

Research Article

The Analysis of Catalytic Conversion of Carbon Dioxide into Fuel

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ABSTRACT:

Among different greenhouse gases, which are released in the atmosphere, CO₂, is released in the atmosphere, on the highest volume and tonnage, and has a major contributor to the phenomenon of climate change. Its prevalence, causes great interest for use as a source for the production of valuable products, special fuels, and Chemical products. Environmental aspects of it also is important. This article will focus on efforts to use, CO₂, to the production of fuels, additives and biochemical substances. CO₂ gas, as a greenhouse gas, in terms of emissions, has topped the list of the same gases, and published in space. The similar gases are, CO and methane, CFC₅. Increasing greenhouse gas emissions, significantly cause to change climate, and consequently the next successive consequences, such as global warming and respiratory problems. China released 24 percent of total emissions, is located at the top of the list. United States with 18 percent, after China placed. India's share is 6 percent. Emission sources of CO₂, are classified into three categories: power generation stations, vehicles, and natural resources. CO₂ emissions from volcanoes, is an example of the release of CO₂ from natural sources. Fossil fuel resources such as oil and coal will take a major share of CO₂ emissions. According to the International Energy Outlook 2011, the increase in global energy-related CO₂ emissions in 2008 from 30.2 BMT to 35.2 BMT in 2020 and in 2035 is estimated 4302 BMT. According to recent scenarios to reduce CO₂ emissions in the atmosphere, is greatest challenge and requires new ideas and technologies. The possible ways to reduce CO₂ include new alternative fuels to replace fossil fuels and convert CO₂ into useful products through chemical conversion.

Keywords: *Greenhouse Gases, Fuel, Climate Change, Natural Resources*

[I] NTRODUCTION

Abundance and low price, is the benefits of CO₂ as a promising feedstock, in organic synthesis. CO₂ is an interesting C1 structure that can replace ready for life-threatening molecules like phosgene, in some industrial processes. Attempts have been made to the CO₂ in commercial applications including food and beverage carbonation processes used. In recent years CO₂ has been able to attract the attention of the chemical industry as a sustainable raw material used in the production of various products. However, it 110MMT (million metric ton) of CO₂ used in the chemical

industry that is less than one percent of overall emissions. [1]

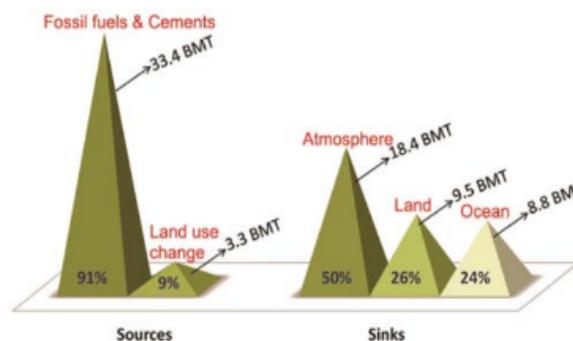


Figure 1 CO₂ generated from different sources

The resulting product of CO₂ and catalysts used

Sakara bunch of different reactions, using CO₂, can lead to products, in the form of (2) have shown.

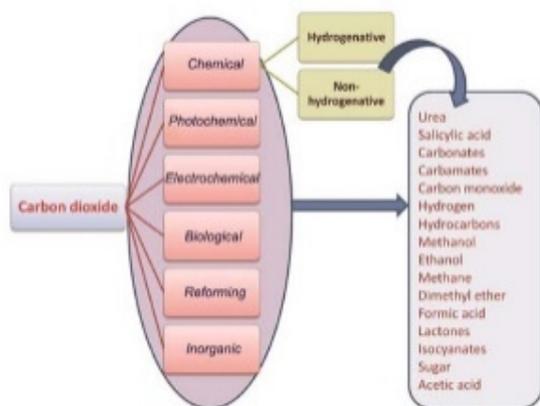


Figure 2: Sakarva bunch of different CO₂ reactions

Production of certain chemicals such as urea and carbonates using CO₂ are known. Between the chemicals, energy production from CO₂, is one of the most important aspects of CO₂ emission. Worldwide demand for fuel is two times more chemicals. CO₂ emissions can be used as a fuel fabrication business. Such a process, in addition to fuel supply, causing the greenhouse effect is moderated. [1]

Hydrocarbons

Fisher-tropsch synthesis, the most popular response, which by hydrogenation of co, it has become a hydrocarbon. In a modified process, FT, is hydrogenation syngas (H₂ + co) that contain significant amounts of CO₂, or by hydrogenation of CO₂, along with co, and CH₃OH, hydrocarbons can be extracted.



The main criteria for this reaction, is additional duties of catalyst to form hydrocarbon. Although FT catalytic process has been well established, but only a few studies, for catalytic hydrogenation of CO₂, to produce hydrocarbons have been reported. CO₂ emissions from the Transportation fuels, along with H₂, which may be obtained from solar

power plants, can be used. This is one of the most effective and possible ways to continue the carbon cycle. Processes such as photochemical, electrochemical, and Thermochemical, for catalytic conversion of CO₂, which were harmful in two previous methods, are applicable. However, Thermochemical conversion of CO₂, is preferred for the production of hydrocarbons. Transition metal catalyst, for catalytic hydrogenation of CO₂, or synthesis gas into hydrocarbons have been reported. In some studies, FT process is controlled by simultaneous injection of CO₂, and synthetic gas to produce hydrocarbons. Iron-based catalysts for the FT process, for the production of hydrocarbons were promising, and efforts to increase the conversion has been done. Dorner has reported, the production of hydrocarbons by using ceria modified iron catalyst. They have reported that the addition of ceria, increases the conversion of CO₂, and selectivity for the C₂-C₅. Cobalt-based catalysts have been studied for FT process, and to produce long chain hydrocarbons, are not so attractive. Iron-based catalysts FT, for processes with high temperatures have been reported, while cobalt-based catalysts FT, have been reported for low temperature processes. CO₂ and CO in the process of hydrogenation, goes through different routes, and this difference is based on the nature of the catalyst. For example, catalysts based on iron, encourage the production of hydrocarbons with CO structure, while catalysts based on cobalt, directly converted CO₂ based on the reactivity limit wgs to methane, in addition to this, the base and the promoter also plays a role in the process of hydrogenation of play. Although attempts have been made to the production of hydrocarbons from CO₂, specific techniques and methods, is necessary to strengthen selectivity. [1]

Methanol

Methanol is an important chemical material that is used in many industrial processes. It was found that consumption of methanol from 2003 to 2008, increased by one per cent and two per cent from 2008 to 2013. Such an increase, clearly there is a high potential market, and efforts continuously to

meet global demand were to increase production. Methanol can be used directly as fuel, or additive fuel instead of gasoline, and can also be used as a basis for the synthesis of different chemicals. More recently, the focus has been on methanol to produce biodiesel (fatty acid methylesters), trans esterification of vegetable oils (Vegetable oils). Generally, methanol can be produced from CO₂/CO and H₂. Company MHTL, one of the largest producers of methanol, with a capacity of 4MMT / year is found that CO₂ is a better material for the production of methanol, to CO because active carbonates / formates form on the catalyst surface, which is desirable for reaction. It also observed that injections of small amounts of CO₂, facilitate the production of methanol from synthesis gas.



Production of methanol from CO₂ hydrogenation by using homogeneous catalyst is as good as heterogeneous catalyst. Homogeneous catalysts are generally worked at a lower temperature than the heterogeneous catalysts for methanol production. Design of homogeneous catalysts, to enhance the reactivity and selectivity, is one of the main challenges. It has been reported that hydrogenation of CO₂, through reactions RWGS, happens. Produced water, is prevented from increasing the percentage of conversion. Therefore, it is necessary to design catalysts in a way that have appropriate activity in low temperature, and control water production reducing. Recently leitner and colleagues, ruthenium phosphine complex molecule, as a homogeneous catalyst for enough hydrogenation of CO₂ to Methanol, have reaction under mild conditions. Copper-based heterogeneous catalysts for the reaction of methanol production were studied effectively. Catalyst performance in terms of selectivity and reduced water is still not clearly understood. Inexpensive catalyst that can overcome the process obstacles in converting CO₂ into methanol are needed. Crossing and his team

from the Research Center in Freiburg, Germany, studied and have developed a method for production of methanol from CO₂ and H₂, produced methanol is converted to gasoline through the process known as MTG. Methanol production under high pressure are done by combining CO₂ and H₂. Their goal is to control CO₂ emissions and catalyst design, to raise reaction rates. Metal oxides is used for reactions at low temperatures, and they found that nanoparticles containing catalysts are more active for methanol production. [1] Methanol is raw material for many chemical products. This material is considered key material in chemical group c1. Methanol is used for the manufacture of other chemicals including formaldehyde, acetic acid, dichloromethane and a number of others. Even prominent solvent has recently been used as a clean synthetic fuels. Barriers in the production of methanol was resolved when it became clear that CO₂ is effective in the reaction mixture for the production of methanol. The main reaction in the

hydrogenation of CO₂ are as follows:



Direct production of methanol from CO₂ and water



Both reactions are exothermic and reversible.

However, the price of such processes of hydrogenation of CO₂ is higher than using a combination of CO + CO₂ (cost). In other words, the use of CO₂, which in many reactions, is considered as waste gas, is needed. Methanol synthesis through the process of hydrogenation of CO₂, provides such an opportunity. Industrial methanol synthesis catalyst to produce by hydrogen, carbon monoxide and small amounts of CO₂ have been developed. Therefore, it is required that catalysts and processes for the use of larger volumes of CO₂ to be designed. This issue is discussed in numerous articles. A number of researchers, using a catalyst Cu/ZnO, is more effective than use of copper-based catalysts. Molar composition of Cu: Zn in industrial catalysts based on Cu/ZnO has been reported equivalent 70:30.

Fujitani has found a linear relationship between the methanol synthesis activity and the copper surface. A number of researchers have found that the copper catalyst, includes zirconium, is active in the synthesis of methanol from CO₂ and H₂. Orтели, be considered zirconium based catalysts stable in terms of mechanical and thermal. Development of a new active catalyst and in the presence of CO₂ not only to pick promoter (promoter) but also requires estimation of concentration. In the meantime, adding gallium, cerium, palladium, lanthanum and chromium to catalyst cu/zno/zro₂ has been more attention. Me in Article browsing, reported that the addition of Ga or Cr on the catalyst cu / zn / Al increases the activity of the catalyst compared to the cu level. Fornero has achieved the highest activity of methanol synthesis for 2wt%cu/6wt% Ga₂O₃/ZrO₂. Toyir during the evaluation of copper-based catalyst with promoters gallium, found that choice zno as a base, would be more appropriate choice than SiO₂. Fujitani claimed that copper surface of the catalyst cu / zno / Ga₂O include up to forty percent more than copper surface of sketetal copper catalysts for methanol synthesis added some cr₂O₃ the copper surface is described. Here we consider the effects of different promoters on the catalyst cu / zno / zro₂ for the process of synthesis of methanol from CO₂. Uniform methods, is selected by using citric acid to prepare the catalyst. During testing, the six different catalysts were prepared. Catalyst compounds, the surface of BET area and active area of cu are in Table (1). [3]

Catalyst cu /zn /zr with the distribution of pore volume and maximum diameter of 20nm is known. Adding gallium change the distribution of pore sizes. Holes with an average diameter, 3-11nm has appeared. This marked change in pore size (from 0.0812 cm³ / g to 0.1014 cm³ / g) have changed surface of S_{BET} characteristics area. Catalytic test results as a graph in Figure 4 is shown. Analysis catalytic results show significant improvement in catalytic properties, which is due

to the addition of promoters (promoters) to the catalyst cuo / zno / zro₂. Temperature dependence of CO₂ conversion percentage is in the figures. The highest percentage conversion is related to cr and la.

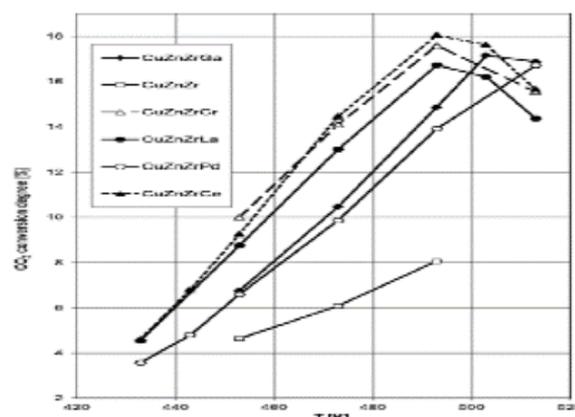
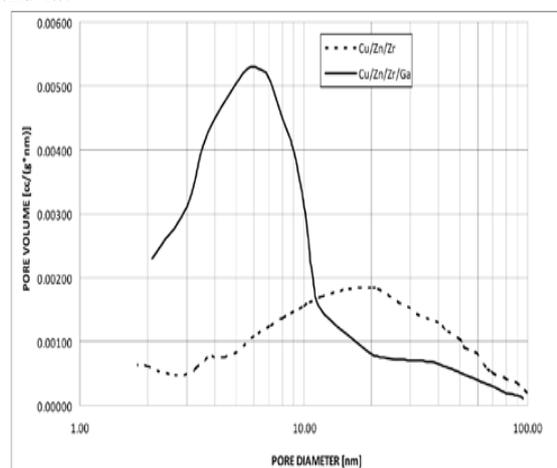


Figure 4. Catalytic test results

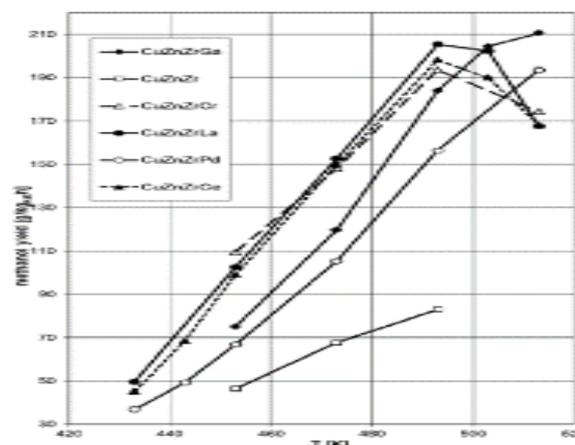


Figure 5 shows the dependence of Methanol Yield High temperature has positive effect on parallel reactions and more CO₂ be converted to co, and

Methanol Yield is reduced. For most active catalysts and ce, Ga and La additives, which reached higher converts percent at low temperatures, in Figure (5) Methanol Yield reached to the maximum value. The addition of a suitable promoter, has helpful consequences on the copper-catalytic properties. Depending on the type of used promoter, catalyst performance can be doubled. Most of the methanol catalyst with promoters la, cr or ce has been achieved at 493c temperature. For higher temperature, catalyst with promoter Ga reached the best condition. [3]

Dimethyl ether (DME)

Di methyl ether (CH₃OCH₃) (DME) is the first derivative of methanol as an alternative to LPG is used effectively. Traditionally, the dehydrogenation of methane leads to DME in the presence of acidic catalysts.



Because of the balance between products and reactants should be very careful in the usual reaction conditions. CO₂ hydrogenation or synthesis gas for the production of DME is an alternative.



Generally, metal oxides are used for the production of methanol and acid catalysts for the dehydrogenation reaction. According to the Korea Gas Technology Information Cooperative, this country received a contract from Unitec Technologies, up to set up a unit to produce 300,000 tons annually and catalytic DME, through a process of by using Tri-Reformed Syngas. Provided that the feed supply from Syngas generated from natural gas. They successfully accomplished this project in accordance with the one-step method (One-Step Model), with a capacity of 10 tons / day. Thermodynamically, CO₂ is much more stable than H₂O. This facilitates the formation of DME at higher temperature through the Feed 1: 1 CO₂ / H₂. In general, a two-step process (Two-Step Process) is going on, because methanol is thermodynamically through

dehydrogenation reaction is more favorable leading to the DME. Catalysts based on Copper (Copper-BASED) for selective production of methanol from CO₂ hydrogenation are known, Interestingly, membrane shell catalysts with central base made of copper (CU), have shown direct synthesis of DME from CO₂. [1]

Methane

Methane is used as fuel synthesized and generated through the hydrogenation of CO₂ with the help of Sabatier reaction. Methane can be obtained from hydrogenation co or CO₂. The end of the previous process is less exothermic process. Methanation called hydrogenation of co or CO₂, and used in units of ammonia, for purification of syngas, reduction of the remaining carbon dioxide in the hydrogen-rich gas refining and polymer electrolytes anodes.



Selective Methanation of CO in gas mixtures rich in CO₂ in recent years due to advantages as a sustainable alternative to selective oxidation of co, is taken into consideration. In this case CO because of its higher absorption energy than CO₂, strongly absorbed on the catalyst surface. Ease of access and low cost, has raised nickel-based catalysts (Ni) as a promising catalyst for industrial units Methanation. With increasing temperature, and occurrence of sintering, caused problems such as low active surface of Ni catalyst, and low catalytic activity. The problem may be resolved by selecting the appropriate supporters that are mechanically and thermally stable. Metals such as co, Ru, Rn containing catalysts have also been studied for Methanation. Particle size, operating temperature and supports, play major roles in the Methanation reaction. Expansion a new technology, which selectively produce methane from co/CO₂, is considered as significant. Active catalyst design, and determine the protocol for distributing the catalyst on a reasonable support, and extract the optimal operating conditions for such systems, is one of the main obstacles.

(Methanogens) methanogens also called Archea.) Normally a billion tons of methanol produced per year from CO₂. Hence the microbes, are expressed as one of the effective sources of methane production, And Europe has already started this process. Dry convert methane, in reaction to synthesis gas (syngas) (the ratio of H₂/CO₂ equivalent to one), is one of the main structures for the production of fuel.

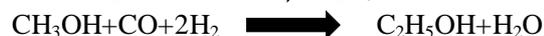


The main advantage of the dry reforming process, is the use of two greenhouse gases (CO₂, CH₄), therefore, it is preferred to Steam Reforming and partial oxidation of methane. Essentially, a dry reforming methane is an endothermic reaction, and requires high temperatures 700°C and an average conversion percentage. Dry conversion methane is a catalytic process, and the development and processing of a suitable catalyst, which is stable under high temperatures without loss of activity, and produce large amounts of synthesis gas, is a primary key of efforts in this reaction. Ni, because of the low price, ease of access, is used more effectively, than the noble metals such as Rh, Ru, Pd and Pt-containing catalysts that for this reaction are active. Coke formation which reduces the activity of the catalyst is the main obstacle to the use of Ni. It has been reported that support plays a crucial role in this reaction. Catalysts containing Ni, with different foundations, and associated promoters have been discovered, most recently Labrecque and Lavoie studied the activity of the catalyst Fe in the presence of electric current and realize that, the excess water vapor electron current playing an important and decisive role in converting methane. Develop a technology which improve carbon sequestration resistance, and the design of a suitable catalyst base and promoter, which possible reactions at low temperatures, the main challenges identified is converting CO₂ to methane. [1]

Ethanol

Ethanol (C₂H₅OH) is one of the greatest alternative fuels which are produced from by-

products of the fermentation process. Ethanol can be produced through the hydrogenation process co / CO₂.



Although the direct hydrogenation of CO₂ to C₂H₅OH is possible but indirect method of cloning methanol (Homologation) for ethanol production is underway. Hydrogenation of C₂ oxygen-containing compounds (such as acetaldehyde and acetic acid derived from synthesis gas, which can be obtained from CO₂) to produce ethanol are most common methods. The number of the center active catalysts, which can restore CO₂ to co-allowed entering group OH-, is the most important criteria for such a reaction. Composite catalysts because of their multiple nature are met the above criteria. Copper catalysts with potassium base, have shown good activity for this reaction, potassium here acts as a promoter for C-C bond formation reactions. Rh catalysts have also been studied and found that promoters play an important role in the selectivity of ethanol. Attempts to reform the catalyst is made to meet the requirements of the reaction conditions, catalysts containing Rh have most important result. Basically catalysts that are active, to produce ethanol from synthesis gas and R_wgs, for methanol homologation reaction are also active. Without any doubt it is proved that best replacement for fuel and ethanol enzyme products. Catalyst design, with production so sure, ethanol from CO₂, is the challenging task for a number of researchers. [1]

Formic acid Formic acid (HCOOH) is the simplest carboxylic acid that its global production in 2009 is estimated to be about 720,000 tons. This acid has a variety of applications including fuel cells. Commercially, formic acid is produced through four processes. Hydrolysis of methyl formate, hydrocarbon oxidation, hydrolysis formaldehyde and formic acid preparation from formate. Direct hydrogenation of CO₂, is the best alternative reaction to produce formic acid, homogeneous transition metal catalysts and

catalyst combination zinc selenide / zinc telluride have been included most important studies on the subject. British Petroleum has developed a multi-step process, using the Ru complex as a catalyst, in the presence of nitrogen-containing base. Although there have been efforts to produce formic acid, with the help of homogeneous catalysts, recent studies predict that formic acid through the use of heterogeneous catalysts with high selectivity of CO₂ is produced. Such a secure method of production that is the biggest task and challenge of researchers. [1]

Fuel additives.

Attempts to produce fuel additives from CO₂ has been done without the use of hydrogen sources. Generally, this non-hydrogenation process leads to the production of carbonate and the carbamate. The carbonate can be considered as an additive fuel. From the reaction of CO₂ with methanol, dimethyl carbonate was produced. Methanol is produced from hydrogenation of CO₂, second reaction with CO₂, dehydrogenation and eventually be converted to dimethyl carbonate. Also oxygenation of CO, which is produced with the help of RWGS from CO₂, is another way to produce dimethyl carbonate. This section pays to non-hydrogenation conversion process of CO₂ or (CO) to dimethyl carbonate. Dimethyl carbonate, is a linear alkyl carbonate, which is considered as potential gasoline additive. There are several methods for the production of dimethyl carbonate from methanol. Toxicity of phosgene gas and hydrochloric acid production, dimethyl carbonate production process obstacles is phosgene-based processes. Alternative methods is preparation CO and CO₂ as raw material for the production of DMC from methanol. Lummus Technology has developed a method in which reaction between methanol, carbon monoxide and oxygen in the presence of a copper catalyst leading to the DMC and water. Injecting small amounts of HCL to the reactor stabilize the activity of the catalyst and by-products produced (CO₂) can be used to produce CO. Production of DMC, by using CO₂, and methanol is a better way. It was found that the

thermodynamic limitations of the reaction, the catalyst deactivation, and hydrolysis of DMC by produced water, leads to low conversion of methanol, and low production of DMC. Selective synthesis of DMC, under the influence of either regions, either acidic or basic areas on the catalyst surface. The reaction temperature is an important factor for the production of DMC. At higher temperatures, due to the decomposition of DMC, reduced methanol conversion and DMC selectivity, and resulted in the production of byproducts. Various catalysts for the production of DMC from CO₂ and methanol reaction have been reported. Several attempts to reform the catalyst, and add co-reagents, to increase the selectivity of DMC has been done. Strengthening of methanol conversion, with an increase in the production of DMC, for the commercialization of this production are essential. [1]

Biochemical derivatives

Biomass (Biomass) is usually constituents of Lignocelluloses and related issues, oils and fatty acids and proteins. It is estimated that biomass produced annually 170BMT. 4% of this production is used in food production. Biomass use in the production of CO₂ is to produce energy. Atmospheric CO₂ concentration is increasing every year and in 2011 was 391ppm. CO₂ concentration can be controlled by turning it into valuable products such as fuels. Fuel shortages caused to be considered this conversion. [1]

CONCLUSION

Methanol is the most important product of the revival of CO₂ that can be achieved, because conventional methods can also be converted to other chemical products and fuel. There are mixed reactions to convert CO₂ into methane, the most important reaction, is Sabatier Process reaction, where CO₂ and H₂ at high temperature and pressure in the presence of nickel catalyst are converted to methane and water.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

It was discovered by the French scientist Paul Sabatier. This process

had been proposed as a key step in reducing the cost of discovery of life on Mars. After water production, with hydrogen coming from Earth and CO₂ that was taken from the atmosphere of Mars, oxygen is obtained from the decomposition of water (electrolysis) that can be used as rocket fuel. Stoichiometry of the progress of the reaction is 1: 8 (8 pounds per pound of hydrogen to oxygen for the fuel needs). And if would just send light hydrogen and heavy oxygen achieved at the site, leading to a significant reduction in the weight of cargo that was supposed to be sent to Mars. However, the expensive techniques of electrolysis process, in Sabatier process for separating hydrogen and oxygen from water, is not affordable for testing road cars. In other words electrochemical systems used, for the revival of CO₂ to methane or methanol, according to consumer costs (including fuel and high-potential electrodes), compared with the value of products, have not Capability. Catalytic hydrogenation of CO₂ to methanol due to the high temperature reaction is not too much attention and satisfaction. Even electro catalytic restoring of CO₂ to formic acid or CO in the presence of a catalyst pd, pt and Hg was not affordable. The cost of producing methanol from CO₂ production processes, such as high-temperature catalytic reaction in the vapor phase CO₂, with water vapor and restore the electrochemical /thermochemical CO₂ has no economic value. Such endothermic reactions, is the main cause of be uneconomical recovery of CO₂ to methanol and other chemicals. According to the thermodynamic state of process of reduction of CO₂, the revival of CO₂ that would be affordable if renewable energy such as solar energy should be used as an energy source. In fact, for a long time, has been studied, photosynthetic plants, to identify the details of its mechanism, and then generalize their knowledge to provide energy for the needs of the community. Solar energy can be used to convert co:

1. Artificial photosynthesis by loading homogeneous and heterogeneous systems

2. The revival of electrochemical, by using solar electrical power

3. The hydrogenation of CO₂ with hydrogen generated from the sun (eg, using an electrochemical cell)

Although these methods represent the ability to convert CO₂ to CH₃OH and HCOOH, HCHO, CH₃OCH, CO and so on, but suffer from limitations such as poor performance, lack of stability of associated catalysts, and semiconductors in water, the uncertainty of electrolyte, cathode inferior materials recovery, and so on. [5]

Results, Challenges and Outlook

1. CO₂ concentration in the atmosphere is increasing every year, controlling the concentration can be controlled by turning it into valuable products such as fuel. Fuel shortages caused that the conversion be highly regarded.

2. In the production of methanol from CO₂ and use of the copper catalyst, adding promoter improves the catalytic properties. In this regard, the best catalysts CuO/ZnO /ZrO₂ and the best promoters La, Cr and Ce been detected.

3. Such endothermic reactions, is the main cause of be uneconomical recovery of CO₂ to methanol and other chemicals.

4. Due to the thermodynamic state of process of reduction of CO₂, its revival would be affordable if renewable energy such as solar energy should be used as an energy source.

5-In CO₂ conversion to CH₄, the main challenge is to design a catalyst with suitable base and promoter, which makes it possible to perform reaction at low temperatures.

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Table (1) surface of BET area and active area of cu

Catalyst	CuO %wt	ZnO %wt	ZrO %wt	Promoter	Promoter concentration %wt	S m ² g ⁻¹	Cu active area m ² g ⁻¹
Cu/Zn/Zr	62.4	25.0	12.6	—		20	6.1
Cu/Zn/Zr/Ce	65.3	26.3	.5	Ce ₂ O ₃	3.9	15	7.9
Cu/Zn/Zr/Cr	65.2	26.3	7.7	Cr ₂ O ₃	0.7	24	8.7
Cu/Zn/Zr/Ga	65.3	26.3	4.5	Ga ₂ O ₃	3.9	21	8.7
Cu/Zn/Zr/La	65.3	26.3	4.5	La ₂ O ₃	3.9	16	7.3
Cu/Zn/Zr/Pd	65.2	26.3	4.5	Pd ₀	3.9	24	6.7

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Catalyst	Temperature, conversion degree and selectivity for maximum methanol yield				Catalyst activity parameters for T=473 K		
	a %	W_{MeOH} g{(kg h) ⁻¹	S_{MeOH} %	T K	a %	W_{MeOH} g{(kg h) ⁻¹	S_{MeOH} %
Cu/Zn/Zr	8	83	61	493	6	68	73
Cu/Zn/Zr/Ce	15	202	69	493	12	146	65
Cu/Zn/Zr/Cr	18	194	68	493	14	148	69
Cu/Zn/Zr/Ga	17	211	71	513	10	120	74
Cu/Zn/Zr/La	17	205	70	493	13	152	67
Cu/Zn/Zr/Pd	17	199	73	513	10	105	80