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# The role of Gadolinia Doped Ceria support on the promotion of CO<sub>2</sub> methanation over Ni and Ni–Fe catalysts

P. Frontera <sup>a,d,\*</sup>, A. Macario <sup>b</sup>, G. Monforte <sup>c</sup>, G. Bonura <sup>c</sup>, M. Ferraro <sup>c</sup>,  
G. Dispenza <sup>c</sup>, V. Antonucci <sup>c</sup>, A.S. Aricò <sup>c</sup>, P.L. Antonucci <sup>a,d</sup>

<sup>a</sup> Department of Civil, Energy, Environment and Material Engineering, Mediterranean University of Reggio Calabria, Salita Melissari, 89124 Reggio Calabria, Italy

<sup>b</sup> Department of Mechanical, Energy and Management Engineering, University of Calabria, Via P. Bucci 87036, Arcavacata di Rende, Cosenza, Italy

<sup>c</sup> CNR, Institute of Advanced Technologies for Energy “Nicola Giordano” – ITAE, Salita S. Lucia sopra Contesse, 5, 98126 Messina, Italy

<sup>d</sup> INSTM, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Via G. Giusti, 9, 50121 Firenze, Italy

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## ABSTRACT

In the present work, CO<sub>2</sub> methanation was investigated over Ni, Fe, Ni<sub>3</sub>Fe<sub>1</sub>, Ni<sub>1</sub>Fe<sub>1</sub> and Ni<sub>1</sub>Fe<sub>3</sub> catalysts supported on Gadolinia Doped Ceria (GDC) in the temperature range 200–400 °C. Both CO<sub>2</sub> and H<sub>2</sub> conversion decreased in the order Ni/GDC > Ni<sub>3</sub>Fe<sub>1</sub>/GDC > Ni<sub>1</sub>Fe<sub>1</sub>/GDC > Ni<sub>1</sub>Fe<sub>3</sub>/GDC. No catalytic activity was displayed by Fe/GDC. Maximum CO<sub>2</sub> conversion (>90%) was observed at 400 °C, with almost 100% selectivity to CH<sub>4</sub>. The catalysts were characterized by X Ray Diffraction (XRD), N<sub>2</sub> adsorption/desorption, H<sub>2</sub> – Temperature Programmed Reduction (H<sub>2</sub>-TPR), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and CO<sub>2</sub> Temperature Programmed Desorption (CO<sub>2</sub>-TPD). The superior activity of monometallic Ni/GDC with respect to bimetallic Ni–Fe/GDC catalysts was ascribed to the presence of surface oxygen vacancies induced by the GDC support, an enhanced basicity of the Ni-rich samples, as well as to the ability of the Ni-GDC to interact with CO<sub>2</sub>, as suggested by XPS data.

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## Introduction

CO<sub>2</sub> fixation for the synthesis of chemicals has great potential interest as this process can contribute to the reduction of CO<sub>2</sub> emissions in the atmosphere. Being an abundant and

renewable carbon source, CO<sub>2</sub> represents an advantageous primary source for sustainable processes involving low GHG emissions.

Amongst viable catalytic processes, CO<sub>2</sub> methanation (Sabatier reaction) [1] is one of the most preferred because of its favourable thermodynamics: CO<sub>2</sub> + 4H<sub>2</sub> = CH<sub>4</sub> + H<sub>2</sub>O

\* Corresponding author. Department of Civil, Energy, Environment and Material Engineering, Mediterranean University of Reggio Calabria, Salita Melissari, 89124 Reggio Calabria, Italy.

E-mail address: [patrizia.frontera@unirc.it](mailto:patrizia.frontera@unirc.it) (P. Frontera).

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( $\Delta G^\circ = -114$  kJ/mol). Moreover, if hydrogen produced by renewable energy sources is employed, such a process would be able to solve the problems connected with the storage and transportation of hydrogen. In other words, methane would become the preferential hydrogen carrier due to its appropriate storage properties (for example, as liquefied natural gas, LNG) and transportation options in the existing infrastructures [2,3].

CO<sub>2</sub> methanation has been widely investigated in the past years on several catalytic systems based on noble metals (e.g., Ru, Rh) [3,4,10,11,13,14] although most of the studies concerns with oxide-supported Ni [5–7,9,12], because of its lower cost.

As for noble metals, Ru has been reported to be the most active and stable methanation catalyst, the reaction selectivity depending on the support [8]. In Ref. [13], turnover frequencies of the reaction were shown to decrease in the order Ru/Al<sub>2</sub>O<sub>3</sub> > Ru/MgAl<sub>2</sub>O<sub>4</sub> > Ru/MgO > Ru/C, suggesting that the catalytic performance was significantly affected by metal-support interactions. Also the preparation method of the catalyst plays a decisive role on the catalytic activity; exemplarily, Ru/TiO<sub>2</sub> prepared by a barrel-sputtering technique was able to achieve a 100% yield at only 433 K, that is much higher in comparison with wet impregnation [14].

Also Al<sub>2</sub>O<sub>3</sub>-supported Rh was reported to be very active and selective to methane [15], and insights on the reaction mechanism have been recently given [16].

Because of the property of Pd in dissociating molecular hydrogen, a bifunctional Pd–Mg/SiO<sub>2</sub> was investigated for CO<sub>2</sub> methanation, which demonstrated high selectivity (>95%) towards methane, with 59% CO<sub>2</sub> conversion [17]. Also Pt, supported on high surface area titania nanotubes, showed good activity in the reaction carried out at low temperature (100 °C) [18].

For what concerns Ni-based systems, main approaches in attempting to discover efficient catalysts have included investigations related to the influence of i) the nature of the support, ii) the preparation method and iii) the design of a suitable catalyst surface constituted by a combination of more than one metal.

Both nature of the support and preparation method play a decisive role in the metal-support interaction, therefore influencing the dispersion and the overall catalytic performance in terms of activity and selectivity. Alumina and amorphous silica-supported Ni were the most extensively investigated catalysts, prepared by different techniques (ion exchange, deposition-precipitation, impregnation) [19–24]. Also ZrO<sub>2</sub> and Ce–ZrO<sub>2</sub>-supported Ni have shown very high CO<sub>2</sub> conversion and selectivity to CH<sub>4</sub> [7,25,26].

A novel class of methanation catalysts was recently discovered starting from calculations using density functional theory (DFT). According to refs. [27–29], the two important properties of a metal surface in determining the rate of the methanation reaction are the energy barrier for CO dissociation and the stability of the main intermediates on the surface, atomic C and O. DFT calculations of these parameters for different metal surfaces have shown to be linearly correlated in the so-called Bronsted-Evans-Polanyi relation, leading to a volcano-shaped dependence of the rate on the dissociation energy of adsorbed CO. For a weak adsorption, the energy barrier for dissociation is high, thus decreasing the reaction

rate. On the other hand, strong adsorption leads to low rates of removal of adsorbed C and O from the surface to form reaction products, as shown in Ref. [27].

According to this analysis, Ni<sub>3</sub>Fe and NiFe should be good candidates for catalysts having higher activity than the single metals and close to the best ones, Ru and Co. Successive investigations have experimentally proven that NiFe alloys, supported on MgAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>, have significantly higher activity and selectivity to methane in comparison with monometallic Ni and Fe catalysts for both CO and CO<sub>2</sub> hydrogenation [30,31]. A more recent study has substantially confirmed previous evidences, showing that Ni<sub>0.7</sub>Fe<sub>0.3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst achieved high carbon dioxide conversion and CH<sub>4</sub> selectivity [32].

The number of papers dealing with the catalytic CO<sub>2</sub> hydrogenation to CH<sub>4</sub> has dramatically increased in the last decade [33]. Nevertheless, no definitive understanding of reaction mechanism has been reached, this goal being necessary for a rational design of a high performance catalyst [34].

On the other hand, utilization of CO<sub>2</sub> as a renewable and environmental friendly source of carbon represents a very attractive approach in view of the use as chemical storage of the excess of electrical energy produced by renewables [35]. In this process, hydrogen used to reduce CO<sub>2</sub> can be preferably produced by electrolysis supplied by renewable energy, making sustainable the entire process.

In order to find new metal-support combinations able to achieve high CH<sub>4</sub> yields, in the present paper results of CO<sub>2</sub> methanation on Gadolinia Doped Ceria (GDC)-supported Ni–Fe catalysts are presented. The choice of such a support is made on the basis of previous studies [36,37] that have demonstrated the “self de-coking” capability of GDC, i.e. removal of carbon species via gasification promoted by the oxygen supplied through the oxide support.

## Experimental

### Catalysts preparation

Catalysts were prepared by wet impregnation. Two different impregnation procedures were carried out. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were used as metal precursors. The support was Gadolinia 0.2 Doped Ceria 0.8 (GDC). The precursors were simultaneously solubilized in aqueous ethanol solution (50%) and then impregnated onto the support at room temperature for 6 h. Then, the catalysts were dried at T = 100 °C for 8 h and calcined at T = 600 °C for 4 h to form the metal oxides that are reduced successively. Five catalysts were prepared in all (monometallic Ni/GDC and Fe/GDC, Ni<sub>3</sub>Fe<sub>1</sub>/GDC, Ni<sub>1</sub>Fe<sub>1</sub>/GDC, Ni<sub>1</sub>Fe<sub>3</sub>/GDC). The total metal loading was 50%wt deposited onto 50% wt GDC.

### Catalysts characterisation

X ray diffraction (XRD) patterns of the powders were recorded on a Bruker D2 Phaser using Cu K $\alpha$  radiation at 30 kV and 20 mA. Peaks attribution was made according COD Crystallography Open Database.

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