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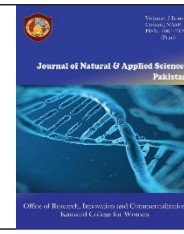

CATALYTIC CONVERSION OF CO2: A MINI-REVIEW

Almas Hamid[1], Marzia Saleem[1], Munifa Azhar[1*]
[1]Department of Environmental Sciences, Kinnaird College for Women, Lahore.

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*Corresponding Author
Email: munifa392@gmail.com

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Abstract

CO2 is a major greenhouse gas. Due to its high emissions in the environment, the transformation of CO2 to useful products is of great interest. In the recent years, much focus has been put on the catalytic conversion of carbon dioxide. Different catalysts have been introduced to convert CO2 into value added products. This mini review provides overview of catalytic conversion of CO2 and includes review of published papers from 2009 to 2019. It focuses on metallic nanocatalysts designed and prepared to catalyze the conversion of CO2. It also summarizes the different mechanisms for CO2 conversion and factors that can affect the conversion of CO2 into desirable products. Many useful products can be obtained through hydrogenation of CO2 which include CO, CH4, methanol, carbonates, carbamates and other valuable chemicals and fuels. Recently, many challenges are facing in catalytic conversion of CO2 but these challenges can be overcome by doing more research in this field.

1. Introduction

Global warming is one of the biggest issues people are facing today. Carbon dioxide is one of the major greenhouse gases that contributes to global climate change. Climate change has posed a great threat for the survival of living organisms on the Earth. Increase in concentration of greenhouse gases is the main driver for the change in climatic conditions all over the world. According to United States Environmental Protection Agency (USEPA), carbon dioxide emissions contribute larger to the global warming than other gases (Tappe *et al*, 2018).

As increased CO_2 concentration has caused many issues, there is need to take appropriate action to reduce its concentration in the environment. The solution to this urgent issue is the reduction of CO_2 emissions and conversion into useful chemicals. Furthermore, upstream introduction of CO2 in the productive cycle through several manifolds for the synthesis of polymers and fuels might lead to emission reduction by partial replacement of oil derived feedstocks and allow the temporary transformation of CO2 into useful substrates (Porosoff *et al*, 2016).

2. Mechanism of CO_2 conversion

CO_2 can be converted into value added products through various mechanisms which include catalytic hydrogenation of CO_2, photocatalytic conversion of carbon dioxide, electrochemical reduction of CO_2 and plasma-catalytic reduction of CO_2.

2.1. Catalytic hydrogenation of CO_2

During the past few years, much attention has been given to catalytic hydrogenation of CO_2. It involves the conversion of CO_2 to hydrocarbons such as liquefied petroleum gas, gasoline, aromatics, lower olefins etc. The hydrocarbons can be produced either directly or indirectly.

2.1.1. Direct conversion into hydrocarbons:

The hydrocarbons can be directly produced from syngas (CO + H_2) based on Fischer–Tropsch synthesis (FTS). FTS involves the series of chemical reactions to form hydrocarbons. The direct route is economical and environmental friendly. The direct CO_2 hydrogenation involves the combination of the reduction of CO_2 to CO via RWGS (Reverse Water Gas Shift) reaction and subsequent hydrogenation of CO to hydrocarbons via FTS. Different kinds of FTS catalysts with unique catalytic selectivities have been evolved for the selective production of diverse hydrocarbons. Catalysts including Fe, Co, Ru and Ni supported on SiO2, γ-Al2O3, TiO_2, and carbon nanomaterials can be used in hydrogenation process. Supporting materials play an important role in this process (Yang *et al*, 2017).

2.1.2. Indirection conversion into hydrocarbons

The two main indirect routes towards CO_2 hydrogenation into hydrocarbons involve conversion of CO_2 into methanol and subsequent transformation into hydrocarbons in a separate stage and conversion of CO_2 into CO via RWGS and then hydrocarbons are synthesized by using the modified FTS process which is based on two-stage reactors (Yang *et al*, 2017).

2.1.2.1. Synthesis of LPG

LPG is a good substitute for fuel in spark ignition engines and is used as an alternative for aerosol propellants and refrigerants (Yang *et al,* 2017). Therefore, direct synthesis of LPG from CO_2 hydrogenation is a desirable path for changing the carbon dioxide to valuable products (Porosoff *et al*, 2016).

2.1.2.2. Synthesis of gasoline

Gasoline is a very important transportation fuel which is widely used all over the world. It can be produced from CO_2 either directly or indirectly (Yang *et al,* 2017). Carbon dioxide can be converted into methanol and then into gasoline (Porosoff *et al*, 2016).

2.1.2.3. Synthesis of olefins

Lower olefins are basic carbon-based building blocks. They are used in the chemical industry and are traditionally produced through thermal or catalytic cracking of a range of hydrocarbon feed stocks, such as naphtha, gas oil, condensates and light alkanes (Yang *et al,* 2017). The reaction path as reported by Yang *et al*. for the formation of isoalkane is as follows:

$$\mathbf{CO_2/H_2 \longrightarrow CH_3OH}$$

$$\mathbf{CH_3OH \longrightarrow C_1, C_4}$$

$$\mathbf{CH_3OH \longrightarrow C_1, C_2, C_3, C_4, C_5}$$

$$\mathbf{C_3 + CH_3OH \longrightarrow \textit{i}\text{-}C_4}$$

$$\mathbf{C_2 + C_3 \longrightarrow \textit{i}\text{-}C_5}$$

Hydrogenation is considered to be one of the easiest and environmentally friendly mechanism of catalytically converting CO_2 to other valuable products. This phenomenon is supported by a study conducted in which hydrogenation was carried out with the help of tandem catalysis in which the catalysts used are dimethylamine and ruthenium. This research evidently showed that with the catalyst dimethylamine, some valuable products are also obtained along with methanol. The valuable product generated is dimethlyformide which is used extensively in pharmaceutical industry as well as in agricultural sector for pesticide formation (Rezayee *et al,* 2015).

2.2.Photocatalytic conversion of carbon dioxide

The conversion of CO_2 into useful products is of great commercial and environmental interest. However, as CO_2 is enormously stable, the input energy required for this conversion is a large limiting factor in the system's overall performance. By utilizing energy from the sun through various key routes this problem can be overcome (Fu *et al,* 2019).

This process is similar to the photosynthesis process of plants. Photo catalysts are used that convert CO_2 into fuels by using UV and visible light. This reaction consists of four steps. In the first step, UV or visible light activate the catalyst which causes the valence electron to jump into conduction band. Simultaneously, the holes are left in the VB and form the negative electron and positive-hole pairs. Then, separation of electron hole pairs takes place and they transport to the catalysts surface. In the last step, CO_2 is reduced by negative electron and desirable products are formed such as CH_4, CH_3OH, and CO (Fu *et al,* 2019).

A comparative study was conducted to evaluate to the efficacy of conversion of CO_2 conducted under direct UV radiation outdoor and the other conduction in laboratory through exposure to artificial UV illumination. This study utilized the nanotubes incorporated with catalysts such as copper or platinum and placed outdoor in the sunlight. The results showed that nanotubes having catalysts placed in direct sunlight produced a 20 times greater hydrocarbon load as compared to nanotubes exposed to UV illumination in lab experimentation (Varghese *et al,* 2009). TiO_2- based photo catalysts have been widely used for photocatalytic conversion of CO_2. Developments have made in Ti_2O based nanostructure i.e. 1-D, 2-D and hierarchical nanostructures (Razzaq *et al,* 2019).

2.3. Electrochemical reduction of carbon dioxide

It is a green chemistry way of reducing carbon dioxide into useful products. It does not involve the use or generation of hazardous chemicals. Different metal nanocatalysts are used for the conversion. These include gold (Au), silver (Ag), lead (Pd), nickel (Ni), bismuth (Bi), copper (Cu), cobalt (Co), tin (Sn) and molybdenum (Mo) based nanocatalysts (Yin *et al*, 2019). It involves conversion of carbon dioxide on electrodes powered by electric bias. It requires high energy to start the reaction because carbon dioxide is highly stable. At cathode, carbon dioxide is electrochemically reduced to fuels and other desirable products and at anode oxygen is produced (Whang *et al*, 2019).

The use of different metal nanocatalysts was studied for electrochemical carbon dioxide reduction reaction (CO_2RR) which showed that Au, Ag and Pd based nanocatalysts are highly selective for the conversion of CO_2 into CO. For formate production, Ni, Bi, Co, Pd, Mo and Sn based nanocatalysts are used. They showed high efficiency for the conversion of carbon dioxide into formate. Cu nanocatalyst has high selectivity for the production of hydrocarbons. However, Cu nanocatalyst shows different catalytic properties because it is chemically unstable (Yin *et al*, 2019).

Metal nitrogen doped carbon materials (MNCs) are considered to be one of the most promising nonmetallic alternatives which are highly selective for the reduction of CO_2 into CO. These materials are widely studied as a low cost alternative to the platinum based fuel cell. Different factors affect the performance of MNCs towards CO_2RR. These include structure and composition of catalyst and reaction conditions. For example, their efficiency is high in neutral or alkaline pH. Lu *et al*. studied the efficiency of Ni-Nx sites which were encapsulated in carbon nanotubes. They showed 95% efficiency for the formation of CO (Varela *et al*, 2019).

In another study, the electrochemical reduction through copper catalyst placed on copper cathodes is shown. This research highlights the different types of electrodes used and designed such as dendritic, honeycomb and electrodes having a 3D edifice. Results obtained showed that with honeycomb cathode, the products obtained are ethane and ethene while methane formation is prevented. Hence the primary result of this study was that electrochemical reduction of CO_2 to hydrocarbons does get effected by the amount of copper catalyst placed on the electrode as well as the structure of the electrode (Gonçalves *et al*, 2013).

3. Composition of catalysts

Catalysts can reduce the need of energy for reactions. For enhancing CO_2 conversion, various catalysts have introduced. Following catalysts can be used for CO_2 conversion:

3.1. Precious metals:

Pt, Rh and Ru are some precious metals that can be used for dry reforming of methane (DRM) and RWGS. DRM involves the use of two greenhouse gases i.e. CO_2 and methane to form syngas. These metals are highly active for DRM and they also resist coke deposition. For example, Ru/ZrO_2-SiO_2 catalyst can be used for DRM and it shows high durability (Whang *et al*, 2019).

3.2.Other catalysts:

Ni or Co can also use as catalyst for DRM. They have low price and are highly abundant.

3.2.1. Nickel and nickel nanoparticles:

Ni catalysts are highly active and they have activity comparable to precious metals. Ni-Fe alloy catalyst can also be used for DRM. Small sized metal nanoparticles have more catalytic activity than large sized metals. Monometallic Fe catalyst shows poor durability because it is inactive for DRM. Supporting material plays an important role in conversion process. Different supporting materials can be used which are SiO_2, γ-Al_2O_3, TiO_2 and La_2O_3. To prevent sintering of nanoparticles, a layer of inorganic oxide is formed on Ni nanoparticles. An average size of Ni nanoparticles is 5nm. These particles are coated with porous SiO_2 to avoid coke formation (Whang *et al,* 2019).

Reduction of CO_2 to methane with the help of nickel catalyst does not entirely depend on the nickel catalyst size as illustrated in a study. Research into this subject revealed that the optimum size range for a nickel catalyst is between 1.6 to 7.3 nm and in this size range the nickel catalyst observes a specific reactivity as well as stability. Their major drawback is that nickel type catalysts tend to easily deactivate even due to slight operational changes and this leads to their loss in activity and their changed selectivity for associated products generation. This thus causes a decrease in the H_2/CO ratio and selectivity for CO_2 conversion. But the research is still going on to evaluate whether particle size and the type of supporting material used does affect the overall efficiency of conversion (Alaba *et al*, 2017).

In another comparative study using nickel catalyst for converting CO_2 to methane used a plasma reactor embedded with nickel catalyst while other used only nickel catalyst without any plasma system. Results indicate that using a plasma reactor, the nickel catalyst got divided into smaller particles and were evenly spread in the plasma system thus their activity increased. While on the other hand, where only nickel catalysts were used, the CO and CO_2 conversion rate was only about 15%. Thus, it showed that nickel catalysts efficiency is increased when combined with plasma system (Jwa *et al*, 2013).

3.2.2. Copper:

For Reverse Water Gas Shift (RWGS) reaction, copper can be used as a catalyst. Carbon dioxide oxidizes Cu^0 to Cu^+ generating CO, and H_2 reduces Cu^+ to Cu^0 forming H_2O. These reactions further produce value added products. For RWGS, Cu shows high activity and selectivity. Among all metal elements, only Cu has been identified to exhibit the ability to catalyze CO_2 hydrogenation to methanol on an industrial scale (Whang *et al*, 2019).

3.2.3. Gold and gold nanoparticles:

For Reverse Water Gas Shift (RWGS) reaction, gold can also be used as catalyst. Gold nanoparticles can be used for enhancing the interaction between metal and support. Gold shows high activity and CO selectivity (Whang *et al*, 2019).

3.2.4. Transition Metal Carbides (TMCs):

They are considered to be best catalysts for RWGS because they can break the bonds between carbon, hydrogen and oxygen. Examples are TiC, TaC, ZrC, WC and NbC (Whang *et al*, 2019).

3.2.5. Transition Metal Catalysts:

Among the transition metals used for CO_2 catalytic reduction, the commonly used are Platinum, Copper, Cobalt, Ruthenium, Rhodium as they are known to actively reduce the CO_2 through the process of hydrogenation. They can be applied either solely or could be combined with other transition metals in order to produce a multilayered catalyst that has enhanced catalytic activity as well as selectivity. For instance, blending Platinum and Cobalt will result in a greater amount of CO yield and on the other hand mixing Nickel and Gallium will promote the methanol synthesis (Gonçalves *et al*, 2013).

3.2.6. Metal Oxides:

Under this category, the most popularly used catalysts are Zinc oxide, Titanium oxide, Ga_2O_3 etc. are some of the examples. They can also be used separately or in combined form. One of their advantage is that they show synergistic effect with other catalyst types such as copper and their mutually beneficial nature makes the overall conversion process a success (Alaba *et al*, 2017).

3.2.7. Iron Based Catalysts:

These types of catalysts also show a higher selectivity and activity rate towards conversion mechanism. Their activity is improved when they are combined with a metal oxide because in this case the iron gets easily dispersed and then combines with CO_2 to cause hydrogenation. Their advantage is that iron based catalysts are considered to synthesize a better yield of hydrocarbons and especially olefins as compared to Copper type catalysts. These catalysts also show a greater CO_2 conversion rate as compared to copper and nickel catalysts as they tend to increase the reverse gas water reaction mechanism (Alaba *et al*, 2017).

Iron used as a catalyst for photochemically reducing CO_2 into useful compounds is known to be a green catalyst that works sustainably. This mechanism is supported through a study by Bonin et al in which iron used is in the form of tetraphenyl porphyrin and this type of iron catalyst showed an efficient conversion rate for CO from CO_2. Moreover, this catalyst's operational life was high with about greater than 50 hours and over this time period the catalyst was not deactivated (Bonin *et al*, 2014).

3.2.8. Organic Catalysts:

This category includes the epoxides and they potentially reduce the CO_2 through cyclic reactions and thus producing cyclic or organic carbonates. These types of catalysts act as intermediary products that tend to produce other valuable products like polycarbonates, isocyanate-free polyurethanes, solvents, ionized components for electrolysis and other chemicals that can be used in pharmaceuticals or drug synthesis. Their only drawback is that they require a high temperature and pressure for maintaining the catalyst's reactivity and selectivity (Tappe *et al*, 2018).

3.2.9. Zinc and Zinc Complex Catalysts:

These catalysts are used to synthesize carbamates from CO_2 reduction reactions. Zinc catalysts are highly recommended as they are not environment degraders and the zinc catalyst are a stable material which can be used again many times and also it carries a high chemical selective nature (Tappe *et al*, 2018).

Catalytic reduction of CO_2 by zinc oxide along with copper precursor was examined in a research study. The catalyst is derived by the reaction between diethyl zinc and copper precursor and a precatalytic solution was obtained of copper nano particles along with dimethyl zinc and ethyl zinc. These catalysts showed high conversion activity rate of about greater than 55 mmol/g *ZnOCu*/h of methanol. This research study concluded that the optimum ratio of ZnO/Cu is 55:45 and using the synthesized catalyst diethyl zinc was successful in producing methanol at a rate equivalent to methanol production commercially (Brown *et al*, 2015).

3.2.10. Zeolite Catalysts:

Their activity and selectivity are highly dependent on the zeolite catalyst's characteristic property such as their shape, structure, strength and acidic nature and all these properties can be mended under controlled conditions to enhance their functionality. They can actively produce hydrocarbons as well as olefins (Yang *et al*, 2017).

3.2.11. Vanadium Catalysts:

Potassium carbonate is used for carbon dioxide hydrogenation because it has low corrosivity, low volatility, high thermal stability and high tolerance to gaseous impurities. But it has a major disadvantage i.e. low reaction rate with CO_2. To overcome this limitation, a promoter can be introduced in a solvent system. Vanadium is used to enhance the adsorption of carbon dioxide in carbonate solutions. It occurs due to presence of two vanadium species which are HVO_4^{2-} and $HV_2O_7^{3-}$. Vanadium also acts as a corrosion inhibitor. The speciation of vanadium depends on different factors which are solution conditions, pH of solution, concentration of vanadium and temperature (Nicholas *et al*, 2014). The catalytic activity of vanadium was studied. Vanadium complexes were derived from aminotriphenolate ligands. These complexes formed strong binary catalysts with ammonium salts. They help in conversion of epoxides and carbon dioxide into their respective COCs (Chemicals of concern) (Miceli *et al*, 2017).

3.2.12. Amine based compounds:

Amine based compounds are used to increase the absorption of carbon dioxide in carbonate solvents. They are cheap and show great potential for the CO_2 absorption. But disadvantages associated with their use are that they are highly toxic, highly corrosive and have high vapor pressure which results in loss of solvent (Nicholas *et al,* 2014).

To capture CO_2 and convert it into useful products is a very complex and energy consuming process. Using amine-based compounds to effectively capture CO_2 was evaluated through a research study which used the compound known as monoethanolamine. This compound showed a greater affinity and absorption capacity for CO_2 and one of their greatest advantage shown is that they require a very less energy for operation. But unfortunately, research is still going on and modifications are examined to evaluate the optimized conditions and amine compounds (Luis, 2016).

4. Factors affecting the catalytic reduction

Several factors affect the activity of catalysts during conversion process. These factors include temperature, pressure, H_2/CO_2 ratio and Gas Hourly Space Velocity (GHSV) (Alaba *et al,* 2017).

4.1. H_2/CO_2 ratio

Increase in H_2/CO_2 ratio favors the carbon dioxide conversion but it declines the CO selectivity. In addition, increase in H_2/CO_2 ratio favors the methane selectivity (Alaba *et al,* 2017).

This ratio is dependent primarily on the size of the cations used or the composition of electrolytes as illustrated in a study conducted by Thorson et al. It showed that if large cations are used then hydrogen production will be minimized and carbon monoxide production will increase but on the other hand CO_2 selectivity will be decreased and thus the size of the cation used effects its hydration rate as well as the adsorption capacity onto the electrodes used (Thorson *et al,* 2012).

4.2. Temperature and pressure

Increase in temperature and pressure increases the collision among particles which results in increased reaction rate. As the temperature increases, the production of methanol increases but it starts decreasing when the system reaches its thermodynamic limit. The type of catalyst determines the thermodynamic limit of the system (Alaba *et al,* 2017).

4.3. Effect of space velocity

Space velocity plays an important role in catalytic conversion of carbon dioxide. As GHSV increases, the selectivity of methanol increases whereas CO selectivity decreases. However, when the catalytic activity reaches the thermodynamic limit, further increase in GHSV will decrease the performance of the catalytic activity (Alaba *et al,* 2017).

5. Products that are obtained through Conversion

The most prominent products that are obtained from catalytic carbon dioxide conversion are carbon monoxide, methane, methanol, carbonates, carbamates and other valuable chemicals and fuels (Porosoff *et al*, 2016).

5.1.Products Significance and Use

5.1.1. Carbon Monoxide

This product is obtained through the reduction of carbon dioxide in the process of reverse water – gas shift. This mechanism inculcates the advantageous property through a low hydrogen consumption and higher conversion efficiency rates as compared to other conventional methods. This product is valuable in the context of it being used as an intermediary substance that aids in the formation of other downstream valued chemicals or fuels (Porosoff *et al*, 2016).

5.1.2. Methane

Carbon dioxide emissions are adequately controlled by the methanation process where CO_2 is transformed into methane. This process is widely used in many areas as it requires no complex infrastructure for handling and distributing the methane formed. This product also serves as a storage facility for renewable energy (Baudouin *et al*, 2013).

5.1.3. Methanol

Similar to carbon monoxide, methanol synthesis is also carried out through the reverse water – gas reaction (Porosoff *et al*, 2016). This product also serves to be an important contribution in the production of other valuable products and chemicals. However, the only drawback with this product synthesis is that it requires more than one catalyst as well as reactor for the reaction to go into completion and this renders the whole conversion mechanism to be highly costly (Gonçalves *et al*, 2013). Methanol as a fuel alternative serves to be a justified choice as it carries a greater capacity for hydrogen storage, higher energy content as compared to other fuel products, economically feasible and the most suitable property of this product is that it serves as a good transportation fuel because it remains to be in liquid phase at normal temperatures and also can be efficiently used in arctic regions due to its greater freezing capacity (Din *et al*, 2019).

5.1.4. Valuable Chemicals and Fuels

Carbon dioxide reduction through catalytic processes not only yields the valuable products as aforementioned, but also some intermediary chemicals and carbon-based fuels are produced that provide other valuable end products. Some of the useful chemicals formed are methyl amines, formic acid, salicylic acid (which helps in the formation of aspirin) and acrylic acid (Tappe *et al*, 2018). Moreover, other green energy sources are generated that shift the consumption of fuel fuels to more renewable fuels like methane, methanol and dimethyl ether. The benefit of such green fuels' usage is that they do not produce any harmful by products that degrade the environment as is the case with other fuels that produce SO_x and NO_x. In addition, these fuels show a higher performance rate with a decreased emission rate and also a less flammability chance thus making these fuels environmentally friendly (Ma *et al*, 2009).

5.1.5. Carbonates and Carbamates

Conversion of CO_2 to dimethyl carbonate not only reduced the greenhouse gas effect but it also provides a new resource for carbon-based products (Gonçalves *et al*, 2013). CO_2 conversion also forms cyclic organic carbonates which are further converted into biological agents used in pharmaceuticals, or are made into polycarbonate chains and these are considered as renewable softeners. Moreover, some carbamates are also produced that have their significance in terms of usage in medicinal purposes, production of insecticide products as well as polyurethane (Tappe *et al*, 2018).

5.1.6. Hydrocarbons

Methanol formed from carbon dioxide conversion can be further processed to produce hydrocarbons such as olefins, gasoline hydrocarbon products, a variety of alkane products and aromatic products. Olefins are primary sources of carbon and they are extensively used in chemical industries to synthesize other chemicals. Another great utilization of carbon in carbon dioxide is the production of LPG (liquefied petroleum gas) and this product is widely used as a fuel for engines that stand a greater chance of ignition and in place of aerosols in refrigerators and coolants (Yang *et al*, 2017).

Table 1: Advantages and Disadvantages of CO_2 Converted Products

Product Type	Advantage	Disadvantage
Carbon Monoxide	Intermediary substance and aids in formation of other valuable products Requires less hydrogen for reaction Carriers a great potential for conversion as is not very stable chemically Low cost conversion mechanism	A greenhouse gas and is very reactive Forms reactions with other substances in atmosphere to produce harmful products Process of conversion requires a high temperature and is catalyst dependent to ensure efficient conversion rate Dual purpose catalyst required for efficient conversion
Methane	Easy to use and handle Does not produce harmful by products Used as a biofuel that comparatively generates less pollution Methanation process plays a significant role in producing a renewable energy resource and regulating CO_2 emissions	Methane is still a greenhouse gas Shows selectivity for products formation Highly temperature dependent Catalyst properties affect the conversion rate for methanation
Methanol	Valuable product as compared to methane and CO because it remains in liquid phase at normal temperature and pressure Used as a feasible alternative for energy and fuel usage Primary product that aids in synthesis of olefins and other aromatic products	High dependence on stable optimum pressure conditions Low pressure environment can introduce poor selectivity for desired end products as compared to methane and CO High pressure conditions need to be maintained throughout the working phase to prevent formation of CO

		Process of methanol formation takes place in a multi stage phenomena due to which the capital costs are risen Requires 2 catalysts and reactors making the process more complex and time consuming
Chemicals and Fuels	Efficient chemical additives and fuels that are environmentally friendly Pollution free products	Chemicals of methylated form can be very toxic in nature Complex reactions require complex substances for synthesis of chemicals Require carefully designed catalyst that react with only selective materials to prevent any side reactions taking place
Carbonates and Carbamates	Used in medicine and pharmaceuticals for drugs Used as good and sustainable softening materials Used as a replacement to aerosols in refrigerants and coolants Used to synthesize industrially usable products that cut down on CO_2 emissions and other harmful gaseous emissions Can achieve removal of CO_2 even from waste flue gas system	Some harmful by products could be produced Highly dependent on high temperatures for increased efficiency Catalyst activity is specific and selective
Hydrocarbons	Cause substantial decrease in CO_2 emission rate Better fuel and chemical additives synthesis	Catalyst are required that are water resistant and are highly selective for olefin Specific catalyst requirement and constant modifications make the overall process too costly and difficult to manage Difficulty in creating suitable catalysts

6. Challenges Faced in Catalytic Conversion of CO_2

There are a number of challenges that needs to be addressed properly while designing and implementing the CO_2 catalytic conversion process.

6.1.Managing Intermediate Products

Throughout the CO_2 conversion process, numerous chemical products are formed that needs to be stabilized in a certain form so that they don't hinder the efficacy of conversion. A certain intermediate product that is formed needs to be identified and managed in a proper way so that the selectivity of the catalyst is not affected in any way. For instance, for efficient conversion to methanol, the right amount of CO has to be maintained within the system. Perhaps managing the key intermediates becomes difficult at all the stages of conversion (Yang *et al,* 2017).

6.2.Inefficiency of Low-Cost Catalysts

For a complete conversion process there has to be a catalyst that is selective and not too costly. But in most cases, these low-cost catalysts become a nuisance as they also bind other intermediary hydrocarbons with them lowering their conversion capacity and also result in other products that either are toxic in nature or hinder the whole conversion process (Yang *et al*, 2017).

6.3. Catalyst Deterioration by Water

Despite other valuable products of the conversion mechanism, the formation of water, in large amount is inevitable. The production of water leads to formation of chemical functional groups called hydroxyl groups that destroy the very function of any catalyst. Thus, water resistant catalysts can be made but they are too costly (Yang *et al*, 2017).

6.4. Unavailability of Sources Producing H_2 free of CO_2

For conversion to take place on a larger scale, and promote a 100% conversion, the source from where hydrogen is obtained has to be free of CO_2 addition in any kind. This too raises the overall cost of the conversion system (Yang *et al*, 2017).

7. Recent Development – Plasma Catalytic Conversion of CO_2

This conversion process using plasma is an entirely a recent development in which research for enhancement is still going on. This type of technology is an improvement to the conventional CO_2 catalytic reduction system where the processes are enhanced via the use of different types of plasma. This technology works to produce optimum conversion processes aimed at lowering the conversion temperatures, strengthening the catalyst stability and elongating their life and selectivity. This type of system contains a dielectric plasma membrane acting as a barrier discharge along with a nickel-based catalyst. Plasma is composed of gas containing ionized molecules such as ions, radicals etc. Whereas on the other hand another type of plasma can also be created which is referred to as non-thermal plasma and it utilizes a high voltage power to convert a non-ionized gas into gas containing charged particles. This process allows the exchanging of ions between cathode and anode electrodes and this also leads to interaction with other molecules causing synthesis of intermediary products that can aid in the CO_2 reduction process. The constant exchanging of ions and their interactions with molecules leads to modification of catalyst and thus their activity could also be enhanced this way. Thus, the plasma and a catalyst work synergistically, improving the efficiency of one another (Dębek *et al*, 2019).

8. Conclusion

There exists a number of ways for reducing the CO_2 emissions through catalytic processes but currently most of the literature supports the use of hydrogenation as a catalytic method of conversion. Whatever the method used, the significant products made are CO, methane, methanol and valuable hydrocarbons that are used extensively in many industries. Every process has their advantage and a challenge which needs to be addressed to mitigate all possible hindrance factors and improve the CO_2 removal from atmosphere so that a safe and healthy environment is gained for everyone. Nonetheless, research is still taking place to come up with a suitable catalyst type and to reduce the cost of producing a H_2 free CO_2 for an economically and scientifically feasible method of CO_2 reduction (Porosoff *et al*, 2016).

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Table 2: Summary Table

Process Type	**Description**	**Catalysts Used**	**Products Obtained**	**Uses**
Catalytic Hydrogenation	Direct and indirect reactions Direct reaction involves CO_2 converted to CO and then to hydrocarbons Indirect Reactions involve CO_2 conversion to methanol and then to CO and hydrocarbons	- Fe, Co, Ru and Ni supported on SiO_2, γ-Al2O3, TiO_2, and carbon nanomaterials	Hydrocarbons such as liquefied petroleum gas, gasoline, aromatics, lower olefins etc. methanol and CO	olefins used as chemical additives in chemical industry LPG, gasoline and methanol used as green fuel
Photocatalytic Reduction	Involves use of UV or visible light which activates the catalyst CO_2 is reduced as negative electrons formed are deposited onto catalyst surface	Metal catalysts or their complexes such as vanadium oxide, copper, platinum, zinc etc.	CH_4, CH_3OH, and CO	Used as biofuels or chemical additives
Electrochemical Reduction	It involves conversion of carbon dioxide on electrodes powered by electric bias It requires high energy to start the reaction because carbon dioxide is highly stable At cathode, carbon dioxide is electrochemically reduced to fuels and other desirable products and at anode oxygen is produced	metal nanocatalysts are used for the conversion such as Au, Ag, Pd, Ni, Bi, Cu, Co, Sn and Mo based nanocatalysts	CO, methane, hydrocarbons Industrial chemicals	useful chemicals formed are methyl amines, formic acid, salicylic acid (which helps in the formation of aspirin) and acrylic acid
Plasma-Catalytic Reduction	contains a dielectric plasma membrane acting as a barrier discharge along with a nickel-based catalyst allows the exchanging of ions between cathode and anode electrodes plasma and a catalyst work synergistically, improving the efficiency of one another	Nickel based catalysts	Hydrocarbons and other valuable industrial chemicals	also forms cyclic organic carbonates which are further converted into biological agents used in pharmaceuticals, or are made into polycarbonate chains and these are considered as renewable softeners