Plasma-catalytic hybrid process for CO_2 methanation

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Abstract

An hybrid plasma-catalytic process at atmospheric pressure was tested for low temperature CO_2 hydrogenation. OES was used to determine the excited species present in the plasma during plasma-catalyst interaction. The coupled plasma DBD – $Ni/CeZrO_2$ system leads to high CO_2 conversions into methane without any external heating source. This low temperature activity can be explained by the formation of highly reactive species from CO_2 and H_2 in the presence of the plasma, further able to react on the surface of the $Ni/CeZrO_2$ catalyst.

I. Introduction

Among the different processes for the catalytic valorisation of CO_2 [1], methanation, i.e. CO_2 hydrogenation, stands as a promising and industrial-scale applicable technology. Although CO_2 conversion into methane is exothermic and thermodynamically favourable at ambient temperature, a catalyst and high temperatures (> 350°C) are needed in order to achieve acceptable methane yield [2,3]. The association of a catalyst with a non-thermal plasma, i.e a dielectric-barrier discharge plasma (DBD), has been recently considered as a tool for boosting CO/CO_2 methanation [4-7]. Concretely DBD plasmas have been successfully coupled with Ni-containing zeolite, ceria-zirconia or hydrotalcite-based catalysts [5-7].

Optical emission spectroscopy (OES) is a powerful diagnostic tool widely used for the characterisation of different types of plasmas [8-11]. It allows the partial determination of the plasma composition without exerting any intrusion or influence over it. Moreover, OES provides crucial information about the excitation state (vibrational and rotational), the electronic temperatures and the energy distribution. In this work, based on the coupled process previously proposed [6], OES information is used with the aim of identifying the contribution of plasma to the overall reaction mechanism.

II. Experimental setup, runs, and OES diagnostics

The activity towards CO_2 methanation under different reaction conditions, i.e. plasma alone (A), catalyst alone (B), plasma + catalyst (C) and plasma + catalyst support (Cbis), was studied at reaction temperatures from 80 to 450°C, in a dielectric barrier discharge (DBD) plasma reactor operating at atmospheric pressure. It consisted of two coaxial tubes

(quartz/alumina tubes), having internal diameters of 10 and 3 mm (2,5 mm gap), and 10 mm of effective length [11]. A high-voltage alternating current in the range of 14 kV (41 kHz) was applied in order to create DBD plasma, corresponding to a power between 3-9 W. Around 300 mg (0.6 cm^3) of catalyst were placed at the annular space of the discharge zone in the reactor.

A reactant gas containing 20% vol. CO_2 and 80% vol. H_2 was fed at 200 mL/min (GHSV = 20,000h^{-1}). The DBD plasma reactor was used either under adiabatic conditions or under isothermal conditions, using an external heating (electric furnace) to reach the desired temperature in this last case. The gas temperature inside the catalytic bed was measured with the aid of a K-type thermocouple (Figure 1).

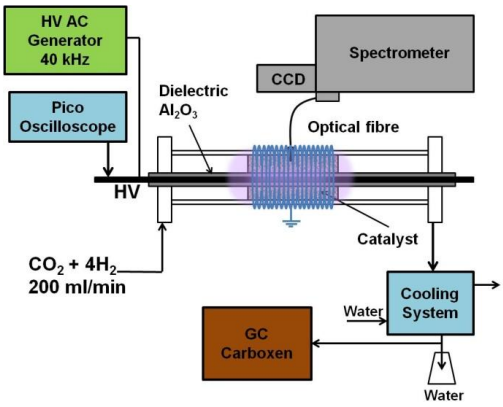

Fig. 1: Experimental setup

The gaseous products exiting the reactor were analysed in a gas chromatograph (IGC-120-ML, TCD detector). The catalyst was a 15 %wt. Ni-containing ceria-zirconia supported catalyst ($Ni/ZrCeO_2$) prepared through a conventional impregnation method [6]. The unloaded ceria-zirconia support was also tested and found to be inactive in CO_2 methanation.

Plasma emission spectra were recorded with a monochromator spectrometer type Czerny Turner with three diffraction gratings (150, 1200 and 3600 lines/mm) coupled with a CCD camera. The opening of the slit was set at 100 μm and the optical fibre was placed vertically along the plasma with a constant distance of 4 mm from the quartz tube. OES spectra were acquired at wavelengths from 200 to 800 nm, 100 ms acquisition time. The OES measures were repeated at least three times.

III. Results and discussion

III.1. Activity in CO_2 methanation

Fig. 3 shows the CO_2 conversions and CH_4 yields measured in the presence of the catalyst alone (B) and in the presence of both the plasma and the catalyst (C), at temperatures from 80 to 450°C. The sole presence of the DBD plasma resulted in zero CO_2 conversion (results not shown). In the absence of plasma and in the presence of the Ni-catalyst, CO_2 conversion is almost negligible at temperatures below 250°C, increasing up to 85% at 450°C. The presence of the DBD plasma greatly boosts the conversion of CO_2 at low temperatures, almost reaching thermodynamic equilibrium conversion, with a methane selectivity always higher than 90% at temperatures lower than 100°C.

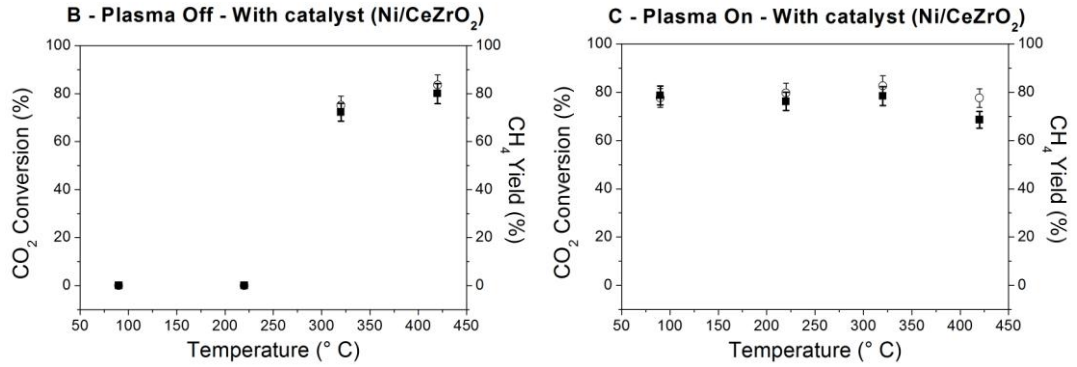

Fig. 2: (○) CO_2 conversion and (■) CH_4 yield measured under different reaction conditions: (B) Plasma off – With catalyst and (C) Plasma on – With catalyst

III.2. Optical Emission Spectroscopy Analyses

Figure 3 shows the OES spectra acquired under different reaction conditions: in the sole presence of the DBD plasma (A), in the presence of both the plasma and the catalyst (C), and in the presence of the plasma and the ceria-zirconia support (Cbis, no Ni).

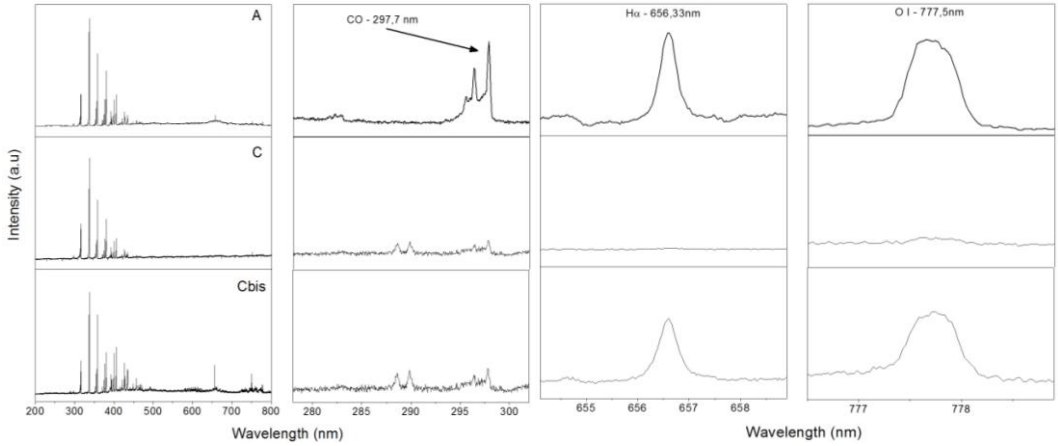

Fig. 3: Emission spectra of the CO_2/H_2 plasmas (A) Plasma on – without catalyst, (C) Plasma on – With catalyst, and (Cbis) Plasma on – CeZr support.

The presence of a CO_2/H_2 plasma into the empty reactor results itself in the formation of several excited species in the gaseous phase, i.e. CO (b-a), H^{α} (655.3nm) and O (777.5 nm). The same species are obtained and can be observed in presence of the plasma-support system (Cbis) and almost totally disappear when the plasma is combined with the Ni-containing catalyst (C). This is specially true for H^{α} and O species. Though the ceria-zirconia support may be able to interact to a certain point with the excited species created by the plasma, the conversion of such species is only possible in the presence of the Ni-active sites present in the $Ni/CeZrO_2$ catalysts. Once these Ni-active sites are ready for reaction, the gaseous excited species created by the plasma react on the catalyst surface and are converted to the reaction products. Although the ceria-zirconia support favours CO_2 adsorption and dissociation and may contribute to oxygen transfer, the presence of Ni is crucial for the methanation reaction,

as well as its dispersion, crystal size and reduction state. These findings are in agreement with previously published results, in a work that indeed compared different types of ceria-zirconia supports having different ceria and zirconia content [6].

IV. Conclusion

The hydrogenation of CO_2 in the presence of a DBD plasma coupled to a $Ni/ZrCeO_2$ catalyst was considered and studied using OES, as a tool for the determination of the excited species and for gaining insight into role of both plasma and catalyst into this coupled process. The methanation reaction did not practically take place in the sole presence of the plasma and in the presence of the plasma combined with the ceria-zirconia support. In the sole presence of the $Ni/ZrCeO_2$ catalyst, reaction did not occur at temperatures lower than 350°C. The coupling of the DBD plasma together with the $Ni/ZrCeO_2$ catalyst yielded almost complete CO_2 conversion at very low temperatures, i.e. lower than 100°C. The OES study of this coupled plasma-catalytic system evidenced the formation of several excited species in the CO_2/H_2 plasma. Though the ceria-zirconia support may contribute to CO_2 adsorption and dissociation, the methanation reaction involving the consumption of the gaseous excited species is only possible in the presence of the Ni-containing catalyst. This finding points to the presence of Ni and to its physico-chemical properties as the crucial issues in the design of active and selective catalysts for this coupled plasma-catalytic CO_2 methanation process.

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