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Catalytic Reduction of Carbon dioxide to Methanol as a Fuel, A Mini Review

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ABSTRACT

CO_2 being a major hothouse gas is primarily emitted to the environment by combustion of fossil fuels. Technological approaches have given carbon dioxide a second life and enabled us to synthesize numerous industrial fuels, domestic fuels and other valuable products by using the process known as catalytic renovation of CO_2. This paper discusses current advancements in the selection and production of many types of catalysts used in catalytic conversion of CO_2. The catalysts are compulsory due to high stability of carbon dioxide molecule. Comparison between conventionally used catalysts and advanced catalysts is shown with respect to carbon dioxide conversion and methanol selectivity. Major research on homogenous catalysts, heterogenous catalysts, photocatalysis, electrochemical methods and polymer catalysts are highlighted in this paper.

Keywords: CO_2 conversion, Catalytic conversion, Chemicals/fuels production, Catalytic processes, Methanol production.

Introduction

High emission rate of carbon dioxide by mankind to fulfil his energy requirements using non-renewable resources has increased the carbon dioxide level in atmosphere up to a life threating level [1]. CO_2, which is a colourless gas, at lower concentrations (250-400ppm) is an odourless gas, but as its concentration increases and go up to 40,000ppm, it becomes harmful for humans. Higher concentrations of carbon dioxide can be the cause of various health effects like headache, higher blood pressure, dizziness, restlessness and even coma. CO_2 is the major gas causing global warming because it remains in the earth's atmosphere for long time. Almost 75-76% of contribution in the overall warming effect is of CO_2. All other greenhouse gases have different capacities for absorbing heat in the atmosphere and thus contributing to global warming, but CO_2 is most important one, because all other greenhouse gases are scaled to the impact of CO_2. This is called Global Warming Potential (GWP). GWP of CO_2 is one. Carbon dioxide is the gas which is most responsible for the earth's climate change. As the amount of CO_2 in the atmosphere increases due to which temperature of atmosphere also increases. This increase in the temperature is everlasting for 1000 years even after the emissions of carbon dioxide stop. The main categories of emission of CO_2 in environment are,

Stationary Sources:

- Power plants.
- Combustion of fossil fuels.
- Industrial processes as cement production, Hydrogen gas synthesis, combustion of biomass etc.

Mobile Sources:

- Residential and commercial buildings
- Automobiles as trains, buses etc.

Carbon Dioxide could not be considered as a surplus product, the only advantage is that, with social imagination, can be utilize in a maintainable mode, since sustainability is at the convergence of ecological and intergenerational management. CO_2 can also be used as a feedstock to yield various chemicals including dimethyl ether, methanol and synthetic fuel etc.

Chemical activity of CO_2 is low at temperature below 200°C but in presence of suitable catalysts and operating conditions CO_2 can be activated by decreasing the activation energy required for reaction. As CO_2 is thermodynamically too strong, its conversion to various chemicals like CO, CH_4, or C_2H_4 is very tough, and formation of effective CO_2 conversion catalyst is a significant task.

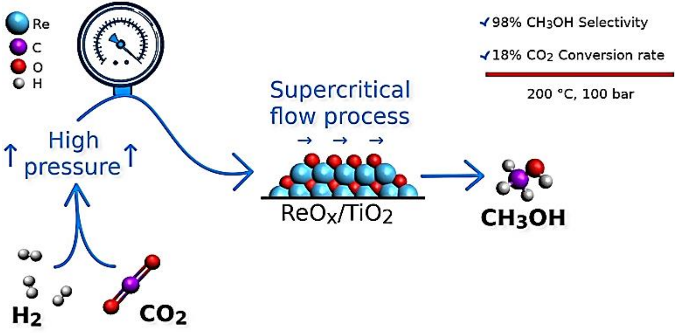

Figure 1. Graphical Representation of Carbon Dioxide Conversion to Methanol. Cloned with authorization from ref.[2]

CO_2 is the major component to be used as a basis in the preparation of carbon based compounds or C_1 molecules like formic acid and methanol is gaining importance nowadays [4]. CO_2 is used to increase the sustainability of products as feedstocks for different processes [5]. Choosing a CO_2 consumption system requires the provision of CO_2 net and waste reduction related to conservative methods of creating the identical end product, it is essential to be efficient, and must not release any further future social glitches to resolve [6]. The improvement of the catalytic efficiency depends upon the attached phenolic groups which is very favorable for different processes under normal conditions [7]. Ethanol, methanol, formic acid etc. can be produced by non-natural photosynthesis method [8].

Great exertions have been dedicated to justifying the CO_2 growth in the air. Though, desorption and compression of CO_2 require additional energy. For dodging this issue, carbon capture and utilization (CCU) plan has been projected whereby CO_2 can be seized and in situ activated at the same time to contribute in the following alteration under slight situations, providing useful products [9]. Thermo, photo and electro chemical process are used to convert CO_2 into fuels. Selectivity of catalysts is very important since it depends on the methodology [10, 11]. From carbon dioxide the production of cyclic carbonates can be attained in which the functional groups like carboxyl an hydroxyl are used as catalyst [12].

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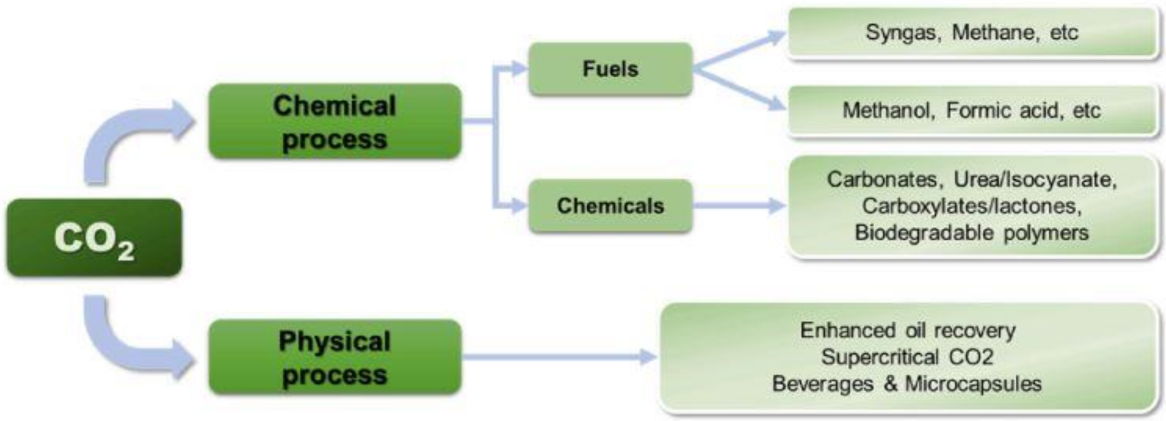

Figure 2 Path for the Carbon Dioxide utilization. Cloned with authorization from ref.[3].

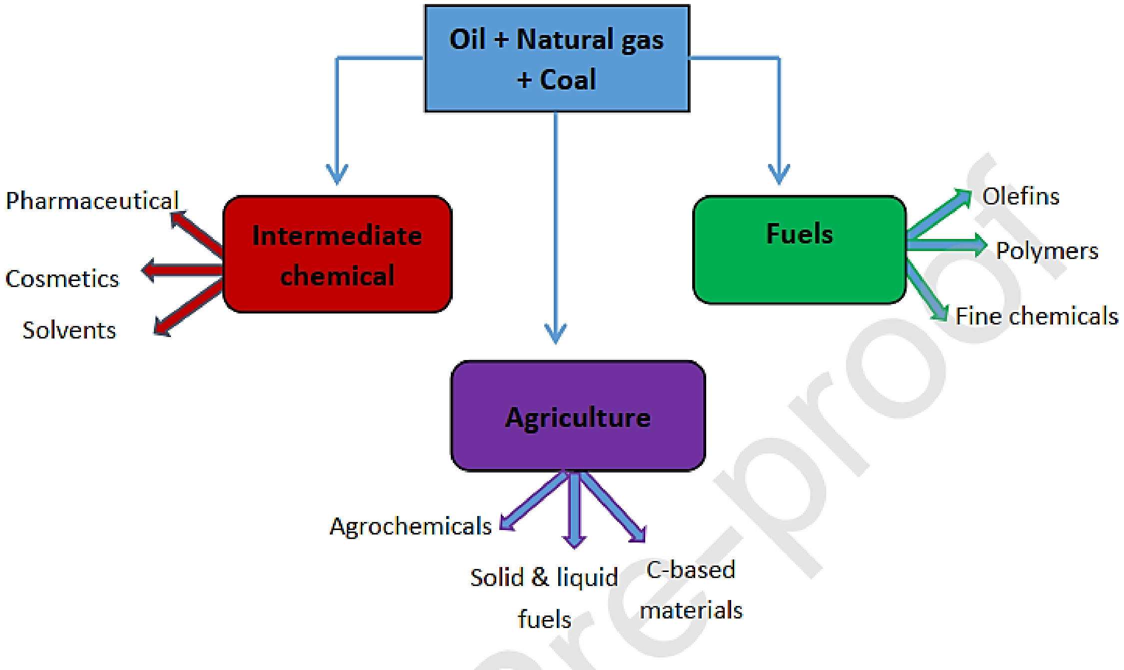

Figure 3 schematic of the materials and fuels made of fossil carbon [13]

Why the need of CO_2 conversion to chemicals/fuels?

Worldwide energy consumption has increased because of population and industry growth, and manmade CO_2 releases have grown quickly as the major energy sources used today are fossil fuels. Increasing the level of CO_2 emissions into the air leads to global warming and a lot of ecological problems [14]. The normal temperature has risen by 0.8° centigrade over the past 70 years. International exertions to decrease CO_2 releases are proposed, as is the international agreement in Paris. Beside this various study have engrossed on the growth and use of energy sources (Renewable), reducing fossil fuel requirement, and the development of technology for capturing and utilizing CO_2. The use of CO_2 will decrease greenhouse gases into air and in the oceans that can be harmful, and CO_2 can also be used to harvest important substances [6]. Solar energy is very efficient to attain useful fuels by converting carbon dioxide in photocatalytic cells [15]. Processes which convert CO_2 to oils deliver great advantages to decrease an important quantity of CO_2 and stock renewable fuel [16]. Including these, the process in which carbon dioxide is recycled and methane is generated as a renewable source is known as power-to-gas technology. Altering CO_2 into energies and other CO_2 resulting substances by electrically powered methods are a good strategy for handling these energy problems, with the addition that they can assist to reduce level of CO_2 in atmosphere. But the growth of such procedures is not so easy, as CO_2 is very steady and comparatively unreactive molecule. Catalysts are crucial to trigger CO_2 and initiate its conversion into anticipated products

[17]. The most significant challenge is the greenhouse gases nowadays. So, the method to lessen greenhouse gas releases must be by means of carbon causes which do not create additional CO_2 to the air [18].

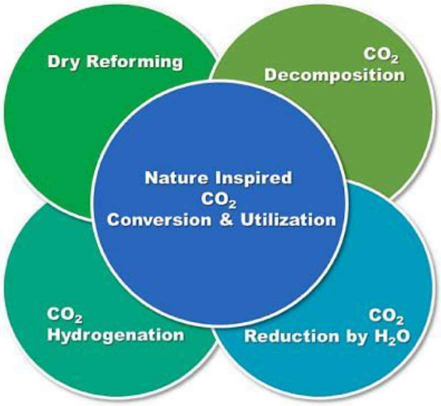

Figure 4 Carbon Dioxide Cycle. Cloned with authorization from ref.[3].

Mechanism of CO_2 Conversion

Carbon Dioxide can be converted into useful fuels and their precursors like formic acid, methanol, carbon monoxide, ethylene and methane by electrochemical process in which the reaction occurs in the cell which is electrolytic having CO_2 reduction at cathode [19].

The main catalytic reaction is:

$$CO_{2(g)} + 3H_{2(g)} \xrightarrow{\text{catalyst}} CH_3OH_{(g)} + H_2O$$

The intermediates which take part in the process procedure for hydrogenation of CO_2 are $HCOO^*$, $HCOOH^*$, $CH_3O_2^*$,CH_2O^* and CH_3O^* [20].

The reaction mechanism is [21].

$$H_{2(g)} + 2^* \rightleftharpoons 2H^*$$
$$CO_{2(g)} + * \rightleftharpoons CO_2^*$$
$$CO_2^* + H^* \rightleftharpoons HCOO^* + *$$
$$HCOO^* + H^* \rightleftharpoons HCOOH^* + *$$
$$HCOOH^* + H^* \rightarrow H_2COOH^* +*$$
$$H_2COOH^* +* \rightarrow H_2CO^* + OH^*$$
$$H_2CO^* + H^* \rightarrow H_3CO^* + *$$
$$H_3CO^* + H^* \rightarrow CH_3OH^* + *$$
$$CH_3OH^* \rightarrow CH_3OH_{(g)}$$
$$OH^* + H^* \rightarrow H_2O^* +*$$
$$H_2O^* \rightarrow H_2O_{(g)} +*$$

Catalysts used for CO_2 Conversion to MeOH

There are different types of catalysts used for methanol synthesis:

- Homogenous catalysis
- Heterogenous catalysis
- Photocatalysis
- Electrochemical catalysis
- Polymer catalysis

Homogenous Catalysis

By the term homogenous catalysis, we mean a chemical reaction in which the reactants that are taking part in the reaction and the catalyst are in the same phase. For instance, if the reactants are in liquid phase, catalyst will also be in liquid phase, and same concept applies for solids and gases. The advantage of using homogenous catalyst is that it can be easily diffused into the solution of the reactants, so the heat and mass transfer can easily take place. However, the main disadvantage of homogenous catalyst is that it can be difficult at times to remove it from the solution to reuse it [22]. The homogenous catalysis of CO_2 can be achieved at the lowest possible temperature of 80℃. So, this means that homogenous hydrogenation is more effective than heterogeneous and can be done under milder conditions. For more cost-effective production of carbon dioxide to methanol, non-noble based catalysts should be used. For instance, copper, cobalt, manganese and iron etc. [23]. Reactants H_2 and CO_2 are present in the gaseous state. So, for homogenous catalysis of CO_2 to methanol, the catalysts will also be present in gaseous state. Some of the homogenous catalysts that are used for the catalytic hydrogenation of CO_2 are [24].

1. Ruthenium phosphine
2. Cobalt catalyst
3. Cascade catalysis
4. Manganese catalyst

The ruthenium phosphine system comprises ruthenium (III) acetylacetonate and the tridentate ligand Triphos (1,1,1-tris (di-phenyl-phosphino-methyl- ethane) along with an organic acid which in this case was MSA (methane sulfonic acid). This acid is used to increase activity of MeOH formation. The pressure of carbon dioxide was kept at 10bar, and that of H_2 was 30bar. The temperature of this reaction was 140℃ [25]. The result of this study was that CO_2 can be hydrogenated to methanol using a homogenous catalyst under mild conditions [26].

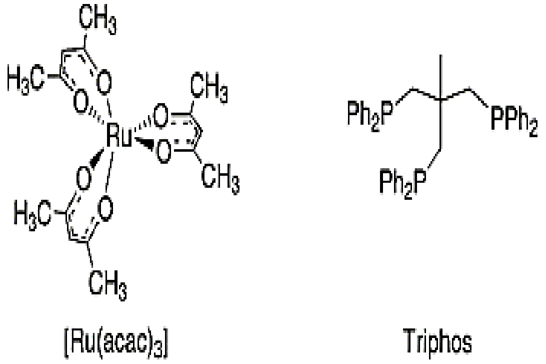

Figure 5 Structure of Ruthenium Phosphine. Cloned with authorization from ref. [27].

The homogenous iridium catalyst was used after ruthenium phosphine complexes, for indirect MeOH production from carbon dioxide at normal temperature. But, as iridium is an expensive noble metal, so for cost effective production, non-noble metals such as Copper, Iron and Cobalt were proposed to use. The research done for cobalt catalyst was made basis for further investigations [28]. In cascade catalytic reaction of CO_2 to get methanol as product, three different catalysts are used in sequence. That's why it is called cascade catalysis. The three catalysts are: $(PMe_3)_4Ru(Cl)(OAc)$, $Sc(OTf)_3$ and $(PNN)Ru(CO)(H)$. Due to the reaction of carbon dioxide and hydrogen in the existence of first two catalysts at 75℃ to produce methyl formate. ($HCOOCH_3$). Then, the temperature is increased to 135℃ and the third catalyst is introduced in the vessel and methanol is produced. The turnover number (TON) of the cascade catalysis is 21 [29].

$$CO_2 + 3H_2O \xrightarrow[75℃]{A,B} HCOOCH_3 + H_2O$$

$$HCOOCH_3 \xrightarrow[135℃]{C} CH_3COOH$$

Where A, B and C catalysts' structures are shown below:
TON can be demarcated as the relationship between the number of molecules which reacts to the number of active species of catalyst. TON is the highest quantity of substrates molecules that can be converted to product per unit time by the catalyst activity[30]. The unit of turnover number is per second [31]. For the reduction of CO_2 to MeOH using manganese Mn(I)-PNP pincer as a catalyst consists of two steps:

1. CO_2 and H_2 react to form N-formyl of amine
2. Reduction of formamide to methanol

The Mn pincer catalyst acts in both of these steps. Yield of methanol is up to 84% and the TON is [32].

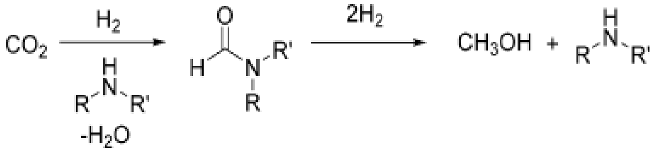

Figure 6 Manganese Catalysed Reaction. Cloned with authorization from ref. [33].

Heterogenous Catalysts

Synthesis of methanol was initially carried out using Cu coupled with ZnO catalysts in 1946, in which Cu is catalyst and ZnO behave as a promoter in the catalyst. High stability of CO_2 deactivates the conventional Cu-ZnO catalyst[34]. Due to low activity, conversion to methanol remains less than 20%. Another primary drawback was the production of excess water during methanol production reactions, large amount of water increases the probability of crystallization of Cu and ZnO along with production of undesired products [35]. In order to address all these problems make the 'Methanol Economy' as much as possible, an extensive research and systematic study is done and still continued for improvement in catalyst activity, its properties, morphology and conversion [36]. In order to get results essential for the improvement in the choice of the catalyst, it is of remarkable significance to comprehend the insights of Cu-ZnO reaction mechanism [37]. Experiments showed that the overall increase in MeOH production using non-conventional catalysts in the order Au/Cu(111) < Cu(111) < Pd/Cu(111) < Rh/Cu(111) < Pt/Cu(111) < Ni/Cu(111). On Au/Cu(111) and Cu(111). Most useful and promising method of conversion of carbon dioxide after its increased concentration in the environment as a greenhouse gas is presented using $Cu/ZnO/Al_3O_2$ also known as conventional cupper based catalysts providing one pass 95% conversion and 98% methanol selectivity at 360 bar pressure [38]. Using Cu/ZnO catalyst, methanol and carbon monoxide are produced in parallel pathways as a result of hydrogenation of CO_2 and reverse Water Gas Shift reactions, but formation rate of CO decreases with time and of methanol increases in a slow monotonic manner [38]. The synergistical interaction of binary Cu-ZnO catalyst is categorized in six different ways:

1. Electronic interaction of Cu and ZnO
2. Development of Cupper cations on ZnO phase
3. Structure of Cu-Zn pair alloy
4. Schottky-type Junction effects at the metal oxide interface
5. Specific reaction at metal oxide interface
6. ZnO stabilizes the active Cu [39]

By far cupper is assumed to be the most effective catalyst but the activity of cupper enhances when the metal surface is partially covered by oxygen. For that purpose ZnO promoter is used to provide the higher reducing potential as a result of which more oxygen vacancies spread over Cu. Deficiency of oxygen vacancies makes the ZnO surface wetted with Cu, on the contrary, under oxidizing conditions, ZnO does not get wet by Cu [40]. Effect of Ru, Rh, Pd and Ag as promoting metals on Cu/ZnO catalyst is investigated and palladium and silver supported on Al_2O_3 (Pd/ Al_2O_3 and Ag/Al_2O_3) are found to be most effective. These catalysts are stable against poisoning by water and the promotion in carbon dioxide hydrogenation is due to hydrogen spill over from palladium to cupper. Promotion in conversion was achieved by using Pd/ Al_2O_3 + $Cu/ZnO/Al_3O_2$ physical mixtures and Pd impregnated using $Cu/ZnO/Al_3O_2$ catalysts[41]. Carbon Nanotubes abbreviated as CNTs are carbon cylindrical rolled-up sheets used to enhance the activity of Cu-ZnO-Al_3O_2 catalyst. These nanotubes have property of adsorbing large amount of hydrogen at normal conditions having a temperature range from 298 K upto 573 K[42]. Experiments are carried out for different percentages of CNTs added to Cu–ZnO–Al_2O_3 catalyst versus CNT-free Cu-ZnO-Al_3O_2 catalyst using H_2-TPD at 492 K and 5 MPa. Results show 25% increase in conversion after using 15.5% CNTS as compared to CNT-free Cu-ZnO-Al_3O_2 catalyst [43]. CO conversion and CH_3OH growth rate at alternative temperatures over a series of catalysts are shown below in figure 6.

(a) $Cu_6Zn_3Al_1$-12.5%CNTs
(b) $Cu_6Zn_3Al_1$-10.0%CNTs
(c) $Cu_6Zn_3Al_1$-15.0%CNTs
(d) $Cu_6Zn_3Al_1$-0%CNTs

Cu coupled with ceria is a strong catalyst for RWGS reactions (a), then further reduction of carbon monoxide to MeOH by CO hydrogenation (b) MeOH synthesis by hydrogenation of CO.

$$CO_2 + H_2 \rightarrow H_2O + CO \dots\dots\dots (a)$$
$$CO + 2H_2 \rightarrow CH_3OH \dots\dots\dots (b)$$
$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \dots\dots\dots (c)$$

It follows the following mechanism deposition of carbon dioxide is facilitated at basic sites of ceria where Ce^{3+} stabilizes the $CO_2^{\delta-}$ using strong inverse metal/oxide interactions. The oxygen vacancies favour the response of $CO_2^{\delta-}$ and surface hydroxyls to form intermediate ($HCOO^-$) species [45]. Experimental results are comparable with the theoretical research based on alteration of CO_2 to MeOH using CeO_2(110). The reaction conditions are the pressure of hydrogen and carbon dioxide is 4.5 atm and 0.5 atm respectively. [46]. In comparison with cupper-zinc catalysts, reaction can take place at temperature below 60 deg C in case of ceria supported cupper catalyst [47].

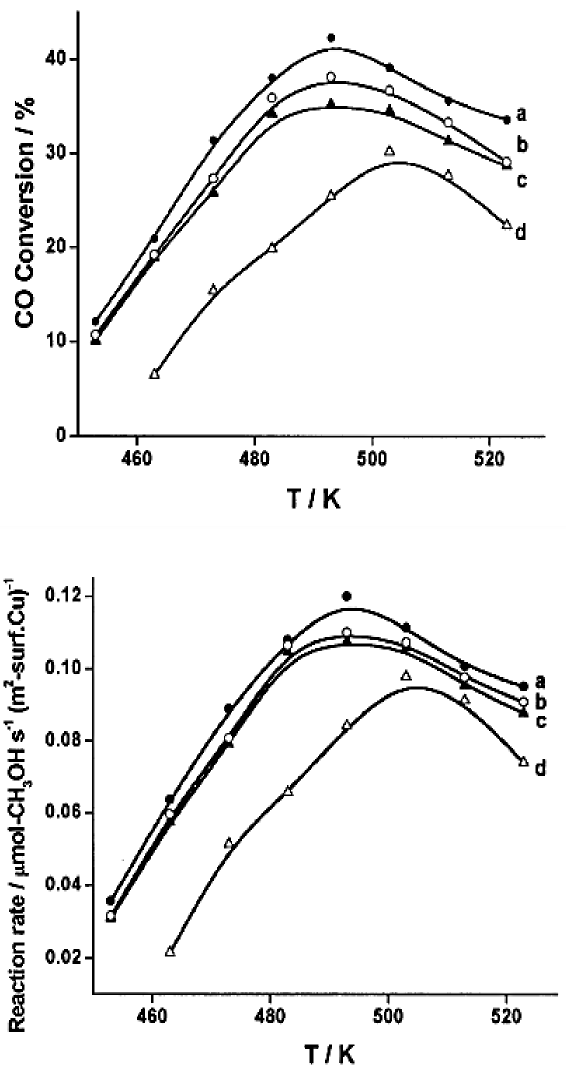

Figure 7. : Conversion versus Temperature over Series of Catalyst listed above. Cloned with authorization from ref.[44]

The catalytic performance of CeO_X-Cu(111) turned out to be highest among ZnO coupled with Cu(111) and Cu(111) as a result of surface study by catalyst using ambient pressure X-ray photoemission spectroscopy and infrared reflection absorption spectroscopy. This is because of greater accumulation of nanoparticles of CeO_X on Cu surface than ZnO, showing the considerable impact of interfacial interactions between metal and oxide [48]. Decrease in activation energy is showed in the figure 8,9 as a result of using CeO_X/Cu(111), ZnO/Cu(111) and Cu(111). Results show highest decrease in activation energy for CeO_X/Cu(111).

MeOH. Cloned with authorization from ref. [49].

After a series of experiments for the synthesis of Ni-Ga catalysts with different ratios of Ni and Gallium, Ni_5Ga_3 catalyst is discovered to be another considerably selective and yielding greater production of methanol in contrast with the typical heterogenous catalysts $Cu/ZnO/Al_2O_3$. Silica supported Ni-Ga based catalyst has enabled the conversion of CO_2 into MeOH at ambient pressure along with the reduced rate of RWGS (Reverse Water Gas Shift) that is the primary source for the production of CO as a by-product in case of conventional utilization of catalyst [50]. Characterization of Ni-Ga catalysts using XRD and TMD followed by conversion of carbon dioxide by reacting with hydrogen is compared with cupper-based catalyst $Cu/ZnO/Al_2O_3$. Production of methanol is highest for Ni_5Ga_3 /SiO_2, it is even higher than $Cu/ZnO/Al_2O_3$ at temperature greater than 220 ^oC.

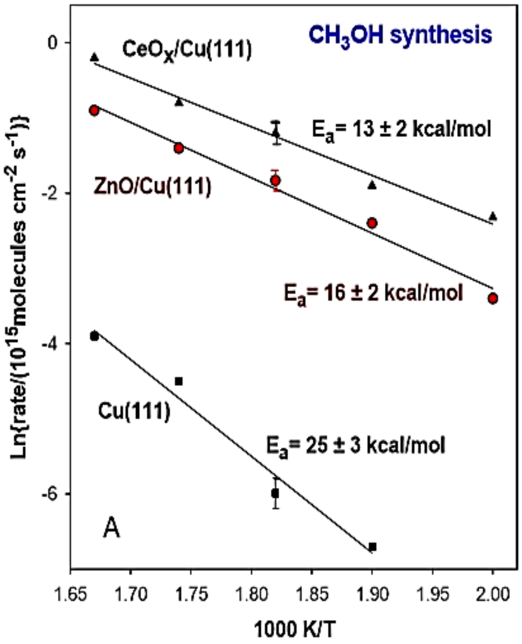

Figure 8. Arrhenius Plots for the Reduction of CO_2 to MeOH. Cloned with authorization from ref. [49]

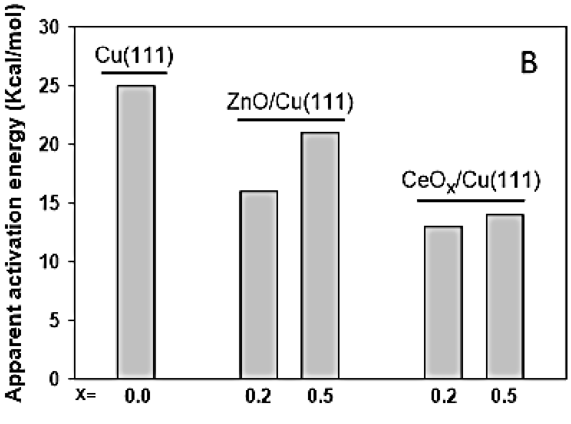

Figure 9. Activation Energies for the reduction of CO_2 to

The greater efficiency of Ni-Ga catalyst is because it does not need any promoter as Cu requires Zn as a promoter for activity. Selectivity of Ni-Ga catalysts, except Ni_3Ga, towards Methanol and all other products less carbon monoxide, is higher than Cu/Zn catalyst because of greater number of active sites of Ni and Gas available as compared Cu/Zn active sites. CO production is less for Ni_5Ga_3 /SiO_2 because Gallium rich sites facilitates the MeOH synthesis whereas Ni rich sites facilitates CO and Methane production. When the Ni rich sites get poisoned by C, the sites get blocked and no reaction (RWGS) further takes place, hence no CO is produced. On the other hand, cupper does not form a strong bond with C, hence rate of RWGS is higher in case of cupper-based catalysts.

Morphology and structures of three main types of Ni-Ga catalysts are studied using different characterization techniques as SEM, WAXRD, SAXRD, TEM, XPS. Three different catalysts synthesized were:

1. Ni-Ga alloy Catalyst
2. Ni-Ga mixed oxide Catalyst
3. Ni-Ga/ mesosilica – Showed highest efficiency in production of methanol by conversion of carbon dioxide.
4. Methanol is produced at high pressure at centralized production units as coal fired, gas and nuclear power plants, hydro-electric dams and large solar power stations. But decentralized hydrogen production using solar energy based on silicon supported Ni_5Ga_3 catalyst requires smaller distributed units, less complicated infrastructure and can operate on low pressures with better quality of fuel by reducing the RWGS reactions activity [51].

Photocatalysis

Converting the CO_2 to MeOH not only reduces the greenhouse effect in our environment but also important for chemical manufacturing industry as methanol is later used in medicines and different chemical substances. To get these results and benefits, CO_2 is converted into methanol using copper loaded with carbon and modified with titanium oxide using ultraviolet and sunlight [52]. The photocatalytic conversion of CO_2 is not only limited to Cu-Ti catalyst, but it can also be used with other various combination of catalysts made from metals in transition group. It can also be stated that alone photocatalysis cannot be used to reduce the CO_2 to MeOH, but the provision of radiations and natural sunlight enhances the chemical reactions including the use of other catalysts[53]. Hence Graphene-TiO_2 is also used and in the incidence of visible light, the chemical reaction is enhanced, and the process is made quicker.[54].

Another combination of catalysts that are used in the presence of UV light are CuO-loaded $NaTaO_3$ catalysts. These catalysts were discovered in 1979 and after a few years, it was observed that in the presence of radiations with wavelength of about 365nm along with these catalysts, carbon dioxide was easily converted into methanol[56]. However, it must be noted that temperature is the key parameter in the whole process, which must be controlled between 25 °C to 28 °C. Here is the schematic diagram of the reaction [57].

Recently, for efficient reduction and conversion of CO_2 to MeOH has drawn attraction of many people related to the chemical field as this process results in many useful products like methane, methanol etc. Carbon dioxide also be converted into MeOH by using Zinc Ferrite doped with Tin oxide (p–n) heterojunctions under visible light irradiation[59]. This process is very essential in industrial process as it gives us the highest amount of yield with very less impurities. That’s why this photocatalyst based reaction is used in solar fuel-based devices and results in saving a lot of energy. Here is the mechanism of the reaction [60].

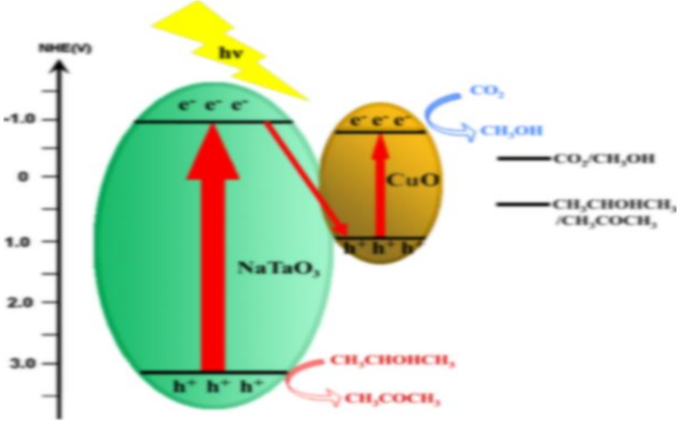

Figure 10: Graphic Diagram for Photo-catalytic Transformation of CO_2 to MeOH using CuO based catalysts. Cloned with authorization from ref. [58].

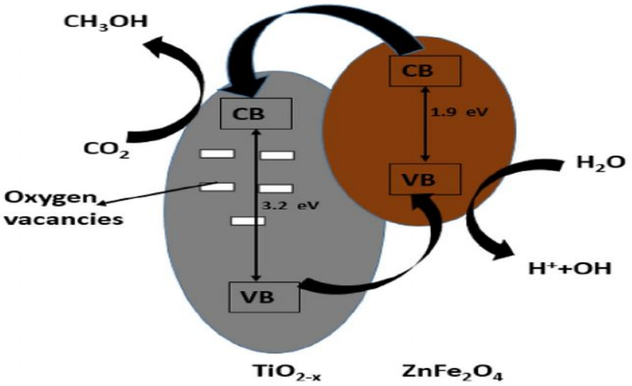

Figure 11: Photocatalytic Reduction of CO_2 by using Zinc based hybrid of iron with tin oxide Catalyst. Cloned with authorization from ref.[61].

CO_2 can also be converted into MeOH by using visible light active Bismuth Vanadate ($BiVO_4$) photocatalyst. The mechanism for this process is simple as CO_2 can be easily dissolved in water as Hydrogen carbonate and carbonate ions and the overall reaction can be written like this:

$$\mathrm{n-Ti}O_2 + 6\mathrm{h}\nu \rightarrow 6\mathrm{ecb} + 6\,\mathrm{hvb}$$

$$6\mathrm{H} + + 6\mathrm{ecb} \rightarrow 6\mathrm{H}$$

$$\mathrm{CO_2} + 6\mathrm{H} \rightarrow CH_3\mathrm{OH} + H_2\mathrm{O}$$

The net reaction is given by:

$$2\mathrm{CO_2} + 4H_2\mathrm{O} \rightarrow 2CH_3\mathrm{OH} + 3\mathrm{O_2}$$

It is vital to mention here that nano particles of catalyst were used to provide more surface area and enhance the catalytic activity [62, 63].

For scientists, it is very important to understand the active sites to design the best photocatalysts. Hence it was observed that the material with the peak of (110) facet of Cu_2O photocatalyst particle is photo-catalytically very effective for carbon dioxide reduction to MeOH while the material with (100) facet is catalytically inert [64].

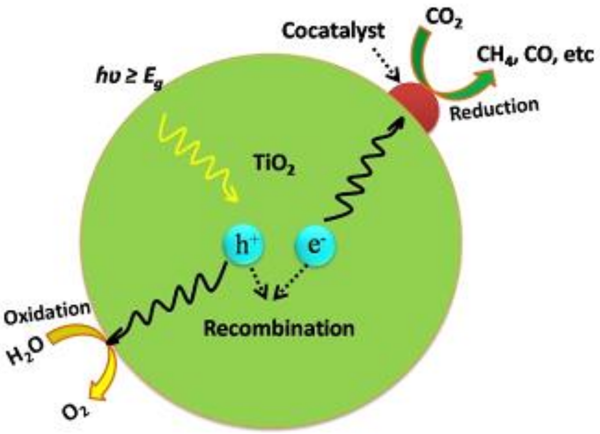

Figure 12. Photo catalytical Reduction of CO_2 on semiconductor TiO_2 [12]

Since this reaction is based upon the nature of light, it is very important to have such a reactor which enhances the presence of light and uses it in such a way that the yield from the reaction is maximum[65]. Therefore, many photocatalytic reactions for transformation of carbon dioxide into MeOH are performed in gas phase batch reactor [66].

Since Methanol can also be used as a fuel, a lot of research has been done for the conversion of CO_2 into MeOH by using natural light and without needing expensive catalysts and transition metals. Hence it was experimentally observed that the use of Cu_2O in the presence of light, gives 70% yield of methanol which can be used as fuel later[67]. It can also be said that solar energy can also be stored and supply in the form of MeOH, which can then be used later when required [57].

The impurities that might be there while converting CO_2 into methanol with the help of photocatalysts are hydrogen, methane, unreacted CO_2, carbon monoxide and formic acid. These impurities sometimes require further processes to be performed to make methanol pure and to be usable for desired purpose [68]. Zinc oxide quantum dots and KNb_3O_8 nanosheets are also used in the presence of light to convert CO_2 into methanol. This reaction is easy to perform as it can be performed at ambient conditions. But the disadvantage of this process is that it does not give us the good yield which is the result of unique shape and assembly of the warped NbO_6 octahedron and the larger external surface area of the nanosheets [69]. Another important aspect that was found in different research was that different radiations can be combined to get maximum conversion of CO_2 into methanol. These radiations can be from sun, ultraviolet–visible lamp, and from laser [70].

Most of the times, Cocatalysts can be utilized to enhance the impact of photocatalysts e. g doping of transition metals such as Pt, Ag etc catalyse the overall reaction by receiving electrons from photocatalysts [71]. It can be deduced from different research that have been done already that photocatalysis of CO_2 into methanol is somehow like the natural process of photosynthesis since both processes require natural light and radiations. However, it is stated that reduction of CO_2 into MeOH requires high energy and intense radiations [72].

Electrochemical method

Converting the CO_2 by electrochemical method into valuable synthetics using the renewable energy is the most efficient approaches to address the problem of rise in atmospheric CO_2. Renewable resources must be more utilized and stored in order to decrease the dependence of mankind on fossil fuels [73]. Various strategies and techniques are being used to diminish the quantity of CO_2 in the atmosphere. But for carbon dioxide electrochemical valorisation is the best technology available that appears to be significant in which the potential is applied between the two electrodes, enabling the CO_2 gas to be transformed into valuable chemicals such as methanol which has added growing and renewed devotion in the research community [74]. The requisites to tackle the deadly growing carbon dioxide emissions in the environment may include:

i) Minimal Consumption of hydrogen
ii) Production of easily transported and stored fuels
iii) Using sustainable energy sources [75]

From among options the most favoured option is to produce lower alcohols e.g. methanol.

Electrochemical cell with filter press, for uninterrupted electrochemically reduction of gas phase carbon dioxide gas-diffusion electrodes is applied. Gas dispersion electrodes are organized with carbon papers being deposited with mercantile Cu_2O and Cu2O-ZnO mixtures. This process mainly produces the methanol while some fractions of ethanol and n-propanol are also produced [76].

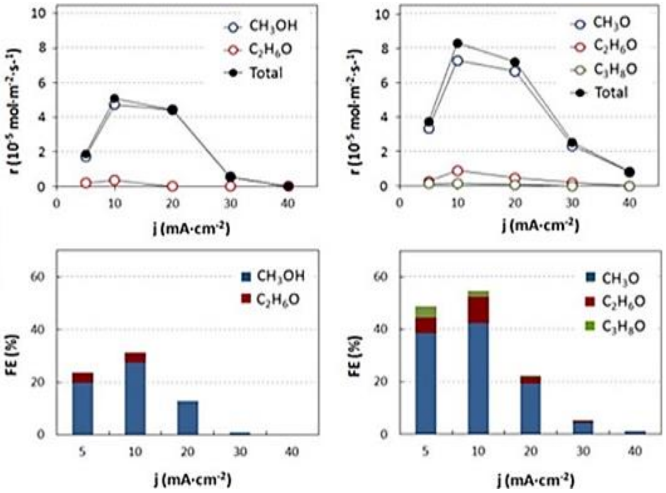

Figure 13: Electrochemical cell diagram and data. Cloned with authorization from ref. [77].

Gas diffusion electrodes are suggested to enhance the mass transport restrictions through the catalyst surface and the gas-liquid interface, this make the reduction process much improved [78, 79]. Polymer adhesive catalyst particles and a carbon backing are used to make a gas diffusion electrode. Besides their high permeability and high hydrophobicity, GDEs from G-S-L three phase interface, that allow on the catalyst surface a homogenous distribution. For CO_2 reduction in gas phase these properties of GDEs make them perfect for the duty. In electrochemistry the advantages of Cu-backed materials may be fruitful as the process can be conducted out at normal terms. For electrochemical formation of hydrocarbons and alcohols i.e methanol, the literature exhibited the appreciating stableness and encouraging catalytic efficacy of Cu_2O-supported surfaces[80]. The key for maintaining catalytic activity may be the introduction of ZnO. ZnO also fortify the Cu-CO' bond, hence enhancing the targeting to methanol and in the hydrogenation, reaction resulting in the stabilizing Cu [81]. Aiming for the electroreduction of the carbon dioxide in the form of gaseous phase, the sieve-press electro-chemical system receives three stimulus i.e catholyte, anolyte and carbon dioxide separately and two outputs produced are catholyte-carbon dioxide and anolyte. Figure (13) represents the gas-diffusion electrode cell for the electrochemical reduction of CO_2 conveyed lineally with gas phase.

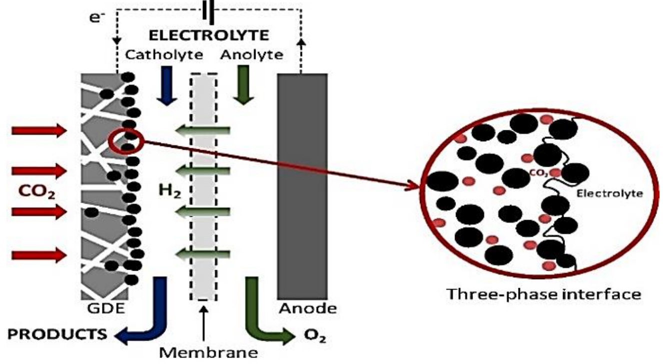

Figure 14: Electrolyte configuration and three-phase interface. Cloned with authorization from ref.[77].

In abidance with previous findings of formation at copper oxide acreages, the electroreduction of carbon dioxide at the Cu_2O-based GD electrodes directed to the constitution of methanol. Additionally, little amounts of ethanol and propanol were also identified [82].

Figure (15) shows for the main liquid-phase product i.e methanol, the grade of the applied voltage, E and constitution rate, over time for the carbon dioxide electrochemical reduction at both the electrodes under the room temperature.

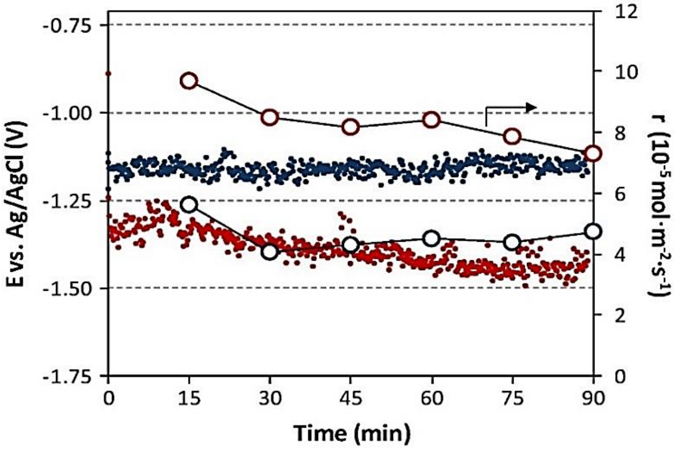

Figure 15: E potential vs Time graph. Cloned with authorization from ref.[77].

For electro-reduction of CO_2 to MeOH, a glassy carbon substrate supporting the novel catalyst containing Pt-nanoparticles on histamine-reduced graphene oxide plates (Pt@His-rGO) has been developed. For the utmost current densities and faradic efficiency inclined to methanol achievement, methanol optimization of nanocomposite in times of pH, Carbon dioxide cleansing time, provided potential and Pt- loading time has been carried out [83].

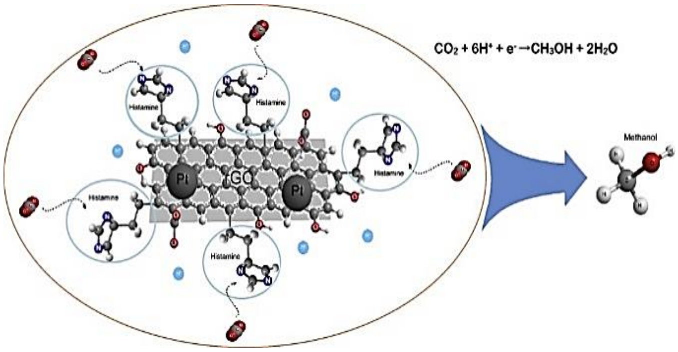

Figure 16: Glassy carbon supporting Pt@His-rGO. Cloned with authorization from ref.[84]

For enhanced faradic along with conversion effectiveness of the reduction function, alteration of electrocatalysts is important. Recent modifications in the production of efficacious catalysts have been carried out in order to dominate the massiveness of nanoparticles with mono-dispersive conformation [85]. Among various metallic electro-catalysts platinum doped nanoparticles are being used for carbon dioxide reduction. Usually platinum-supported catalysts convert CO_2 to CO but by utilization of the electrolyte media which can alter the pathway of reduction their behaviour could be changed. Nowadays, to optimize the properties of the catalysts, by detecting the active sites of catalysts the catalytic behaviour of nanoparticles can be assessed more precisely [86].

Graphene oxide (GO) contains the carbon atoms with the very small size of a few mm and texture of smaller than 1 nm, interconnected to each other forming extremely thin layers. Graphene oxide (GO) constitute of the functional groups having oxygen such as carbonyl, carboxyl, hydroxyl and epoxy etc [87]. Reduction of graphene oxide (GO) is carried out and outcome is the changing of GO to reduce graphene oxide (rGO) which result in change in oxygen content. Moreover, it enhances the chemical properties toward specific concerns like CO_2 reduction. Hence, graphene oxide is used in vast applications [63] and particularly catalysts [88].

In electro-reduction of CO_2, a glassy carbon substrate was altered with Pt@His-rGO. In this process an intermediate i.e formic acid was formed by histamine which is the most important for the electroreduction of CO_2 [89].

Polymer Catalyst

"Acidic etching bimetallic self-assembly" method with ZIF-8 as corrodible model was used for the victorious establishment of the novel bimetallic Cu/Zn-BTC coordination polymer. As compared to the many of the bimetallic coordination polymers found, this technique had short manufacturing time when the amount of the two metals becomes equal. By the hydrogenation of carbon dioxide to methanol, the highly dispersed Cu doped with ZnO catalyst was synthesized using the Cu/Zn-BTC as precursor, which also exhibited excellent catalytic performance [90].

Coordination polymers (CPs) or metal-organic frameworks (MOFs) were crystallic materials containing nano porous built out of organic ligand and metal-based node connected by a coordination bond [91].

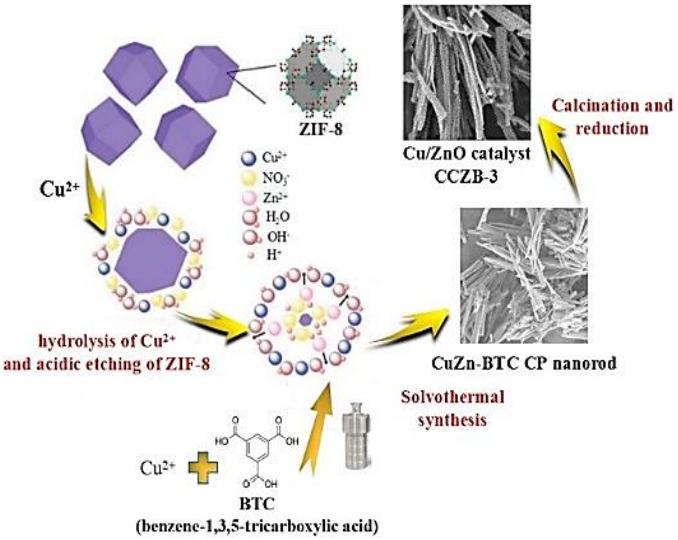

Figure 17: Production of Hetero-metallic coordination polymers. Cloned with authorization from ref.[93]

Recently, due to the outstanding structural topology and the strong applications as precursor for manufacturing various . metal-supported or carbon-supported nanomaterials, the preparation of hetero-metallic MOfs doped CPs had established an intense attentions[92]. But the production of hetero-metallic CPs is still a dare for researchers. So far, different techniques had been adopted to produce hetero-metallic coordination polymers including post-synthetic approaches and one-pot methods. But unluckily all the techniques to make the Cu doped with Zn bimetallic CPs has gone in vain [94]. Copper doped Zinc bimetallic coordination polymer with core-shell structure could only be synthesized by Post Synthetic exchange. To enhance the catalytic interest spots and enhanced catalytic activity, a thoroughly dispersed Cu-ZnO based catalyst was more beneficial instead of core-shell structure [95]. Hence new method is necessary to synthesize the bimetallic coordination polymer. An intended synthesis of Cu-Zn bimetallic CPs containing 1,3,5-benzenetricarboxylic acid (BTC) as organic ligand and Zn^{2+}, Cu^{2+} as metal ions is being reported in this article with an “Acidic etching self-assembly” method. ZIF-8 a kind of zeolitic imidazolate framework and linked by Zn^{2+} and 2-methylimidazole (2-Melm) is used as a starting material [32]

Table 1: Comparison of different type of Catalysis

S.NO	Catalyst material	Catalyst type	Reactor type	CO2 conversion	Energy efficiency	Fuel/Chemical	Ref
1	Ceria encouraged iron oxide catalyst	-	Dielectric barrier discharge (DBD) reactor	24.5 %	13.6%	CO	[96]
2	γ-Al_2O_3	-	DBD	18.3%	10.2%	CO	[96]
3	10Fe	-	DBD	13.3%	7.4%	CO	[96]
4	$7Fe_4Ce$	-	DBD	12.1%	6.7%	CO	[96]
5	$3Fe_7Ce$	-	DBD	9.5%	5.3%	CO	[96]
6	10Ce	-	DBD	28.2%	15.7%	CO	[96]
7	Photocatalys**t**	Heterogeneous	Fabricated stirred set annular type Pyrex Reactor	-	-	Methanol	**[97]**
8	g-C_3N_4	Heterogeneous	Photoreactor	-	-	CO2 as a promoter or soft oxidant in the oxidation Reaction	**[98]**
9	g-C_3N_4 with Ag NP	Heterogenous	Photoreactor	-	-	For carboxylation of terminal alkynes	**[99]**
10	g-C_3N_4 with melamine	Heterogenous	Photoreactor	5.6%		Epoxides to produce cyclic carbonates	**[100]**

11	Mesoporous g -C_3N_4 with melamine	Heterogenous	Photoreactor	34.0%	-	Epoxides to produce cyclic carbonates	**[98]**
12	Mesoporous g -C_3N_4 with urea	Heterogenous	Photoreactor	28.0%	-	Epoxides to produce cyclic carbonates	**[98]**
13	Ga_3Ni_5	-	plug flow reactor	-	-	Methanol	**[101]**
14	Copper-Zinc-alumina catalysts	-	Jacket reactor	7%	-	Syngas/methanol	**[102]**
15	Alloys of copper Metal. Bio metallic and Zn/Mn catalysts.	Heterogenous	-	-	-	Methanol	**[103]**
16	Sn catalysts. Bi catalysts. Cu, Pt catalyst.	Heterogenous	-	-	-	Formic Acid	**[103]**
17	Nanocrystals of Cu. Nano particles of Cu.	Heterogeneous	-	-	-	Ethylene	**[103]**
18	Composite catalysts of copper.	Heterogenous	-	-	-	Methane	**[103]**
19	Cu-Tio$_2$	Heterogenous	Solar Reactor (Liquid Phase/Solid Phase	-	-	Ethanol, acetaldehyde, Methanol.	**[104]**
20	Au catalysts	Heterogenous	Flow Reactor	-	-	Carbon monoxide	**[105]**
21	Photo catalyst	Heterogenous	Parr reactor	-	-	Methanol	**[106]**
22	$TiO_2$and $BaTiO_3$in plasma	Heterogenous	Dielectric barrier discharge (DBD)	-	-	Synergistic effect of plasma catalysts	**[107]**
23	Cu based Catalysts	Heterogenous	Proton Exchange Membrane (PEM)	-	-	Syn-fuels	**[108]**
24	Silver based	Heterogenous	-	-	-	Fuels	**[109]**
25	Ruthenium	Homogenous	-	-	-	Methanol	**[110]**
26	CeO_2 based Catalysts	Heterogenous	-	-	-	Methane Methanol	**[111]**
27	Bio catalysts	Heterogenous	-	-	-	Formic acid	**[112]**
28	Photo catalyst	Heterogenous	Photo reactor	-	-	Methane Methanol	**[113]**
29	Photocatalyst with ZnO/g-C_3N_4	Heterogenous	Stainless steel reactor	-	-	Fuel	**[114]**
30	Cascade Formaldehyde dehydrogenase	Heterogenous	Enzymatic membrane reactor	-	-	Methanol	**[115]**
31	Copper and its Derivatives	Heterogenous	-	-	-	C_3 to C_4 components	**[116]**

32	(FDH) with dithionite reduced methyl viologen	Heterogenous	-	-	-	Formic acid	**[117]**
33	Metal catalysts	Heterogenous /Homogenous	-	-	-	CO	**[118]**
34	Cu, Pt with TiO_2 nanoparticles	Heterogenous	-	-	-	Hydrocarbon fuels	**[119]**
35	TiO_2-based photocatalysts	HeterogenoUs	Photocatalytic reactor	-	-	Fuels	**[120]**
36	Nano catalysts	HeterogenoUs	catalytic reactor	-	-	CH_4	**[121]**
37	Electrocatalysts	HeterogenoUs	Electrochemical reactor	-	-	Fuels like methanol, acetone, H_2.	**[122]**
38	Photo catalysts	HeterogenoUs	Photo reactor	-	-	Hydrocarbon fuels	**[123]**
39	$Ni/MgAlO_x$ catalyst	HeterogenoUs	Fixed bed reactor	-	-	Syn gas	**[124]**
40	Nano porous catalysts	Heterogenous /Homogenous	-	-	-	Fossil fuels	**[125]**
41	carbon xerogels with metals	Heterogenous	-	-	-	C_1 to C_4 Compounds	**[126]**
42	Electro catalysts	Heterogenous	Electrocatalyst reactor	-	-	Liquid fuels	**[127]**
43	Electro catalysts	Heterogenous	-	-	-	C_1 to C_2 fuels	**[128]**
44	Electrocatalysts with CNT	Heterogenous	Electrocatalyst reactor	-	-	Solar fuels	**[129]**
45	Photocatalysts	Heterogenous	Photoreactor	-	-	Fossil fuels	**[130]**
46	Cobalt created Catalysts	Heterogenous	-	-	-	Formate	**[131]**
47	Electrocatalysts with Bismuth	Heterogenous	-	-	-	CO	**[132]**
48	TiO_2 with Ag-Pt Nanoparticles	Heterogenous	Photoreactor	-	-	Hydrocarbons	**[133]**
49	Single catalysts	Heterogenous	-	-	-	CO and O_2	**[134]**
50	Acid catalysts	Homogenous	Batch reactor	-	-	Fuels Biodiesel	**[135]**
51	Photocatalysts with $CuO-TiO_2$	Heterogenous	-	-	-	Methane	**[136]**
52	TiO_2 with Cu-Pt Coating	Heterogenous	Photocatalytic reactor	-	-	Light Hydrocarbons	**[137]**
53	Cobalt oxide with Ru nanorods	Heterogenous	Fixed Bed Microreactor	-	-	Methane	**[138]**
54	Electrocatalysts of transition metals	Heterogenous /Homogenous	Electrochemical reactor	-	-	Methane	**[139]**
55	Cu/Zn catalysts	Heterogenous	Absorbent reactor	-	-	Urea	**[140]**
56	Photocatalysts like $TiO_2$with Au particles	Heterogenous	Stainless steel reactor	-	-	Hydrocarbon Fuels	**[141]**

Conclusions

Carbon free society can be maintained by reducing large amount of carbon dioxide emitted by fossil fuel combustion using competitive catalytic technologies to convert it from a greenhouse gas to transportation fuel i.e., methanol. Many efforts have been spent for the advancement of catalysts for hydrogenation of CO_2. The catalytic conversion of CO_2 to methanol has a very great potential as compared to the other carbon capturing technologies in terms of sustainability and environment friendliness. However, these technologies also have their limitations and challenges that must be solved before they could be applied commercially in carbon capture and utilization. Keeping activity/cost ratio in mind, conventional Cu doped ZnO based catalysts are most widely used in this field. But improvements in certain areas are essentially required as low temperature activity, formation of by-product, formation of water, deactivation of catalyst need to be addressed. Development and synthesis of potential catalysts to improve the performance, durability and stability of the catalyst under harsh conditions and high yield of the catalyst are need. Deep study is necessary to determine the details of interfacial and local properties of Cu doped ZnO based catalysts. Activity/selectivity from precursor to the catalyst is immensely based on catalyst performance. Molecular level study of process structure of hydrogenation of CO_2 in presence of different catalysts is necessary to get the insights of the process. Experimental characterization, theoretical and modelling work may enable us most to develop and select the most efficient promoter to increase the performance rate of catalyst. Catalysts based on Palladium, Ni-Ga, Gold etc. and other techniques of conversion of CPO_2 to methanol has great potential to beat the problems occurring in the typical catalysts but still advancements are required in these areas to be used industrially. A comparison of certain active catalysts based on techno-economic assessment of CO2 reduction are required including heat integration and catalyst regeneration scheme under various hydrogen sources.

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Disclosure

The authors report no conflict of interest for this work.

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