Innovative Catalysts for H₂ Conversion to SNG via CO₂ Methanation

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The depletion of fossil fuels increased the interest towards the power-to-gas technologies for the conversion of energy excess (such as photovoltaic energy) in valuable chemicals. In this direction, the CO_2 hydrogenation to substitute natural gas strikes the double target to reduce a greenhouse emission and to exploit solar energy surplus. These papers addressed on the study of innovative catalysts for the CO_2 hydrogenation (Sabatier reaction), by paying attention on the role of active phase and chemical support. In particular, the effect of nickel loading was investigated, evidencing that in one hand the higher amount of active specie increased the activity and reduced the onset temperature of the catalyst, in the other hand too large loadings could suppress the dispersion of the metal, thus reducing the CO_2 conversion. The employing of ceria and ceria-zirconia as catalytic supports improved the sample reducibility, so increasing the CO_2 conversion and reducing the activation temperature of the catalytic system; in particular, CeO_2-ZrO_2 sample showed a higher selectivity towards the Sabatier reaction. The high exothermicity of the reaction is better managed by employing highly conductive structured catalysts that assured an enhanced redistribution of the heat in the whole reaction volume, thus assuring higher conversion values and mainly higher selectivity towards methane production.
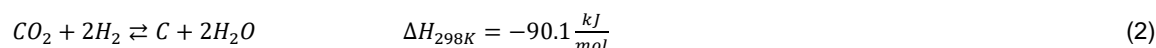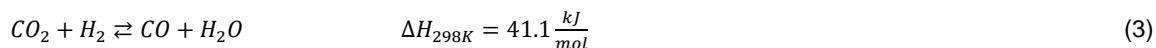
1. Introduction

Renewable energy sources have a significant potential to reduce greenhouse gas emissions in electricity generation. However, due to their intermittent and fluctuating characteristics, their increased implementation is accompanied by major challenges within energy systems because power swings, technically called cycling, lead to an increase in harmful emissions and a rapid wear of machinery. Overcoming this problem, with storage systems to be integrated into the electricity grid, is the goal to achieve for the future and the Power-to-Gas technology is a possible solution.

PtG technology uses renewable energy surplus, which cannot be fed into the public electricity grid, for hydrogen production by electrolysis of water, and H_2 obtained by reacting with carbon dioxide from combustion fumes leads to Substitute Natural Gas (SNG) production through methanation reaction Eq(1), known as Sabatier reaction (Götz et al., 2016). SNG has the same characteristics of the natural gas so it can be directly injected in the existing natural gas distribution grid network.

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \qquad \Delta H_{298K} = -164.7 \frac{kJ}{mol} \qquad (1)$$
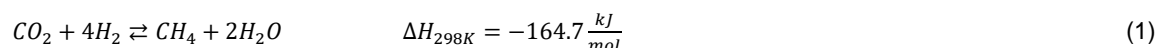
The methanation process is favoured from the thermodynamic point of view by low temperatures, high pressures and high H_2/CO_x ratios (Su et al., 2016). Research is geared towards a more efficient production of methane through the use of catalysts that can accelerate the reaction of methanation of CO_2 and inhibit unwanted reactions such as Eq(2) and Eq(3).

$$CO_2 + 2H_2 \rightleftarrows C + 2H_2O \qquad \Delta H_{298K} = -90.1 \frac{kJ}{mol} \qquad (2)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad\qquad \Delta H_{298K} = 41.1 \frac{kJ}{mol} \qquad\qquad (3)$$

Moreover, the main problem of this technology is the high exotermicity of Sabatier reaction, so researchers' aim is to study innovative reactor solutions able to guarantee a good thermal control, and to find more efficiency catalytic formulations with high activity at low temperature and high stability at high temperatures.

Sabatier and Senderens (1902) discovered the CO and CO_2 methanation processes in 1902 and have been studied and developed for over 100 y. In their early studies, Sabatier and Senderens discovered that nickel was able to catalyse the reaction between carbon monoxide and hydrogen to form methane and water; to date, about 100 y later, it has been seen that many metals between VIII and X group are active for the methanation reaction. Although noble metals are very selective to methane at relatively low temperatures, they are very expensive to be used on an industrial scale for the production of SNG. Nickel has been recognized as the most appropriate catalyst given its selectivity, activity and low price (Rönsch et al., 2016).

The activity and selectivity of CO_2 hydrogenation is sensitive to the Ni load present in the catalytic formulation. Zhou et al. (2016) discovered that the catalytic activity of the Ni/TiO_2 catalyst grew with the increase of Ni load from 5 to 15 wt% and stabilized by increasing the load from 15 to 20 wt%. Excellent for methanation at low temperatures was the 15 % Ni/TiO_2 catalyst.

Garbarino et al. (2014) investigated the hydrogenation of CO_2 to CH_4 and CO on a catalyst based on Ni/Al_2O_3 at atmospheric pressure. They noted that the catalysts with small Ni particles given by a moderate Ni load showed a high selectivity to CH_4, while those with larger particles, attributable to higher Ni loads, showed a high selectivity to CO. The hydrogenation of CO_2 to produce CH_4 and CO was investigated on the Ni/Al_2O_3 catalyst by Garbarino et al. (2014) they discovered that the catalysts with very small Ni particles after reduction and with a moderate Ni load had a high selectivity to methane. High selectivity to CO was found on high-Ni catalysts with larger particles.

Commonly used metal supports are metal oxides with a high surface area such as Al_2O_3 (alumina), SiO_2 (silica) or TiO_2 (titania). Among these the alumina, above all the γ-Al_2O_3 turns out to be the most used (Rönsch et al. 2016). However, in the last period, the focus is on the use of rare earth oxides as structural and electronic supports to improve the activity, selectivity and stability of the catalytic systems.

Among them, CeO_2 appears particularly interesting for its redox properties (Trovarelli et al. 2001). In addition, a property of this oxide, which makes it particularly interesting for methanation, is its ability to promote the dissociation of R-OH-type molecules (de Lima et al., 2008). Using catalysts supported on CeO_2 for the Sabatier reaction, the high oxygen mobility, a consequence of the Oxygen Storage Capacity, allows the gasification of carbon deposits, thus preserving the active surface area of the catalytic system. Furthermore, ceria promotes the complete oxidation of CO_2 coke. A well-known doping agent for CeO_2 is zirconium, which can increase oxygen mobility, thermal resistance and low temperature activity in mixed CeO_2-ZrO_2 oxide systems (Alifanti et al., 2003). Aldana et al. (2013) studied the methanation of CO_2 on the catalyst based on $Ni/Ce_{0.72}Zr_{0.28}O_2$ with a Ni load variable between 5 wt% and 15 wt%. To show the best performance was the catalyst with a load of Ni equal to 10 wt% showing a high activity and stability for 150 h with a conversion of CO_2 and selectivity of CH_4 respectively to 75.9 % and 99.1 %. These results are due to the high oxygen storage capacity of cerea-zirconia and to the high dispersion of Ni on its surface.The mixed oxide of cerium and zirconium appears to be a promising support for its ability to activate CO_2, interactions between Ni and ceria-zirconia detect a direct hydrogenation as the main mechanism of CO_2 methanation without passing through the intermediate reaction which leads to CO.

The catalyst geometry also plays a crucial role in the reaction performances: the catalyst transferring on a high conductive structured carrier enabled an optimal thermal management that could lead to a better exploiting of the catalytic volume (Palma et al., 2016). In particular, exothermic reactions takes advantages by this phenomenon, since a temperature flattening occurs in the reaction volume, that avoid undesired phenomenon that mau cause an early deactivation of the catalyst (Palma et al., 2011)

Starting from these premises, the aim of this work is to investigate new catalytic formulations at low metal content for the sabatier reaction. In particular, it will be analysed both the nichel load effect and the role of chemical supports on catalytic performances.

2. Materials and methods

All the experimental procedure (catalyst preparation, characterization and experimental tests) was carried out at the ProCEED labs in the University of Salerno.

2.1 Catalysts preparation

In order to investigate the effect of nickel load on CO_2 methanation reaction, different powder samples were prepared by wet impregnation method by selecting a CeO_2-ZrO_2 solid solution (provided by Rhodia) as support, and varying Ni loading from 3 wt% to 13 wt%. Support were previously calcined at 600 °C for 3 h with a heating ramp of 20°C/min, then it was prepared an aqueous solution of the precursor salt of about 500 mL, using distilled water. Wet impregnation was carried out using nickel nitrate hexahydrate $Ni(NO)_2 \cdot 6H_2O$ as nickel precursor salt. Once dry, the sample is left in the oven overnight at 120 °C to eliminate any residual water from the porosity of the solid and then it is again calcined at 600 °C. The role of the support was also assessed: once fixed the nickel loading, two other samples were prepared by deposing the same active phase on alumina and on ceria. All powder samples (summarized in Table 1), were compacted and sieved in 180 - 355 μm spheres. Finally, the most promising formulation was transferred on highly thermal conductive structured carriers: a honeycomb silicon carbide monolith (SiC) and an aluminum open cell foam were selected as substrate. Once shaped substrates as 88 x D1.6 mm cylinders, a ceria-zirconia slurry was deposed by dip coating (2 g of slurry), then nickel was deposed by wet impregnation method (the procedure was described elsewhere (Palma et al. 2017).

Table 1 Investigated formulations

Sample N.	1	2	3	4	5	6
Formulation	3%Ni/CeO$_2$-ZrO$_2$	7%Ni/CeO$_2$-ZrO$_2$	10%Ni/CeO$_2$-ZrO$_2$	13%Ni/CeO$_2$-ZrO$_2$	10%Ni/Al$_2$O$_3$	10%Ni/CeO$_2$

2.2 Catalysts characterization

Properties of the powder catalysts have been investigated through different characterization techniques. The specific surface area (B.E.T.) measurements were evaluated with a Costech Sorptometer 1040 (Costech International), by dynamic N_2 adsorption measurement at -196°C, the samples were previously treated at 150 °C for 30 min in a flow of helium. The X-ray fluorescence analytical technique was applied with the aim of determining the effective load of active specie on powder catalysts by means of ARL QUANT'X ED-XRF spectrometer (Thermo Scientific). Finally, the Temperature Programmed Reduction (TPR) analysis was done in situ feeding 500 Ncm^3/ min of 5 % H_2 in nitrogen, with a heating rate of 5 °C/min reaching 600°C, in order to obtain the metal active phase.

2.3 Catalytic reaction system

The experimental tests on powder samples were carried out in a tubular (O.D. 12.7 mm, thk 1.0 mm) AISI 316L reactor, placed in an annular furnace for the temperature control. An amount of 2 g of catalyst samples (in powder, pelletized to 180-355 μm grains) was placed in the middle of the tubular reactor, and hold through 2 quartz-wool flakes. In order to reduce the pressure drop along the catalytic bed, coarser quartz spheres (500-710 μm) were added to catalytic powder up to reach a volume of 4 mL. Experimental tests were carried out at atmospheric pressure by fixing feed ratio ($H_2/CO_2 = 4$), diluted in nitrogen ($N_2/CO_2 = 5$) and space velocity (WHSV= 30 NL h^{-1} g_{cat}^{-1}), defined as the ratio between the volumetric feed rate and the catalyst weight. The reaction temperature range investigated was between 200 °C and 500 °C with an increasing rate of 2 °C/min. Tests for monolithic samples were carried out in a ø 1" quartz reactor, by fixing gas inlet temperature, and by thermally insulating the reaction zone in order to approach an adiabatic reaction volume. For comparison, powder catalyst was also tested in the same conditions, by diluting catalytic powder with 500 - 710 μm quartz spheres in order to have the same volume of structured samples.

3. Results and discussion

3.1 Catalysts characterization

Main results of sample characterization are summarized in the Table 1. The evaluation of the specific surface area remarked that the alumina assures the highest SSA value, as expected. The utilization of ceria is promoted by the quite low temperature of the system that assures a relatively high surface area for the ceria-supported sample. On the other hand, the addition of zirconia to the sample causes a significant reduction in SSA value, resulting about half than the only ceria-supported catalyst. The XRF analysis confirmed a reasonable agreement between the experimental end nominal loading of nickel: beside a systematic gap between experimental and nominal value, the evaluated loading increasing seems compatible with the nominal one.
The TPR analysis results were summarized in Table 2 and in Figure1. The Ni-CeO_2-ZrO_2 samples evidenced 3 main reduction peaks: the first two, occurring at temperature below 450 °C, are attributed to the reduction of the NiO species on the sample. It was also appreciable that the increasing in nickel loading produced an increasing in the intensity of the middle temperature peak: it suggests a stronger interaction between Ni and Zr on the

sample, responsible to the lower temperature reduction peak. The highest reduction peak, occurring at temperature around 400 °C, could be attributed to the reduction of the support. The influence of supports on the reduction profile is summarized in Figure 1. The employment of rare earths oxides as support produced a clear improving in sample reducibility, since peaks moved to lower temperatures. In particular, ceria-zirconia supported samples resulting in a reduced temperature of NiO, evidencing the advantages of the combination of such material that enhances the mobility of oxygen within the support lattice.

The evaluation of the hydrogen uptake (Table 2), and in turn of the nickel loading, further confirms a good accordance between experimental and nominal values. The slightly higher values observed for the ceria- and ceria-zirconia-supported samples could be devoted to the spillover phenomenon, peculiar of rare earth oxides-based catalysts.

Table 2: Sample characterization

| Samples	*BET analysis* Catalyst SSA [m²/g]	*XRF analysis* Experimental Ni loading [%wt]	Nominal Ni loading [%wt]	----------------------*TPR analysis* ---------------- Peak Temperature [°C]	Experimental Ni loading [mmol]	Nominal Ni loading [mmol]
3%Ni/CeO₂-ZrO₂		2.6	3	220; 320	1.4	1.1
7%Ni/CeO₂-ZrO₂		5.2	7	300; 420	2.1	2.4
10%Ni/CeO₂-ZrO₂	61.9	8.2	10	310; 400	5.8	3.4
13%Ni/CeO₂-ZrO₂		10.9	13	350; 460	5.1	4.4
10%Ni/Al₂O₃	160.9	9.2	10	283; 589	2.6	3.4
10%Ni/CeO₂	114	8.1	10	161; 296	3.8	3.4
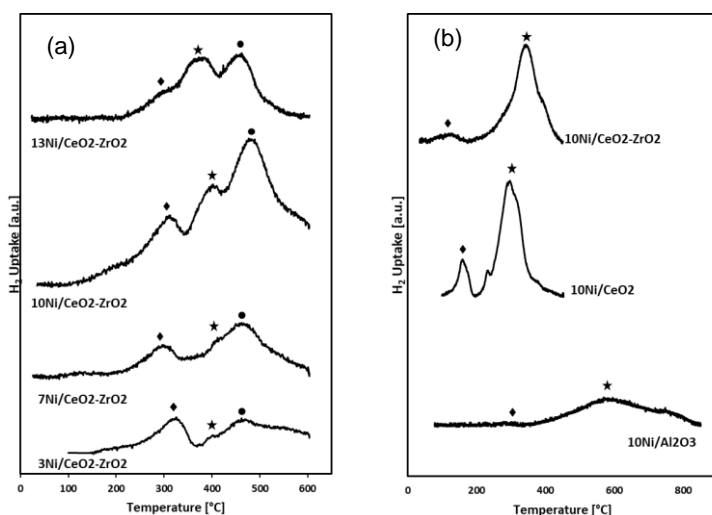
Figure 1: Temperature programmed reduction results for CeO₂-ZrO₂ samples with different Ni loading (a) and for different support (b).

3.2 Activity test

A first approach to the catalytic study of the methanation reaction concerned the role of nickel load on catalytic performances (Figure 2). The activity and selectivity of CO_2 hydrogenation is sensitive to nickel loading: the increasing in metal loading assures higher conversion values up to 10 wt% of Ni; the further increasing in nickel loading did not lead to higher conversion values, and also caused a worsening in the approach to the thermodynamic values. On the other hand, by considering a CO_2 conversion threshold of 40 %, it could be observed that the amount of active species strictly contributed to reduce the onset temperature, since the catalysts activation starts at lower temperature with the increase of Ni load. Conversely, the methane yield, and thus the process selectivity, strictly depended by the nickel loading, since the best approach to thermodynamic equilibrium could be observed for the 13 % Ni catalyst.

The effect of the support was also investigated; results are summarized in Figure 3. Reported results evidenced that the choice of the support material plays a crucial role in the reaction mechanisms: the employing of rare earths in the samples supports assured clear enhancements in the catalytic activity, since higher conversion

values could be observed in the whole investigated temperature range with respect to the alumina-based sample. Ceria and ceria-zirconia samples also enabled a clear reduction in onset temperature, being 320°C for the Ni/Al_2O_3 sample, and around 240 °C for the other two samples. Such achievement was in well accordance with results of TPR analysis, in which the better reducibility of rare earths-based samples was evidenced. In particular, ceria-based sample showed slightly better performances with respect to the ceria-zirconia sample, probably due to the higher surface area of the support that also suggests a higher dispersion of the active phase. On the other hand, ceria-zirconia sample assured a better approach to the equilibrium in terms of methane yield, due to the higher selectivity of the sample. Such result is in accordance to the higher reducibility of the Ni/CeO_2-ZrO_2 sample that enhances the activation of hydrogen and in turn the hydrogenation of the carbon dioxide.
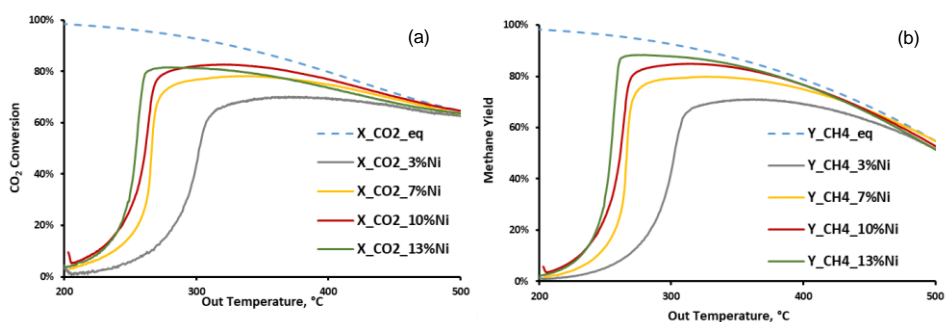

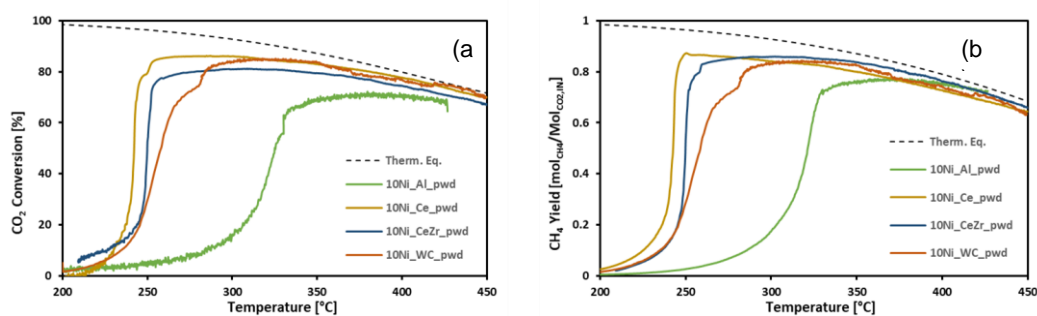Figure 2: Effect of Nickel loading on CO_2 conversion (a) and methane yield (b).

Figure 3: Effect of catalytic support on CO_2 conversion (a) and methane yield (b).

3.3 Structured Catalysis

The 10%Ni/CeO2-ZrO2 formulation was also transferred on structured carrier, and catalytic tests were performed by fixing the inlet gas temperature: results are summarized in Figure 4.
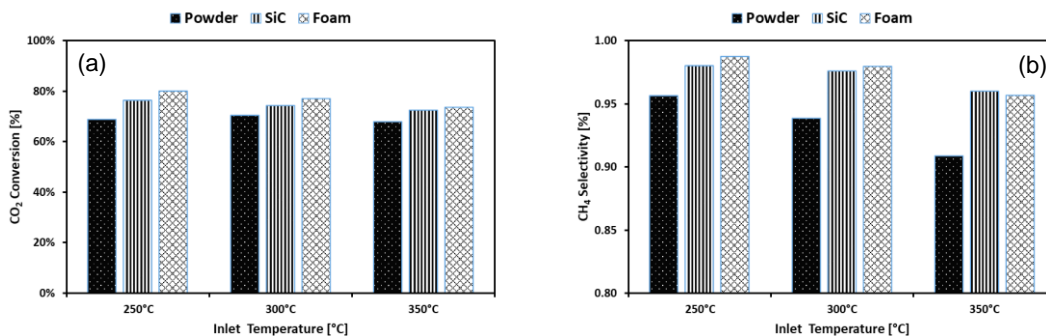

Figure 4: Effect of carrier on CO_2 conversion (a) and methane selectivity (b).

As evidenced by experimental results, the transferring of the catalyst on the structured carrier allowed a sensible increasing of catalytic performances in terms of CO_2 conversion: the highest performances were observed for the aluminum foam supported catalyst. The evidenced gain in catalyst activity could partially attributed to the enhanced transport properties related to the monolithic structure; but the main contribution is due to the optimal thermal management assured by the highly conductive structured catalysts, that enabled an optimal redistribution of the temperature along the catalyst. Therefore, in one hand the outlet temperature was reduced, taking thermodynamic advantages, in the other hand hotspots and temperature peaks along the reaction volume were mitigated, assuring a better exploiting of the whole catalytic volume. Such achievement also affected the process selectivity that resulted in a sensible increasing for the structured samples.

4. Conclusions

Catalysts for the CO_2 hydrogenation reaction aimed to the synthesis of methane are investigated. Nickel was selected as active specie, due to its relatively low cost, and the effect of the metal loading on a ceria-zirconia support was investigated. The physical-chemical characterization evidenced that the nickel amount clearly improves the reducibility of the support, enhancing the interactions between the metal and the support. Catalytic tests revealed that the active phase loading strongly affects the catalytic performances, since higher loadings assured higher conversions and lower onset temperature. However, a too high amount of nickel seems to not advantages the sample activity, probably due to a limited metal dispersion on the catalytic surface. The evaluation of active phase role indicated that the reaction takes advantages by the employment of rare earths oxides, that showed a higher reducibility with respect to alumina, however the metal dispersion, and in turn the support specific surface area, is a crucial parameter in the catalyst activity, both in terms of CO_2 conversion and onset temperature. It was also evidenced that ceria-zirconia supports assured a higher selectivity to methane, probably due to the more pronounced activation of hydrogen towards the CO_2 hydrogenation. Finally, very interesting improvements could be achieved by transferring formulations on highly thermal conductive structured carrier. The optimized thermal management inside the catalytic volume enhanced the methanation reactions kinetics and suppressed side reactions, allowing to higher performances in terms of CO_2 conversion and selectivity to methane. This effect evidences that the substrate optimization enables for a better exploiting of the catalytic formulations.

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