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***Plasma DBD activated ceria-zirconia-promoted Ni-catalysts for plasma catalytic CO<sub>2</sub> hydrogenation at low temperature***

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**Abstract**

The activity of Ceria-Zirconia supported Ni catalysts was measured in a hybrid cold dielectric barrier discharge (DBD) plasma-catalytic process for the hydrogenation of carbon dioxide into methane at low temperatures. Hydrogen DBD plasma treatment at room temperature was chosen as an alternative activation to conventional reduction performed at high temperature. The plasma-catalytic tests performed in the presence of the plasma-treated catalyst clearly show that the hydrogen plasma treatment can replace the high-temperature reduction in hydrogen.

**Keywords:** CO<sub>2</sub>-methanation, catalytic plasma activation, nickel catalysts

## 1. Introduction

With the increase of energy consumption leading to global warming, CO<sub>2</sub> emissions will be controlled. Thus, CO<sub>2</sub> valorisation processes need be developed in order to stabilize the future CO<sub>2</sub> emissions. Among them, CO<sub>2</sub> methanation, i.e. Sabatier reaction, is considered as one of the most effective technologies for CO<sub>2</sub> valorisation, offering moreover a feasible route for renewable H<sub>2</sub> storage and utilisation [1,2] and syn-methane production. CO<sub>2</sub> methanation is catalytic reaction in which Ni and Ni-Ru supported on diverse porous materials [1,3-6]. However, relatively high temperatures are needed to reach acceptable conversions. Recently, it was shown that a plasma DBD catalytic process can lead to high conversions of CO<sub>2</sub> and high CH<sub>4</sub> selectivity at temperatures lower than 200°C [3,7,8,9]. Plasma technologies can also be used for catalytic synthesis [10-15]. In general, there are three main trends in catalyst preparation using plasma technologies: plasma chemical synthesis of ultrafine particle catalysts [11,12], plasma assisted deposition of catalytically active compounds on various supports [13-15] and plasma enhanced preparation or plasma modification of catalysts [12,16,17]. A recent work evidenced that radio frequency or microwave plasma treated catalysts led to higher catalytic efficiency in NO<sub>x</sub> abatement for hydrocarbon SCR (Selective Catalytic Reduction) in comparison to classical calcined catalysts [15,18].

A non-thermal hydrogen plasma reduction pre-treatment is proposed herein as an alternative to conventional high-temperature reduction. The activity and selectivity of both plasma-treated and conventionally reduced 15%Ni/CeZrO<sub>2</sub> catalysts in the coupled DBD-catalytic CO<sub>2</sub> methanation is compared.

## 2. Experimental

### 2.1. Catalysts synthesis and activation

Catalysts were prepared through conventional wet impregnation of a commercial ceria-zirconia mixed oxide ( $\text{Ce}_{0.58}\text{Zr}_{0.42}\text{O}_2$ , Rhodia-Solvay). The Ni loading was 15 wt.% ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  used as precursor). After impregnation, the Ni-impregnated ceria-zirconia were dried overnight at  $100^\circ\text{C}$  and subsequently calcined at  $550^\circ\text{C}$  for 4h. The calcined materials were then activated under different conditions. The catalyst Ni15RED470 was reduced under  $\text{H}_2$  through temperature-programmed reduction ( $5^\circ\text{C}/\text{min}$ ) followed by isothermal reduction at  $470^\circ\text{C}$  for 2h, as described elsewhere [8,9]. Three other catalysts were activated 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 8 and 2.7 mm (2.15 mm gap), and 100 mm of effective length. A high-voltage alternating current in the range of 15 kV (42.5 kHz) was applied in order to create DBD plasma, corresponding to a power at  $8 \pm 0.5$  W (adiabatic bed temperature of  $100^\circ\text{C}$ , due to the exothermicity of the reduction process). 300 mg ( $0.6 \text{ cm}^3$ ) of catalyst were placed at the annular space of the discharge zone in DBD reactor. Pure  $\text{H}_2$  was fed at 160 mL/min ( $\text{GHSV}=16,000 \text{ h}^{-1}$ ), for 20, 40 and 60 minutes. The resulting catalysts were named Ni15PDBD20, Ni15PDBD40 and Ni15PDBD60.

### 2.2. Physico-chemical characterization

The specific surface area (BET) was calculated from  $\text{N}_2$  adsorption isotherms acquired at  $-196^\circ\text{C}$  (degas:  $150^\circ\text{C}$ , 4h, BELSORP-MINI-II-BEL JAPAN). X-ray diffraction (XRD) patterns were recorded in a diffractometer (PANalytical,  $\text{CuK}\alpha$  source). Temperature-programmed reduction (TPR) and  $\text{CO}_2$ -TPD were performed using a BEL-Japan-BELCAT-M. TPR were carried out using under 25 mL/min of a 5% vol.  $\text{H}_2/\text{Ar}$  mixture ( $10^\circ\text{C}/\text{min}$ , 25-

950°C) with 50 mg of activated catalysts. CO<sub>2</sub>-TPD experiments were carried out on activated catalysts with an adsorption at 80°C with 10% vol. CO<sub>2</sub>/He for 1h followed by desorption under He for 20 minutes at 80°C, then from 80 to 900°C with a heating rate of 10°C/min.

### 2.3. Hybrid Plasma-Catalytic Methanation

The activity in CO<sub>2</sub>-methanation was evaluated under adiabatic conditions, at temperatures from 120°C (3W) to 170°C (16W), in the same dielectric barrier discharge (DBD) plasma reactor used for activation/reduction. In all the cases a gas mixture of pure hydrogen and carbon dioxide with a H<sub>2</sub>/CO<sub>2</sub>=4:1, at a flow rate of 200 mL/min (GHSV=20,000 h<sup>-1</sup>), was fed to the reactor.

In the hybrid plasma-catalytic methanation experiments, an alternative current (AC) high voltage (operating frequency: 40-42.8 kHz) of 13-18 kV was applied to the discharging electrode to create non-thermal plasma. It varied in the range of 73-378 μJ/cycle, corresponding to a power between 3 and 16W, with electricity consumption lower than 50 kJ/mole<sub>CH<sub>4</sub></sub> in the best case (40 min, (4W)). The voltage applied to the plasma-catalytic reactor was measured with a digital oscilloscope (PicoScope 5243A) using a probe (ELDITEST GE 3830).

The concentration of CO<sub>2</sub>, CO, H<sub>2</sub> and CH<sub>4</sub> in the inlet and outlet gas streams were measured with the aid of a Varian 490 microGC equipped with a 5m PBQ/10m MS and 10m PPU columns, and TCD detectors. The CO<sub>2</sub> conversion ( $X_{CO_2}$ , %), and CH<sub>4</sub> selectivity ( $S_{CH_4}$ , %), and CH<sub>4</sub> yield ( $Y_{CH_4}$ , %), were calculated as follows:

$$X_{CO_2} = \frac{(n_{CO_2}^{in} - n_{CO_2}^{out})}{n_{CO_2}^{in}} \times 100 \quad (\text{eq. 1})$$

$$S_{CH_4} = \frac{n_{CH_4}^{out}}{(n_{CH_4}^{out} + n_{CO}^{out})} \times 100 \quad (\text{eq. 2})$$

$$Y_{CH_4} = X_{CO_2} \times S_{CH_4} \quad (\text{eq. 3})$$

A blank on-plasma test was performed in the absence of catalysts at 430°C. This test yielded almost no CO<sub>2</sub> conversion and zero selectivity to CH<sub>4</sub>.

### 3. Results and discussion

#### 3.1. Characterization of activated catalysts

The values of BET surface areas for both the Ni-catalysts (Table 1), obtained from their corresponding N<sub>2</sub> adsorption isotherms, are 87, 84, 85 and 84 m<sup>2</sup>/g for Ni15PDBD20, Ni15PDBD40, Ni15PDBD60 and Ni15RED470 respectively, which are in agreement with previous studies [9].

The diffraction patterns are shown in Figure 1. For the plasma treated catalysts (Ni15PDBD20, Ni15PDBD40, Ni15PDBD60), the XDR patterns evidence several marked diffraction peaks corresponding to NiO and Ni<sup>o</sup> crystalline phases. Whereas on reduced catalyst Ni15RED470, only the Ni<sup>o</sup> phase is present. The crystal sizes for NiO and Ni<sup>o</sup> calculated from the diffraction patterns using Scherrer equation, using (311) diffractions, are shown in Table 1. At the sight of these XRD analyses it can be already concluded that the hydrogen plasma treatment lead to the formation of Ni<sup>o</sup> particles similar to the ones obtained by a classical reduction at high temperature. It is however remarkable that the plasma treatment does not lead to a complete reduction of NiO to Ni<sup>o</sup>.

The basicity of these catalysts was evaluated by means of temperature-programmed desorption of CO<sub>2</sub> (TPD-CO<sub>2</sub>). Basicity may play a role in the methanation reaction since it is required in the adsorption and activation of CO<sub>2</sub> [19]. The results of TPD-CO<sub>2</sub> are presented

in Table 1. For all the catalysts, very similar values of CO<sub>2</sub> desorption were measured, with very similar desorption profiles. However, it seems that the plasma activation slightly enhances the basicity of the materials since the total amount of CO<sub>2</sub> desorbed follows the sequence: Ni15PDBD60 > Ni15PDBD40 = Ni15PDBD20 > Ni15RED470. The CO<sub>2</sub>-desorption profiles (not shown) were deconvoluted into 3 contributions at different temperatures: i) 120°C, ii) 200-250°C, and iii) 300-350°C. The desorption peaks with the maximum at approximately 120°C and 200-250° corresponding to the support, can be ascribed to the presence of basic centers of low and/or medium strength (e.g. OH and O groups) [20-23]. It has been already proposed that such weak and medium basic sites are necessary to the methanation reaction [20,24]. The third peak centered at 300-350°C has been ascribed to strong basic sites (e.g. O<sup>2-</sup>) [22,23]. Particularly in the case of the plasma treated catalysts, the incorporation of nickel to a ceria-zirconia support leads to the creation of new strong basic sites and to decrease the amount of weak basic ones. In fact, since strong O<sup>2-</sup> sites may come from Ni that has been incorporated to the ceria matrix, this points to a strong interaction between Ni and ceria from the support that seems to be reinforced as a consequence of the plasma treatment.

### 3.2. Hybrid plasma-catalytic methanation: Effect of power supply on catalytic activity

The CO<sub>2</sub> steady-state conversions measured for the conventionally reduced catalyst, H<sub>2</sub>-470°C (Ni15RED470), are presented in Fig 2. They increase from 65% to 80% with increasing power supply from 4 to 16W. However, a plateau is already obtained at around 8 W, pointing to an optimal in terms of power supply for this plasma-catalytic process. In all cases, the selectivity to CH<sub>4</sub> was found to be higher than 97%.

Fig. 3 shows the CO<sub>2</sub> conversion and methane yield measured during CO<sub>2</sub> methanation in the presence of a calcined catalyst that was not submitted to any pre-treatment

(either thermal or plasma). Power supply was varied from 5 to 25W. The CO<sub>2</sub> conversion is very low below 10W and reaches 77% for power supplies higher than 12W. This fact points to a progressive activation of the catalysts under the plasma conditions used for the catalytic CO<sub>2</sub> methanation experiment. This in-situ activation is however not successful at low power supplies, since the activity of the non-pretreated catalyst only equals the one measured for the thermally pretreated Ni15RED470 catalyst, i.e. 80% CO<sub>2</sub> conversion, at power supplies higher than 13W. The selectivity to CH<sub>4</sub> was found to be around 95% in all experiments, except for the test performed at 23W, in which a large amount of CO is observed.

The CO<sub>2</sub> conversion and selectivity to methane measured for the hydrogen-plasma pre-treated catalysts at different time-on-stream, i.e. 20, 40 and 60 min, are presented respectively in Fig 4 a and b. Already for power supplies between 5 and 6W the CO<sub>2</sub> conversions reached are in any case very similar to those obtained for the thermally treated Ni15RED470 catalyst, pointing to this plasma treatment as an effective reduction treatment promoting the activity of these Ni-based catalysts in CO<sub>2</sub> methanation.

Only in the case of the experiment performed at 4W, some differences in terms of CO<sub>2</sub> conversion can be observed for the plasma pre-treated catalysts at 20, 40 and 60 min. Under these experimental conditions the CO<sub>2</sub> conversion is slightly higher for the plasma pre-treated catalysts for 40 min, i.e. Ni15PDBD40 = 73% > Ni15RED470 = 63% > Ni15PDBD60 = 61% > Ni15PDBD20 = 35%. This points to an optimal in terms of time-on-stream for this hydrogen-plasma activation pre-treatment, which allows obtaining CO<sub>2</sub> conversions even higher than those measured for the conventionally thermal reduced catalyst. The XRD patterns of the plasma pre-treated and the thermally reduced catalysts (Fig.1, Table 1) evidence slightly smaller Ni<sup>0</sup> crystal sizes for the plasma-treated (around 23 nm, 28 nm for the thermally treated catalysts). The CO<sub>2</sub>-TPD profiles acquired for the plasma pre-treated catalysts evidence an enhanced presence of strong basic sites for Ni15PDBD60, which can



explain the lower CO<sub>2</sub> conversion measured for this catalyst in comparison to Ni15PDDBD40, pointing as well to a stronger interaction between Ni and the support as the duration of the plasma pre-treatment increases. Let us note here that H<sub>2</sub>-TPR performed on the Ni15PDDBD20 catalysts confirmed the presence of non-reduced NiO species remaining on the surface of this plasma-treated catalyst, thus explaining its low activity in CO<sub>2</sub> methanation and confirming that 20 min treatment is not enough to fully reduce Ni-species.

#### 4. Conclusion

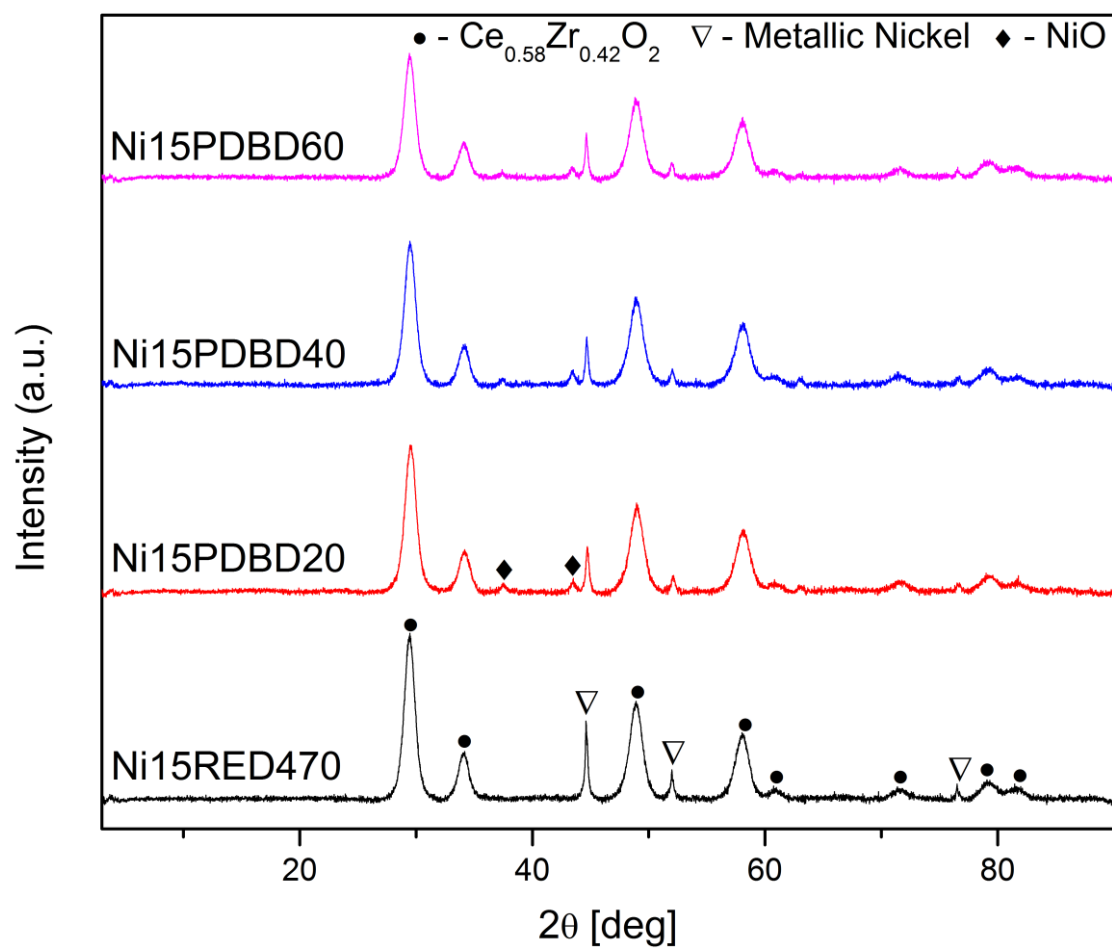
Ni-based ceria-zirconia supported catalysts were prepared and pretreated through both a conventional thermal reduction pre-treatment and an ambient temperature hydrogen-plasma pre-treatment. The activity towards CO<sub>2</sub> methanation in a hybrid plasma-catalytic adiabatic process was very similar for both thermally and plasma pre-treated catalyst. CO<sub>2</sub> conversions as high as 80% were obtained at low power supplies around 5-6W. This proves that this hydrogen-plasma activation can effectively replace a conventional thermal reduction pre-treatment. The Ni-support interaction was strengthened in the catalysts submitted to longer hydrogen-plasma exposure, resulting in slightly higher catalytic activity.

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**Fig 1.** X-Ray Diffractograms of studied catalysts

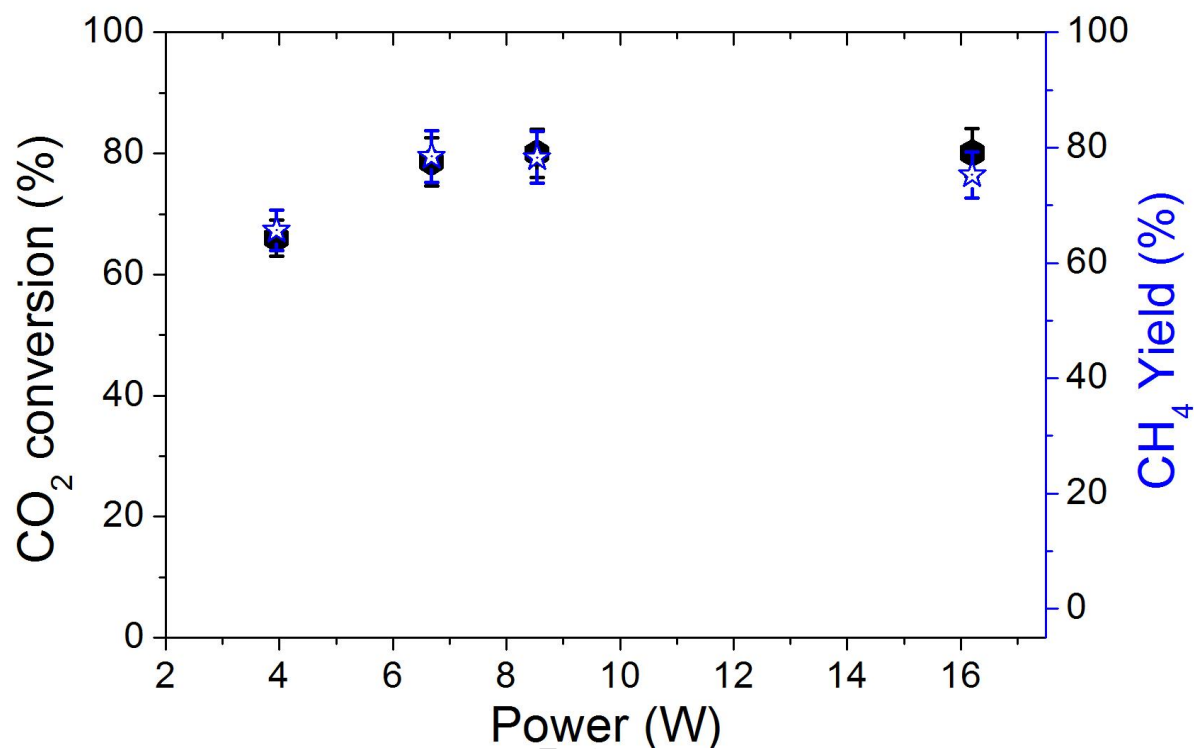
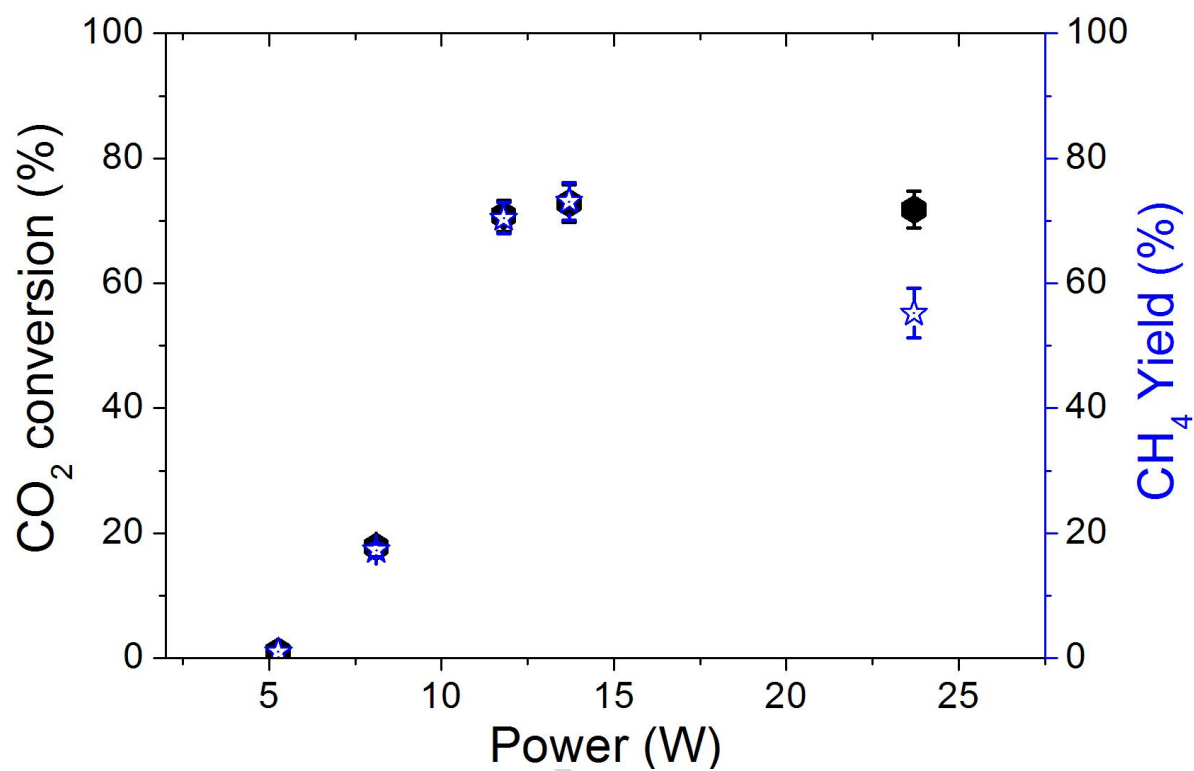
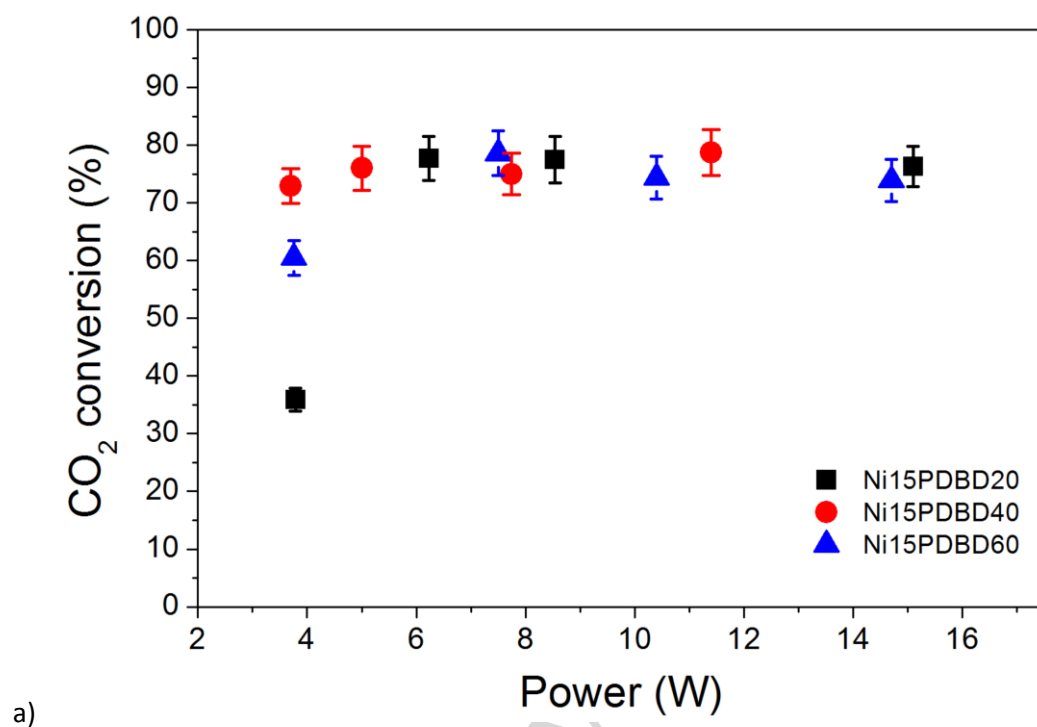


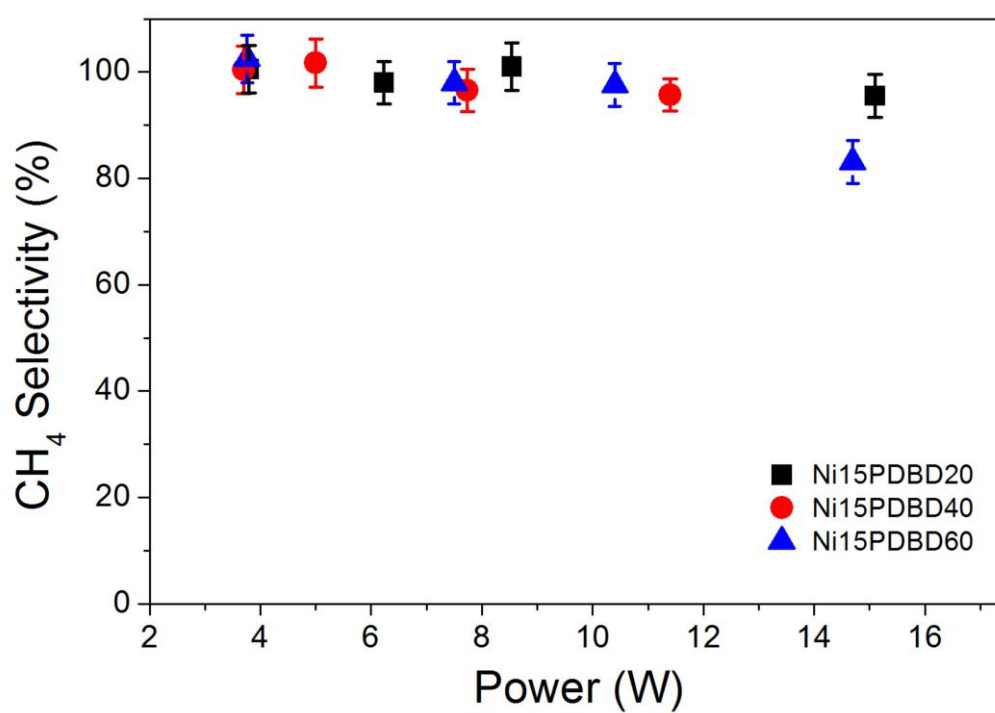
Fig. 2. CO<sub>2</sub> conversion and CH<sub>4</sub> yield over Ni/CeZrO<sub>2</sub> reduced at 470°C in hydrogen



**Fig. 3.** CO<sub>2</sub> conversion and CH<sub>4</sub> yield over calcined Ni/CeZrO<sub>2</sub>



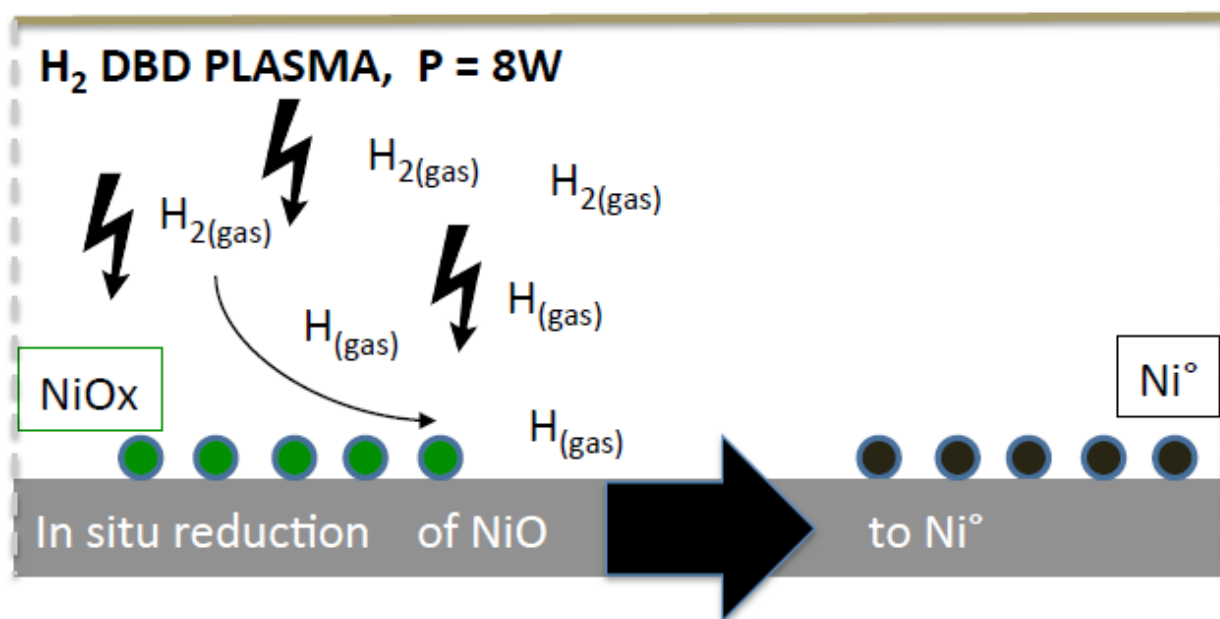
a)



b)

**Fig. 4.** Activity of Ni/CeZrO<sub>2</sub> pretreated in hydrogen plasma for 20, 40 and 60 minutes

a) CO<sub>2</sub> conversion, b) CH<sub>4</sub> Selectivity



Graphical Abstract

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**Table 1.** Basicity (CO<sub>2</sub>-TPD), Ni-crystal size (XRD), and textural properties for the used catalysts.

<b>Catalyst</b>	<b>1st Peak basicity [μmol/g]*</b>	<b>2nd Peak basicity [μmol/g]*</b>	<b>3rd Peak basicity [μmol/g]*</b>	<b>Total basicity [μmol/g]*</b>	<b>NiO crystallite size [nm]</b>	<b>Ni<sup>0</sup> crystallite size [nm]</b>	<b>S<sub>BET</sub> [m<sup>2</sup>/g]</b>
Ni15RED470	50	100	48	198	-	28.1±0.3	84
Ni15PDBD20	41	77	94	212	20.9±0.3	23.0±0.3	87
Ni15PDBD40	33	73	108	214	21.7±0.3	23.1±0.3	84
Ni15PDBD60	39	80	112	231	25.8±0.3	22.4±0.3	85

\* calculated from CO<sub>2</sub> TPD

\*\* calculated from Scherrer formula (XRD patterns)

**Highlights**

- Ni-supported on Ceria-Zirconia for CO<sub>2</sub> methanation under DBD plasma
- Hydrogen-plasma pre-treatment proved alternative to thermal reduction
- Plasma pre-treated catalysts show high catalytic activity at low power supply
- Duration of plasma pre-treatment influences Ni-support interaction

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