# METHANATION OF CARBON DIOXIDE

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## Abstract

This paper describes the $CO_2$ conversion to methane by reduction with hydrogen on a Ni catalyst. The catalyst has been characterized in terms of number of surface sites. The effect of $H_2S$ poisoning on catalytic activity has been evaluated too.

## Introduction

The growing use of fossil fuels (solids, liquids and gaseous) as the main primary energy sources, inevitably leads to an increasing amount of carbon dioxide released into the atmosphere. As a matter of fact, growing efforts are devoted to control the accumulation of atmospheric $CO_2$. Carbon capture technologies are a well stabilized route to reduce greenhouse gas concentration. Besides the $CO_2$ capture and its geological sequestration, a number of synthetic processes using this gas as feedstock are operating. However, the only product consumed at the same rate that generates the $CO_2$ is a fuel; so, there is a growing interest in the hypothesis to treat the $CO_2$ in a reducing environment to convert it to methanol [4,5] or methane [6,7,8]. Our interest is focused on the conversion to methane [9], due to the opportunities to be locally used or easily stored or transported. According to the Sabatier's reaction, in which one mole of methane can be obtained by the reaction of one mole of carbon dioxide and four moles of hydrogen:

$$CO_{2\,(g)} + 4\,H_{2\,(g)} \rightleftarrows CH_{4\,(g)} + 2\,H_2O_{\,(l)}$$
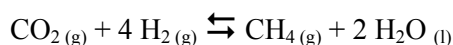
The temperature is the main parameter that affects the equilibrium. The methanation reaction is exothermic and spontaneous at room temperature: $\Delta H = -165$ KJ/mole e $\Delta G = -113.5$ KJ/mole. The Gibbs free energy increases rapidly with temperature, and over 500 °C becomes positive, making spontaneous the opposite reaction to that of methanation, which is the reforming of methane.

## Experimental

We have carried out our experimental measurements using a quartz tubular reactor (PFR) in ideal displacement conditions characterized by no longitudinal or lateral mixing in the stream of reacting gas. Three different $CO_2/H_2$ feed molar ratios were used, and the operation pressure was at atmospheric pressure. On leaving the gas mixture was analyzed by gas-chromatography. Due to the kinetic barrier in this reaction, it is necessary to introduce a catalyst that increases the reaction rate. The catalysts commonly used are metals such as Rh, Ru and Ni: in our study we filled

the quartz reactor with Ni powder (average particle size 43 nm) as it is or supported on rock-wool. The length of the fixed bed catalyst was ranging from 3.5 cm to 17 cm; depending on the flow rate, the contact time was ranging from 0.07 s to 50 s.

## Results and discussion

In the figure 1, we report the $CO_2$ to $CH_4$ conversion yield ($\Re$) vs. the reaction temperature ranging from 25 °C to 500 °C, when the feed gas is composed only of carbon dioxide and hydrogen in the ratio of 1:3, 1:4 and 1:5. As it can be seen from the figure, there is a threshold around 200 °C, then the yield increases rapidly and reaches a maximum value just before 300 °C. When the $CO_2/H_2$ ratio is 1/4 and 1/5 the maximum yield is close to 100 %, while when the ratio $CO_2/H_2$ is less than the stoichiometric ratio, the maximum yield is about 75%. In all the cases a further increase in temperature corresponds to a reduction in yield that is more remarkable as far as we are away from stoichiometric ratio**.**
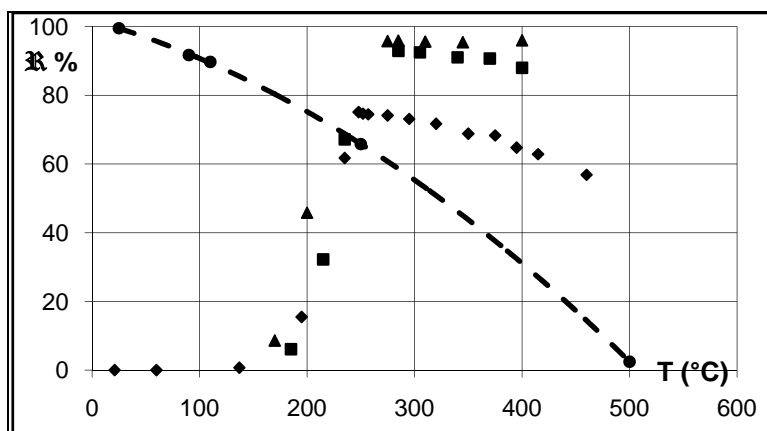


**Figure 1.** Methanation yield vs. temperature: $CO_2/H_2 = $ ♦ 1/3; ■ 1/4; ▲1/5; ● thermodynamic yield.

The observed behaviour is congruent with expectations: as the temperature increases the methanation regress in favour of the reforming. The kinetic barrier moves the maximum methane yield of nearly 300 degrees.
The methanation reaction on Ni is a typical example of heterogeneous catalysis dominated by gas-solid interactions, so it is important to characterize the surface of the solid catalyst in terms of surface active sites. The most common analysis for gas-solid interactions is that of Langmuir where one consider the rate of reaction (J) directly proportional to the fractional coverage of the surface (θ ) i.e. the part of the total surface area of the catalyst occupied by molecules of the reactant. We can calculate θ within the Langmuir restraints, namely: 1) only the molecules that reach the free surface of the catalyst can be adsorbed, while the others are elastically

reflected, 2) adsorption is limited to obtaining one molecular layer, and 3) no interactions between the adsorbed molecules. Therefore a catalyst could be characterized, for each gaseous species, by the maximum volume adsorption (Vm) that contains a number of molecules covering the surface with a monolayer.

We measured Vm for $H_2$ and $CO_2$. First, we report the adsorbed volume (Va) of $H_2$ and $CO_2$ as a function of partial pressure of $H_2$ and $CO_2$ ($p_{H2}$ and $p_{CO2}$) respectively, to verify the Langmuir adsorption.

The volume adsorbed was calculated as follows:

$$(Va)_{H2} = 4\,\Phi_{H2}\,\frac{R\,T}{pH2}\,\Re \qquad\qquad (Va)_{CO2} = \Phi_{CO2}\,\frac{R\,T}{pCO2}\,\Re$$

For the experimental conditions described in the next table we have for $H_2$ and $CO_2$ the curves plotted in the figure 2, according to the previous equations. We note that the trend is typically Langmuir for the hydrogen, while for the carbon dioxide we can not apply the same type of analysis.

Catalyst: 6 g of Ni in 78,2 g of rock-wool

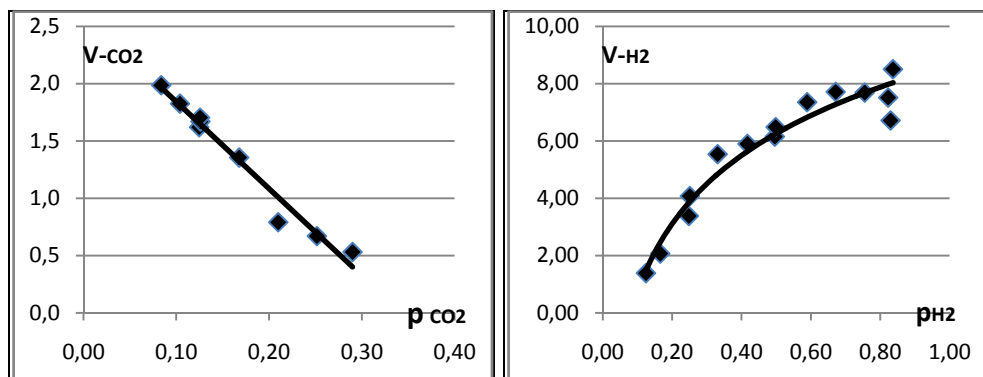| P = 1 atm | $\Phi_{H2}$ = 150 - 1000 sccm |
|---|---|
| T = 300 °C | $\Phi_{CO2}$ = 150 sccm |
| $\Phi_{tot.}$ = 1200 sccm | $\Phi_{N2}$ = 900 - 50  sccm |



**Figure 2.** Volume (l) of the adsorbed $CO_2$ and $H_2$ in function of their partial pressure (atm).

The decrease of $(Va)_{CO2}$ with the  increase of  $p_{CO2}$ suggests a rapid absorption of $CO_2$ with a rapid saturation of its sites. Assuming the adsorption of  hydrogen independent and dissociative ($H_2 \leftrightarrows 2\,H_{ads}$), we can write for $H_2$:

$$\frac{1}{Va} = \frac{1}{p^2}\frac{1}{Vm\sqrt{K}} + \frac{1}{Vm}$$

Plotting $1/Va$ as a function of $1/p^2$, we can obtain the value of $Vm$. Then for hydrogen, the yield is measured as a function of $p_{H2}$, keeping the temperature, the total flow and the $p_{CO2}$ constants to get $Vm$. The result gives $(Vm)_{H2} = 8.69$ l.

From the value of $Vm$ we can estimate the number of active sites (S) on the surface of the catalyst. For $H_2$ we get a number of active sites $S = 1.15\ 10^{22}$. Calculated S, we can calculate the TON (turnover number) which is the number of product molecules ($CH_4$) for active site and per g of catalyst. The behavior of the TON as a function of $p_{H2}$ and $p_{CO2}$ is shown in the following figure 3.

The procedure just described has been applied to evaluate the performance of the catalyst in different conditions. For example, when 0.2074 grams of Ni are dispersed in 0,597 g of rock-wool, we get a $(Vm)_{H2} = 97.3$ ml and a number of surface sites $S = 1.39\ 10^{21}$. The number of catalytic sites per gram of Ni, in the reported cases, are: $1.9\ 10^{22}$ sites/g Ni and $0.7\ 10^{22}$ sites/g Ni respectively. These two last results, obtained by two differents experimental runs, show us that the procedure can be usefully applied to compare different catalysts. The S value was used to evaluate the effect of poisoning on the catalyst when it is exposed to pollutants. The most common pollutant present in a syngas or in an exhaust is the hydrogen sulphide ($H_2S$).
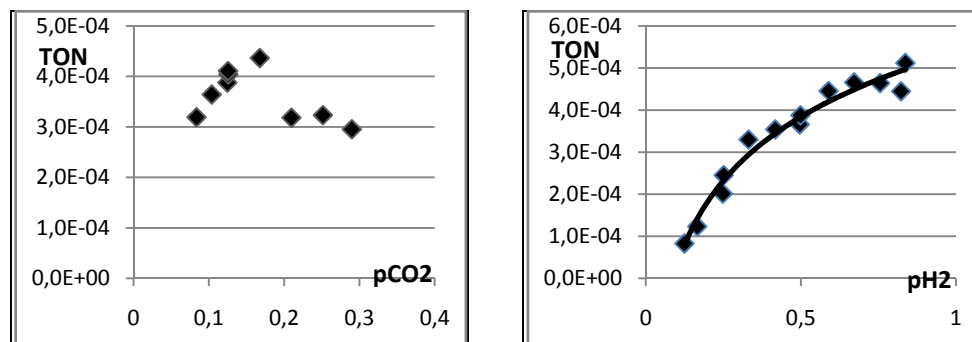


**Figure 3.** TON as a function of partial pressure of $CO_2$ and $H_2$ (atm).

To simulate the effect of $H_2S$ on the methanation reaction, we flushed our catalyst with 50 sccm of a mixture of $H_2S$ (2%) in $N_2$ and measured the $CO_2/CH_4$ conversion yield in function of the exposition time. $H_2S$ content of 2% is higher than those found in a real effluents, where the $H_2S$ is present in few tens of ppm, so our conditions were particularly stressful for the catalyst. R versus time of poisoning is reported in the next figure 4.
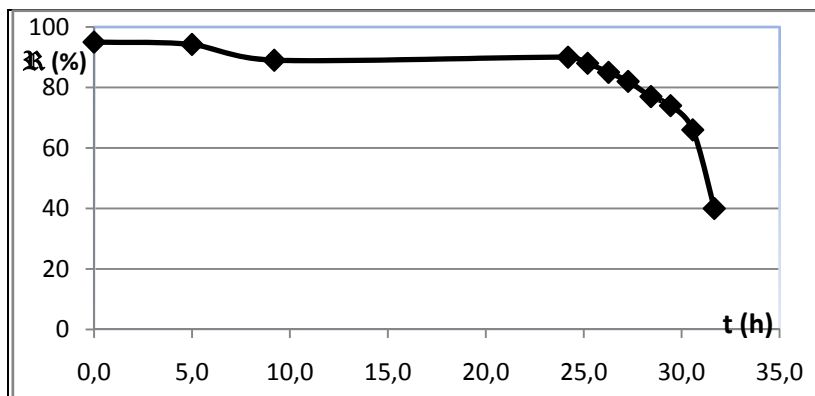
**Figure 4.** Effect of time of exposure to $H_2S$ on the conversion yield.

As shown the catalyst maintains its efficiency virtually unchanged up to 25 h and then degrades quickly with the time of poisoning. On the poisoned catalyst, i.e. when the efficiency dropped to 40%, was applied Langmuir analysis and calculated the number of active sites. We report the results directly:

Ni Catalyst: 6,085 g

|  | Pristine catalyst | After poisoning |
|---|---|---|
| $(Vm)_{H2}$ : | 350 ml | 51 ml |
| S: | $7.8 \, 10^{20}$ sites / g Ni | $1.4 \, 10^{20}$ sites / g Ni |

From these data we can see that the number of sites per g of Ni before poisoning is less than first reported for Ni supported on rock wool: it is clear the effect of the dispersion that makes more accessible the Ni particles. It is also evident the effect of poisoning, with a reduction in the number of sites per gram of catalyst, which accounts for the decrease in conversion efficiency. Therefore the measurement of Vm is a valuable tool for the characterization of the catalyst.

**Conclusions**
$CO_2/CH_4$ conversion is a viable route to help to reduction the accumulation of atmospheric $CO_2$. The methanation of carbon dioxide is a easy reaction that proceeds at relatively low temperature with high yield. We have reported experimental results on the characterization of Ni used as catalyst. The effect of $H_2S$ poisoning on the catalyst has been studied.

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