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## CO<sub>2</sub> as carbon source for fuel synthesis

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### Abstract

The growing use of fossil fuels (solid, liquid and gas) as the main primary energy sources, inevitably leads to an increasing amount of carbon dioxide released into the atmosphere. On the other hand, the increasing CO<sub>2</sub> concentration in the atmosphere is indicated as the main cause of the greenhouse effect on the planet with consequent climate change. These reasons motivated in recent years growing efforts, from both technical-scientific and political communities, to control the accumulation of the atmospheric CO<sub>2</sub>. Carbon capture technologies are a well stabilized route to reduce the concentration of the greenhouse gas (CO<sub>2</sub>) from the atmosphere. However, the introduction of these capture processes always requires additional costs regardless of the adopted technology (post-combustion capture, pre-combustion capture or oxy-combustion). Despite higher costs, the adoption of efficient technologies for capturing CO<sub>2</sub> is essential for the preservation of the environment. Besides the capture of CO<sub>2</sub>, its final sequestration in geologically stable sites is currently proposed for storing enormous quantities of gas involved. However, the geological storage of a given amount of CO<sub>2</sub> avoids the possible use of C for about 27% wt. Therefore it seems reasonable to question if we can take advantage of this huge amount of carbon. As a matter of fact, the CO<sub>2</sub> could become an important source of carbon for the synthesis of organic and inorganic compounds. In particular, there is a growing interest around the possibility to treat the CO<sub>2</sub> in a reducing environment to convert it to methanol or methane. This option is an alternative to the well documented reduction of CO<sub>2</sub> to carbon monoxide. Our interest is focused on the conversion to methane by hydrogen reduction. When the hydrogen is obtained by renewable energy, the method is a good way to store the electricity generated from renewable sources such as chemical energy; it is easily accessible and transportable thanks to the widespread presence of methane distribution network.

We investigate the hydrogenation of CO<sub>2</sub> on various Ni based catalysts. The conversion yield, the time stability and the poison sensitivity has been studied up to the temperature of 723 K and at atmospheric pressure.

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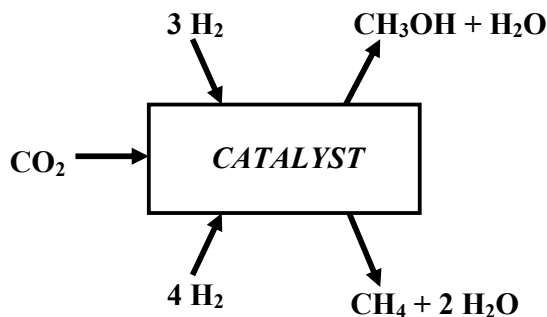
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## 1. Introduction

The use of carbon oxides as useful precursors in the synthesis of fuels is a subject well addressed in the early of the last century. The Sabatier reaction, namely the hydrogenation of carbon dioxide to give methane and water is of 1902 (1), while the F-T synthesis introduced by Fischer and Tropsch in the 1920s has been extensively used to obtain fuels by hydrogenation of carbon monoxide (2).

Nowadays are the environmental requirements to impose the control of the accumulation of CO<sub>2</sub> in the atmosphere since this gas is considered the main responsible for the greenhouse effect. The most commonly studied technology to limit CO<sub>2</sub> emission is the CCS (Carbon Capture and Sequestration) that consists in the capture of CO<sub>2</sub> from a flue gas, transportation and underground storage. However carbon dioxide turns out to be attractive C1 building block and CCS is often replaced by the abbreviation CCUS where U stands for utilization. Currently, the utilization of CO<sub>2</sub> as chemical feedstock is limited to a few processes, mainly synthesis of urea, salicylic acid and polycarbonates. Other applications of carbon dioxide are due to its good solvent properties (3, 4). Moreover CO<sub>2</sub> find application in the pressurization of fossil fuel deposits for enhanced oil recovery (EOR).

Thus the CO<sub>2</sub> conversion to fuel is a good way to chemically store both the renewable energy and the excess electricity loads (5). The direct reaction of CO<sub>2</sub> and H<sub>2</sub> produces mainly gaseous methane or methanol depending on the catalyst used according to the following scheme:



The methanol synthesis occurs with temperatures ranging from 513 K to 533 K and pressure of 4.9 MPa -9,8 MPa. The most used metal catalysts for methanol synthesis are copper based type supported on oxides: Cu/ZnO, Cu-Zn based multicomponent catalyst: Cu/ ZnO-ZrO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> or Cu/CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> [6]. However our main interest is focused on the conversion to methane due to the opportunities to be locally used or easily stored or transported.

Hydrogenation of CO<sub>2</sub> toward methane has been investigated using catalytic systems based on supported VIII group metals (e.g., Ru, Rh, Co, Fe, Ni) on various oxide supports (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, MgO, NiO-MgAl<sub>2</sub>O<sub>4</sub>, NiO-K<sub>2</sub>O-MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, ksr, MgO-ksr, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-CaO, La<sub>2</sub>O<sub>3</sub>) [7]. However, supported nickel catalysts remain the most widely studied materials due to its low cost and its good catalytic activity. As a contribution to this topic, we will briefly review the various types of catalyst used. The hydrogenation of CO<sub>2</sub> on various Ni based catalyst both commercial type one and home-made one is presented. The conversion yield, the time stability and the poison sensitivity has been studied up to the temperature of 723 K and at atmospheric pressure.

## 2. Experimental

We 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. Two types of catalysts were tested: a commercial one and a home-made one. The commercial catalyst was Ni/Al<sub>2</sub>O<sub>3</sub> supplied by BASF and indicated by RP-75 and GI-85 containing 10-12 % of Ni and 50 % of Ni respectively.

The home made catalysts (H-M) was prepared by using Ni powder (mean particle size < 100 nm) supported on alumina. For Ni on rock-wool, the metal particles was simply mixed with the support in aqueous dispersion and a physical adhesion was obtained. The resulting material was dried and then treated with hydrogen at 673 K for 2 h. This catalyst will be denoted as HM-1.

For Ni on alumina ( denoted as HM-2) the procedure was as follows:

- 1) 3.874 g of Ni powder was dissolved in HNO<sub>3</sub> conc. than 3.652 g of alumina was added to the Ni<sup>2+</sup> solution;
- 2) The pH of the solution was increased by adding NH<sub>3</sub> in order to precipitate the nickel hydroxide (pH = 5); after filtration, the resulting material was dried at 373 K for 18 h;
- 3) The anhydrous nickel hydroxide was treated with hydrogen at 673 K for 2 h.

The resulting catalyst contains 44,3 % w/w of Ni.

The concentration of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> in the out-coming gas mixtures was monitored by micro-gas chromatography (Micro-GC Agilent 490). More detail on the experimental apparatus and procedure are reported elsewhere [8].

All the experiments were carried out using CO<sub>2</sub>/H<sub>2</sub> molar ratio at the stoichiometric value, i.e. 1/4.

Prior each new experimental run, the catalyst was treated with hydrogen at 673 K for 4 hours, than the temperature was set to the given value and the CO<sub>2</sub> was added. The occurrence of the methanation reaction was noticed immediately by an increase in the temperature and more the methane conversion yield, more the temperature increase.

## 3. Results and discussion

In the figure 1 the methane conversion yield (i.e. the moles of produced methane over the moles of in-coming carbon dioxide) in the function of the temperature in the range 300 K - 900 K is reported. The reactant gas mixture was composed by 160 sccm of H<sub>2</sub> and 40 sccm of CO<sub>2</sub> and the pressure was one atmosphere. The catalysts were 0.392 g of GI-85; 0.390 g of RP-75 and 0.401 g of HM-2.

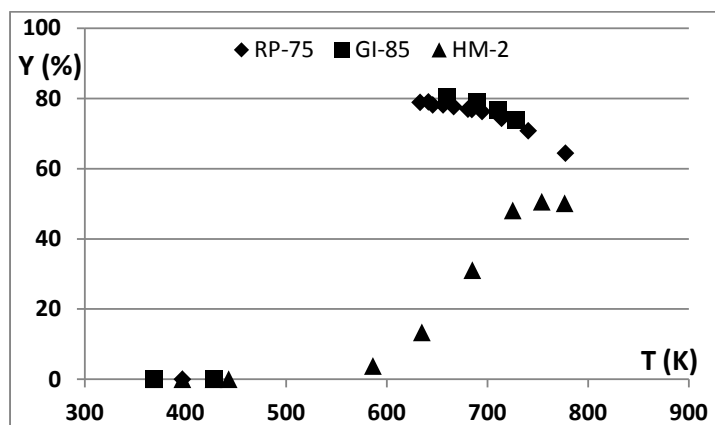


Figure 1. Methane conversion yield in the function of temperature for commercial catalyst and for Home Made catalyst on alumina

As the figure 1 shows the commercial catalysts has higher activity respect to the home-made one. The onset temperature for BASF catalysts was about 450 K while the onset temperature for the HM catalyst was about 600 K. The maximum conversion yield for BASF and HM catalysts were 80 % and 50 % respectively. In spite of the higher catalytic activity, G1-85 and RP-75 catalysts exhibits lower surface area than the HM catalysts. The BET values, calculated by N<sub>2</sub> absorption at 77 K, were:

$$\text{G1-85} = 123 \text{ m}^2/\text{g}$$

$$\text{RP-75} = 130 \text{ m}^2/\text{g}$$

$$\text{HM-2} = 313 \text{ m}^2/\text{g}$$

This occurrence demonstrates a high turnover number (TON) for commercial catalysts, but we was not able to calculate it because the inability to measure the H<sub>2</sub> uptake and the CO<sub>2</sub> uptake.

An important issue for a catalyst is the ability to operate for a long time without loss in catalytic activity. For methanation the main factors that contribute to catalytic decay are i- the thermal deactivation with the possibility of sintering of the catalytic particles; ii- the surface carbon deposition due to the accumulation of carbonaceous material formed during methane synthesis (9, 10); iii- catalytic poisoning mainly due to the sulphur compounds (11).

A slight decrease in catalytic activity has been registered for both the BASF catalysts after 21 hours of work. In the figure 2 are reported the SEM images of G1-85 sample before (2-a) and after (2-b) 21 h of work.

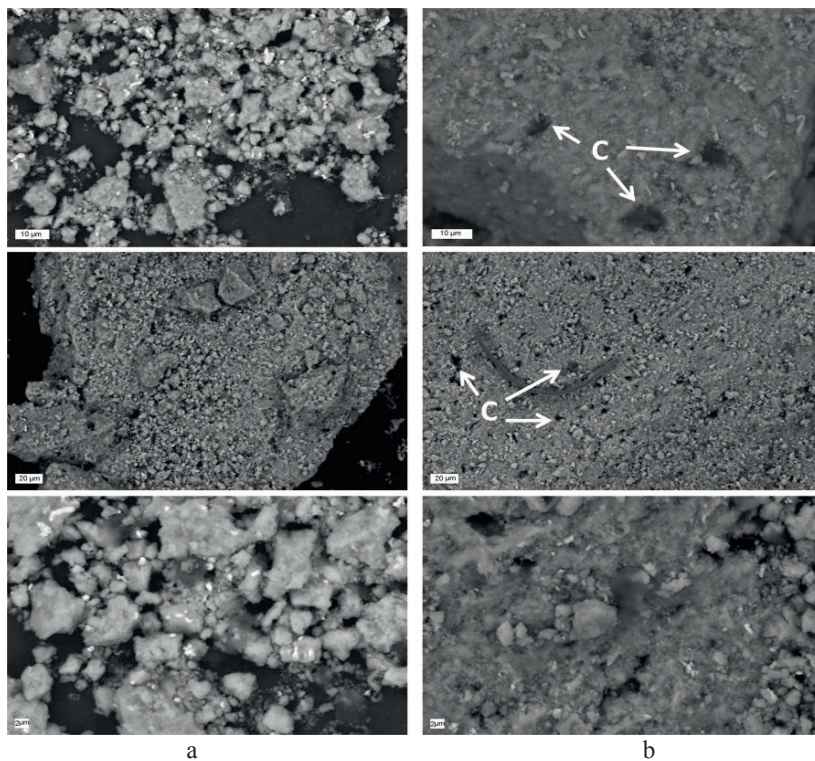


Figure 2. SEM images for G1-85 catalyst: a- pristine catalyst; b- catalyst after 21 h of work

As can be seen, several spots of carbon deposition appear on the catalyst after its use, however a large part of the catalyst is free thus it still show a high activity. The HM-1 catalyst shows a noticeable loss of activity during the work: the pristine catalyst, constituted by 0.216 g of Ni dispersed in 0.624 g of rock wool, has a methane conversion yield of 38 %, whereas after 22 h the methane conversion yield reduces to 13 % due to the deposition of carbonaceous material on Ni particles surfaces. This carbonaceous material produces a reversible deactivation of the catalyst that is able to recover its activity by hydrogen regeneration treatment. For catalyst HM-1 that reduced its activity to 13 % after 22 h of work, the methane yield rises to about 40 % when H<sub>2</sub> is flushed at 493 K for 1 h.

Unlike carbon deposition, sulphur causes an irreversible damage to the catalyst, due to the formation of stable nickel sulfide. Therefore it is essential to provide the methanation equipment with a suitable sulphur compounds absorber prior to the catalyst. This occurrence points out the significant of the gas treatment before the methanation reaction.

#### 4. Conclusions

The catalytic upgrading of the mixture of carbon dioxide and hydrogen coming from a flue gas or from gasification of coal or biomass is becoming advisable due to not only the availability of efficient catalysts, but also for the economically attractive of the process. The hydrogenation of CO<sub>2</sub> on various Ni based catalysts has been studied and the aging and doping effects reported. A crucial role is played by the system of capture and processing of gas before the methanation.

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