



# REDUCTION OF CO<sub>2</sub> EMISSION TO METHANE USING HYDROGENATION WITH NICKEL (110) SURFACE CATALYST

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## ABSTRACT

The day-to-day development in industries and manufacturing process, all the industries are using chemicals and fuel to produce a product. While manufacturing, they may release some harmful gas in the atmosphere like carbon dioxide, carbon monoxide etc. When compared with all other gases carbon dioxide will cause the environment and approximately the industries are releasing highest percentage of CO<sub>2</sub>. To reduce the CO<sub>2</sub> emission there exist some methods like inject the CO<sub>2</sub> gas by dried up oil wells or deep in ocean or convert the useful organic compounds by using catalyst. The new procedure is proposed that the carbon dioxide is to convert methane by using hydrogenation process using catalyst which is less expensive than other catalysts like platinum, palladium, ZnO, CuO, Al<sub>2</sub>O<sub>3</sub> etc.

**Keywords:** Co<sub>2</sub>, Hydrogenation, Methane, Methanol, Nickel(110) Surface catalyst.

## I. INTRODUCTION

In the present days the pollution increases rapidly. Mainly, the air pollution came from traffic and industries. Because of industries the environment may be affected with their released gases. Mostly, the manufacturing industries utilize chemicals to produce a product. While producing, it generates some harmful gases which may affect nature. On the survey, the carbon dioxide will produce more when compared with other gases.

**Table : List of Pollutants**

<b>Fossil Fuel Emission Levels - Pounds per Billion Btu of Energy Input</b>			
<b>Pollutant</b>	<b>Natural Gas</b>	<b>Oil</b>	<b>Coal</b>
Carbon Dioxide	117,000	164,000	208,000
Carbon Monoxide	40	33	208
Nitrogen Oxides	92	448	457
Sulfur Dioxide	1	1,122	2,591

There are some methods for reducing the carbon dioxide in the atmosphere :

- 1) energy efficiency and conservation practices
- 2) carbon – free and reduced –carbon energy resources



3) capturing and storing carbon either from fossil fuels or from the atmosphere

**Energy efficiency and conservation:**

In general terms energy efficiency is achieved through the application of technology such as insulation upgrades, compact fluorescent bulbs, high efficiency furnace. Energy conservation is achieved through behavioral changes such as turning off lights when it is not needed.

It is the one of the technique that reduce the consumption of carbon based fuel like natural gas, oil, coal and decreasing carbon dioxide emission.

**Carbon – free and reduced –carbon energy resources:**

Another way to reduce carbon dioxide emission is to use carbon-free or reduced-carbon sources of energy. Carbon free sources of energy as its own impact, these technology generate energy without producing and emitting carbon dioxide to the atmosphere. Carbon free energy sources include solar power, wind power, geothermal energy and nuclear power. Alternatively switching from high carbon fuel to low carbon fuel will also result in reduced carbon dioxide emission.

**Capturing and storing carbon:**

A third for reducing carbon dioxides in the atmosphere is carbon sequestration. It involves the capture and storage of carbon dioxide which is present in the atmosphere. Carbon dioxide can be removed from the atmosphere and stored within plants. another way to capture the carbon dioxide is done by burning either before or after fossil fuel, and then we stored within the earth.

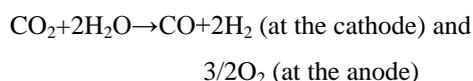
The objective of proposal solution to reduce the carbon dioxide emission using hydrogenation with the help of nickel(110) surface catalyst. Other catalyst are also used in the hydrogenation process which are very expensive. the Ni(110) surface has a larger catalytic activity compared to the other surfaces, and that Ni is a better catalyst for hydrogenation of carbon dioxide

**II. EXISTING SYSTEM**

The carbon dioxide emission reduction using hydrogenation as follows:

**1) To Methanol:**

Methanol is produced from carbon dioxide dissolved in water by electrolysis followed by hydrogenation of the carbon monoxide formed. A method of producing methanol by reductive conversion of any available source of carbon dioxide, which comprises electrochemically reducing the carbon dioxide in a divided electrochemical cell comprising an anode in one cell compartment and a metal cathode electrode in another cell compartment that also contains an aqueous solution or aqueous methanolic solution of an electrolyte of one or more alkyl ammonium halides, alkali carbonates or combinations therefore to produce a reaction mixture containing carbon monoxide and hydrogen which can be subsequently used to produce methanol while also producing oxygen in the cell at the anode.



The CO and H<sub>2</sub> produced at the cathode are subsequently reacted over Cu and Ni based catalysts to produce high yields of methanol (CH<sub>3</sub>OH).





Though this method is an efficient method of utilization of carbon dioxide the technology used is a little sophisticated. It involves the installation of a separate unit in an Industry. The carbon dioxide used should be as pure as possible for the method of conversion to be effective.

In another method the production of methanol from reactions between  $CO_2 + H_2$  and  $CO + H_2$  has been studied over platinum catalysts supported on  $Nb_2O_5$ ,  $ZrO_2$ ,  $MgO$ ,  $SiO_2$  and  $TiO_2$ . Zirconia- and niobia-supported Pt catalysts showed the highest activity for reactions of both  $CO_2$  and  $CO$ . This method is also as effective as the previous method. But the disadvantage is that the carbon dioxide used should be very pure not containing any gaseous or particulate impurities. In such situation obtaining pure carbon dioxide from flue gases plays a major role

**2) Carbon dioxide hydrogenation to methanol at low pressure and temperature:.**

The measurements obtained were used to investigate the methanol synthesis reaction from pure carbon dioxide and hydrogen over binary ( $CuO/ZrO_2$ ) and ternary supported catalyst ( $CuO/ZnO/Al_2O_3$ ).

A comparison of different catalysts the influence of the most important reaction parameters, i.e temperature, pressure, space velocity and feed gas composition is examined at moderate temperatures ( $\leq 300^\circ C$ ) and pressure ( $\leq 20$  bar)

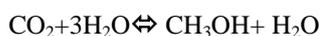
The methanol synthesis was first performed over zinc oxide-chromium oxide catalyst. The catalyst, which was used at 250-350 bars and temperature  $300-450^\circ C$ , was highly stable to the sulfur and chlorine compounds present in the synthesis gas. In 1966, the copper based catalyst was introduced for the methanol synthesis for sulfur free synthesis gas containing a high proportion of carbon dioxide. This copper oxide and zinc oxide catalyst, thermally stabilized by alumina, was extremely active and highly selective. The synthesis could be carried out at  $220-250^\circ C$  and 50 bars, thereby avoiding premature aging of the catalyst due to sintering of copper.

All currently used low pressure catalysts contains copper oxide and zinc oxide with one or more stabilized additives.

*Table 1: Summary of typical catalysts composition for low pressure methanol synthesis*

Manufacturer	Components			
	Cu [% at.]	Zn [% at.]	Al [% at.]	C (graphite) [% at.]
BASF	65 - 75	20 - 30	5 - 10	-
Süd Chemie	65 - 75	18 - 23	5 - 10	-
ICI	61	30	9	-
Du Pont	50	19	31	31
Haldor Topsøe	50 - 60	21 - 25	15 - 28	6 - 8

Methanol synthesis has nearly always been expressed in terms of hydrogenation of carbon dioxide using copper based catalysts



Methanol synthesis has nearly always been expressed in terms of hydrogenation of carbon monoxide



The reaction between  $\text{CO}_2$  and  $\text{H}_2$  and  $\text{CO}$  and  $\text{H}_2$  both are exothermic reaction. They are also thermodynamically unfavorable.

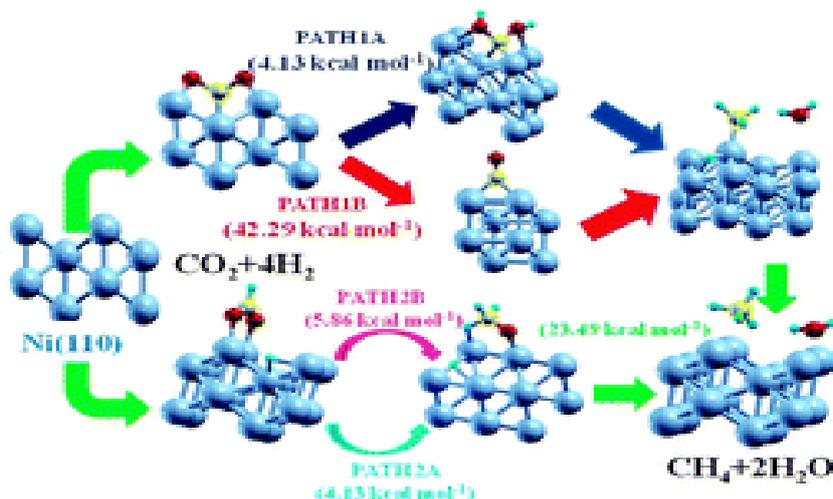
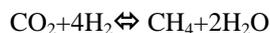
### III. PROPOSED METHOD

The new concept is introduced for reduction of carbon dioxide emission to methane using hydrogenation process with help of nickel(110) surface catalyst. The highest percentage of carbon dioxide which is released from the industries, Because of industries using high amount of fuels and chemicals. Reduction of carbon dioxide emissions can be obtained by applying carbon dioxide removal. In this technique,  $\text{CO}_2$  is separated during or after the production process and subsequently stored or disposed of outside the atmosphere. In some cases the recovered  $\text{CO}_2$  can be used for other purposes.

The  $\text{CO}_2$  removal process can be split into three separate steps:

- i) recovery of the  $\text{CO}_2$  (often including drying and compressing),
- ii) transport of the  $\text{CO}_2$  to a location where it is handled further, and utilization,
- iii) storage or disposal of  $\text{CO}_2$ .

The carbon dioxide emission reduction using hydrogenation with the nickel(110) surface was done in the following reaction



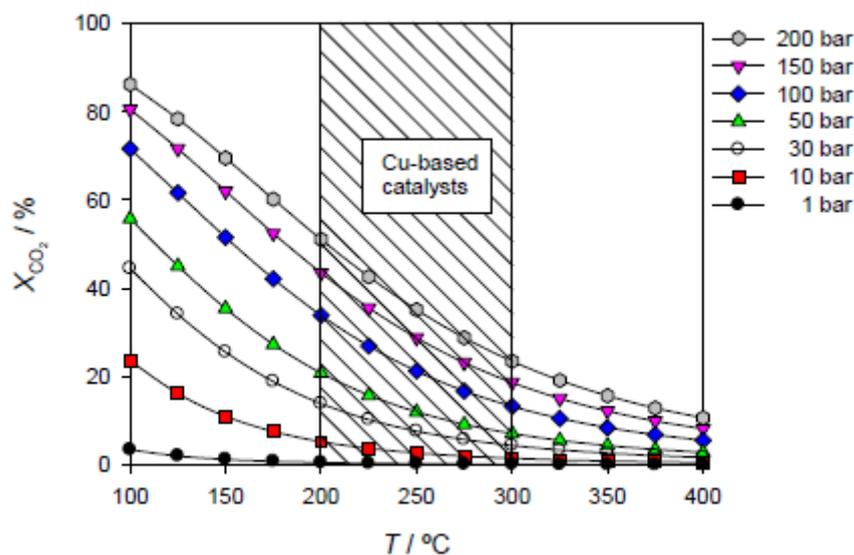
The complete hydrogenation mechanisms of  $\text{CO}_2$  are explored on Ni(110) surface catalyst using density functional theory. the possible hydrogenation mechanism to form product methane from the stable adsorption-co-adsorption intermediates of  $\text{CO}_2$  and  $\text{H}_2$  on Ni(110) surface. Clearly it shows the methane formation *via* hydroxyl carbonyl intermediate requires a lower energy barrier than *via* carbon monoxide and formate intermediates on the Ni(110) surface.

The methanation reaction of CO<sub>2</sub> have been conducted at low temperatures. It would be important to carry out CO<sub>2</sub> reductions at lower temperatures(150-300°C), in order to improve the flexibility of the operation, especially when the CO<sub>2</sub> and/or H<sub>2</sub> sources are intermittent, and to improve the energy efficiency of the process.

#### IV. RESULTS AND COMPARISONS

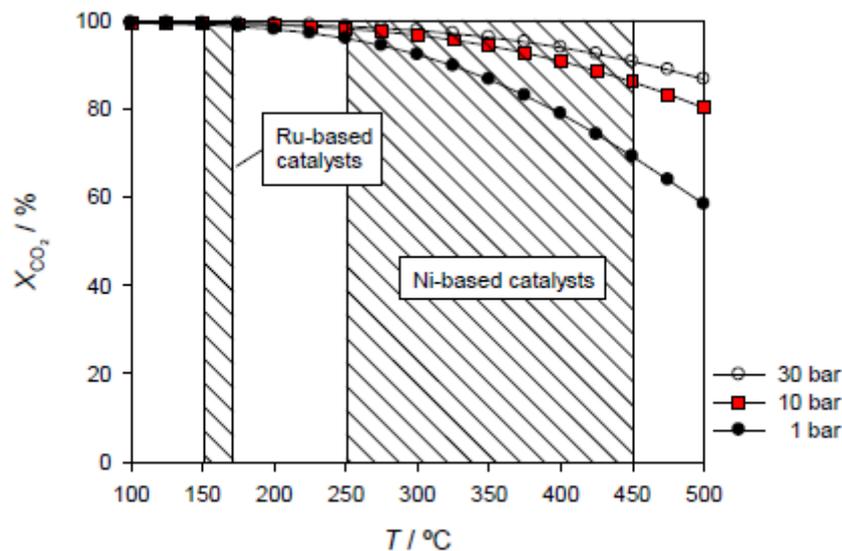
The hydrogenation of carbon dioxide emission may produce methanol and methane. Hydrogenation of CO<sub>2</sub> to methanol is thermodynamically more favourable, needing only six electrons. Methanol has the disadvantage that, compared to methane, there is no complete infrastructure already built to handle it for transport and end-user utilization.

Strategies for CO<sub>2</sub> valorisation on CH<sub>4</sub> or CH<sub>3</sub>OH , thermodynamic analysis was performed using the continuous Gibbs reactor model. Carbon dioxide equilibrium conversion was determined for hydrogenation into methane or methanol as a function of pressure and temperature. The carbon dioxide conversion into methanol over methane requires high pressures, particularly the active catalysts in industries. The following analysis on methanol and methane at different temperatures and pressures:



**Fig: Conversion of Carbon dioxide to methanol at different temperature and pressure**

The above graph represents the conversion of carbon dioxide to methanol based on copper catalyst with different pressures from 1 bar to 200 bar.



**Fig: Conversion of Carbon dioxide to methane at different temperature and pressure**

The above graph represents the conversion of carbon dioxide to methane based on Ru and Ni catalyst with low pressures which is less than 30 bar.

Methane can be used in organic chemicals, as fuel, and in the generation of electricity in fuel cells. Special applications have been proposed for space travel, to obtain drinking water by combining the on-board rocket fuel with carbon dioxide which is released.

The carbon dioxide conversion to methane can be done using different catalyst in the hydrogenation process which are Rh, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Pd, Ru and also nickel. But when compared with all catalysts, the nickel is most effective and cheapest surface catalyst suitable for the carbon dioxide with hydrogenation.

## V. CONCLUSION

In the growth of industries, while manufacturing the product when the carbon dioxide is released it immediately captured and stored by using carbon sequestration. That carbon dioxide is removed by converting into methane using nickel(110) surface catalyst in the hydrogenation process. Since hydrogenation process, the carbon dioxide is to convert the methanol and methane but methane has more advantages compared with methanol. Methane can generated with different catalysts but the nickel(110) surface catalyst is most effective and less expensive when compared with other surfaces.

## VI. ACKNOWLEDGEMENT

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**REFERENCES**

- [1]. Charles Christopher Kankam, K.Praneeth Raj, "RECYCLING OF CARBON DIOXIDE TO PROVIDE RENEWABLE ENERGY AND FOR THE MITIGATION OF GREEN HOUSE GAS EMISSIONS", *2011 2nd International Conference on Environmental Science and Technology IPCBEE vol.6, IACSIT Press, Singapore, PP:257-260.*
- [2]. Carlos V. Miguel, Miguel A. Soria, Adelio Mendes, Luis M. Madeira, "Direct CO<sub>2</sub> hydrogenation to methane or methanol from post-combustion exhaust streams - A thermodynamic study", *Journal of Natural Gas Science and Engineering*, PP:1-8.
- [3]. X. Ding, L. De Rogatis, E. Vesselli, A. Baraldi, G. Comelli, R. Rosei, L. Savio, L. Vattuone, M. Rocca, P. Fornasiero, F. Ancilotto, A. Baldereschi, M. Peressi, "Interaction of carbon dioxide with Ni(110): a combined experimental and theoretical study".
- [4]. George A. Olah G.K. Surya Prakash , "Electrolysis of Carbon Dioxide in aqueous media to Carbon Monoxide and Hydrogen for production of Methanol," US patent application 12/171,904, patent number: 7704369, winston & strawn LLP, Patent Department, Washington DC, US.
- [5]. Olah, G.A., Goepfert, A., Prakash, G.K.S., 2006. *Beyond Oil and Gas: the Methanol Economy*. Wiley e VCH Verlag GmbH & Co, Weinheim.