Topic number: 3

Oxidation of methane in a DBD – catalyst system using $He/CH_4/CO_2$ or $Ar/CH_4/CO_2$ mixtures

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Introduction

The use of a non-thermal plasma (NTP) for methane conversion is an interesting alternative to steam reforming and has been the subject of many studies [1]. A NTP process can reach methane conversion values comparable to or higher than those obtained through the thermal process but the product selectivities are poor [2]. The coupling of the plasma with a catalyst improves the selectivity for selected products. This is a synergistic effect on the catalysts due to the plasma pre-activation of the reagents.

In this work, we studied the production of *Syngas* using $He/CH_4/CO_2$ or $Ar/CH_4/CO_2$ mixtures in a DBD – catalyst system. On a DBD-only discharge we obtained maximum conversion rates of 65% (CH_4) and 50% (CO_2), and selectivity values of 80% (H_2) and 70% (CO). With a catalyst positioned after the discharge, the CH_4 and CO_2 conversion rates have increased up to 10%, depending on the catalyst temperature. Other products with significant selectivities include ethane (up to 30%), propane (up to 12%) and ethylene (3%).

Experimental setup

The results were obtained in a reactor with cylindrical geometry, built from a 10 mm I.D. glass tube and a ∅ 5 mm SS electrode, supported by ™MACOR fittings. The external (ground) electrode is an aluminum thin foil stretched around the glass. The chamber has a porous glass on one end to support a catalyst set at a few mm from the round tip of the internal electrode.

The gas flow was controlled with standard mass flow controllers ranging from 2 to 6 L/h. The gases used had a purity of at least 99.99%. We changed the CH_4/CO_2 ratio from 0.1 to 2.0 and the rare gases concentration from 60% to 93%.

We have tested three different catalysts: a commercial 5% Rh - Al_2O_3 catalyst and two other catalysts developed by the group based on Cu-Ce or Pr-Ni oxides [3, 4].

The power supply allowed a maximum RMS voltage of 10 kV in a frequency range of 4-6 kHz. The values of Specific Input Energy (SIE)[1] consumed in the discharge system and in the plasma were obtained from the applied voltage and external current using a combination of methods [5]. The output gas composition was analyzed on-line by gas chromatography using a Restek ShinCarbon ST column (L=2.0 m, f=1/8 in., ID=1 mm, 100/200 mesh) and a Shimadzu 9A GC equipped with a thermal conductivity detector (TCD) and a 6-port gas sampling valve with a 0.250 µL loop.

Results with a DBD-only system

For fixed rare gas concentrations, the CH_4/CO_2 ratio affects the CH_4 and CO_2 conversion rates, the former decreasing and the latter increasing with an increase of this ratio (figure 1(a)).

However, it is the rare gas concentration that has a higher impact on the conversion rates, e.g. for a SIE of 10 kJ/ L the CH_4 conversion rate changes from 20%-35% to above 60% when the helium concentration changes from 85% to 72%.

Argon has the advantage of being easier to separate from the products than helium. However, preliminary results with argon replacing helium indicate that for the same values of concentration, the breakdown voltage is higher and that the conversion of CH_4 requires higher SIE.

[1] SIE = Power consumption / gas flux

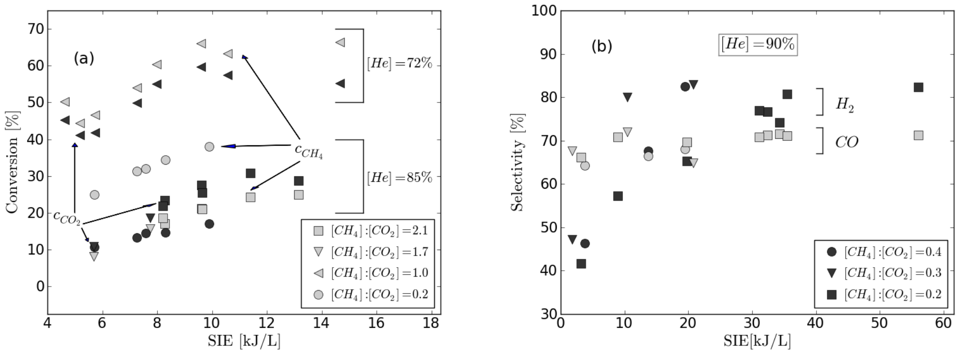

Fig. 1: (a) CH_4 and CO_2 conversion rates as a function of the specific input energy for two values of helium concentration. Light symbols: CH_4, dark symbols: CO_2. (b) Values of selectivity for H_2 and CO as a function of the specific input energy. Light symbols: CO, dark symbols: H_2

Results with a DBD – catalyst reactor

All catalysts show similar results at low temperature. The results were obtained under two (2) conditions: without external heating, and with the DBD discharge chamber inside an oven at 600 K. In the second case, however, we found that the discharge was unstable, easily developed an arc, and had a narrow useful range of working voltages.

Figure 2 shows preliminary results obtained for the CH_4 conversion rate with and without catalyst.

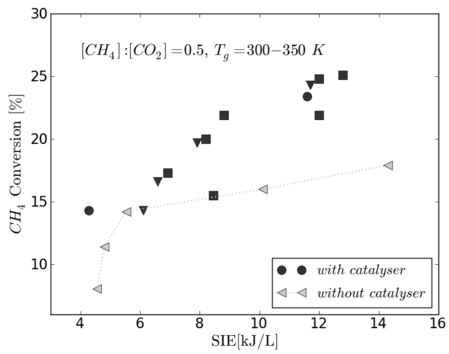

Fig. 2: Comparison of CH_4 conversion rate obtained on the DBD discharge with and without a catalyst. The black symbols identify different catalysts.

Acknowledgments

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