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# Hybrid plasma-catalytic methanation of CO<sub>2</sub> at low temperature over ceria zirconia supported Ni catalysts

Magdalena Nizio<sup>a,b,c</sup>, Abdulkader Albarazi<sup>a</sup>, Simeon Cavadias<sup>a</sup>,  
Jacques Amouroux<sup>a</sup>, Maria Elena Galvez<sup>b,c</sup>, Patrick Da Costa<sup>b,c,\*</sup>

<sup>a</sup> Institut de Recherche de Chimie Paris, Equipe 2PM, 11 rue Pierre et Marie Curie, 75005 Paris, France

<sup>b</sup> Sorbonne Universités, UPMC, Univ. Paris 6, Institut Jean Le Rond d'Alembert, 2 place de la gare de ceinture, 78210 Saint Cyr L'Ecole, France

<sup>c</sup> Institut Jean Le Rond d'Alembert, CNRS, UMR 7190, 2 place de la gare de ceinture, 78210 Saint Cyr L'Ecole, France

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## ABSTRACT

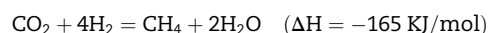
A hybrid plasma-catalytic system was used in for the hydrogenation of carbon dioxide (CO<sub>2</sub>) into methane (methanation) at atmospheric pressure and very low temperature using a dielectric barrier discharge (DBD) plasma reactor packed with Ni-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts. 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.

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## 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].



\* Corresponding author. Sorbonne Universités, UPMC, Univ. Paris 6, Institut Jean Le Rond d'Alembert, 2 place de la gare de ceinture, 78210 Saint Cyr L'Ecole, France.

E-mail address: [patrick.da\\_costa@upmc.fr](mailto:patrick.da_costa@upmc.fr) (P. Da Costa).

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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 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 12 kJ/mol 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 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.

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## Experimental

### 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.

### 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 min 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 h at 470 °C. The X-ray diffraction (XRD) patterns were acquired in a

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