input power… the effect of those parameters was shown elsewhere [4]. In this study, we will only present the influence of the molar ratio CH_4/CO_2 on the reactants conversion before describing the plasma-catalyst interaction .

Materials and Methods

The experiments were performed in a cylindrical dielectric-barrier-discharge (DBD) alumina reactor. Plasma was generated by a monopolar pulsed electric generator and a AC power supply delivering a sinusoidal signal. The study on the influence of the CH_4/CO_2 ratio was performed at a fixed discharge power of 8 watt (applied voltage: 15kV, frequency : 300Hz) by varying the molar ratio of methane to carbon dioxide from 0.25 to 4, the total CH_4+CO_2 concentration was 33.3 %, helium was used as dilutant (66.7%) the flow rate being fixed at 22.5mL/min. The gaseous products were analysed by a µGC (Varian Quad CP4900). The catalyst used was composed of nickel (2wt%) deposited on a alumina washcoated cordierite monolith [5]. The study on the plasma –catalyst interaction was performed with a molar ratio CH_4/CO_2 equal to 0.5.

Results and Discussion

The conversion of CO_2 was not significantly modified by the CH_4/CO_2 ratio whereas the conversion of CH_4 increases when an excess of CO_2 is used. These results can be explained by the high reactivity of oxygenated species resulting from CO_2 dissociation (O, OH) with methane according to : $CH_4 + O \rightarrow CH_3 + OH$. The distribution of the reactant products is greatly influenced by the CH_4/CO_2 feed ratio (Table 1). An increase in the methane concentration favours the production of hydrocarbons and particularly the C2 selectivity. A larger amount of CO_2 in the feed led to higher selectivity to carbon monoxide. The sum of the selectivities were always less than 100% showing that unidentified compounds were produced, one should be coke, particularly when an excess of methane was present. The analysis by mass spectroscopy of the viscous liquid deposited over electrodes after reaction revealed the presence of compounds such as : 2-methyl-2-hexanol, 3-methyl-2-heptanone, 3-butyl-octanol, 4-dodecene… proving the formation of heavy molecules under our experimental conditions.

Table 1. Influence of the CH_4/CO_2 ratio in the feed on selectivities

Ratio CH_4/CO_2	Conversion (%)		Selectivity (%)					
	CH_4	CO_2	CO	C2	C3	C4	oxy.*	other
0.25	27.6	11.0	81.0	1.8	1.2	0.6	0.4	5.0
0.5	20.9	12.5	71.9	5.2	3.2	1.6	1.1	7.0
1	17.6	13.3	58.3	11.4	6.6	3.4	1.7	18.6
4	12.3	11.8	29.5	24.8	13.5	7.0	2.4	22.8

* oxy : oxygenated compounds

The combination of a catalyst with the plasma did not increased significantly the reactant activation when a pulse power supply was used (Figure 1) CH_4 and CO_2 conversion are approximately the same with the support alone and the catalyst composed of 2wt% Ni over an alumina washcoated support. With a sinusoidal signal, the behavior is different, very low conversions are obtained with the support alone but the presence of the catalyst allows to increase sharply the conversions (more than 200% for CH_4 and CO_2). According to the work of Chen et al.[6], the energy carrier generated could explain the results obtained here. Indeed, we can assume that the electron energy delivered by the pulse power supply was too high to assists the catalyst, the species with lower energy (vibrational state) more readily generated by the sinusoidal signal could be responsible for the synergy between plasma and catalyst.

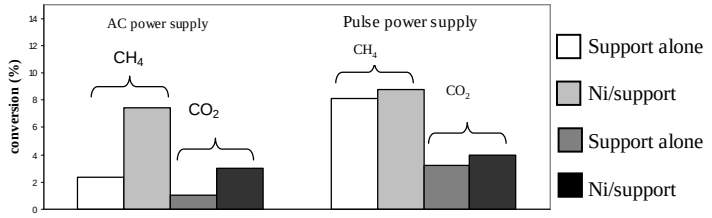

Figure 1. Effect of the applied voltage form on CH_4 and CO_2 conversions

Significance

We showed that it is possible to obtain an interesting synergy between plasma and a catalyst, for the conversion of CH_4 and CO_2, as soon as the most energy effective species are generated.

References

1. Kado, S., Urasaki, K., Sekine, Y.,Fujimoto, K., Chem. Commun., Vol. 5, 415-416 (2001)
2. Kim, S., Lee, H., Na, B., Song, H., catal. Today, 89, 193-200 (2004)
3. Eliasson, B., Liu, C.J., Kogelschatz, U., Ind. Eng. Chem. Res., 39, 1221-1227 (2000)
4. Goujard, V., Batiot-Dupeyrat, C., Tatibouët, J.M., Appl. Catal. A: General, in press 2008
5. Villegas, L., Masset, F., Guilhaume, N., Appl. Catal.: A: General, 320, 43-55 (2007)
6. Chen, H., Lee, H., Chen, S., Chang, M., Appl. Catal. B: Environmental, in press 2008