

## Optimization of Ni-based catalysts for Substitute Natural Gas synthesis via CO<sub>2</sub> methanation

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### Highlights

- Catalytic supports strongly effects Sabatier reaction performances
- Nickel dispersion appeared a crucial parameter for reactions kinetics
- Highly thermal conductive carriers enable a better exploiting of catalytic formulation

### 1. Introduction

Power to Gas (PtG) technology is emerging as a possible solution able to counter the need to exploit green pathways for energy production, by realizing an alternative energy storage system. In particular, through the PtG technology it could be possible to convert the excess of renewable energy (e.g. solar, wind, etc.) into hydrogen by electrolysis of water; moreover, produced hydrogen could react with carbon dioxide, derived from combustion fumes, so achieving Substitute Natural Gas (SNG) production by means of methanation reaction, known as *Sabatier reaction*, resulting a carbon free process.



Sabatier reaction typically occurring at a temperature of 250-550°C, so suffering of both thermodynamic and kinetic limitations. In addition, the strong exothermicity of the process results in a difficult thermal control of the process, affecting both reaction selectivity and catalyst lifetime. The scientific research aims 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.

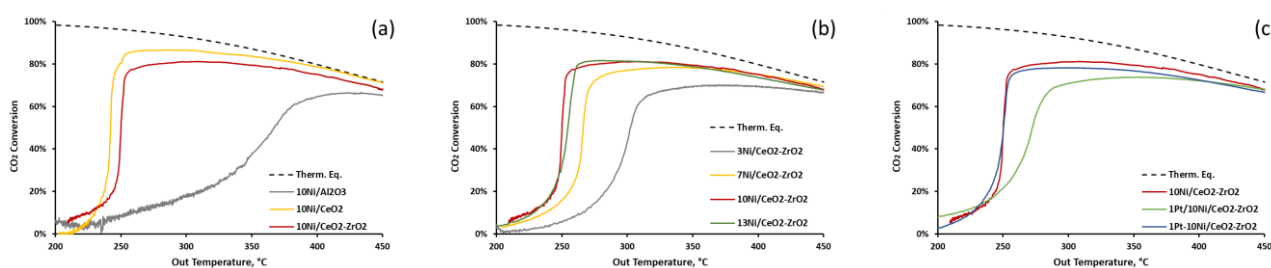
Typically, Sabatier reaction could be catalyzed by nickel catalyst, due to its selectivity, activity and low price [1]. Generally, active species are supported most commonly on  $\gamma\text{-Al}_2\text{O}_3$ , but recently researchers are directed towards the use of rare earths oxides to improve the activity, selectivity and stability of the catalytic system. The aim of this work is to investigate the role of structured carrier, chemical support, and active phase loading in the Sabatier reaction, by paying attention both to system activity and to selectivity. In addition, the effect of the addition of a noble metal in traditional formulation was also evaluated.

### 2. Methods

Three catalytic formulations were prepared by fixing active metal content (10 wt% Nickel), deposited on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub>. Furthermore, four catalytic formulations were prepared on CeO<sub>2</sub>-ZrO<sub>2</sub> support by varying nickel loading from 3 wt% to 13 wt%. All the samples were prepared with the impregnation-precipitation method (described elsewhere [2]), and tested in powder shape ( $d = 180 \div 355 \mu\text{m}$ ). Finally, bimetallic formulations were prepared by adding Platinum (1 wt%) to the 10%Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst both by co-impregnation and subsequent impregnations (Nickel, then Platinum) methods, in order to also stress the preparation method effect on catalytic performances. Finally, 2 structured catalysts were prepared by depositing a 5%Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> based catalysts on two carriers: a silicon carbide honeycomb monolith and an aluminum open cell foam; both carriers were shaper as a cylinder ( $D = 1.6 \text{ mm}$ ;  $L = 88 \text{ mm}$ ), on which an amount of 2 g of catalytic washcoat was deposited. Powder formulations were tested in a tubular (i.D. 10 mm) AISI 316L reactor, by using 2 g of catalyst, diluted with coarser quartz spheres (500-710  $\mu\text{m}$ ) up to reach a total volume of 4 mL to reduce pressure drops. Structured catalysts were tested in a tubular quartz reactor (i.D. = 21 mm), by wrapping the monoliths in an expanding mat in order to avoid bypass phenomena. Samples were characterized through in-situ temperature-programmed reduction. Experimental tests were carried out at atmospheric pressure by fixing feed ratio ( $\text{H}_2/\text{CO}_2 = 4$ ), dilution ratio ( $\text{N}_2/\text{CO}_2 = 5$ ) and space velocity ( $\text{WHSV} = Q_{\text{tot}}/m_{\text{cat}} = 30 \text{ NL h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ). For the powder catalyst, reaction temperature ranged between 200°C and 450°C with an increasing rate of 2°C/min. For the structured catalysts, tests were carried out by fixing oven temperature at 250°C, and by evaluating temperature profile along the catalytic bed.

### 3. Results and discussion

In a first stage, the role of the chemical support was investigated. As summarized in figure 1(a), the rare earths based supports were responsible for the best performances, probably due to their intrinsic basicity and to the OSC properties. Conversely, the acid sites of alumina support depress the carbon dioxide adsorption, thus resulting in a less pronounced activity. The ceria-based catalyst evidenced the highest conversion, probably due to the higher surface area, and in turn the higher nickel dispersion, than ceria-zirconia sample. On the other hand, the ceria-zirconia sample showed a higher selectivity, suppressing the reverse-WGS reaction, thus achieving a comparable methane yield than ceria sample (not reported). The investigation on nickel loading (figure 1(b)) confirmed that the nickel dispersion plays a crucial role on the system performances, since CO<sub>2</sub> conversion raised by increasing nickel loading up to 10%, while no difference was observed between 10% and 13%. The effect of the addition of a noble metal was also investigated (figure 1(c)): as reported the platinum addition method resulted detrimental for the performances of the system because it promoted the reverse-WGS + CO-methanation mechanism, resulting in a global lower reaction rate. On the other hand, platinum addition promoted lower activation temperature, in particular for the co-precipitation method, in which both benefits of platinum and nickel catalytic activities were observed.



**Figure 1.** Effect of chemical support (a), nickel loading (b) and platinum addition (c) on carbon dioxide conversion.

Finally, the effect of structured carrier was investigated, by comparing the performances of structured catalysts with a powder catalyst, diluted with quartz up to reach the same volume of monoliths. As reported in Table 1, clearly better performances were observed for structured catalysts with respect to powder sample, probably due to a better thermal management along the reaction volume. The high conductivity of aluminum carrier was able to better redistribute the exothermicity of the reaction along the catalytic bed, so raising temperature also in the inner section of the catalyst, thus resulting in an overall improved reaction rate.

**Table 1:** Structured catalysts performances, Toven = 250°C

	Powder	SiC Honeycomb	Foam
CO <sub>2</sub> Conversion	66.8%	70.5%	81.9%

### 4. Conclusions

Substitute Natural Gas production through the conversion of CO<sub>2</sub> from exhausted gas is an interesting solution in the depollution direction. The role of catalytic components for a “low-cost” formulation was investigated. The reported study evidences that catalytic support plays a crucial role on the catalytic activity, whereas the support basicity and textural properties enabled a better activation of reactants. Moreover, an optimal nickel loading maximized CO<sub>2</sub> conversion, remarking the role of active specie dispersion in the catalyst. Platinum addition seems to reduce activation temperature of the system although the optimization of the bimetallic catalyst preparation is required. Finally, the transfer of the catalytic formulation on an appropriate structured catalyst could result in a better exploiting of the properties of the catalytic formulation.

### References

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### Keywords

Power-to-Gas; Process Intensification; Structured Catalysts.