



Low-temperature studies of hydrocarbon synthesis

CO₂ hydrogenation in the presence of Ni- and Fe-based catalysts was evaluated as a potential reaction for abiotic production of hydrocarbon in geologic time. The methane production was experimentally studied in an atmosphere of H₂ and CO₂ (5:1) at 1 bar and 50 °C with NiO, Fe₂O₃ and Fe₂O₃xFeO (magnetite) powders as catalysts. The measurements showed evident traces of methane/ethane on NiO and ethylene on iron oxide and magnetite

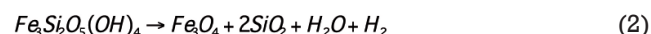
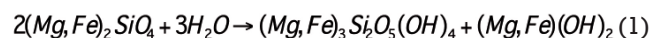
■ Alfonso Pozio, Massimo De Francesco, Stefano Galli

DOI: 10.12910/EAI2014-64

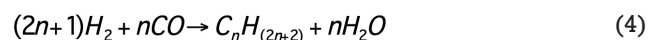
Introduction

In nature, most hydrocarbons were produced by microbial processes or thermogenic degradation of organic matter in sedimentary rocks (i.e., biotic hydrocarbons). This biogenic explanation does not explain some hydrocarbon deposits, as the presence of oil and methane within non-sedimentary rocks upon the Earth. In general, most of the articles published about abiotic hydrocarbons, concerned its detection in a specific experimental environment, trying to define possible mechanism for its production. Although it has been traditionally assumed that abiotic hydrocarbons is mainly related to mantle-derived or magmatic processes, a new generation of data is showing that low-temperature synthesis related to gas-water-rock reactions is more common than previously thought [1]. Particularly, among the various theories, methane and/or hydrocarbons could be produced by low-temperature, gas-water-rock reactions in continental settings, even at shallow depths [1,2]. Specifically, a growing interest was focused on the role of serpentinization of ultramafic rocks, either on land or seafloor [2,3]. Serpentinization is an alteration process of low-silica,

ultramafic rocks, rich in olivine and pyroxene minerals and characteristic of the lower oceanic crust and upper mantle. Water-rock reactions result in the oxidation of ferrous iron from olivine and pyroxene, resulting in the precipitation of ferric iron in magnetite (Fe₃O₄) and other minerals (serpentine, brucite) (eq. 1), and in the release of hydrogen (eq. 2) [3]:



At low temperatures (< 150° C) these reactions result in extremely alkaline pH (above 10). The combination of H₂ and CO₂ or CO (from decomposition of limestone or via circulating meteoric waters) under highly reducing conditions could lead to methanation (Sabatier Reaction - SR) and/or other hydrocarbons through Fisher-Tropsch (FT), which involve the reduction of CO₂ and/or CO by H₂ on a catalytic surface to form bound methylene groups that polymerize into long chain hydrocarbons (eqs. 3 and 4). [3,4,5]



As an example, abiotic CH₄ at the Earth's surface has been found to be related to low-temperature serpentinization in ultramafic rocks, such as in the submarine Lost City Hydrothermal field (LCHF) [6]

■ Alfonso Pozio, Massimo De Francesco, Stefano Galli
ENEA, Technical Unit for Renewable Energy Sources



and, on land, in ophiolites or igneous intrusions in the Philippines, Oman, New Zealand, Turkey, Italy, Greece, and Japan, [1]. Methane has also been measured in other sites with active serpentinization, but the data required to determine the CH_4 origin are incomplete or not available.

FT and SR are catalyzed by transition metals/oxides, so that the conversion of the gas molecules occurs on the metal surface. The Sabatier reaction (SR), is reversible and exothermic ($\Delta H = -167 \text{ kJ/mol}$) and proceeds spontaneously and catalytically at relatively low temperatures (250°C). Experimentally, FT synthesis have been widely reported under hydrothermal conditions, at temperatures above 200°C and high pressures, using Ni, Fe and Cr, which are the most abundant transition metals in ultramafic rocks [7-9]. Recently, the methanation under wider geologic conditions, low temperature ($<50^\circ \text{C}$) and pressure was suggested, as a possible generation mechanism of the abiogenic heavy methane in some geological sites [10,11].

In the past, very few works did analyse these kinds of reactions with temperature lower than 200°C and atmospheric pressure due to the lacking industrial interest. For natural gas formation in coalbed the mechanism of hydrocarbons hydrogenolysis on Fe and Ni natural catalysts in an atmosphere of H_2/CO_2 (4:1) at 1 bar and 180°C was tested experimentally [12,13]. It was evidenced that iron and nickel minerals, which can be present in coals at low levels, can become active under geologic conditions [12,13].

Other works demonstrated the possibilities of hydrocarbon generation at lower temperature on ruthenium (46°C) and rhodium (25°C) [14-17]. However, from a geological point of view platinum group elements occur in rocks only in trace amounts (orders of hundreds of ppb), so their catalytic role in nature should be quantified. On the other hand, the most abundant catalysts available in rocks, like chromium (e.g., chromitites in peridotites), iron (magnetite) and nickel (e.g., in awaruite) could support a more abundant production of abiotic hydrocarbons over longer time scales. Such a slow methanation is theoretically possible but not yet experimentally demonstrated in the laboratory.

The present work has analysed the hydrocarbon synthesis from a mixture H_2/CO_2 at low temperature and pressure on Ni- and Fe-based catalysts in order to verify the possible production of abiotic methane in particular geological environments, in the presence of these metals. The work is aimed at evaluating, through laboratory experiments, the process of hydrocarbon generation and CO_2 removal, with particular emphasis on methanation at low temperature conditions.

Experimental

Catalysts

Two grams of a commercial, nickel-based catalyst (CRG-F Syntex), Fe_2O_3 and $\text{Fe}_2\text{O}_3 \cdot x\text{FeO}$ 99.9% powders (Aldrich) were used just as received. CRG-F is commonly used in the industrial pre-reforming process to convert heavy hydrocarbon feed to methane and for the Sabatier Reaction (SR) its composition is: NiO 75 wt%, SiO_2 0.2 wt%, K_2O 0.35 wt% and the rest as Al_2O_3 balance. The Ni-based catalyst was chosen because it is a traditional catalyst for SR and it is known to be quite effective. On the other hand, Fe-based catalysts were selected since iron is the most abundant metal in the ophiolite minerals.

Experimental apparatus and product analysis

Tests were performed in a quartz reactor, the experimental apparatus of which is shown in Fig. 1. Catalyst powder under test is deposited on an inert septum placed in the 41 ml quartz reactor R (\varnothing 18 mm). The reactor can be alternatively fed with helium or a 5:1 H_2/CO_2 mixture (eq 3. evidence for a ratio not lower than 4), with flow rates separately controlled by two thermal mass-flow controllers (Bronkhorst) at 10 mL min^{-1} . Both gas supplies come from cylinders (Air Liquide, 99.9%).

The reactor can be by-passed (V2) by submitting the gas stream directly to the MS/GC (580GCMS Perkin Elmer) analysis for checking the gas composition. The spectrometer was calibrated with a 10 mL min^{-1} flow from a certified 0-60-120 ppm CH_4 , ethane, ethylene in H_2/CO_2 (Air Liquide). The mass spectrometer, equipped with a multi-port inlet automated valve, is in-line with the reactor. A $100 \mu\text{L}$ sample of the gas coming out from

the reactor is sent to the spectrometer and analyzed. The Mass Spectrometer (MS) analysis parameters were: Source Temperature: 200° C, mass scan: 10–80 amu.

Measurements were carried out at 50° C by means of a proportional–integral–derivative, thermo-controlled, heating sleeve placed around the reactor. Before each test, the reactor temperature was increased up to 130° C in Helium stream for 30 min in order to drive the desorption of hydrocarbons from the powder under test. After such a preliminary desorption, the reactor temperature was set to 50° C and then three testing procedures were performed with different scopes. In the first set up (S-1) the test temperature was fixed (50° C) and the H₂/CO₂ stream was sent through the reactor for 10 min. Then, the reactor was by-passed (V2) and closed at its lower end (V3), creating a fixed H₂/CO₂ atmosphere inside the reactor. After a prefixed short incubation time (1-5 hours), the H₂/CO₂ stream was sent through the reactor again (V2, V3) and immediately analysed. The chemical analysis of the stream from the reactor outlet was measured and compared with that of the H₂/CO₂ by-passed stream to reveal the net production of hydrocarbons. (incubation tests at 50° C were performed also in He atmosphere, in order to verify in advance the absence of hydrocarbons in the powders).

Along the above tests in the quartz reactor, other long-time tests were performed. One gram of each catalyst was placed in a glass vial (20 mL). The vial was vacuumed and then gas-filled with H₂/CO₂ (5:1) at 3 bar and heated in oven at 50° C. After a three-month

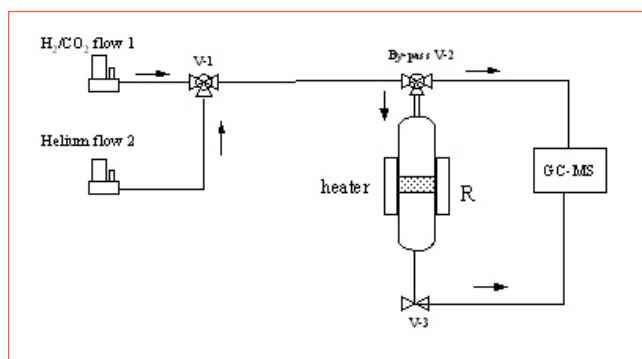


FIGURE 1 Schematic of the measurement apparatus

thermostated incubation the gas inside the vials was sampled at 25° C with a 100 µL gas-tight syringe and analysed using a Fison Instrument GC-8000 Series gas-chromatograph by means of a Photoionization detector (PID).

In a different measurement set (S-2) the test temperature was fixed at 50° C and the H₂/CO₂ stream was sent through the reactor for 10 min in order to have gas adsorption. Then, the Helium stream was sent through the reactor non-stop for 12 hours and immediately after the H₂/CO₂ stream was sent through the reactor again and analysed.

In a third set-up (S-3), the reactor temperature was fixed at 50° C and the H₂/CO₂ stream was sent through the reactor for 10 min in order to have gas adsorption. Temperature was then increased to 130 °C and Helium was sent through the reactor for 10 min in order to have gas desorption. Finally, the Helium stream was sent through the reactor non-stop for 12 hours at 50 °C, and immediately after the H₂/CO₂ stream was sent through the reactor again and instantly analysed.

The above tests (S-2 and S-3) were aimed to verify/exclude the mechanical effect of the stream gas and of the temperature onto the adsorbed species in order to establish a correct analysis method.

Results

Figures 2 and 3 show the results obtained on all the catalysts at 50° C in the first three hours with the S-1 set up apparatus. Reported data represent an average of at least three different measures for every catalyst.

The Ni-based catalyst showed a substantial presence of methane but also some ethane trace with a methane/ethane ratio of about 4-4.5. Conversely, the magnetite and ferrite catalysts did not produce methane or ethane, but they showed a significant presence of ethylene. All hydrocarbons were produced in little amount due to the low operative temperature and pressure and to the consequent slow kinetics.

These results suggest that a direct Sabatier's reaction (SR) occurs on the NiO-based catalyst following Eq. 3, and partially a two-stage Fischer-Tropsch (FT) reaction, too, where the first stage hydrogenates CO₂ (Reverse Water Gas Shift - RWGS), whereas the second stage

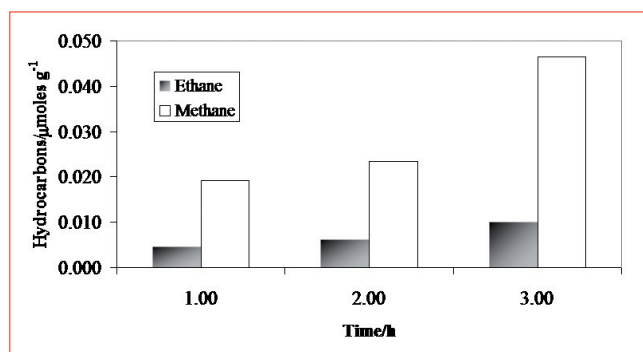


FIGURE 2 Hydrocarbon production for gram of catalyst on the NiO-based catalyst at 50 °C at different time values with S-1 setup

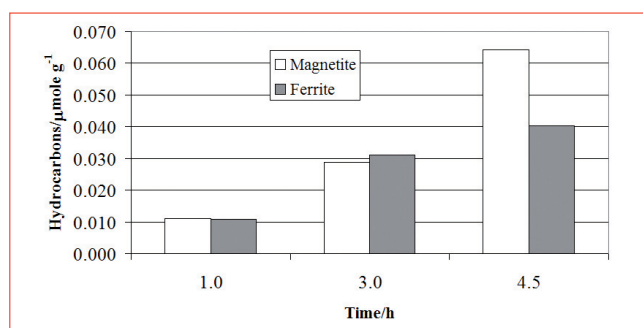
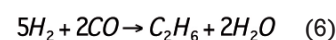
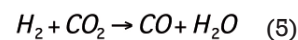
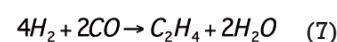


FIGURE 3 Ethylene production for gram of catalyst on Ferrite and Magnetite catalyst at 50 °C at different time values with S-1 setup

follows the standard FT hydrogenation of CO to form ethane (Eq. 6):



On the iron-based catalyst the ethylene product can be explained with a different second stage:



Carbon dioxide hydrogenation to CO (eq. 5) is a reversible reaction and leads to equilibrium. This equilibrium is very much influenced by temperature but it also depends on the H_2/CO_2 ratio. As an example, Puskas et al [18] showed that the equilibrium conversion of CO_2 to CO at 50° C was about 2.3%, with an H_2/CO_2 ratio 4:1.

Table 2 shows the results obtained after three months of incubation at 50 °C, sampling vial with gas-tight syringe. The Ni-based catalyst showed a substantial presence of methane but also some ethane trace with a methane/ethane ratio of about 32. Conversely, the magnetite and ferrite catalysts did not produce methane nor ethane but they showed a significant presence of ethylene. Surprisingly, the amount of measured methane and

Catalyst	CH_4		CH_3CH_3		$CH_2=CH_2$	
	ppm	*μmole g ⁻¹	ppm	*μmole g ⁻¹	ppm	*μmole g ⁻¹
Ni-based	34	0.047	11	0.010	-	-
FeO-Fe ₂ O ₃	-	-	-	-	31	0.029
Fe ₂ O ₃	-	-	-	-	34	0.031

* For gram of catalyst

TABLE 1 Hydrocarbon production in H_2/CO_2 5:1 at 50 °C and 1 bar after 3 hours

Catalyst	CH_4		CH_3CH_3		$CH_2=CH_2$	
	ppm	*μmole g ⁻¹	ppm	*μmole g ⁻¹	ppm	*μmole g ⁻¹
Ni-based	9.90	8.83×10^{-3}	0.31	2.77×10^{-4}	-	-
FeO-Fe ₂ O ₃	-	-	-	-	0.31	2.77×10^{-4}
Fe ₂ O ₃	-	-	-	-	0.14	1.25×10^{-4}

TABLE 2 Hydrocarbon production in H_2/CO_2 5:1 at 50 °C and 3 bar after three months

ethane were respectively 2÷5 and 17÷36 lower than those produced in the short time configuration. Moreover, the methane/ethane ratio produced and measured in this configuration was about 8, i.e. higher than those obtained in the previous configuration. This effect could be due to the higher volatility of methane with respect to ethane, evidenced for the long incubation time.

Again comparing the results (Table 2 and Figures 2-3), the amount of measured ethylene was of a magnitude order of about twice as lower as those produced in the short-time configuration ($1.1\div 6.4\times 10^{-2}$ $\mu\text{mole g}^{-1}$ for magnetite and $1.1\div 4.0\times 10^{-2}$ $\mu\text{mole g}^{-1}$ for ferrite).

Based on all these evidences, we can suppose that the different sampling method (syringe or on-line sampling) influenced the analysis results. The gas-tight syringe sampling at 25° C had the limit that hydrocarbons, strongly adsorbed on the catalyst, were hardly removed and so they were underestimated.

Figure 4 shows the characteristic signal for fragment CH (m/z 13) and CH₃ (m/z 15), obtained on NiO- and

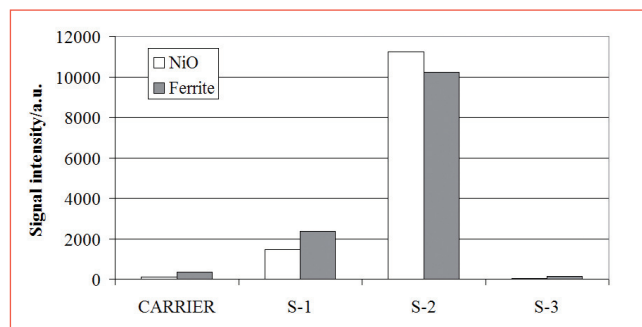


FIGURE 4

Fe₂O₃-based catalysts at 50° C in S-1, S-2 and S-3 set up apparatus compared with the signal for the H₂/CO₂ carrier bypassing the reactor.

Figure 4 shows qualitatively that, when the H₂/CO₂ stream was sent through the reactor for 10 min (S-2 setup), these gases adsorbed strongly onto the catalyst powder and they were not removed by the Helium stream flowing through the reactor non-stop for 12 hours. Conversely, if the reactor temperature was previously increased to 130 °C and Helium was sent through the reactor for 10 min (S-3), then H₂/CO₂ gases were desorbed completely and the analysis after 12 hours in Helium stream did not reveal hydrocarbons. These results, revealed by the S-2 setup, explain the reason why the hydrocarbon analysis on these catalysts was strictly related to the sampling method used. We can rationalize the results in two points:

- 1) the analysis of the produced hydrocarbons depends on the use of a gas able to desorb them;
- 2) a conditioning temperature is required in order to remove completely H₂/CO₂.

Table 3 compares literature data at temperature ≤ 50° C on different kinds of catalysts. Unlike the Ni and Fe catalysts, tested in this work just as received, all the others listed in Table 2 underwent a reduction treatment in pure hydrogen at 200-300° C. Some details of these experiments must be stressed. The artificial reduction treatment, very useful to activate the catalyst, does not normally occur in nature, where only iron and nickel in the oxidized form are available in the rocks. In the works of Tampi et al [10-11], a UV source was needed in order to obtain methane, while in dark conditions the methane production was very reduced. Jacquemin

Catalyst	Temperature °C	H ₂ /CO ₂	CH ₄ $\mu\text{moles g}^{-1} \text{h}^{-1}$	(Other)	Weight g	Metal %	Reference
Rh/Al ₂ O ₃	25	(9-300)	2400	-	0.15	1.0%	[16]
Ru/TiO ₂	46	12	105(26) ¹	-	0.10	3.8%	[14]
NiO/Al ₂ O ₃	50 °C	5	0.046	(0.019) ²	2	59%	This work
Fe ₂ O ₃	50 °C	5	-	(0.011) ³	2	70%	This work
Fe ₂ O ₃ xFeO	50 °C	5	-	(0.011) ³	2	72%	This work

¹Dark, ²Ethane, ³Ethylene

TABLE 3 Comparison with literature data

et al. [12] performed a particular two-stage experiment with a very high H_2/CO_2 ratio. As reported, two known quantities of carbon dioxide (0.0417 and 1.33 mmol) were introduced in the reactor with Helium. Hydrogen was then kept flowing into the cell for 15 min at a rate of 20 mL min^{-1} . The authors observed that the production of CH_4 was higher when very small amounts of CO_2 flowed in [12].

In the past, Medina et al. [12,13] working at much higher temperature ($180 \text{ }^\circ\text{C}$) than all the previous ones, reported that methane can be produced as the only product from CO_2 hydrogenation only if Ni catalyses the reaction but, methane, ethane, and propane were detected immediately after the beginning of the reactions.

However, ethane and propane were converted to methane after several hours of reaction, so by the end of the reaction, methane was the only component of the gas. The Medina data [12,13] partially confirm the results on NiO in this work, where both methane and ethane was detected in the first hours.

Moreover, Medina et al. results [12,13] evidenced that small fractions of ethane and propane were found in addition to methane in the products from Fe-catalyzed reactions. In this case, methane and propane appeared after several hours of reaction, but in contrast to the Ni-catalyzed reactions, their amounts increased steadily. In this case our data were different because only ethylene was detected in the very first hours.

In order to evaluate the possibility of hydrocarbon generation in geologic environments, with particular emphasis on the methanation under low temperature conditions, it is important to normalize the obtained results with the natural abundance of the elements reported in Table 3. Since these materials are present in the earth's crust, it is plausible to assume the production of hydrocarbons by inorganic reaction through the serpentinization. Table 3 data can be normalised with

Catalyst	Temperature $^\circ\text{C}$	CH_4 $\mu\text{moles kgcrust}^{-1} \text{ h}^{-1}$	Reference
Rh	25	0.24	[16]
Ru	46	0.00276 (0.00068) ¹	[14]
Ni	50 $^\circ\text{C}$	0.0065	This work
Fe	50 $^\circ\text{C}$	0.922	This work
Fe	50 $^\circ\text{C}$	0.892	This work

TABLE 4 Normalisation of Table 3 data with respect to the abundance of elements in the earth's crust

respect to the abundance of elements in the earth's crust [19]: Fe $5.63 \times 10^4 \text{ mg/kg}$, Ni $8.4 \times 10^{-1} \text{ mg/kg}$, Ru and Rh $1 \times 10^{-3} \text{ mg/kg}$, evidencing (Table 4) that for high crust rock amount and in geological times both oxides could produce relevant hydrocarbons amount.

Conclusion

Our results showed that both high-concentration Ni and Fe oxides without any particular reducing treatment could produce light hydrocarbons (methane and/or ethane, ethylene) at low temperature and pressure conditions similar to those present in particular geologic environments.

The data obtained have bridged the lack of literature references at low temperature for the Ni- and Fe-based catalysts, adding useful information to the mechanism comprehension. In addition, the different tests have established the correct analysis method for this kind of measures. ●

Acknowledgments

This work was carried out under the contract: Low temperature methanation in geologic environments (n° 31/2012/COMMOHI07), funded by the Italian National Institute of Geophysics and Volcanology (INGV).

- 1) G. Etiope, B. Sherwood Lollar, "Abiotic methane on earth", *Reviews of Geophysics*, 51 (2013) 1-24.
- 2) N. H. Sleep, A. Meibom, Th. Fridriksson, R. G. Coleman, D. K. Bird, " H_2 -rich fluids from serpentinization: Geochemical and biotic implications", *Proceedings of the National Academy of Sciences of the United States of America*, 101/35 (2004) 12818-12823.
- 3) M.O. Schrenk, W.J. Brazelton, S.Q. Lang, "Serpentinization, Carbon, and Deep Life", *Reviews in Mineralogy & Geochemistry*, 75 (2013) 575-606.
- 4) R.B. Anderson, 1984. *The Fischer-Tropsch Reaction*. Academic Press, London.
- 5) Y.A. Taran, G.A. Kliger, E. Cienfuegos, A.N. Shuykin, "Carbon and hydrogen isotopic compositions of products of open-system catalytic hydrogenation of CO_2 : Implications for abiogenic hydrocarbons in Earth's crust", *Geochimica et Cosmochimica Acta*, 74 (2010) 6112-6125.
- 6) G. Proskurowski, M.D. Lilley, J.S. Seewald, G.L. Früh-Green, E.J. Olson, J.E. Lupton, S.P. Sylva, D.S. Kelley, "Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field", *Science*, 319 (2008) 604-607.
- 7) D.I. Foustoukos, W. E. J. Seyfried, "Hydrocarbons in hydrothermal vent fluids: the role of chromium-bearing catalysts", *Science*, 304 (2004) 1002-1005.
- 8) T. M. McCollom, J. S. Seewald, "Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions", *Earth and Planetary Science Letters*, 243, (2006) 74-84.
- 9) Y.A. Taran, G. A. Kliger, V. S. Sevastyanov, "Carbon isotope effects in the open-system Fischer-Tropsch synthesis", *Geochimica et Cosmochimica Acta*, 71 (2007) 4474-4487.
- 10) G. Etiope, G., M. Schoell, H. Hosgoromez, "Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars", *Earth and Planetary Science Letters*, 310 (2011) 96-104.
- 11) G. Etiope, B.L. Ehlmann, M. Schoell, "Low temperature production and exhalation of methane from serpentinized rocks on Earth: A potential analog for methane production on Mars", *Icarus*, 224/2 (2013) 276-285.
- 12) J.C. Medina, S.J. Butala, C.H. Bartholomew, M.L. Lee, "Low temperature iron- and nickel-catalyzed reactions leading to coalbed gas formation", *Geochimica et Cosmochimica Acta*, 6474 (2000) 643-649.
- 13) J.C. Medina, S.J. Butala, C.H. Bartholomew, M.L. Lee, "Iron-catalyzed CO_2 hydrogenation as a mechanism for coalbed gas formation", *Fuel*, 79 (2000) 89-93.
- 14) K.R. Tampi, J. Kiwi, M. Gratzel, "Methanation and photo-methanation of carbon dioxide at room temperature and atmospheric pressure", *Nature*, 237 (1987) 506-508.
- 15) M. Gratzel, J. Kiwi, R. Tampi, "Mixed ruthenium catalyst", Patent US4847231 (1989).
- 16) M. Jacquemin, A. Beuls, P. Ruiz, "Catalytic production of methane from CO_2 and H_2 at low temperature: Insight on the reaction mechanism", *Catalysis Today*, 157 (2010) 462-466.
- 17) P. Ruiz, M. Jacquemin, N. Blangenois, "Catalytic CO_2 methanation process", Patent WO2010006386 (2010).
- 18) I. Puskas, "Can carbon dioxide be reduced to high molecular weight Fischer-Tropsch products?", *Proceedings of American Chemical Society, ACS 213 National meeting (San Francisco, 13-17 1997)*.
- 19) *CRC Handbook of Chemistry and Physics*, David R. Lide, editor, 88th edition. Boca Raton, Florida: Taylor & Francis Group, (2008) 14-17.