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CATALYTIC HYDROGENATION OF CARBON DIOXIDE OVER Pd BASE CATALYST

BY

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Abstract. The performances of the commercial catalysts with various content of Pd in the hydrogenation process of carbon dioxide to methane have been analyzed. Catalytic test for carbon dioxide hydrogenation was conducted in mild reaction conditions (temperature up to 320°C and atmospheric pressure). Optimizing the main parameters such as, reaction temperature, H₂/CO₂ molar ratio, high CO₂ conversion and total methane selectivity were obtained up to 300°C. Also, the performances of these catalysts in the hydrogenation process of carbon dioxide to methane in the conversion and selectivity terms have been highlighted by a mathematical model developed by means of the Table Curve 3D software. The mathematical model corresponding to the characteristic equation provides a good arrangement of the experimental points on the responding surface, simplicity of the characteristic equation and a good determination coefficient that is near unity.

Key words: hydrogenation process; Pd base catalyst; mathematical model.

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1. Introduction

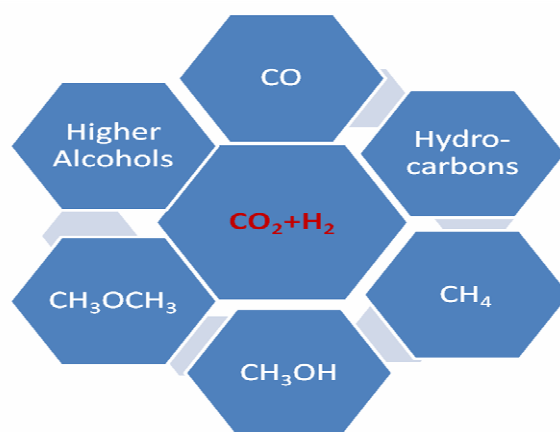
Carbon dioxide (CO₂) as the final by-product of all processes involving the oxidation of carbon compounds represents a possible potential source for C₁ feedstock for the manufacture of chemicals and fuels, alternative to the current predominant use of petroleum derived sources. This study is a small part of the global challenge regarding the reducing of concentration of the greenhouse emission gas by the catalytic transformation of CO₂ sources, as an essential step for substituting the fuels synthesis.

The Sabatier and Bosch processes are two Carbon Dioxide Reduction Systems which have been studied extensively. Current technology for the reduction of carbon dioxide is embodied in the Sabatier reactor. For each mole of CO₂ reduced, this system produces two moles of water and one mole of methane. For this reason, only half of the hydrogen consumed in this reaction can be recovered by electrolysis. The Sabatier reaction, usually utilizes an alumina supported ruthenium catalyst and, in comparison to the Bosch reaction, has the advantage of greater thermodynamic favorability and higher reaction rates. The Bosch reaction produces only water and elemental carbon at 650°C, allowing all of the hydrogen consumed to be recovered by electrolysis.

This realizes the closure of the oxygen-carbon dioxide-water-oxygen loop possible. The primary problems associated with the Bosch reactor are slow reaction rates and the generation of particulate carbon which fouls the catalyst surface and which plugs the catalyst bed. Catalysts are critical to the Bosch process, due to the intrinsically slow kinetics. Iron, cobalt or nickel catalyzed the Bosch reaction and minor additions of ruthenium significantly improve kinetics. Typical reaction temperatures are in range of 450-650°C but even at these relatively high temperatures single pass reduction efficiencies are typically below 10%, hence practical reactor designs require recycle operation. A more significant disadvantage is the inactivation of catalyst surface and the plugging of the reactor caused by a build-up of particulate carbon. While greater efficiencies in terms of material balances aboard spacecraft are possible using the Bosch reaction, much further development work will be required before the system is competitive with Sabatier process from a practical standpoint (Perathoner & Centi, 2014).

The chemical reduction of CO₂ using molecular hydrogen is not thermodynamically viable, because the industrial production of hydrogen from natural gas or petroleum produces CO₂. Recent research has shown that transition metal complexes catalyze the reduction of CO₂ via the intermediacy of hydride complexes, in which the origin of the activated hydrogen is water. While many of such reactions result in a partial reduction of CO₂ to carbon monoxide, the possibility of the further reduction to formaldehyde, methanol and/or methane is alluring, both from the point of view that the reduction becomes increasingly thermodynamically favorable but also because these

multi-electron reduction products are particularly important in chemicals manufacture (formaldehyde and methanol) and as fuels: methane and methanol. Methane from H_2 and CO_2 is receiving particular attention because of applications like: purification of hydrogen used in PEM fuel cells or manufacture of substitute natural gas from coal (Krier *et al.*, 2013).



Among the catalytic reactions, the catalytic hydrogenation of CO_2 over transition metal catalysts to form methane, simply called methanation, is a particularly promising technique that has received a great appreciation because of its possibility to manufacture and substitute natural gas, reducing thereby the price of gas obtained from coal.

In literature many 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, due to the particular attention of the opportunity regarding technological utilization of CO_2 as a possible source of energy. Although many different metals supported on various oxide carriers have been used to catalyze the reaction, palladium is one of the most effective. Furthermore, the palladium catalyst on mesoporous alumina or silica support exhibits variable performances in terms of selectivity and activity for methanation process (Krier *et al.*, 2013; Perathoner & Centi, 2014).

However, there are not data in literature on the catalytic hydrogenation of carbon dioxide to methane by Sabatier reaction on palladium catalysts.

In this context, the primary aim of present work is to testing of the commercial catalysts with various content of Pd in the reduction of CO_2 to methane. Furthermore, we will develop a mathematical model needed to highlight the performances of the Pd based catalysts in the hydrogenation process of carbon dioxide. The mathematical model is obtained with Table Curve 3D software. This program arranges the experimental data in three-dimensional space and it is able to make a quick graphical and numerical

analysis providing the dependency relations between physical quantities that characterize the experimental data obtained, thus providing a mathematical model for the study. The complexity of the software needed to establish is ideal approximation equation is given by the fact that it uses around 36,000 approximation procedures which have different equations (Marinoiu *et al.*, 2015). In literature there are papers with the mathematical models that emphasize the performance of various catalysts in chemical processes (Marinoiu *et al.*, 2015; Marinoiu *et al.*, in press; Sollfrank & Gujer, 1990; Mosey, 1983; McLean & McAuley 2012; Araujo & McElwain, 2004; Mikhailova *et al.*, 2003; Šoóš *et al.*, 2000; Krier *et al.*, 2013; Perathoner & Centi; 2014).

2. Experimental

For the production of methane via Sabatier reaction, commercial catalysts (MGS₅/S₁) from Sud Chemie with various content of Pd were used. These catalysts were tested at temperatures from 260 to 350°C. The catalysts are identified as Pd I, Pd II, Pd III, Pd IV corresponding to 1.0, 1.2, 1.6, 2% Pd respectively. The hydrogen and carbon dioxide for reaction were purchased from Linde Groupe, and were of ultra high purity (UHP). In the reaction system (Fig. 1) three units, comprising a feeding unit, a reaction unit and a product gas analysis unit are included.

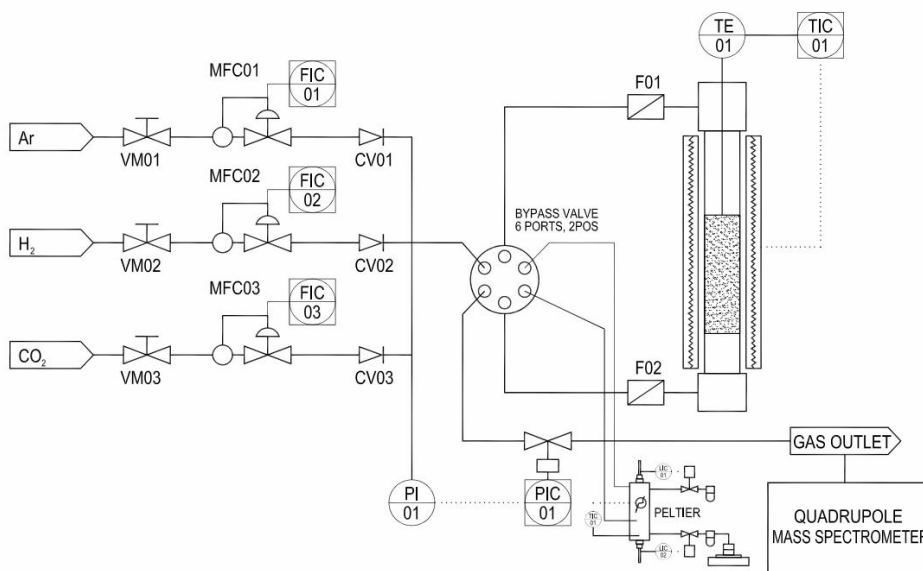


Fig. 1 – A schematic of the conducted reaction system and experimental procedures.

2.1. Catalytic Experiments

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-Reference), 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. In situ catalyst activation and methanation reactions were performed from ambient temperature up to 320°C, with an increment temperature rate of 7°C. Each experiment was repeated twice, and each temperature was maintained for 30 min before the next temperature increment was accomplished. CO₂ and H₂ 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 H₂:CO₂ (3.6:1.0 to 8.0:1.0), while the total flow rate was maintained at a constant 50 mL min⁻¹. The conversion of carbon dioxide is defined as the percentage of reacted carbon dioxide:

$$\text{CO}_2 \text{ conversion}(\%) = \frac{(Q_{\text{CO}_2_inlet} - Q_{\text{CO}_2_outlet}) \times 100}{Q_{\text{CO}_2_inlet}}$$

where: $Q_{\text{CO}_2_inlet}$ and $Q_{\text{CO}_2_outlet}$ are the molar flow rates of CO₂ (mol s⁻¹) at the inlet and the outlet, respectively.

2.2. Characterization of Catalyst

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 H₂, CH₄ and CO₂ compositions was made based on registered partial pressures signals and using standard calibration gas mixtures. X-ray powder diffraction patterns of the samples were obtained using a Rigaku Ultima IV diffractometer. The wavelength of Cu-K α : X-ray radiation

used was 1.5418 A while the beam voltage and current were 45 kV and 40 mA, respectively. The specific surface areas of the samples were determined using the Brunauer-Emmett-Teller (BET) method by performing nitrogen sorption measurements using a Quantachrome Autosorb iQ instrument. The adsorption and desorption experiments were done at 77 K after initial pre-treatment of the samples by degassing at 120°C for 2 h.

3. Results and Discussions

The performances of palladium catalysts as a function of reaction temperature are shown in Fig. 2. All catalysts exhibit similar conversion and selectivities over the range of reaction temperature examined. Except the Pd III catalyst, the conversion of the all catalysts was slightly up to 280°C. As the temperature was increased, the conversion increased rapidly. As temperature greater than 300°C, the conversion reaches nearly 100%.

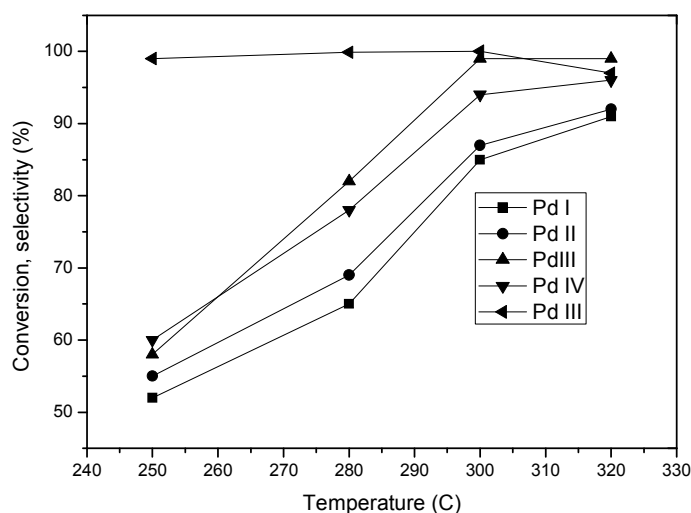


Fig. 2 – The catalytic performances of Pd catalysts in the catalytic hydrogenation reaction of CO₂ to methane. The reaction conditions: GHSV = 10000 h⁻¹, CO₂:H₂ molar ratio = 1:4.

The effect of H₂/CO₂ molar ratios in the range 240-330°C is also examined (Fig. 3). As can be noticed in Fig. 3 the CO₂ conversions are growing continuously with the rise of CO₂:H₂ molar ratio, the rise being faster between 280-340°C. The likely reason is that the higher CO₂:H₂ molar ratio shift equilibrium from CO (detected in ppm range) to CO₂. The CO is more reactive and leads to product loss by transforming into CH₄.

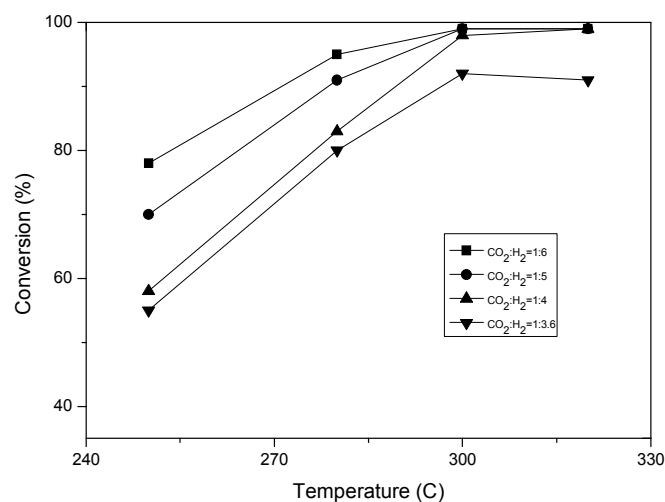


Fig. 3 – Conversions of CO₂ as a function of temperature and various CO₂/H₂ molar ratios, GHSV = 12.000 h⁻¹.

In order to obtain the mathematical model of the hydrogenation process, the obtained experimental data were processed by means of the Table Curve 3 D software by the following procedure steps:

- *Introduction of experimental data;*
- *Graphical representation of the furnished data;*
- *Choosing of the best mathematical model on the basis of the responding surface* by taking into account the best arrangement of the experimental data on the plot, the simplicity of the characteristic mathematical equation and the determination coefficient (r^2).

The value of the determination coefficient represents the ratio between the spreading degree of the experimental points around the plot of the regression equation and the spreading degree of the same points relative to the arithmetic mean of the own ordinates. Apart from this, a regression function is considered to approximate the best the set of the experimental points when the regression coefficient is as close as possible to the unity.

The following notations were made in all equations and graphical representations: x-ratio CO₂:H₂; y-conversion, respective yield or selectivity [%]; z-temperature [°C].

The mathematical model obtained for the catalytic hydrogenation according to conversion.

By processing the obtained experimental data the Table Curve 3D software gives a set of 338 for the total conversion as a relationship between the

experimental results and the values calculated by the equations. After a careful selection and taking into account the determination coefficient values, the simplicity of the equations and the good arrangement of the experimental points of the response surface, the characteristic equations for this performance criterion were obtained. Finally, the best characteristic equation of the mathematical model provided by the Table Curve 3D software for the catalytic hydrogenation according to conversion as well the determination coefficient value are given in Table 1.

Table 1
The Characteristic Equation of the
Mathematical Model and the Determination Coefficient Value

| Equations of mathematical | (r ²) |
|--|-------------------|
| $z = (a+bx+clny+d(\ln y)^2)/(1+ex+fx^2+gx^3+hlny)$ a = -1112.9756; b = 1.1455695; c = 554.26337; d = -68.464612; e = 0.01073501; f = -0.0004504; g = 9.0799208x10 ⁻⁶ ; h = -0.23333199 | 0.9947 |

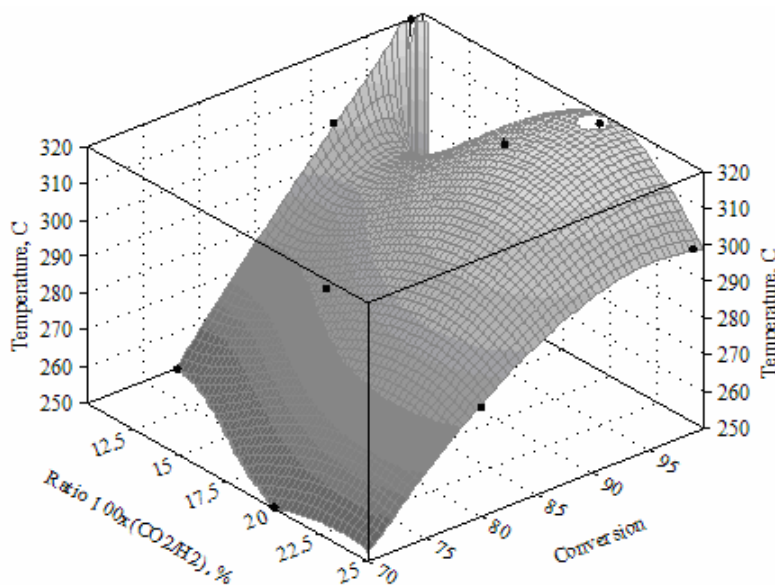


Fig. 4 – The characteristic mathematical model of the catalytic hydrogenation according to conversion.

The mathematical model obtained for the catalytic hydrogenation according to selectivity.

By processing the obtained experimental data the Table Curve 3D software gives a set of 195 for the selectivity as a relationship between the

experimental results and the values calculated by the equations. The selection of the characteristic equation of the mathematical model for this performance criterion was realized as in the previous case.

The characteristic equation of the mathematical model provided by the Table Curve 3D software for the catalytic hydrogenation according to selectivity as well the determination coefficient value are given in Table 2.

Table 2
*The Characteristic Equation of the
Mathematical Model and the Determination Coefficient Value*

| Equations of mathematical | (r ²) |
|---|-------------------|
| $z = a+bx+c/y+dx^2+e/y^2+fx/y$ $a = 27791.539; b = -187.2001; c = -4740352.4;$ $d = -0.03433; e = 2.0251 \cdot 10^8; f = 17622.002$ | 0.9993 |

The mathematical model developed on the basis of this equation is given in Fig. 5.

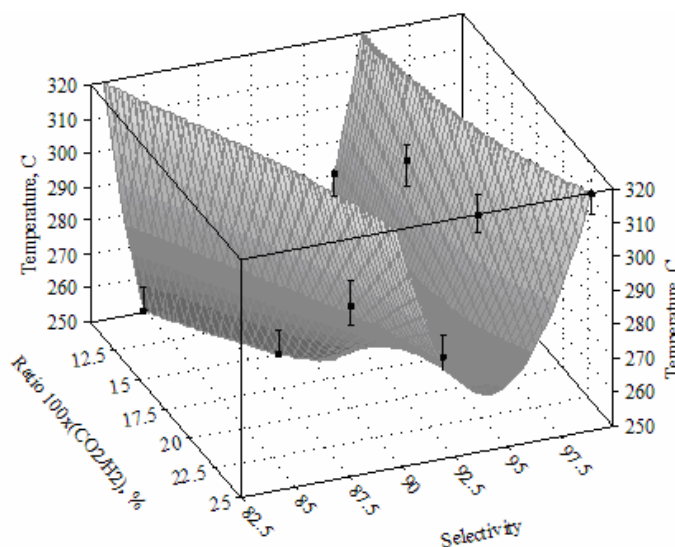


Fig. 5 – The mathematical model characteristic of the catalytic hydrogenation according to selectivity.

The mathematical models from the Figs. 4 and 5 show common characteristics given by the very good placing of the experimental points on the response surfaces. All the estimated values were close and showed small variations with the experimental values. The best fit model was proposed of the largest determination value.

4. Conclusions

Firstly, the performances of the commercial catalysts with various content of Pd were used in the hydrogenation process of carbon dioxide. All catalysts exhibit the similar conversion and selectivity over the range of reaction temperature examined. Except the Pd III catalyst, the conversion of the all catalysts was slightly up to 280°C. Further, the conversion increases quickly with increasing of the temperature. Thus, at a temperature greater than 300°C, the conversion reaches nearly 100%. The experimental results justify the opportunity and possibility of using of the commercial catalysts with various content of Pd in hydrogenation process due to a high conversion and selectivity obtained. For this reason, the tested catalysts could have potential applications in the CO₂ conversion to methane process.

Second, the performances of the commercial catalysts with various content of Pd used in the hydrogenation process of carbon dioxide have been highlighted by a mathematical model developed by means of the Table Curve 3D software. Models given by the software and the equations derived in this study gave close estimated values to the experimental results. Further, the mathematical model corresponding to the characteristic equation provides a good arrangement of the experimental points on the responding surface, simplicity of the characteristic equation and a good determination coefficient that is near unity.

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HIDROGENAREA CATALITICĂ A CO₂ PE CATALIZATORI CE CONȚIN PALADIU

(Rezumat)

Performanțele catalizatorilor comerciali cu conținut diferit de paladiu au fost testate în procesul de hidrogenare a dioxidului de carbon la metan. Testele catalitice realizate în cadrul procesului de hidrogenare a dioxidului de carbon s-au realizat la T=320°C și presiune atmosferică. Optimizarea parametrilor principali, precum: temperatura de reacție, raportul molar H₂/CO₂, conversia și selectivitatea totală la metan au fost obținute la 300°C. Performanțele acestor catalizatori în procesul de hidrogenare a dioxidului de carbon la metan în termeni conversie și selectivitate au fost evidențiate printr-un model matematic dezvoltat cu ajutorul unui software și anume Tabelul Curve 3D. S-a constatat că modelul matematic corespunzător se caracterizează printr-un aranjament bun al punctelor experimentale pe suprafața de răspuns, simplitate a ecuației caracteristice și un coeficient de determinare care este apropiat de unitate.