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# Hybrid Plasma-catalytic methanation of CO<sub>2</sub> at low temperature over Ceria Zirconia supported Ni catalysts

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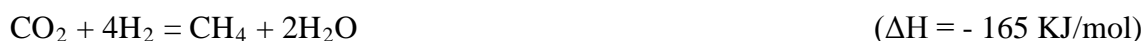
## ABSTRACT

A hybrid plasma-catalytic system was used in for the hydrogenation of carbon dioxide (CO<sub>2</sub>) into methane (methanation) at the atmospheric pressure and a very low temperature using a dielectric barrier discharge (DBD) plasma reactor packed with Ni-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts. Three catalysts were prepared by a conventional wet impregnation method, using 15 wt% of Ni loading over ceria-zirconia mixed oxides having different Ce/Zr ratios. The physico-chemical features of both catalysts and supports were evaluated by means of X-Ray Diffraction (XRD), Temperature-Programmed Reduction of H<sub>2</sub> (H<sub>2</sub>-TPR), Temperature Programmed-Desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) and Transmission Electron Microscopy (TEM). The methanation experiments in the absence or in the presence of plasma were carried out in

the temperature range of 90-420°C. The hybrid plasma 15NiCZ5842 catalyst combination was found to efficiently convert CO<sub>2</sub> into methane even at low temperature. Indeed, CO<sub>2</sub> conversions as high as 80%, together with 100% selectivity toward methane was measured in the presence of plasma at 90°C. On the contrary in the absence of plasma, the same conversion and selectivity were only achieved at much higher temperatures around 300 °C, for the same catalyst.

## 1. Introduction

The increasing concern on the greenhouse gases emissions (mainly CO<sub>2</sub>) forces our society to seek for efficient options towards the stabilization of atmospheric CO<sub>2</sub> concentrations in overall zero-emissions scenario, considering CO<sub>2</sub> recycling, reutilization as an alternative to its geological storage. Catalytic methanation of CO<sub>2</sub> stands as a perspective technology for such purpose [1,2].



In addition the limited resources of oil and natural gas, together with the increasing energy demand, forces us to seek for each time more efficient and cleaner energy production alternatives. Hydrogen has been recently considered as promising energy carrier. However, there are several problems inherent to the utilization of H<sub>2</sub>, from its transportation to its distribution. The transformation of the H<sub>2</sub> molecule by fixing into a carbon-containing compound, i.e. CH<sub>4</sub>, will offer the possibility of using the infrastructure of natural gas transportation network.

Methanation represents both a feasible approach contributing to the reduction of the emissions of CO<sub>2</sub> and a way of transforming hydrogen into a conventional energy carrier. Though many different metals have been used to catalyze the methanation process, the

catalysts mostly based on Group VIII metals, such as Ni and Ru and supported on various porous materials, are among the most commonly studied systems, since they allow achieving considerable methanation rates [3-8]. Ni-based catalysts have been widely investigated, because of their good compromise between high activity and low price [7]. The interaction between the metal and support also plays a very important role in catalyst performance [9] and a key role in the active site dispersion, stability and activity [10]. Ocampo et al. [11] evaluated CO<sub>2</sub> methanation activity of Ni-ceria-zirconia and revealed that Ni-ceria-zirconia exhibited excellent catalytic activity and stability during 150 h on stream. Such outstanding performance was due to the high oxygen storage capacity of ceria-zirconia oxides ~~and~~ together with the presence of highly dispersed nickel. Other studies [12] claimed that CO<sub>2</sub> methanation activity on Ni-ceria-zirconia was related to the particular interaction between Ni<sup>2+</sup> cations and the ceria-zirconia support. Cai et al. [1] studied fractional-hydrolysis-driven formation of non-uniform dopant concentration catalyst nanoparticles of Ni/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> in methanation of CO<sub>2</sub> and showed that a structure with Ce and Ni enriched at the surface improved the conversion of carbon dioxide. Despite the encouraging results observed for Ni-catalysts at around 300°C and atmospheric pressure, the presence of water in the products leads to the sintering of Ni particles, which is the main reason for catalysts deactivation. However, conversion becomes negligible below 250°C. At higher temperatures, (>420 °C), concomitant secondary reactions favor the CO+H<sub>2</sub> formation, thus considerably decreasing the selectivity towards the methane formation.

A hybrid combination of catalysts with Dielectric Barrier Discharge plasma (DBD) may allow us to overcome all the above-mentioned drawbacks. Moreover, DBD catalytic reactors require usually only very low consumption of electricity power, less than 12kJ/mole of CH<sub>4</sub> and, at the same time, they meet all the requirements for large volume methane production [13]. Non-thermal plasma, producing a wide variety of active species such as electrons, ions

and radicals, has been applied to the methanation of CO [14-16]. Song et al. [16] have investigated the production of synthesis gas with the use of a Ni catalyst packed in dielectric barrier discharge (DBD) reactor, and reported that the CO selectivity considerably increased with the application of plasma. Furthermore, Mok et al. found that non-thermal plasma can enhance the rate of catalytic methanation of CO using a coupled plasma catalytic process using a Ni-Zeolite catalyst [3]. No studies in the existing literature have reported so far the influence of working with DBD plasmas for enhancing the catalytic performance in CO<sub>2</sub> methanation.

In the present work we present a hybrid plasma-catalytic methanation process ~~in~~ allowing low temperature conversion of CO<sub>2</sub> to methane. This combined Ni-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts and DBD plasma lead to the high yields necessary for this process to become economically feasible. Structural and chemical characterization was performed on selected Ni-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts prior and after methanation reactions in order to assess the differences in catalytic behavior and durability.

## **2. Experimental**

### **2.1. Catalysts synthesis**

Three catalysts were prepared by a conventional wet impregnation method, commercial ceria-zirconia mixed oxide (Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>) with different Ce/Zr ratios: Ce<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>2</sub>, Ce<sub>0.58</sub>Zr<sub>0.42</sub>O<sub>2</sub> and Ce<sub>0.85</sub>Zr<sub>0.15</sub>O<sub>2</sub> (Rhodia Solvay) were used as support. These supports were impregnated with an aqueous solution of nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Aldrich) as metal precursor. The Ni loading for all catalysts was fixed as 15 wt%, in all the cases. After the impregnation, the catalysts were dried overnight at 100 °C

and subsequently calcined at 550 °C for 4 h in air. The final catalysts were respectively denoted as 15NiCZ1090, 15NiCZ5842 and 15NiCZ8515.

## 2.2. Catalysts characterization

The specific surface areas of both catalysts and supports were determined by physisorption of N<sub>2</sub> at 77 K using a Quantasorb Jr. dynamic system equipped with a thermal conductivity detector (TCD). The specific surface areas were calculated using the BET method. The reducibility of nickel and ceria-zirconia mixed oxide was evaluated by Temperature Programmed Reduction (H<sub>2</sub>-TPR) in a H<sub>2</sub> flow system (BEL Japan BELCAT-M). In the presence of 5 %vol. H<sub>2</sub> /Ar, about 50 mg of each material were heated up to 950 °C at a heating rate of 7.5 °C/min. Before TPR measurements, catalysts were pre-treated at 400 °C under helium flow for 1 h and then cooled down to 100 °C. The H<sub>2</sub> consumed was monitored by a TCD detector. Temperature programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) was carried out in a flow system (BEL Japan BELCAT-M equipped with a TCD detector) using a 10 %vol.CO<sub>2</sub> /He gas mixture. About 50 mg of each catalyst was loaded in a quartz U-tube and flushed at 500 °C for 1 h in He flow and cooled to 80°C. Then, they were exposed to a gaseous mixture of CO<sub>2</sub> (10 vol.%)/helium for 1 h at 80°C in order to adsorb CO<sub>2</sub>. Helium was then flown for 15 minutes in order to desorb the physically adsorbed. Temperature programmed desorption (TPD) of CO<sub>2</sub> was carried out heating the samples at 10 °C/min up to 950 °C under He flow. The desorbed CO<sub>2</sub> was measured with the aid of the TCD detector. CO<sub>2</sub> desorption measurements were performed on the catalysts reduced in 5 %vol. H<sub>2</sub>/Ar for 2 hours at 470°C. The X-ray diffraction (XRD) patterns were acquired in a XRD (Empyrean diffractometer from PANalytica), using Cu-K $\alpha$  anode operated at 45 kV and 40 mA. The scanning range was set from 3° to 90° (2 $\theta$ ), with a step size of 0.01°. High-resolution

transmission electron microscopy (HRTEM) images were acquired on a JEOL JEM 2011 equipped with LaB<sub>6</sub> filament, operating at 200 kV on reduced and used catalysts.

### **2.3. Experimental set-up and methanation test in the absence and in the presence of plasma**

The activity of the different catalyst towards the methanation of CO<sub>2</sub> was tested in a experimental set-up briefly consisting of a quartz tubular reactor, a plasma generator and different devices for gas analysis. A Schematic of the installation is shown in Figure 1. The dielectric barrier discharge (DBD) plasma reactor consists of two coaxial tubes (quartz and alumina tubes). Between the outer tube (10 mm internal diameter, 1 mm wall thickness) and the inner (3 mm diameter) the discharge is sustained in a gap of 2,5 mm with a steel foil wrapped around the outer surface of the quartz tube acting as the ground electrode.

The catalytic reactor was placed in the middle of the quartz tube, consisting of a fixed-bed of particle catalyst, corresponding to a total volume of 0,6 cm<sup>3</sup>. The effective length of the plasma - catalytic reactor is approximately 10 mm.

Temperature was kept constant with the aid of an external convection heater. The reaction temperature was measured by a K-type thermocouple placed close to the catalytic bed after the plasma zone and all experiments were conducted at atmospheric pressure.

In all the cases a gas mixture of pure hydrogen and carbon dioxide with a H<sub>2</sub>/CO<sub>2</sub> molar ratio of 4:1, at a flow rate of 200 mL/min was fed to the reactor. Under such conditions,, the Gas Hourly Space Velocity (GHSV) was found to be around 50,000 h<sup>-1</sup>. Before any catalytic test, the catalyst was previously reduced in the presence of 5% vol. H<sub>2</sub>/Ar mixture at 470°C for 2 hours.

In the hybrid methanation experiments, an alternative current (AC) high voltage

(operating frequency: 40-41 kHz) of 10-15 kV was applied to the discharging electrode to create non-thermal plasma. It varied in the range of 20-35  $\mu\text{J}/\text{cycle}$ , corresponding to a power between 1-3W with electricity consumption  $<12\text{kJ}/\text{mole}_{\text{CH}_4}$ . The voltage applied to the plasma-catalytic reactor was measured with a digital oscilloscope (LT 342, LeCroy) using a probe (ELDITEST GE 3830).

A specific sensor was used to analyze  $\text{CO}_2$ .  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  are analyzed in a gas chromatograph (IGC 120 ML, Delsi Intersmat) equipped with an analytical column (Carboxen) using helium as a carrier gas, FTIR (Fourier transform infrared spectrometer) and MS (mass spectrometer) (Pfeiffer Omistar 422) which moreover allowed following the formation of other possibly products such as formic acid. Water formed as product was continuously removed and condensed from the product gas.

$\text{CO}_2$  conversion was calculated as follows:

$$X_{\text{CO}_2} = 100 \times ([\text{CO}_2]_{\text{ini}} - [\text{CO}_2]_{\text{product}}) / [\text{CO}_2]_{\text{ini}}$$

where  $[\text{CO}_2]_{\text{ini}}$  and  $[\text{CO}_2]_{\text{product}}$  are respectively the concentrations of  $\text{CO}_2$  in the gas entering and existing in the reactor together with the selectivity to methane

$$S_{\text{CH}_4} = 100 \times ([\text{CH}_4]_{\text{product}}) / ([\text{CO}_2]_{\text{ini}} - [\text{CO}_2]_{\text{product}})$$

and  $\text{CO}$  yield

$$Y_{\text{CO}} = 100 \times ([\text{CO}]_{\text{product}}) / ([\text{CO}_2]_{\text{ini}} - [\text{CO}_2]_{\text{product}})$$

### 3. Result and discussion

#### 3.1. Catalytic activity towards Methanation in absence of plasma (Plasma OFF)

Figure 2 contains the results obtained in the methanation tests in the absence of plasma, for the three different catalysts prepared. The thermodynamic equilibrium predicts  $\text{CO}_2$  conversions varying from 100 to 85%, with the temperatures increasing from ambient to



400°C [3,17,18]. Methanation experiments in the absence of plasma evidenced negligible CO<sub>2</sub> conversion at temperatures lower than 280°C. CO<sub>2</sub> conversion rapidly increases in the range 280-450°C, reaching values close to the thermodynamic limit, especially in the case of NiCZ5842, as seen in Figure 2a. In this range of temperature, the selectivity was found to be almost 100%, Figure 2b. Nor formic acid nether formaldehyde were detected by MS and thus one can note that the unique secondary product was carbon monoxide with a yield lower than 2% in the studied temperature range (Figure 2c).

### **3.2. Role of active phase and support**

The values of BET surface areas for both the Ni-catalysts and the ceria-zirconia supports, obtained from their corresponding N<sub>2</sub> adsorption isotherms, are shown in Table 1. Surface area is always higher for the unloaded supports pointing the pore blockage (around 8% BET diminution) occurring to a certain extent upon the incorporation of Ni. 15NiCZ8515 shows the highest BET of this series of catalysts, since the BET surface area of the CZ8515 (Ce<sub>0,85</sub>Zr<sub>0,15</sub>O<sub>2</sub>) is almost 36% higher than the rest of ceria-zirconia supports. The addition of Ni, however, does not seem to modify the crystalline structure of ceria-zirconia support. The diffraction patterns acquired for the different catalysts and supports are shown in Figure 3. XDR patterns evidence the marked diffraction peaks corresponding to NiO particles. The crystal size of such NiO particles calculated from the diffraction patterns are shown in Table 1. NiO Crystal size varies with the type of the support. The larger particles, of around 29 nm, were found for 15NiCZ8515, corresponding to the support containing more cerium oxide. Ni is better dispersed on 15NiCZ5842 (NiO particles of 18,7 nm), which may explain the higher CO<sub>2</sub> conversions measured in absence of plasma.

Fig. 4 shows the hydrogen consumption profiles (H<sub>2</sub> TPR) of the three catalysts, as well as that of the CZ supports. In agreement with literature [12,20], 15NiCZ catalysts present

similar reduction profiles. The hydrogen consumption begins ca. 250°C and ends around 620°C. It is well known that the reduction peak between 380 and 420°C is attributed to bulk NiO while the broad peaks appearing between 250 and 620°C correspond to the reduction of the ceria-zirconia support. The higher the Ni dispersion the lower the temperature at which the peak corresponding to NiO appear in the TPR profiles. This is clearly observed for this series of catalysts since 15NiCZ8515 TPR profile exhibits a marked peak of NiO reduction starting at much lower temperatures than 15NiCZ5842 or even 15NiCZ1090. The increased presence of Zr seems to be thus favoring the dispersion of Ni species on the supports surface. Basic properties of the catalyst surface play an important role in the methanation process since they are required in the adsorption and activation of CO<sub>2</sub> [21]. They can be evaluated by the means of temperature-programmed desorption of CO<sub>2</sub> (TPD-CO<sub>2</sub>). The results of TPD-CO<sub>2</sub> of the different materials reduced at 470°C for 2h presented in Fig. 5. The bare supports CZ showed a strong desorption peak with the maximum at approximately 120 °C. This peak can be ascribed to the presence of basic centres of low and/or medium strength (e.g. OH and O groups) [12,22-25]. For both 15NiCZ5842 and 15NiCZ1090, only the peaks corresponding to the support are present which leads to the conclusion that on these catalysis only exist weak and medium basic sites necessary to methanation reaction [12,20]. In the case of 15NiCZ8515 catalyst a peak appears at temperatures between 450-700°C. This corresponds to the strong basic site (e.g.O<sup>2-</sup>) [23,25,26]. Thus, incorporation of nickel seemed to the formation of strong basic sites and elimination the quantity of weak basic ones. This fact may point a stronger interaction between Ni and ceria from the support, resulting in enhance basicity of 15NiCZ8515 catalyst. According to the literature addition Ni into the ceria-zirconia improved the redox properties of the material favoring oxygen transfer, which would be required for CO<sub>2</sub> activation [25,27,28]. However, the increased presence of zirconium in the mixed oxide support may hinder the strong interaction between Ni and ceria.

Based on the methanation reaction mechanism proposed on such materials [20,29], It was shown that the kinetically relevant step is the adsorption of CO<sub>2</sub> leading to adsorbed CO and adsorbed O. Thus, on 15NiCZ5842 and 15NiCZ1090, low/medium strength basicity is enough to initiate the reaction at sufficiently high temperatures in the absence of plasma, i.e. close to 300°C. Furthermore, the particles of NiO and then of Ni<sup>0</sup> after reduction being better dispersed on 15NiCZ5842, may contribute to achieving catalytic conversion at lower temperature than on 15NiCZ9010 or even 15NiCZ8515.

The TEM images acquired for these catalysts are presented Fig. 6. For the three fresh catalysts (A,C,E), it was not possible to evidence the Ni particles on the CZ bare supports. However, by EDS (Fig. not shown) performed on reduced samples, it was possible to verify that the Ni<sup>0</sup> is well dispersed on the supports.

### **3.3. Hybrid plasma catalytic methanation**

Fig. 7a presents CO<sub>2</sub> conversions in the DBD plasma reactor in the presence of the different catalysts and under plasma in a temperature range of 80–450 °C.

Without plasma (Fig 2), the conversion was almost zero below 250 °C, and it increased to about 85% at 450 °C. In agreement with the literature [3] non-thermal plasma was able to greatly improve the conversion of CO to more than 97%, almost close to the thermodynamic equilibrium conversion with a methane selectivity always higher than 90% at temperatures lower than 260°C. Particularly at low temperatures (T<260 °C) at which catalysis alone did not produce significant methanation rate, the plasma gave rise to a sharp increase in the conversion of CO. Indeed, our hybrid system is more active at even much lower temperature (from 80°C) than ones previously proposed in the literature [23] based on a zeolite catalytic phase.

According to the literature, the catalytic methanation involves the dissociation of CO<sub>2</sub> to CO\*

and O\* in which \* is an active site [3,29-31]. The extent of this reaction is low at low temperatures but it is thermodynamically favorable [3]. The following steps of the methanation consist on the reaction of this dissociated species with hydrogen to produce methane. It is well known that plasma can help to dissociate adsorbed molecules, what will lead to an enhancement in the final CO<sub>2</sub> conversion and CH<sub>4</sub> yield.

Thus, at low temperature and in the presence of the hybrid system NiCZ+plasma, the formation of these adsorbed active molecules is favored in comparison to catalytic methanation alone in which this reaction does not take place for T<250°C. Moreover, since CZ bare supports are well known to act as an oxygen reservoir [32], these CO\* and O\* will be even more ready to react with hydrogen leading to higher conversions at low temperatures. At high temperature, the catalysts are active enough to activate the formation of CO\* and O\* species [12,20,29], and the plasma becomes inefficient and even non-recommendable since CO appears as a non-negligible by-product (Fig 7c), as moreover predicted by thermodynamics.

Let us note here that for sake of comparison, the methanation reaction was also conducted with plasma alone, i.e. in the absence of catalyst (Figure not shown) at low temperature. At 90°C, the CO<sub>2</sub> conversion was found to be around 5%, with CH<sub>4</sub> yield and CO yield of 0% and 5% respectively. This result further confirms the synergetic effect of the hybrid plasma-catalytic system.

### **3.4. Evolution of the active Ni phase during the methanation reaction**

The catalytic activity of 15NiCZ5248 in the presence of the DBD plasma was tested in a long-duration methanation experiment, corresponding to 100 hours time on stream. The catalyst after this long duration test was submitted to further physico-chemical characterizations.

TEM analysis (Figures 6 b, d and f) evidences the absence of any morphological modification of the catalyst after this test.

Moreover TPR was performed on 15NiCZ5248 before and after catalytic test and after hybrid plasma runs (Fig. 8). Similar reduction peaks at low temperature are observed prior and after catalytic runs leading to the conclusion that during this process the Ni species are similar, however the peaks are more intense showing an increase of the active nickel species. Similar results have been presented on another catalytic system based on zeolites [3]. In order to verify that the hybrid catalytic plasma process does not affect the intrinsic basicity of the material, CO<sub>2</sub> TPD measurements were conducted on the 15NiCZ5842 before and after the 100h test (Fig.9). Similar profiles of CO<sub>2</sub> desorption are observed. One can thus conclude that there were no changes in the basicity occurring as a consequence of the 100h duration test

#### **4. Conclusions**

In the present work we present a hybrid catalytic plasma system for CO<sub>2</sub> methanation based on the combination of a DBD plasma and Ni/CeZrOx catalysts. It was clearly demonstrated that the hybrid plasma catalytic process is active at low temperature ( $T < 260^{\circ}\text{C}$ ) on the selective conversion of CO<sub>2</sub> into methane. At low temperature and in the absence of plasma, the conversions of CO<sub>2</sub> were lower than 15%, but they were drastically enhanced and in the presence of plasma reaching 80% at temperatures between 100-300°C, whereas for plasma alone conversions of 5% were observed. In the presence of plasma the CO<sub>2</sub> is activated in both CO\* and O\*, even at low temperatures, leading to higher conversion rates in the presence of the catalysts. Almost no difference in catalyst activity was found for Ni catalysts prepared using different ceria-zirconia supports. On the contrary, in absence of plasma, the 15NiCZ5842 was showing enhanced methanation activity due to the presence of low and medium strength basicity together with a better dispersion of Ni-species, at high ZrO<sub>2</sub>

contents on the mixed oxide support. In order to better define a mechanism for this hybrid methanation process, DRIFT experiments are in course, which will allow the identification of the reactive adsorbed species.

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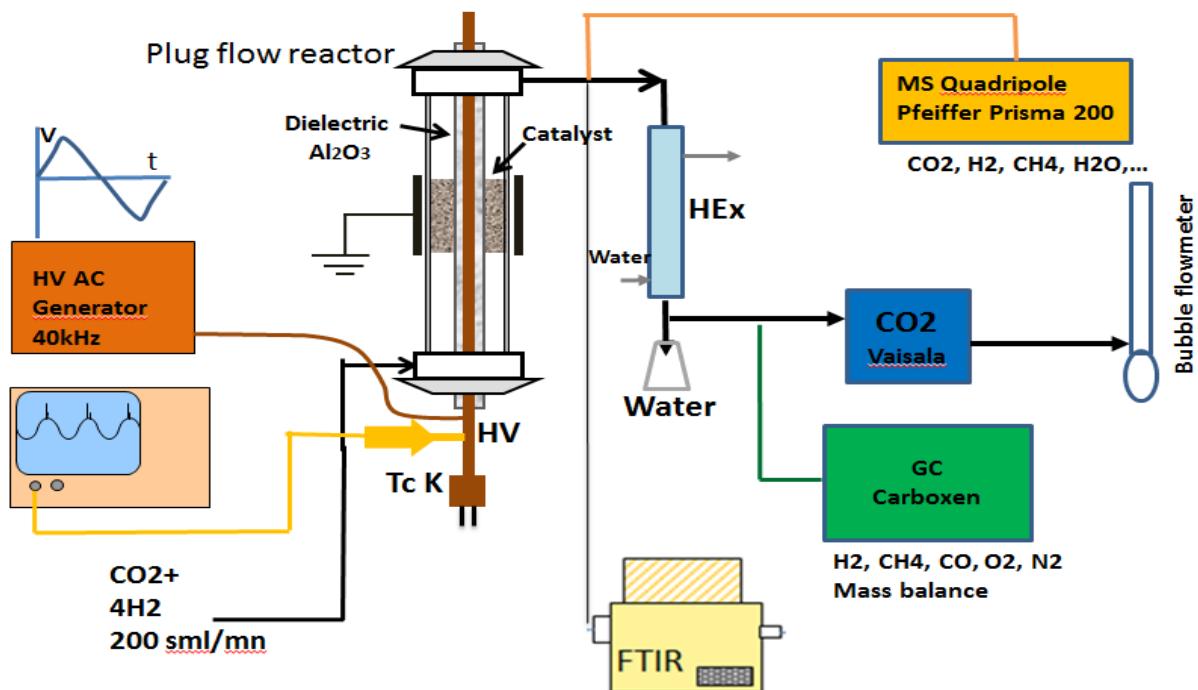
**Table 1 – BET surface area, Crystallite sizes of NiCZ catalysts before reduction, total H<sub>2</sub> consumption**

**Table 1**

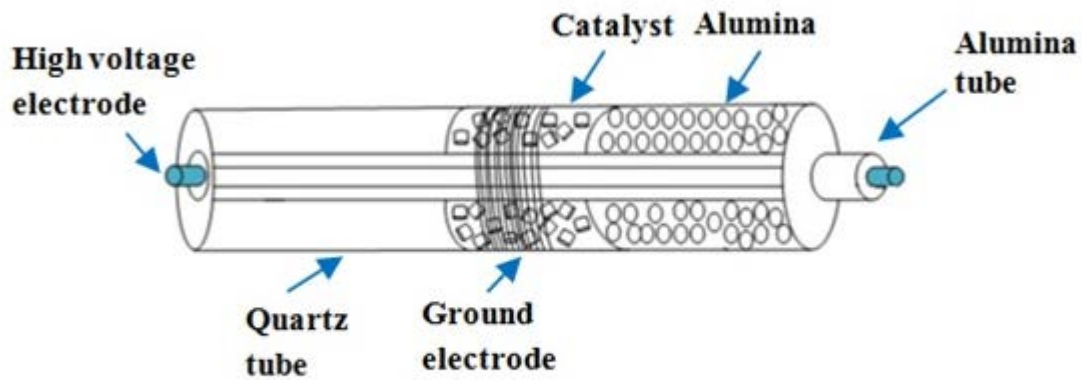
<b>Catalyst</b>	<b>S<sub>BET</sub> (m<sup>2</sup>/g)</b>	<b>D CeZrO<sub>2</sub> (nm)</b>	<b>D NiO (nm)</b>	<b>Total H<sub>2</sub> consumption (mmole/g)</b>
15NiCZ1090	67	10.6	21.5	2.3457
15NiCZ5842	87	7.4	18.7	3.0062
15NiCZ8515	106	5.5	29.0	2.7034
CZ1090	73	8.2		
CZ5842	93	7.2		
CZ8515	115	4.3		
15NiCZ5842 after reduction at 470 °C	86			0.6329
15NiCZ5842 after hybrid plasma- catalytic test	87			1.1408

**Fig. 1 (a) Experimental set-up for the plasma-catalytic methanation of CO<sub>2</sub> and (b) Dielectric barrier discharge plasma reactor**

a)

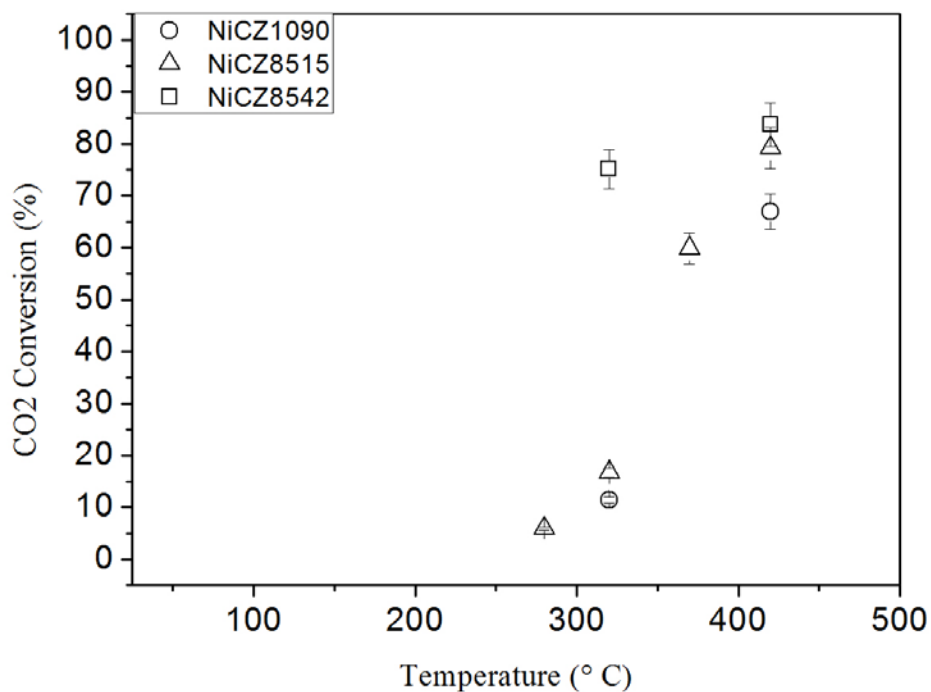


b)

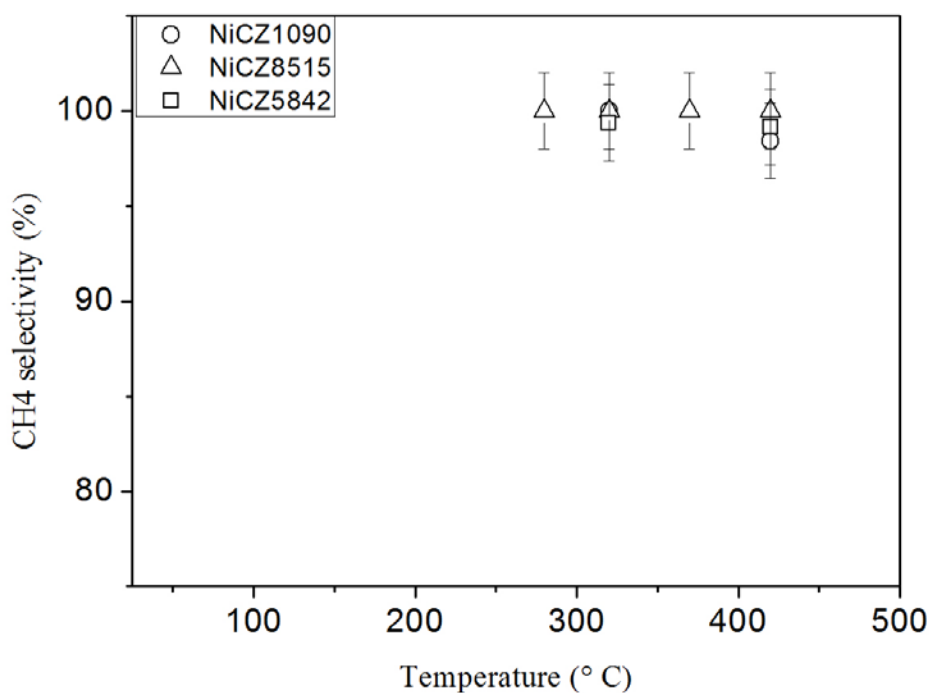


**Fig. 2 (a) CO<sub>2</sub> conversion, CH<sub>4</sub> selectivity and (b) CO yield versus temperature over 15Ni-CeZr catalytic system. Reaction conditions: 20 vol% CO<sub>2</sub>, 80 vol% H<sub>2</sub>, GHSV = 50,000 h<sup>-1</sup>.**

a)



b)



c)

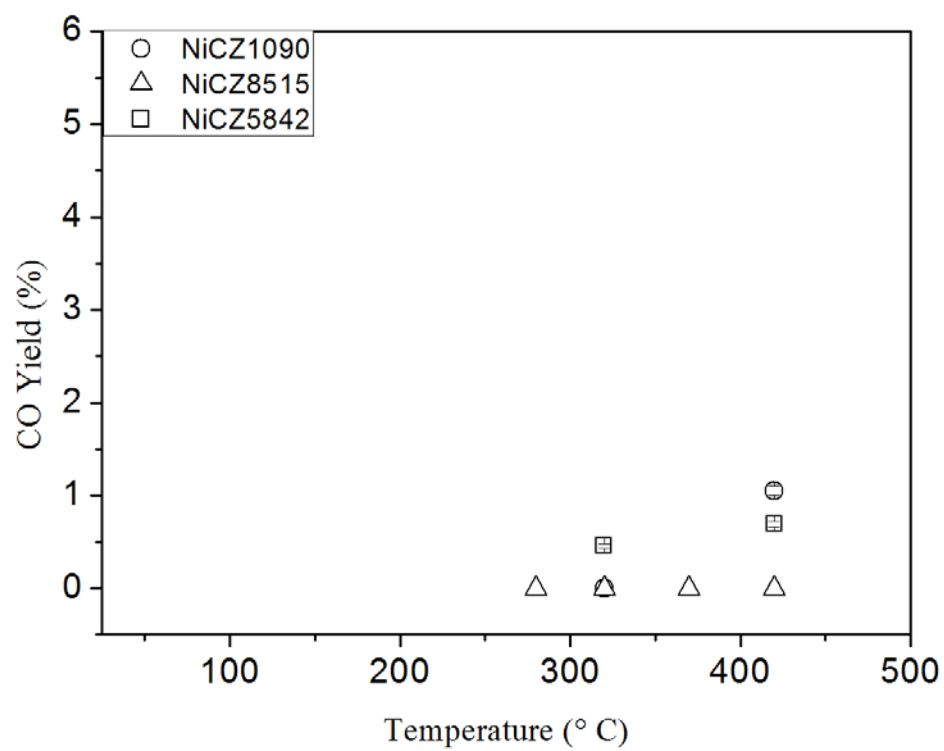


Fig. 3. X-ray diffractograms for the catalysts and the supports before reduction.

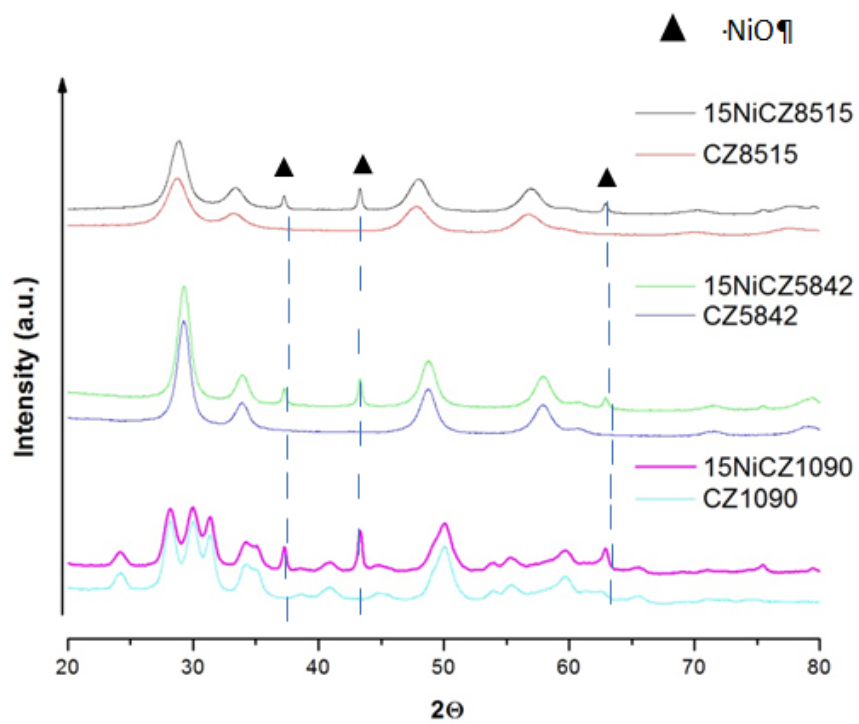


Fig. 4: TPR profiles of the different catalysts and supports.

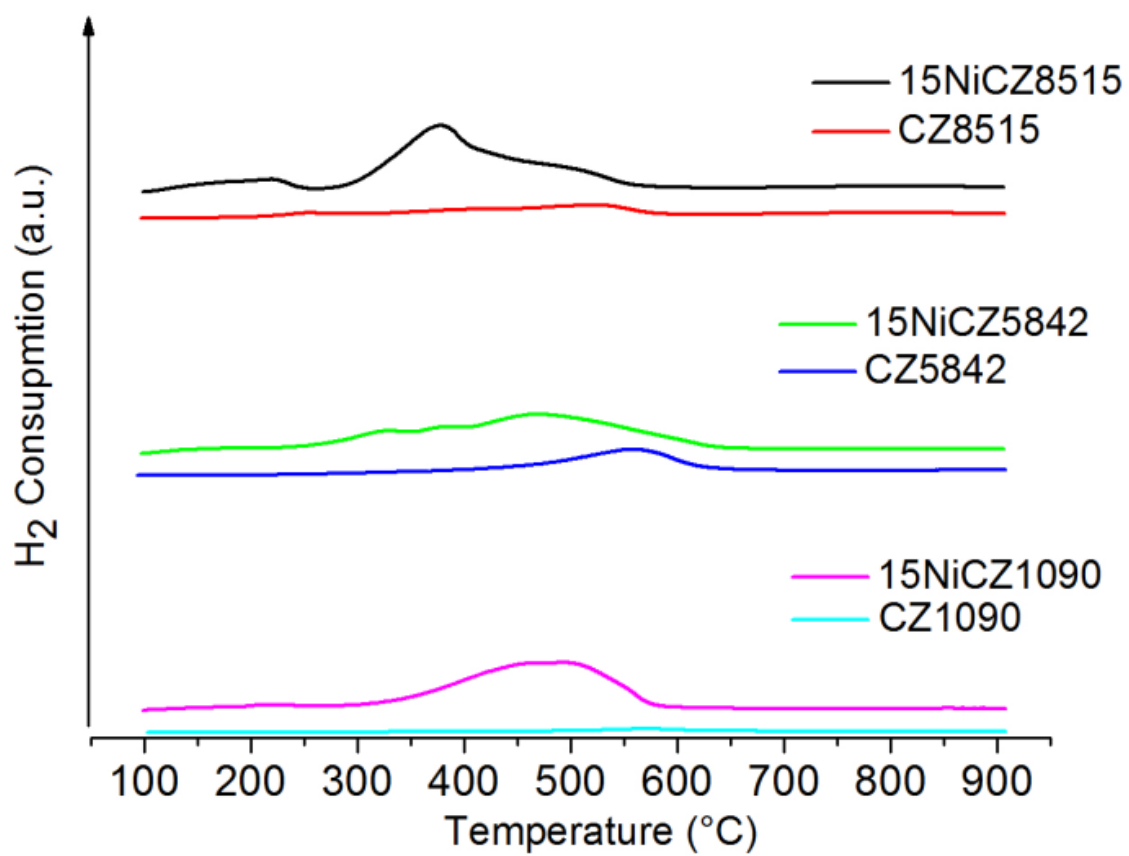
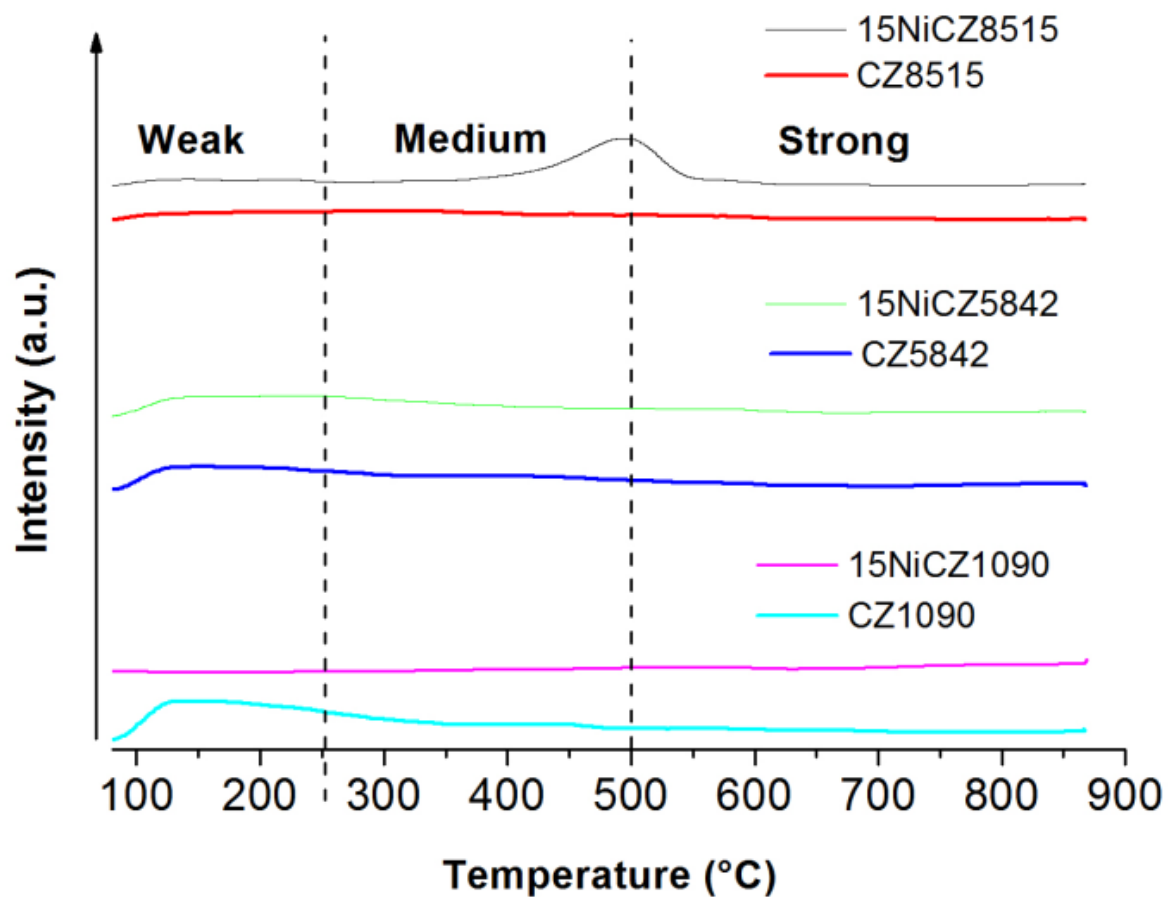


Fig. 5: TPD profiles of CO<sub>2</sub> adsorption on the pre-reduced catalysts and supports.

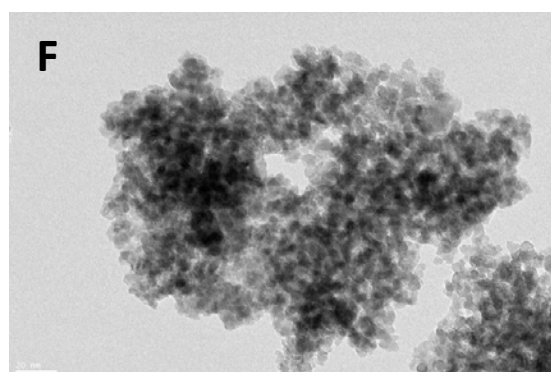
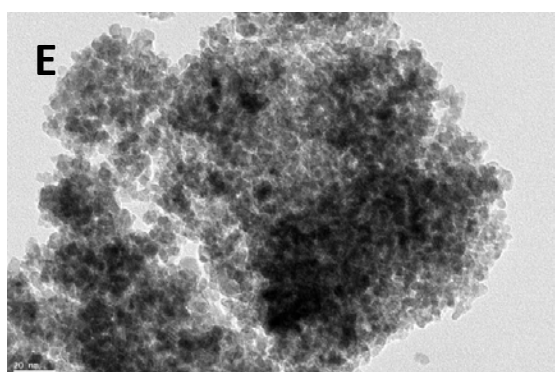
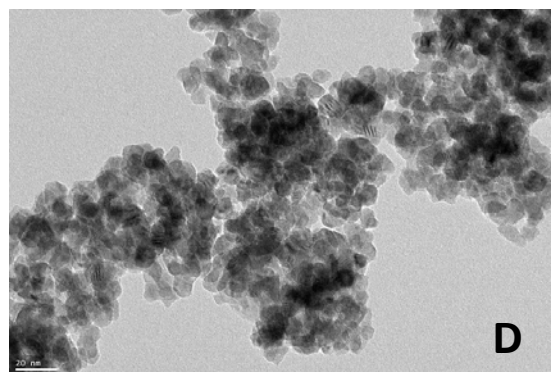
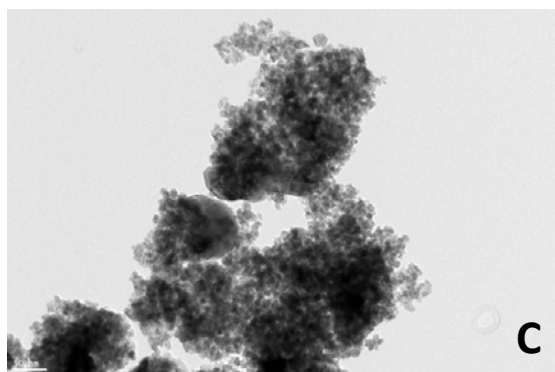
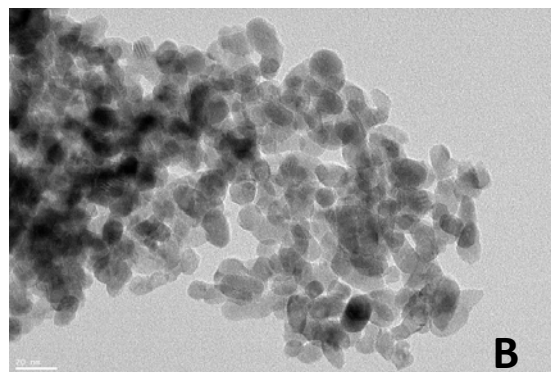
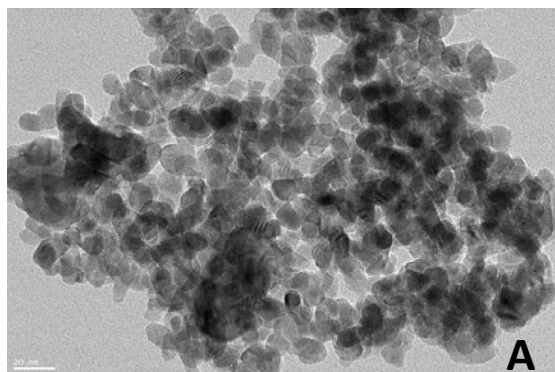




**Fig. 6 – TEM images of the fresh catalysts after hybrid plasma-catalytic methanation . (A, B) 15NiCZ1090, (C, D) 15NiCZ5842, (E, F) 15NiCZ8515**

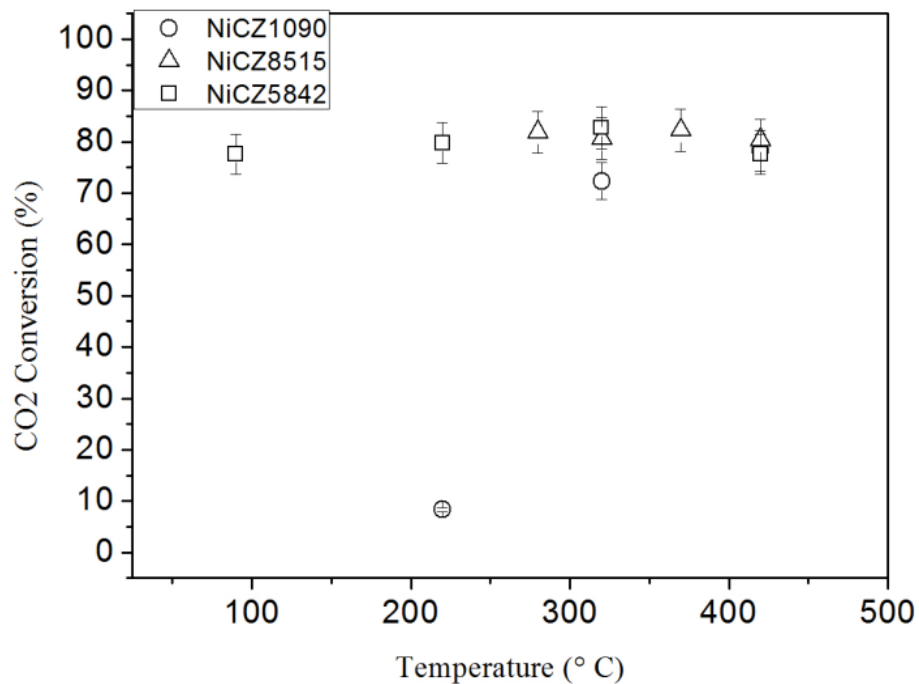
**Fresh**

**after hybrid plasma catalytic methanation**

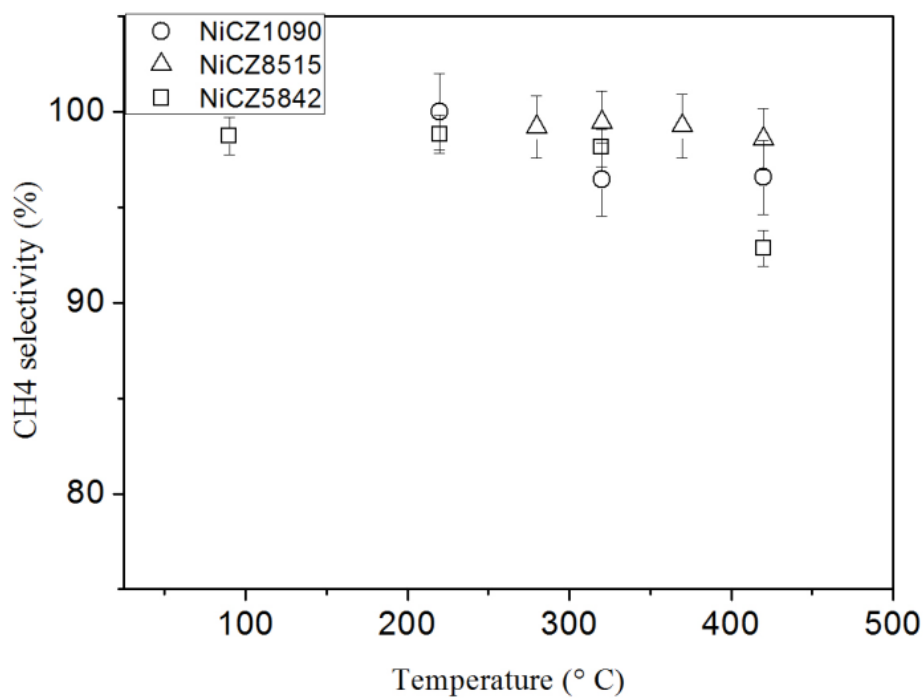


**Fig. 7 (a) CO<sub>2</sub> conversion, (b) CH<sub>4</sub> selectivity and (c) CO yield versus temperature over the different catalysts in the hybrid plasma-catalytic configuration. Reaction conditions: 20 vol% CO<sub>2</sub>, 80 vol% H<sub>2</sub>, GHSV = 50,000 h<sup>-1</sup>.**

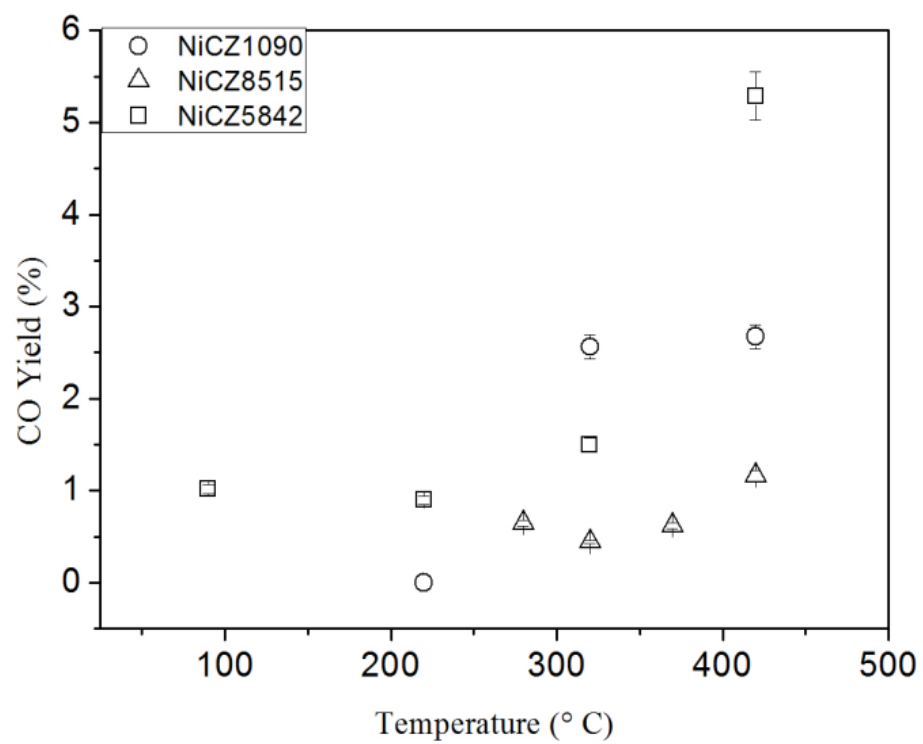
a)



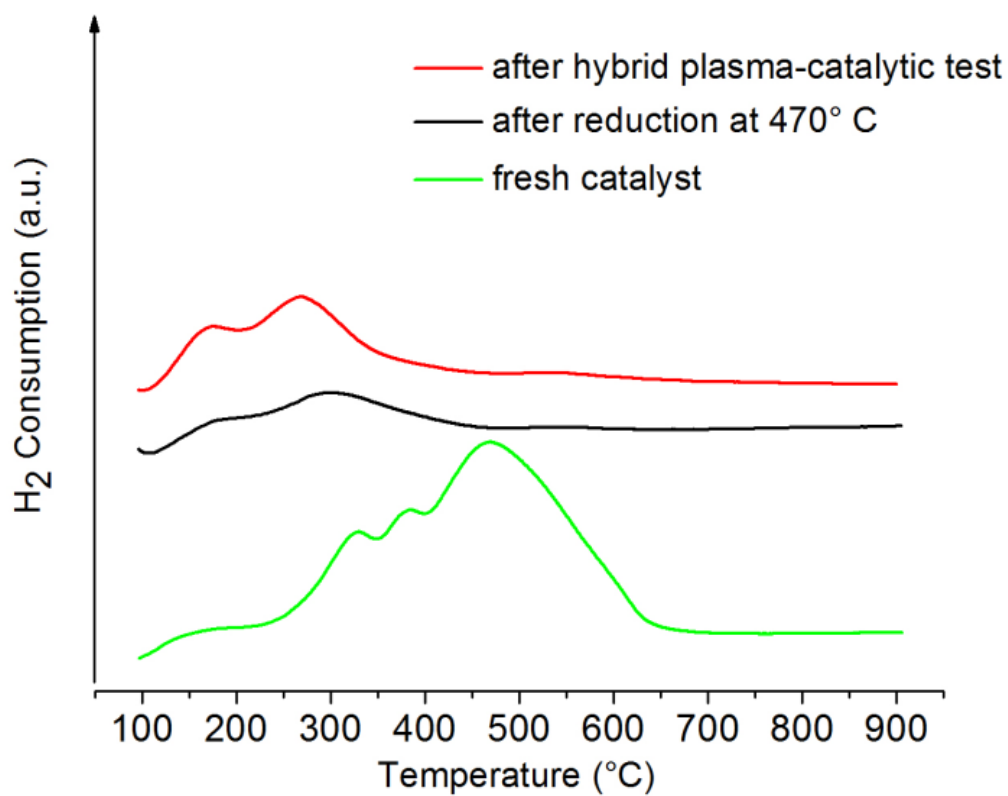
b)



c)



**Fig. 8: Comparison of TPR profiles of the 15NiCZ5842 catalyst, fresh, after reduction at 470°C and after the 100 hours duration hybrid plasma-catalytic methanation test**



**Fig. 9: Comparison of TPD profiles of the 15NiCZ5842 catalyst, fresh and after the 100 hours duration hybrid plasma-catalytic methanation test.**

