Catalytic reactor configuration for coupling of methane assisted by DBD plasma

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Abstract: The effect of Pd/Al_2O_3 catalyst on plasma-assisted coupling of methane in different reactor configurations has been analysed. The methane conversion is determined by plasma power. The catalyst shifts the product distribution towards saturated hydrocarbons, decreasing formation of unsaturated compounds and deposits. A structured reactor with a catalytic layer on the wall of the quartz reactor tube gives the largest effect, decreasing formation of deposits with about 50%.

Keywords: DBD plasma, coupling CH₄, structured reactor, catalyst-plasma synergism, Pd.

1. Introduction

The methane conversion is an interesting alternative to fossil fuels, since methane remains underused and cleaner high value-added chemicals can be produced by coupling methane reaction [1,2]. However, this reaction requires high energy to activate the methane molecules (434 kJ/mol), which involves the use of catalysts and temperatures over 600 °C. Operating at these conditions leads to low methane conversion and significant deactivation by temperature and mainly coke formation [2]. In this context, the co-feed of oxygen increases the methane conversion but the selectivity to hydrocarbons is highly reduced in favour of CO and CO₂ products [3]. Consequently, non-oxidative coupling of methane in a non-equilibrium plasma appears as a promising via for methane conversion into hydrocarbons (mainly alkanes and olefins) [4]. In particular, dielectric barrier discharge (DBD) provides a homogeneous non-equilibrium plasma capable of activating methane molecules at medium temperatures [5]. In this work, the DBD plasma for coupling of methane has been studied at ambient conditions. Different reactor configurations have been addressed in the same reaction conditions in order to study the plasma-catalyst synergism. In addition, the effect of a catalyst is also analysed when placed in different positions along the reactor.

2. Experimental

Non-oxidative coupling of methane has been carried out in a cylindrical DBD reactor at atmospheric pressure and the gas discharge was initiated at room temperature. A quartz tube of 4 mm in internal diameter and 30 cm in length is used as dielectric reactor. A stainless steel rod of 1.6 mm in diameter is placed in the center of the quartz tube as high voltage electrode. The grounded electrode is a cylindric stainless steel of 3.3 cm in length that externally covers the quartz tube. The applied plasma power was set at ~ 6.5 W, applying high voltage of ~ 3-4 kV with a frequency of 23 kHz from an AC power supply. A high voltage probe (TESTEC TT-HVP15 HF), a probe for connecting the ground electrode (TESTEC TT-HV 250), a 3.9 nF capacitor and an oscilloscope (Pico Scope 2000 series) were used to measure the discharge power, which is calculated using the Q-V Lissajous plots.

The reaction products were analysed with an online Varian 450 GC equipped with a Hayesep T&Q, Molsieve 13x and PoraBOND Q columns, and a TCD and FID detectors.

The catalytic tests were performed with a commercial Pd/Al_2O_3 catalyst (1 wt.% Pd, Alfa Aesar). An optimized colloidal suspension were prepared with 14 wt.% of catalyst sieved below 32 µm, 6wt.% of aqueous colloidal alumina solution (20 wt.% Al_2O_3 , Nyacol) and deionized water. The catalytic layer was deposited via washcoating on the internal wall of the quartz reactor in the specific length and position were the plasma is generated. Both, structured reactor and the slurry to generate powder catalyst, were then dried and calcined in air for 8 h at 350 $^{\circ}$ C. The heating ramp was 2 $^{\circ}$ C/min to avoid fissures or pores in the catalytic layer. Afterwards, the catalyst was reduced in 10 % of H₂ at 350 $^{\circ}$ C for 2 h. The catalytic layer was analysed by scanning Electron Microscope.

Coupling of methane reaction was then performed in DBD plasma reactor (blank) and in 4 catalytic DBD plasma reactor configurations: with a catalytic layer loaded on the internal quartz wall in the plasma zone, and with the equivalent catalyst powders placed inside the plasma (0 cm), 1 cm downstream from the plasma, and 5 cm downstream from the plasma. The same amount of catalyst was used in all catalytic configurations.

3. Results and discussion

Previously to the activity tests, the catalytic layer was analysed by SEM (Fig.1). An homogeneous layer was observed, perfectly attached to the internal quartz wall. Several measurement provided an average thickness of the layer of 14.3 μ m, allowing thereby to discard mass diffusional limitations.

The conversion of methane obtained in these tests at room temperature were in the range of 35 - 42 %, much



Figure 1. SEM image of the catalytic layer over the internal quartz wall obtained by wahscoating process for the structured reactor configuration.

higher than e.g. achieved in a conventional thermal reactor with Mo catalysts [6]. The highest conversion was achieved with the blank reactor, while the lowest value was found for the catalytic layer on the quartz configuration. This is explained by the change in the capacitance of the dielectric material, since all the experiments were carried out at the same power input but the presence of the catalyst generates an additional dielectric material in the gap. changing the properties of the plasma.

Hence, the plasma apparently determines the conversion of methane, since is responsible of activating the methane molecules and developing the radical reaction. Indeed, it is clearly noticed that the product distribution obtained in any configuration remains stable in time, whereas the yield of each product varies accordingly to the methane conversion, as observed e.g. with structured reactor configuration (Fig.2).

On the other hand, the catalyst shifts the product distribution. As can be seen in Fig.3, the presence of the catalyst enhances hydrogenation of activated species, thus producing more saturated hydrocarbons, at the expense of unsaturated hydrocarbons and, more important, the undesirable carbon-based deposits. These deposits, mainly coke and polymeric -CH_x - hydrocarbons, are distributed among the internal quartz wall and the central electrode, decreasing the generated plasma power. Besides the significant reduction in deposits formation, the main changes are increasing selectivity to ethane and complete suppression of acetylene when the catalyst was present. The structured reactor configuration, with the catalyst loaded as a thin layer on the internal quartz wall, shows the biggest effects, decreasing formation of deposits and enhancing formation of saturated hydrocarbons (Fig.3). Since the methane conversions achieved by the catalytic configurations (layer or powders) are the same and the hydrogenation effect in this case is even higher than the powdered catalytic configurations, possible reactant bypassing with the structured configuration is discarded.





Comparing the position of the powdered catalytic configuration shows that the hydrogenation effect is significantly reduced when the catalyst is placed outside the plasma zone. Indeed, acetylene is again observed in the product distribution when the catalyst is placed downstream at 5 cm from the plasma. In fact, this extreme case is quite similar to the blank configuration except for the deposits production. This reveals that the effect of the catalyst is almost non-existent at this distance and the lifetime of the plasma activated species is below 1.6 seconds. However, the production of less amount of deposits was still achieved by forming unsaturated hydrocarbons.

The amount of deposits in Fig.3, calculated based on the carbon balance, was also corroborated by weighing the reactors before and after reaction. This results, reported in Table 1, support the decrease of *c.a.* 50 % observed for the structured reactor configuration compared to the blank. Moreover, the amount of deposits measured for the three configurations with powdered catalyst in fixed bed are in

the same range, indicating that this promotional effect occurs in the same extent independent of the position, which could be associated more to the hydrogenation of the formed deposits more than avoid their production. However, in the case of the structured reactor, showing so much less deposits (3.5 mg on the quartz wall), also prevention of forming deposits may contribute, since the internal wall of the reactor is completely covered with the catalyst.



Figure 3. Carbon based selectivities of the products for DBD plasma-assisted coupling of methane at 20 min. of reaction. Saturated HC includes C₂H₆, C₃H₈, iso-C₄H₁₀ and n-C₄H₁₀. Unsaturated HC includes C₂H₂, C₂H₄, C₃H₆, C₄H₈, C₄H₆. Deposit selectivity is calculated from the carbon balance.

Table 1. Carbon-based deposits weighted after plasmaassisted coupling of methane reaction for 3h in different reactor configuration.

Experiment	Deposits on quartz wall (mg)	Deposits on internal electrode (mg)
Blank	6.6	1.0
Layer on Q	3.5	0.7
Powder 0cm	9.9	0.7
Powder 1cm	9.5	1.0
Powder 5cm	7.6	1.0

4. Conclusions

Coupling of methane reaction has been successfully performed in a DBD non-equilibrium plasma at room temperature, achieving around 42 % of methane conversion.

Methane conversion is meanly determined by plasma power. However, the product distribution is shifted by Pd/Al₂O₃ catalyst towards more saturated hydrocarbons and, more importantly, decreasing the undesired amount of carbon-based deposits. The structured reactor exhibits the lowest amount of carbon deposits, an increased selectivity to ethane of *c.a.* 40 % and no formation of acetylene. On the other hand, the use of powdered catalysts resulted in less enhancement of hydrogenation reactions than the structured reactor. The catalytic effect is further decreased when the catalyst was placed downstream, outside the plasma zone and is even almost non-existent when the catalyst in placed 5 cm downstream from the plasma.

5.References

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