



*Dedicated to Professor Zeno Simon  
on the occasion of his 80<sup>th</sup> anniversary*

## CARBON DIOXIDE CONVERSION TO METHANE OVER SUPPORTED NICKEL BASE CATALYSTS

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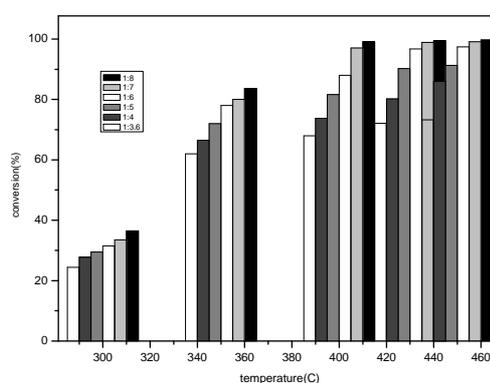
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Catalytic tests for carbon dioxide hydrogenation were reported over nickel base catalysts on various supports in this paper. The tests were carried out under atmospheric pressure and for a temperature range between 300 and 550°C. Based on the results of the catalytic activity tests, it was found that from the three investigated catalysts Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> is the potential catalyst for CO<sub>2</sub> conversion. Several important parameters namely reaction temperature, H<sub>2</sub>/CO<sub>2</sub> molar ratio and regeneration procedures were taken into account and optimized. Temporal distributions of volumetric concentrations for CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> at various reaction conditions are presented. An important conclusion related to the experimental results was that a high catalytic activity obtained at relatively low temperature is correlated with the copper presence.



### INTRODUCTION

With the rapid increase in the emission of greenhouse gas carbon dioxide (CO<sub>2</sub>) from the industry development, the exploitation of CO<sub>2</sub> as a carbon source has received considerable attention in recent years. The use of carbon dioxide (CO<sub>2</sub>) as either a technological fluid for building complex molecules blocks or a raw material in chemical processes as a carbon source for fuels or in biotechnological applications, provides the potential to reduce CO<sub>2</sub> emissions.<sup>1-5</sup> Two main

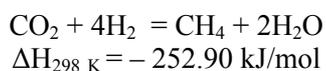
solutions are proposed: (i) capturing CO<sub>2</sub> at its source and storing it in the geological subsurface,<sup>6,7</sup> (ii) promoting the transformation of CO<sub>2</sub> in the presence of an adequate catalyst at high temperature.<sup>8,9</sup>

Because the introduction of carbon capture and storage processes requires additional costs, more efforts should be dedicated to the possible CO<sub>2</sub> conversion into chemicals or fuel synthesis. The CO<sub>2</sub> conversion process is of interest for: (i) the recycling of CO<sub>2</sub> as an energy carrier, thereby reducing its accumulation in the atmosphere, (ii)

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the production of renewable hydrocarbon fuels from CO<sub>2</sub>, water, and renewable electricity for use as transportation fuels, and (iii) as a convenient means of storing electrical energy in chemical form to level the electrical output from intermittent energy sources such as wind and solar.

Many efforts have been made in respect to the catalytic transformation of CO<sub>2</sub>, known as an attractive C1 building block by the organic synthesis into valuable chemicals. One of the promising methods is the obtaining of the methane (CH<sub>4</sub>), by the catalytic hydrogenation (also called the Sabatier reaction) from CO<sub>2</sub> which is highly functional, abundant, renewable carbon source and an environmentally friendly chemical reagent:



Different types of catalysts (noble and non-noble metals, oxide supported metals, oxides, etc.) were tested and studied in relation to their selectivity towards the formation of methane, paraffins, alcohols, especially methanol, and olefins.<sup>5-10</sup> Obtaining the methane has received a particular attention due to the opportunities arising from the CO<sub>2</sub> technological utilization as a possible source of energy.

Hydrogenation of CO<sub>2</sub> toward methane has been investigated using alternative suitable catalytic systems based on supported group VIII metals (e.g., Ru, Rh, Ni, Co, Fe) on various oxide supports (TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, MCM, SBA-15, zeolite). Noble metals such as rhodium, ruthenium, platinum and palladium, exhibit promising CO<sub>2</sub>/H<sub>2</sub> methanation performance, high stability and less sensitivity to coke deposition.<sup>11</sup>

However, supported nickel catalysts remain the most widely studied materials. Relatively high surface area supports, usually oxides, have been used extensively for the preparation of metal catalysts. The nature of support plays a crucial role in the interaction between the nickel and the support, and thus determines catalytic performances toward activity and selectivity for the methanation of CO<sub>2</sub>.

Milder and efficient reaction parameters, recently reported in literature, allowed the obtaining of promising performance for CO<sub>2</sub>/H<sub>2</sub> methanation, as follow: 90% conversion in presence of amorphous alloy Ni-Zr-Sn at 300°C<sup>12</sup>, 43.6% conversion in presence of Pd-Ru-Ni/Al<sub>2</sub>O<sub>3</sub> (200°C, 5 h),<sup>13</sup> 90% conversion in presence of Ru (300°C, 2 atm),<sup>14,15</sup> 75% selectivity for CH<sub>4</sub> over

Rh/TiO<sub>2</sub> at 400°C<sup>15,16</sup> and 20% conversion over Pt at temperatures higher than 450°C,<sup>17</sup> 96% selectivity over Ni/MCM-41, 84.6% conversion on Ni-La/Al<sub>2</sub>O<sub>3</sub>,<sup>18</sup> 64.1% conversion on Ni/MSN, 42.4% conversion on Ni/SiO<sub>2</sub>, 27.6% conversion on Ni/Al<sub>2</sub>O<sub>3</sub> at 300°C,<sup>19,20</sup> 89.4% conversion on NiO/SBA-15,<sup>21</sup> 54.2-63.4% conversion over Ni-Mg base or Ni-Fe base catalysts.<sup>22</sup>

In these cases, either selectivity or conversion was low, or high temperature, or complex catalytic systems or expensive catalysts were required. Nevertheless, nickel remains the favoured catalyst for the reaction by virtue of its life, high activity, selectivity towards methane formation in preference to other hydrocarbons, and its comparatively low cost.<sup>20</sup>

These considerations justify the opportunity of the present study aimed to obtain adequate performances as a straightforward method for generating CH<sub>4</sub> fuel as a possible source of energy.

Our current objective was to study the CO<sub>2</sub> conversion to methane, carrying out the process at 300-550°C and atmospheric pressure, in the presence of nickel base catalysts. Promising methanation performances were expected due to the optimization of different reaction parameters.

## MATERIALS AND METHODS

The hydrogen and carbon dioxide were purchased from Linde Groupe, and were of ultra high purity (UHP). The catalysts employed in this work were commercial samples. Ni/Silica was commercially available from CCE (Catalysts and Chemicals Europe), Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was purchased from BASF, Ni/C was available from VEGA Ploiesti Roumania.

The characteristics of Ni/Silica used in this study were: pellets shape with 4 mm diameter, 4 mm length. Elemental analysis for the CCE catalyst gave the following composition: 45.45% Ni; 0.02% CuO, 0.23% Fe<sub>2</sub>O<sub>3</sub>, 20.18% SiO<sub>2</sub>. The characteristics of Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were: pellets shape with 4 mm diameter, 10 mm length. Elemental analysis for the BASF catalyst was: 17.73% Ni; 5.7% Cu, 1.7% Mn, 45.2% SiO<sub>2</sub>, 22.48% Al<sub>2</sub>O<sub>3</sub>. The characteristics of Ni/C were: pellets shape with 2 mm diameter, 6 mm length. Elemental analysis showed a composition of: 32.03% Ni and 65.8% C.

A schematic conducted reaction system is presented in Fig. 1.

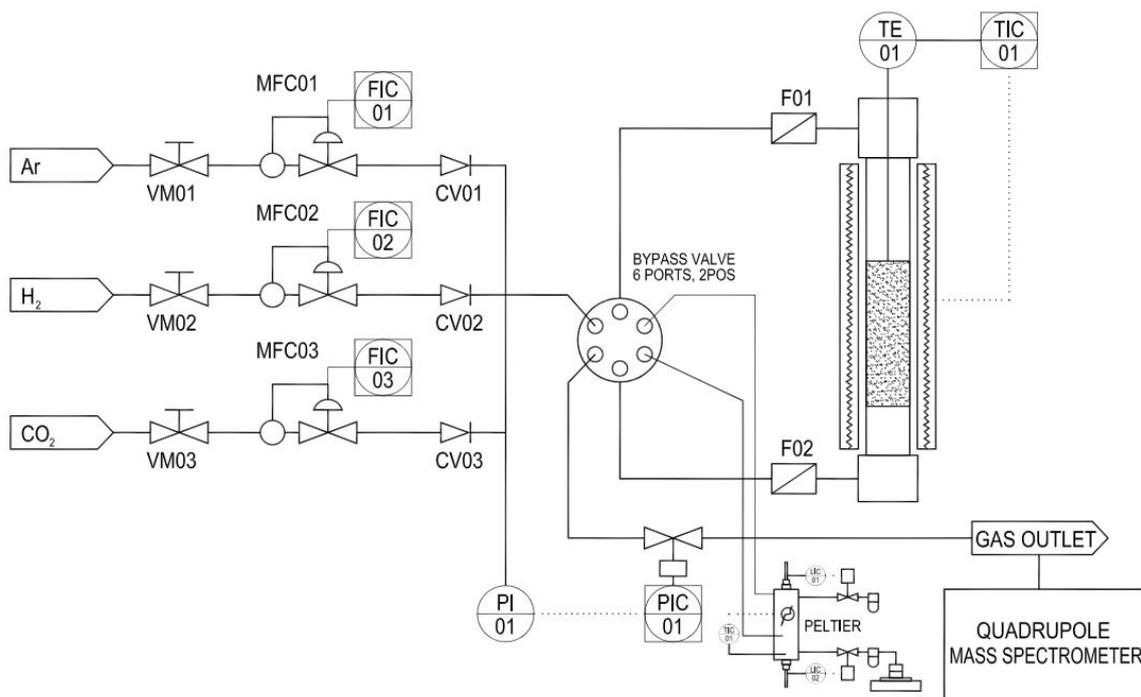


Fig. 1 – A schematic of the reaction system and experimental procedures.

In the reaction system, as can be seen in the Fig. 1, three units (a feeding unit, a reaction unit, and a product gas analysis unit) were included.

All reactions were carried out in a laboratory-scale, continuous-flow reaction system using a tubular specially stainless steel micro reactor (PID Eng&Tech-MICROACTIVITY), placed in a cylindrical conventional tubular furnace, equipped with an electrical heater, operated at atmospheric pressure and fully monitored by computer. The temperature was checked with a thermocouple located inside a quartz thermo well fixed into the catalytic bed. During the operation, the product mixture from the reactor outlet was led to an ice-water trap PELTIER, through the tube wrapped by a heating tape, so as to condense the water produced. This water was regularly removed.

The catalytic bed was composed of a layer of inert glass wool on which is placed the powder catalyst selected within the granulometric fraction of 0.1-0.2 mm. Before starting each catalytic testing, the catalyst was reduced at 550°C in 5% H<sub>2</sub>/Ar for 3h. The methanation reaction was carried out at gas hourly space velocity (GHSV=19000h<sup>-1</sup>). Each experiment was repeated twice, and each temperature was maintained for 30 min before the next temperature increment was accomplished. CO<sub>2</sub> and H<sub>2</sub> were continuously fed into reactor together with argon carrier. Mass flow controllers (ALICAT Scientific model) were used to control

the flow rates of the feed gases in known proportions prior to reaction.

Experiments were carried out under atmospheric pressure in the temperature range of 300-550°C. The compositions of the feed gases were varied by changing the molar ratio of H<sub>2</sub>:CO<sub>2</sub> (3.6:1.0 to 8.0:1.0), while the total flow rate was maintained at a constant value (50 ml min<sup>-1</sup>). The conversion of carbon dioxide is defined as the percentage of reacted carbon dioxide:

$$\text{CO}_2 \text{ conversion}(\%) = \frac{(Q_{\text{CO}_2\text{-inlet}} - Q_{\text{CO}_2\text{-outlet}}) \times 100}{Q_{\text{CO}_2\text{-inlet}}}$$

where:  $Q_{\text{CO}_2\text{-inlet}}$  and  $Q_{\text{CO}_2\text{-outlet}}$  are the molar flow rates of CO<sub>2</sub> (mol s<sup>-1</sup>) at the inlet and the outlet, respectively.

The reactant and product gases composition were measured and continuously monitored by a Hiden HAL VII quadrupole mass spectrometer. Between the experiments, the entire experimental set-up was flushed with He until the mass spectrometer signals reached practically their respective baseline value. Quantitative calibration of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> compositions was made based on registered partial pressures signals and using standard calibration gas mixtures.

## RESULTS AND DISCUSSION

The activity measurements were carried out over mentioned catalysts in order to identify the best performance in terms of conversion in stoichiometric conditions ( $H_2:CO_2=4:1$ ), at atmospheric pressure and isothermal conditions ( $350^\circ C$ ). The results of the activity test at stoichiometric conditions exhibited conversions comparable with those from literature over Ni/C (8%) and Ni/SiO<sub>2</sub> (32%), but superior performance were obtained in the presence of Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (up to 70%).

This behaviour can be explained by two reasons: (i) due to the support, which has a significant influence on the morphology of the active phase, adsorption and catalytic properties, namely the metal-support effect,<sup>20</sup> (ii) due to the superior performances of CO<sub>2</sub> conversion over Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> as a consequence of its chemical composition.

We can suppose that for the first two catalysts, the methane formation didn't occur practically with remarkable results, maybe because of copper absence in the catalyst structure (it is well known that methanation reaction initially occurs by the reduction of CO<sub>2</sub> to CO on the catalyst surface and the dissociation of CO to carbon species is the rate determined step (copper based catalyst is a proper catalyst for CO formation). The Cu catalyst favours CO formation, while the Ni catalyst is active for CH<sub>4</sub> production. The high activity of the third catalyst, Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, can be related to the

observation that methane formation appears to be limited by the dissociation of carbon monoxide to carbon species which further react with hydrogen to produce methane in the carbon monoxide methanation reaction. This is in accordance with the observations of Hwang *et al.*,<sup>22</sup> for the Ni-M-Alumina (M=Fe, Zr, Y and Mg), which concluded that the catalysts used in the CO<sub>2</sub> methanation need to have an optimal CO dissociation energy and weak metal-support interaction of the catalyst to favourable production of methane. In addition, Ni-Cu base catalyst is known for its synergic effect in hydrogenation process.<sup>23</sup>

On the basis of the above observations we focused our experiments on optimizing the reaction conditions for the most promising catalyst, Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Several parameters such as reaction temperature, H<sub>2</sub>/CO<sub>2</sub> molar ratio and regeneration procedures were taken into account and optimized.

For this purpose, different amounts of reactants were preheated at studied temperatures, and after that introduced into the mass spectrometer through the reactor by-pass for checking the composition of the gaseous mixture. Then, the reactants were passed into the reactor, by using an electro-valve. The formation of the methane was observed. The trends for reactants and products were similar but a comparison suggests that a higher H<sub>2</sub>/CO<sub>2</sub> molar ratio leads to a higher obtained CH<sub>4</sub> as a consequence of more CO<sub>2</sub> transformed in methane. For exemplifications, the results obtained at two temperatures were presented in Figs. 2-7.

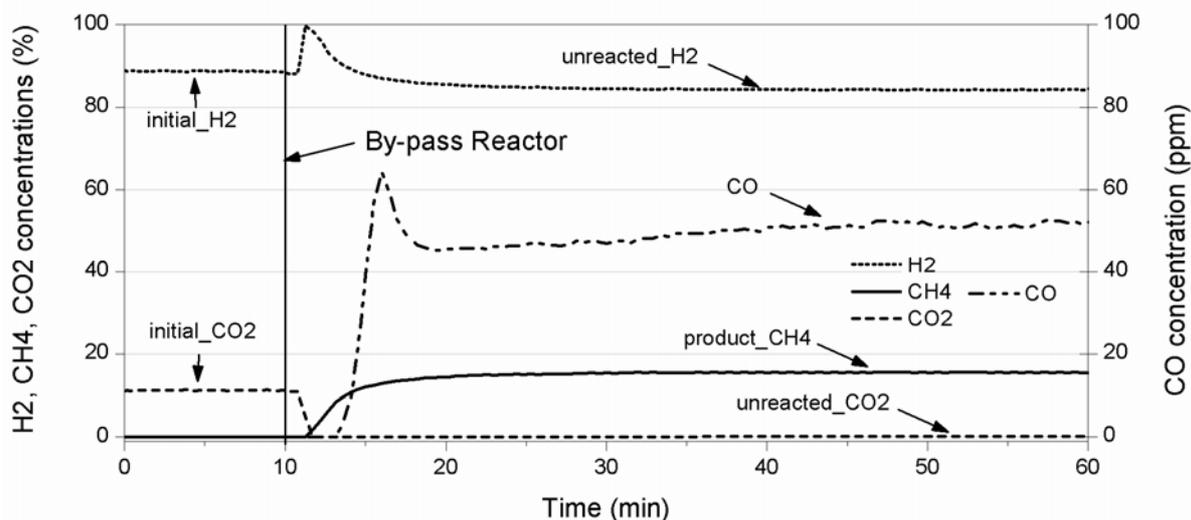


Fig. 2 – Volumetric concentrations of CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and CO at 450°C. Initial CO<sub>2</sub> (2.5 ml/min) + H<sub>2</sub> (20 ml/min) + Ar (20 ml/min). The by-pass reactor was done at 10 min.

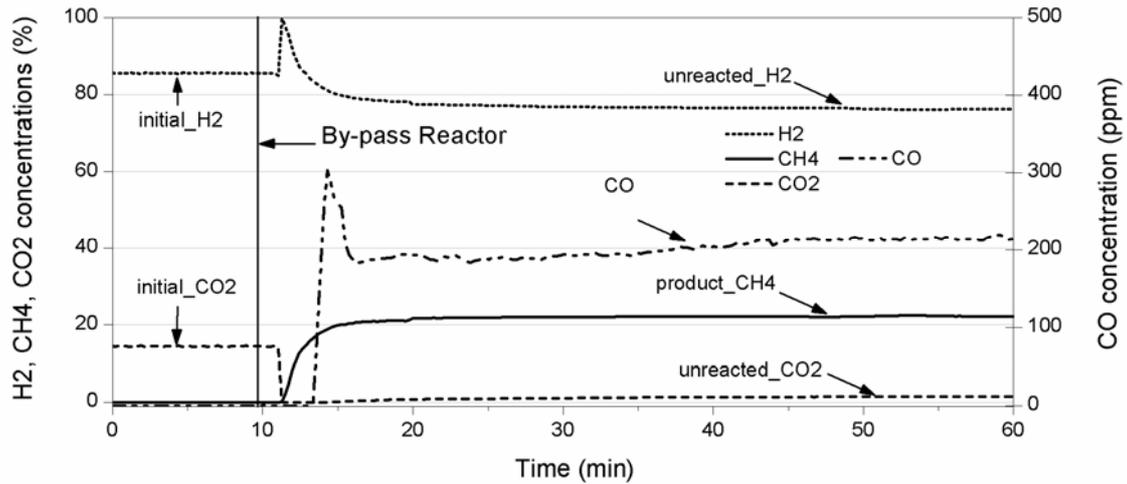


Fig. 3 – Volumetric concentrations of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$  at  $450^\circ\text{C}$ .  
Initial  $\text{CO}_2$  (2.5 ml/min) +  $\text{H}_2$  (15 ml/min) + Ar (20 ml/min). The by-pass reactor was done at 10 min.

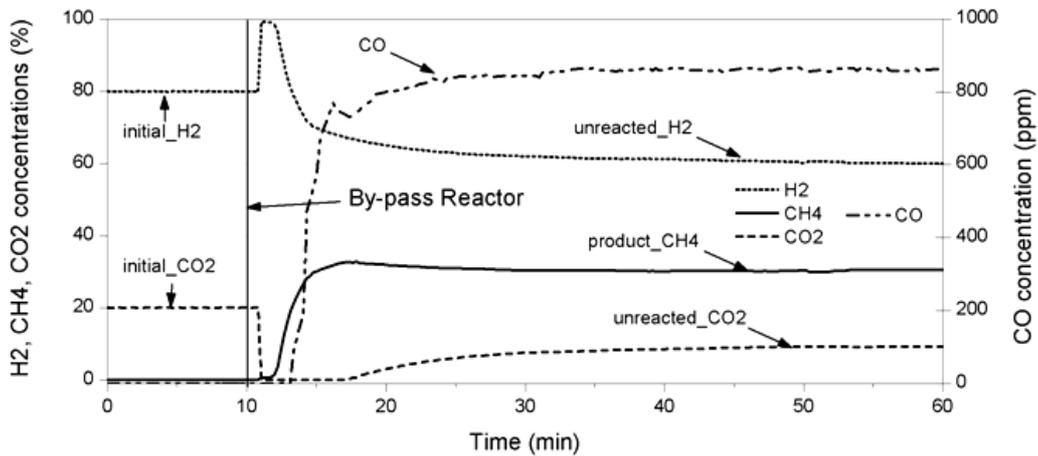


Fig. 4 – Volumetric concentrations of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$  at  $450^\circ\text{C}$ .  
Initial  $\text{CO}_2$  (2.5 ml/min) +  $\text{H}_2$  (10 ml/min) + Ar (20 ml/min). The by-pass reactor was done at 10 min.

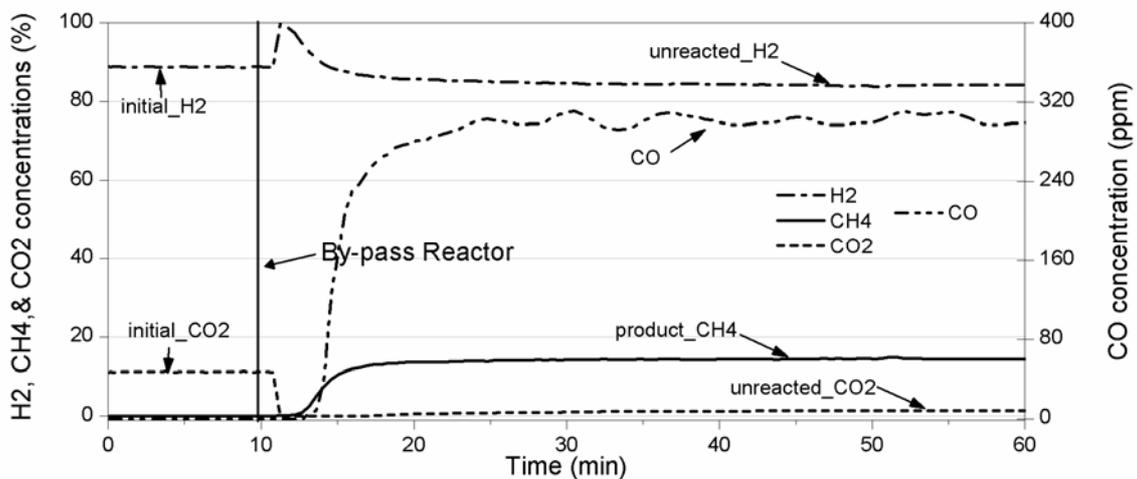


Fig. 5 – Volumetric concentrations of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$  at  $400^\circ\text{C}$ .  
Initial  $\text{CO}_2$  (2.5 ml/min) +  $\text{H}_2$  (20 ml/min) + Ar (20 ml/min). The by-pass reactor was done at 10 min.

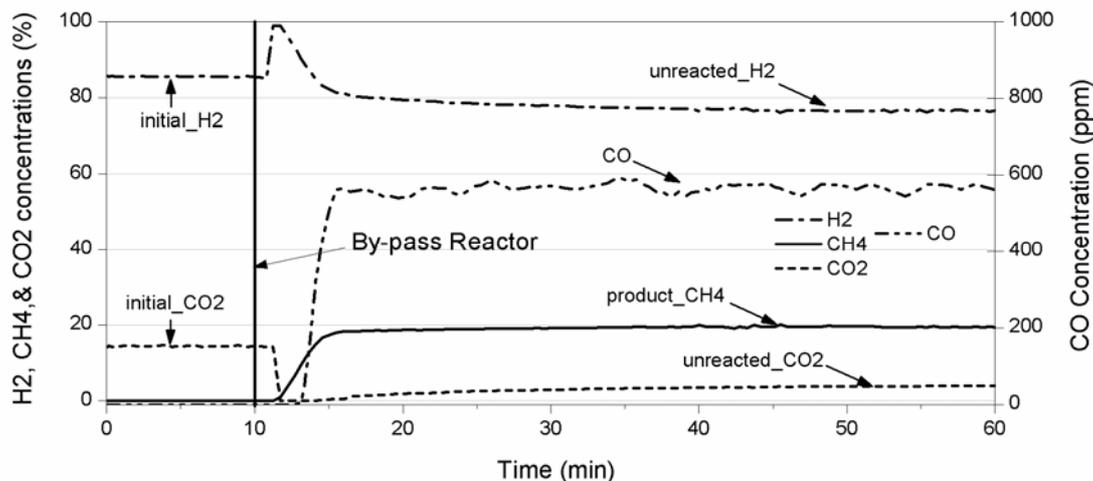


Fig. 6 – Volumetric concentrations of CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and CO at 400°C. Initial CO<sub>2</sub> (2.5 ml/min) + H<sub>2</sub> (15 ml/min) + Ar (20 ml/min). The by-pass reactor was done at 10 min.

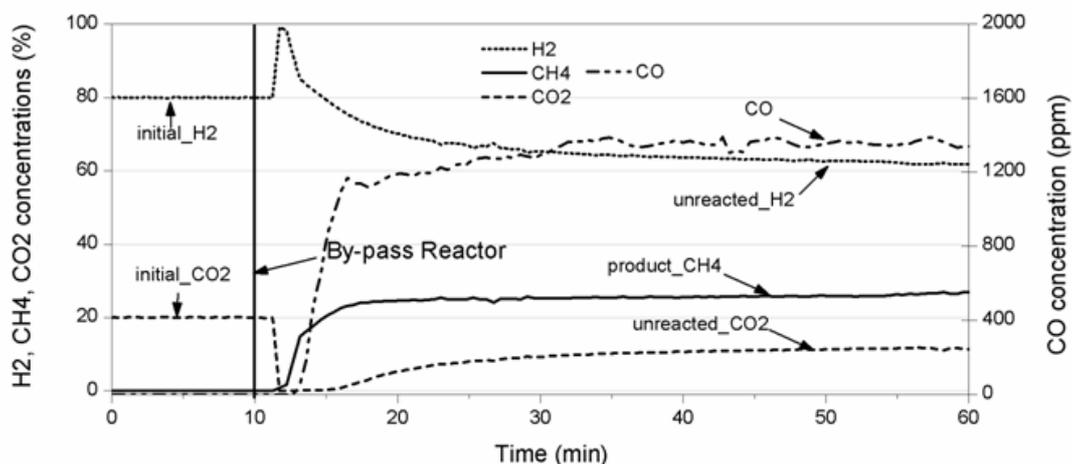


Fig. 7 – Volumetric concentrations of CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and CO at 400°C. Initial CO<sub>2</sub> (2.5 ml/min) + H<sub>2</sub> (10 ml/min) + Ar (20 ml/min). The by-pass reactor was done at 10 min.

The temperature has a significant effect on the CO<sub>2</sub> conversion (Fig. 3). The lowering reaction temperature (below 300°C) leads to a decrease of the overall activity of the catalysts. When we used higher reaction temperatures, the conversion increased continuously, but CO formation drops over 450°C and by-products appear. This reveals that for methanation known as exothermic reaction, a higher reaction temperature over 450°C disadvantages the formation of CH<sub>4</sub>. The optimal agreement for this type of reaction seems to be between 400 and 430°C, because in this range, methane is the unique hydrocarbon molecule formed, consequently the selectivity is almost 100%.

Many studies focused on the methanation of CO<sub>2</sub> under relevant conditions for methane formation at stoichiometric conditions (H<sub>2</sub>:CO<sub>2</sub>=4:1). Only few studies dealt with reaction

with a high excess of hydrogen<sup>20</sup> and no one was varying reactant ratios on Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.

The effect of CO<sub>2</sub>/H<sub>2</sub> molar ratios at different temperatures is also examined in range 1:3.6 to 1:8.0. The CO<sub>2</sub> conversions are growing continuously once with the rise of H<sub>2</sub>/CO<sub>2</sub> molar ratio, the rise being faster at a ratio over 1:5 (Fig. 3). The likely reason is that the higher H<sub>2</sub>/CO<sub>2</sub> molar ratio shift equilibrium from CO (detected in ppm range) to CO<sub>2</sub>. The CO is more reactive and leads to product loss by transforming into CH<sub>4</sub>. It is emphasized that the CO<sub>2</sub> conversion increase with increasing H<sub>2</sub>/CO<sub>2</sub> ratio, without distinction of what the reaction temperature is. This substantiates mechanisms evaluated in recent publications.<sup>24</sup>

CO<sub>2</sub> methanation in sub-stoichiometric H<sub>2</sub> led to a loss of H<sub>2</sub> conversion, faster deactivation and an increase in CO production. The process might thus encounter viability issues when run under

changing conditions in the reactant flow (discontinued  $H_2$  flow). The effect of  $H_2$  sub-stoichiometry could be of interest when considering the conversion of  $CO_2$  with  $H_2$  provided by water electrolysis based on excess electricity. In such a process, the production of  $H_2$  would be discontinuous, only obtained when the electricity demand is low. Therefore, the catalyst performance under a lack of  $H_2$  with respect to the stoichiometry of the  $CO_2$  methanation reaction had to be established in order to better define the global process.

In order to determine its lifetimes, longer term experiments have been carried out and the  $Ni/Al_2O_3-SiO_2$  was found to be significantly stable providing over 97% CO conversion after 72 h. The performances decay steadily to about 82% after 120 h (Fig. 8).

The results indicate that the catalysts, whose deactivation was caused by a temporary deactivation or by the sintering of metallic Ni and by the forming of  $NiAl_2O_4$  species,<sup>25</sup> must be regenerated through a reduction-oxidation method.

Different treatments aiming to verify the effectiveness of the regeneration procedure in

connection with the reusing of the catalyst for methanation reaction, were applied for regenerating the used catalyst. The catalysts used in following reaction conditions 400°C, atmospheric pressure,  $CO_2:H_2= 1:8$  molar ratio and 120 h were regenerated by different treatments shown in Table 1.

The data obtained in this work show that the oxidation at 350°C seems to be the best procedure to regenerate the used catalyst to NiO more than 90%.

## CONCLUSIONS

In actual study we were interested by carrying out the methanation reaction over nickel base catalyst at atmospheric pressure. Based on the results of the catalytic activity tests, it was found that from the three investigated catalysts the  $Ni/Al_2O_3-SiO_2$  is the potential catalyst for  $CO_2$  conversion. Several optimization parameters including the reaction temperature,  $H_2/CO_2$  molar ratio, and, finally, regeneration tests were optimized.

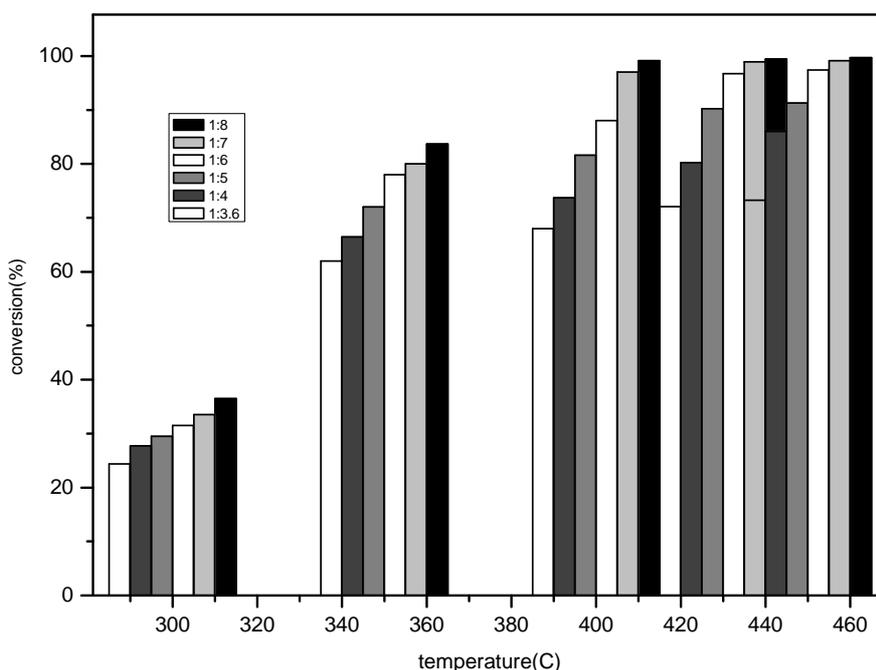


Fig. 8 – Conversions of  $CO_2$  as a function of temperature and various  $CO_2/H_2$  molar ratios.

Table 1

$CO_2$  conversion to methane in presence of regenerated catalysts

Catalyst/ regeneration procedure	Fresh catalyst	Used catalyst/ regenerate 200°C		Used catalyst/ regenerate 250°C		Used catalyst/ regenerate 350°C		Used catalyst/ regenerate 400°C	
		2 h	4 h	2 h	4 h	2 h	4 h	2 h	4 h
Conversion (%)	99.8	28.3	42.2	69.3	83.8	88.6	92.4	87.2	88.4

Regarding the reaction temperature it was found an optimal range between 400 and 430°C, because methane is the unique hydrocarbon molecule formed. Related to the H<sub>2</sub>/CO<sub>2</sub> molar ratio investigated, our study revealed that the CO<sub>2</sub> conversion is growing continuously once with the ratio increasing, and the increase is faster at a ratio over 1:5. Regarding the catalyst regeneration procedure our study indicates that the oxidation at 350°C is the best procedure.

The remarkable values for selectivity (more than 99.8%) were obtained at an unprecedented almost total conversion under moderate hydrogenation conditions from the perspective of methane synthesis, offering without doubt competitive costs for CH<sub>4</sub> obtaining as fuel. It may be concluded from this study that Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems were found to be promising catalysts for CO<sub>2</sub> turning to methane, depending on the technological regime of the reaction conditions. Optimization of these catalysts by compositional variation or doping is being explored.

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