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Catalytic CO2 Hydrogenation - Literature Review: Technology Development since 2014

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Abstract

Global atmospheric carbon dioxide (CO$_2$) concentration from fossil fuel combustion has generated much concern because of the several environmental issues associated with high levels of atmospheric CO$_2$, a major greenhouse gas. In order to reduce the risks associated with global warming, the increase in atmospheric CO$_2$ concentration must be prevented. CO$_2$ capture and conversion not only mitigates the risks associated with increasing CO$_2$ concentration in the atmosphere, but also addresses the problem of fossil fuel depletion by providing sustainable production of industrial demanded fuels and chemicals.

This literature review analyzes several of the most promising products that can be generated via catalytic CO$_2$ hydrogenation and discusses advancements in catalysis. Primary focus is on CO$_2$ conversion, selectivity to desired products, and stability of the catalysts. A summary is included at the end of the review that discusses the most promising catalytic advancements since 2014.

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1. Introduction

Global atmospheric carbon dioxide (CO_2) concentration from fossil fuel combustion has grown dramatically since the beginning of the industrial revolution. The rise in atmospheric CO_2 levels due to fossil fuel combustion has generated much concern because of the several environmental issues associated with CO_2, a major greenhouse gas. This includes the acidification of oceans and the rise in average global temperatures, known as global warming, which can cause the melting of ice caps and increased severity in weather patterns [1]. In order to reduce the risks associated with global warming, the increase in atmospheric CO_2 concentration must be prevented. As a result, CO_2 capture is a developing field with many new publications.

Carbon dioxide capture and sequestration has received much attention, but the recycling of carbon contained in CO_2 through chemical transformation into industrially valuable chemicals and fuels has a more promising outlook. CO_2 capture and conversion not only mitigates the risks associated with increasing CO_2 concentration in the atmosphere, but also addresses the problem of fossil fuel depletion by providing sustainable production of industrial demanded fuels and chemicals.

Considering the global production of CO_2 and the increasing capacity of CO_2 capture, technologies capable of utilizing large quantities of CO_2 as building blocks for commodity chemicals must be produced. A particularly significant developing technology is catalytic hydrogenation of CO_2, important due to its ability to convert large quantities of CO_2 in a short timeframe [2]. However, CO_2 is kinetically and thermodynamically stable; thus CO_2 conversion reactions are endothermic and require efficient catalysts to obtain a high yield of the desired product [1].

2. Carbon Dioxide Hydrogenation

The reactions of CO_2 with hydrogen (H_2) offer various pathways for fuel and industrial chemical production. Primary fuels and chemicals include carbon monoxide (CO), formic acid and formaldehyde, methane, higher hydrocarbons and oxygenates, and methanol as shown in Figure 1. These products can be produced through direct CO_2 hydrogenation or via an intermediate product.

Several products generated from CO_2 hydrogenation are currently demanded in industrial quantities, due to existing infrastructure, while there is potential for other hydrogenation products to be demanded in similar quantities in the coming decades [3]. Renewable energy sources, such as solar, wind, and hydroelectric energy, have been proposed as the energy source for CO_2 hydrogenation. Utilizing renewable energy sources as a means to produce fuels and chemicals is promising as the intermittent energy sources can be converted to stable chemical energy, which can be transported and used as demanded [1, 3].
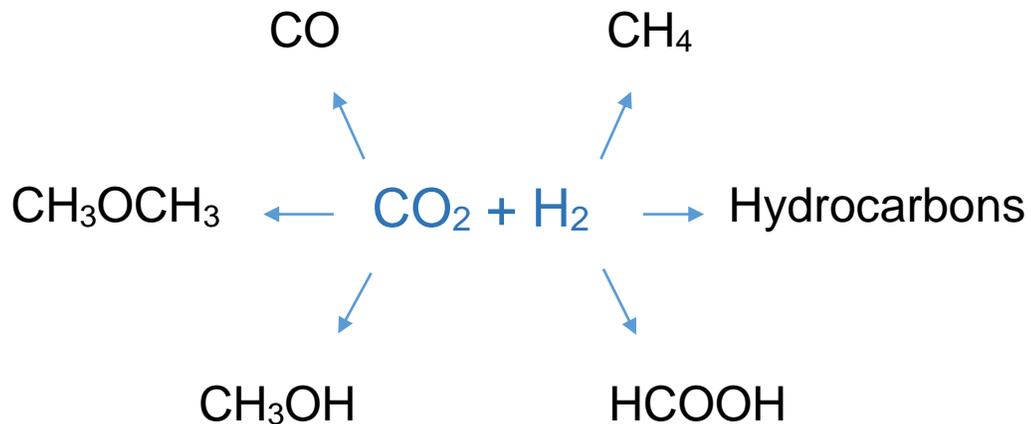

Figure 1. CO_2 hydrogenation pathways to major products discussed in this review.

Due to the kinetic stability of the CO_2 molecule, CO_2 hydrogenation requires efficient catalysts; these processes have historically utilized metal-based catalysts. Precious metals, which are used in the production of formic acid and other chemicals, typically demonstrate good catalytic activity and selectivity, but are expensive and are often deactivated by oxidation. Other metal-based catalysts include copper-based, which have been highly studied for CO production via the Reverse Water Gas Shift (RWGS) reaction, cobalt-based, and nickel-based systems. Copper based systems have poor thermal stability, thus, are not suitable for high temperature reactions without a thermal stabilizer. Cerium-based catalysts have also shown good activity and selectivity for CO_2 hydrogenation process, but are easily deactivated by a small coverage of deposited carbon [4].

All historically utilized catalysts are limited by conversion and selectivity. Various catalytic modifications and supports have been researched in order to enhance the conversion of CO_2 and the selectivity to the desired product. Catalyst optimization will lead to enhanced performance at ideal process conditions [3, 4].

2.1 Synthesis Gas

Methane-CO_2 reforming is utilized to produce synthesis gas, typically called syngas. Traditionally, this mixture of carbon monoxide (CO) and hydrogen (H_2) is produced by steam reforming. In steam reforming, a carbon containing source material, usually methane (CH_4), is converted into a mixture of CO and H_2 via steam injection, as shown.

CH_4 + H_2O

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
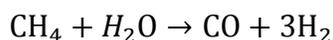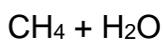
Evaluating the source of H_2 utilized in further CO_2 hydrogenation steps is necessary, as steam reforming requires large energy inputs; thus, large CO_2 emissions are associated with steam reforming plant operations and sustainable operations are not achieved. Instead, syngas can be produced via dry or wet CH_4-CO_2 reforming. In dry methane reforming, methane is converted into a mixture of CO and H_2 via CO_2 injection, as shown.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
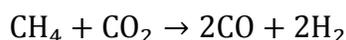
In wet methane reforming, methane is converted into a mixture of CO and H_2 via simultaneous steam and CO_2 injection; this process if often called bi-reforming and produced a different ratio of CO:H_2 than either steam reforming or methane-CO_2 reforming.

$$3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H_2$$

The use of CO_2 as a carbon source for synthesis gas production is advantageous, as it could potentially enable sustainable plant operations via CO_2 recycling. That is, CO_2 produced during fuel combustion can be utilized directly in methane reforming.

Synthesis gas produced via methane reforming has many utilizations. H_2 can be directly utilized as an environmentally attractive fuel, with uses including the Proton Exchange Membrane (PEM) fuel cell or can be used in the production of valuable chemicals and fuels via CO_2 hydrogenation. Carbon monoxide is an industrial gas used as a raw product in many bulk chemical manufacturing and other industrial processes. It serves as a carbon source for the production of hydrocarbon fuels, lubricants, and

oxygenates via FT synthesis [3]. The direct CO_2 hydrogenation reaction to hydrocarbons is similar to the FT synthesis, but favors the production of methane.

2.2 Methane and Higher Hydrocarbons

Methane is the major constituent of natural gas and is widely utilized for both electricity generation and heating. It is currently in high demand due to existing infrastructure for both transport and distribution, but is also in abundance because of development in the production of shale gas and tight gas [3]. Higher hydrocarbons include those used for transport fuels like gasoline and diesel fuel. Transport fuels are currently useful due to the compatibility with existing transportation infrastructure and technology and are expected to remain in high demand as primary uses include use in combustion engines [3].

The primary technology utilized to produce liquid hydrocarbon fuels from synthesis gas is FT synthesis, but CO_2 can also be hydrogenated to hydrocarbons in a similar synthesis. This can occur by either direct or indirect methods and typically favors the production of light hydrocarbons, such as methane. Catalytic hydrogenation of CO_2 to methane, or the Sabatier reaction, is well known. It is a thermodynamically favorable process, but is kinetically limited. Thus, catalysts are required to achieve acceptable rates of methane production. The Sabatier reaction is less promising than other hydrogenation processes due to its larger consumption of H_2 and lower energy per volume [5].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
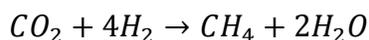
As stated, CO_2 hydrogenation to methane can be completed in either an indirect or direct method. The indirect route can be occur in a single or multi-step process; both

processes perform multiple reactions, typically with a methanol intermediate formation

[5]. The first reaction is the hydrogenation of CO_2 to CO and water.

$$CO_2 + H_2 \rightarrow CO + H_2O$$

The second reaction is the FT synthesis, or hydrogenation of CO, to produce

hydrocarbons.

$$CO + 2H_2 \rightarrow (CH_2) + H_2O$$
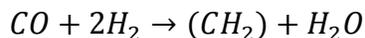
    If a single step process is utilized, a hybrid catalyst can used to simultaneously

catalyze both hydrogenation reactions; if a multi-step process is utilized, a different

catalyst can be used for each reaction.

    Although the indirect route includes more reactions and the use of multiple or

hybrid catalysts, it allows for a higher degree of selectivity. The competition between

CO_2 and CO must be considered and has been widely studied. Zhang et al. have shown

that, using cobalt catalysts, CO_2 hydrogenation proceeds very slowly in the presence of

CO; that is, CO is adsorbed on the cobalt surface to a much greater extent than CO_2.

While the hydrogenation of pure CO or CO_2 show similar catalytic activities, very

different selectivities are seen. That is, CO_2 hydrogenation products contained about

70% more methane than CO hydrogenation product distributions [6]. Figure 2 shows the

selectivity to CH_4 for both CO and CO2 as a function of Time on Stream (TOS) over a

Co-SiO_2 catalyst for pure feed streams of CO and CO_2, respectively. This extreme

difference in selectivity requires that methane formation occurs by two separate and

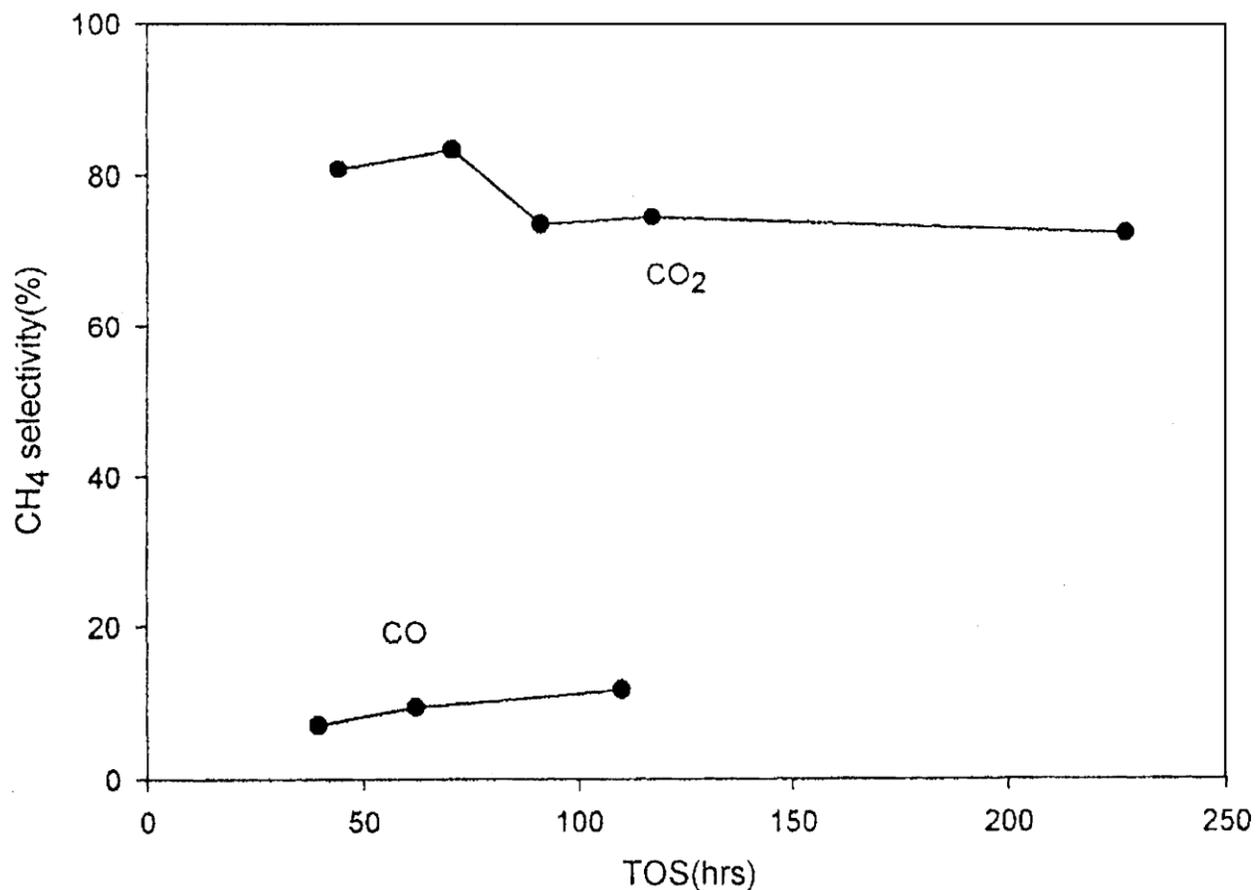different reaction pathways in CO and CO_2 conversion [6].

Figure 2. CO_2 hydrogenation as a function of Time on Stream (TOS) over a Co-SiO$_2$ catalyst.

The indirect route also allows for the enhancement of overall conversion. Figure 3 shows the overall conversion of CO_2 as a function of TOS. Reaction occurred over a Co-Pt/Al$_2$O$_3$ catalysts with a H$_2$:CO ratio of 4:1 in the feed gas [6]. The flow rate of was adjusted to study stability and deactivation. The catalysts did not deactivate after 24 hours when the conversion was approximately 42%; however, when the flow rate decreased, the conversion initially increased to around 55%, but began to deactivate

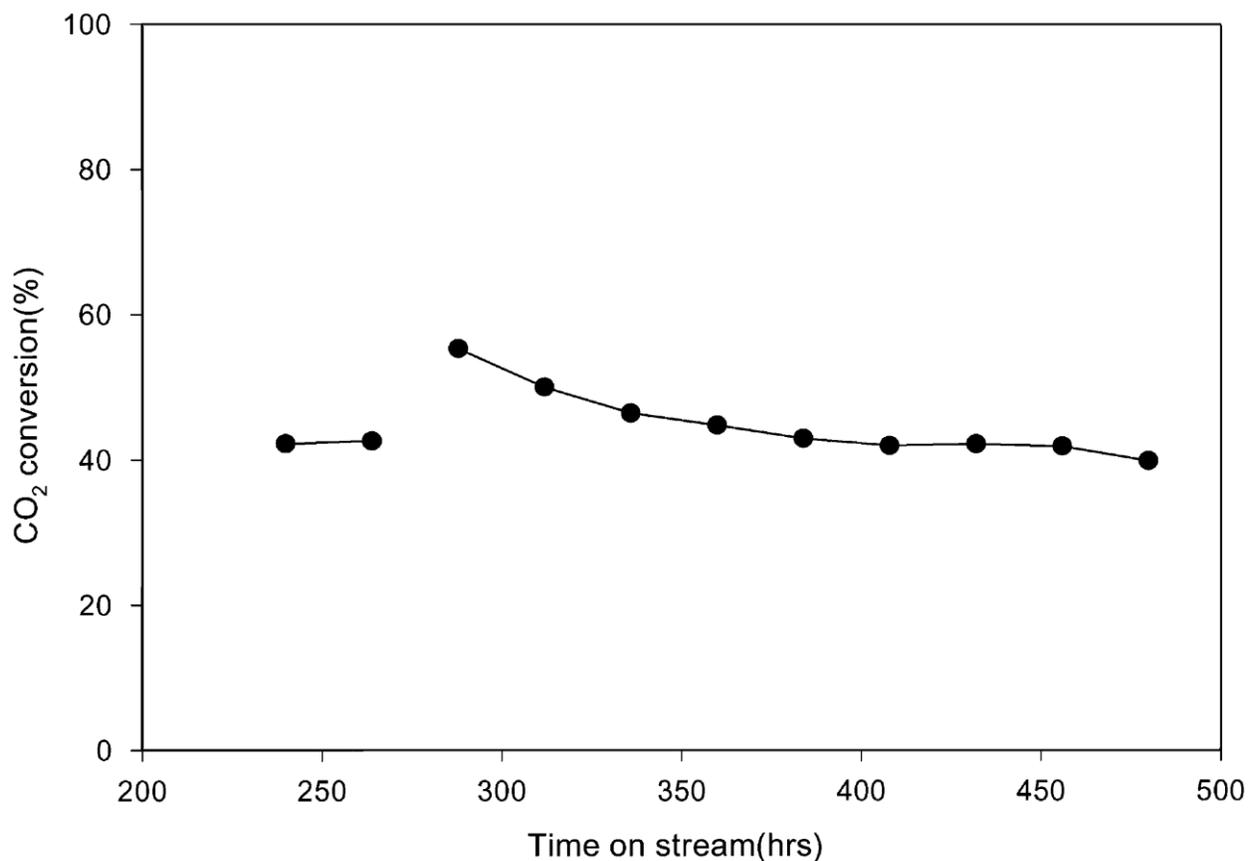slowly until it leveled off at a conversion of approximately 40% [6].

Figure 3. CO_2 conversion via hydrogenation over a Co-Pt/Al_2O_3 catalyst.

As seen above, CO_2 hydrogenation utilizes a different reaction pathway than FT synthesis. However, both syntheses can be utilized to produce methane and higher hydrocarbons [5]. The major drawbacks of these syntheses is that they typically produce a broad spectrum of products; that is, 100% selectivity to a single product is challenging to achieve.

Melaet et al. have recently evaluated the catalytic activity and selectivity of Co/TiO_2 and Co/SiO_2 catalysts with both metallic and oxidized Co. This research was based on the fact that surface science dictates that cobalt (Co) is necessary to disassociate CO and that the metallic state is most likely the active state. Both supports

were investigated as it is known that the nature of the support influences the particle size distribution and dispersion. Melaet et al. have determined that a cobalt oxide catalyst is more active and selective that its metallic equivalent on a TiO_2 support [7].
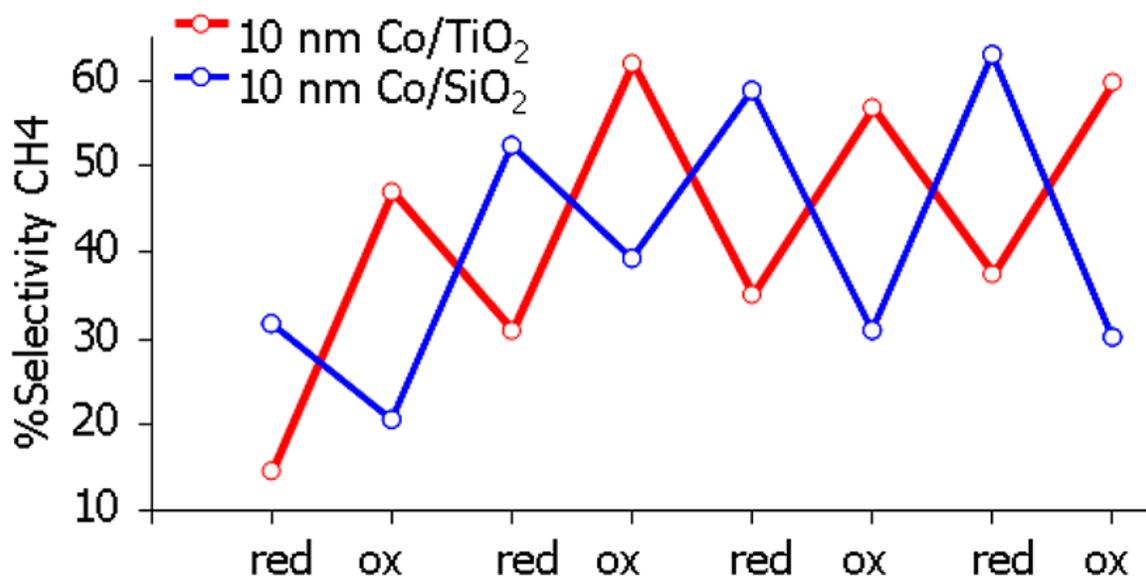

Figure 4. Cobalt catalyst percent selectivity to methane over TiO2 and SiO2 supports in both reduced and oxidized states.

Figure 4 shows that the Co/TiO_2 catalysts performed approximately 5-fold better when in the oxidized rather than reduced state and selectivity for methane was largely improved. Additionally, the Co/TiO_2 catalysts enhanced the selectivity to methane compared to the Co/SiO_2 catalysts in the metallic state. It is believed that oxidized Co forms a catalytically active and unique interface with TiO_2. This interaction enhances the activity of both CO and CO_2 hydrogenation with regards to metallic Co/TiO_2. This catalytic data enhances our understanding of the surface chemistry associated with the FT synthesis and CO_2 hydrogenation reactions and allows the product distribution to be fine-tuned by utilizing metal/metal-support interaction [7].

Both CO and CO_2 hydrogenation relate directly to methane, hydrocarbons, and oxygenates, allowing sustainable production of chemicals and fuels that are highly demanded in today's energy marketplace. Although CO_2 hydrogenation can be used for sustainable production of currently demanded fuels and chemicals, it is also a promising technology for future developments and potentially demanded resources. Primarily, CO_2 hydrogenation could be integral to the formation of a hydrogen economy where H_2 is used as a primary energy storage and transportation medium, enabling sustainable development. Formic acid is considered a necessary chemical in the hydrogen economy.

2.3 Formic Acid

Formic acid is the simplest carboxylic acid and can be used as a building block for commodity chemicals, though its utilization is more limited compared to other products produced via CO_2 hydrogenation. Currently, it is used in the textile industry, cleaning, as a preservative and is produced through the combination of CO and methanol with a strong base.

Formic acid is considered a promising technology for chemical storage of hydrogen. Chemical storage of hydrogen involves media that contain hydrogen in chemically bonded forms; the release of hydrogen begins when the storage media is exposed to thermal or catalytic decomposition. Challenges of chemical hydrogen storage include ease of storage and delivery processes, storage capacity, and stability of the storage material [8]. Formic acid is a promising chemical for hydrogen storage as it has a volumetric hydrogen density of 53 g of H_2 per liter, a low-toxicity, and is liquid under ambient conditions, and decomposes to hydrogen under mild conditions [8, 9].
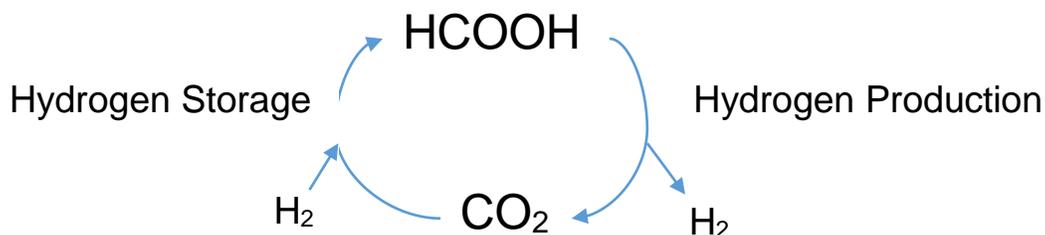
Figure 5. The formic acid and CO_2 cycle for hydrogen storage.

Demand of formic acid could increase significantly within the context of the hydrogen economy with the development of an efficient formic acid dehydrogenation catalyst [3, 9]. Hydrogen production from formic acid has typically been achieved with a variety of homogeneous and heterogeneous catalysts, such as gold-ceria catalysts and other noble metals [8]. The concept of a hydrogen economy would be even more attractive should a viable hydrogenation catalyst become available that is capable of reducing CO_2 with hydrogen in the absence of a base [9].

The conversion of CO_2 into formic acid is highly difficult and controlled by the pH of the solution with basic media being favorable. In a recent study, Moret et al. have recently discovered a homogeneous ruthenium-based catalyst with water soluble phosphine ligands, $[RuCl_2(PTA)_4]$, that hydrogenates CO_2 into formic acid in acidic media, without the need of buffers, amines, or bases. These water soluble ligands include 1,3,5-triaza-7-phosphaadamantane (PTA). Possible catalytic intermediates were discovered using NMR spectroscopy; these intermediates include the monohydride and dihydride species, $[RuH_2(PTA)_4]$ and $[HRu(PTA)_4Cl]$, of the ruthenium complex; a tentative catalytic cycle was proposed based on the observed data and prior literature in which the ruthenium-based catalysts hydrogenates to the monohydride species, reacts with CO_2, and loses a formic acid molecule to return to the monohydride species [9].

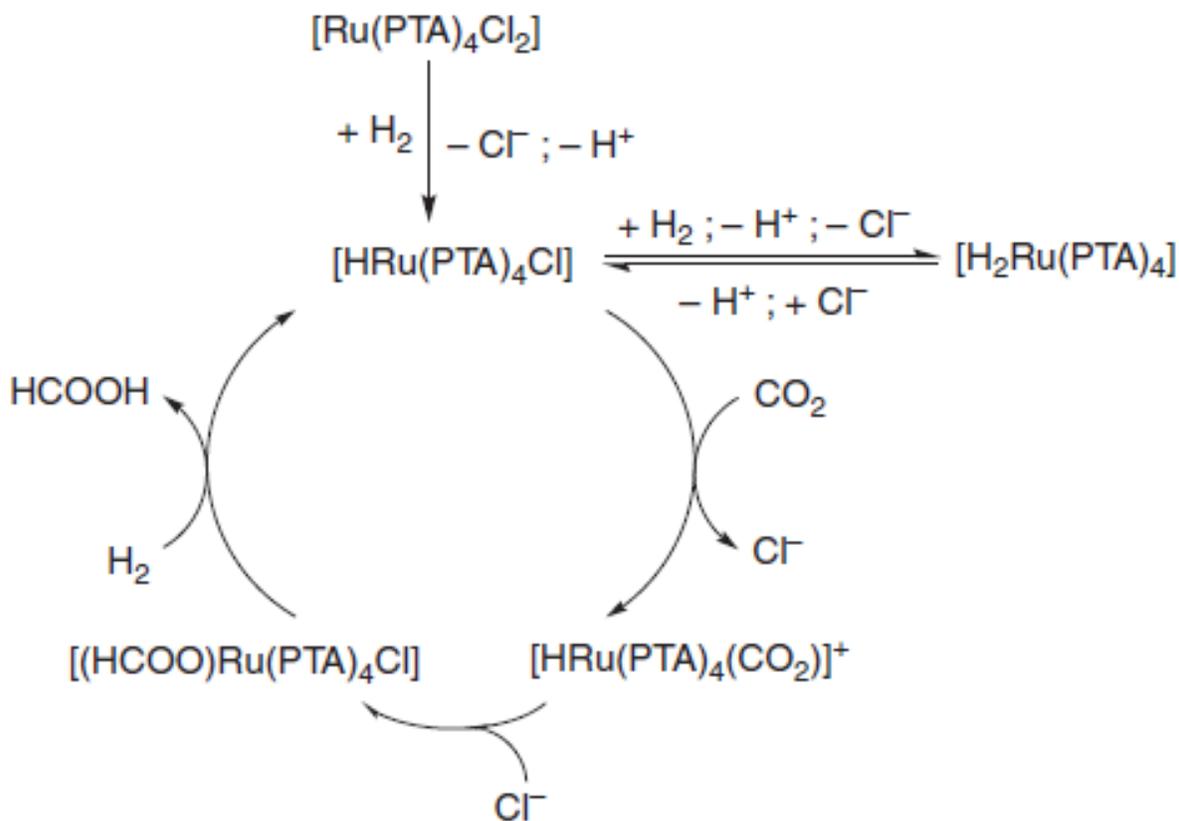Figure 6 shows the proposed catalytic cycle for CO_2 hydrogenation using [RuCl2(PTA)4] catalyst in DMSO.

$$[Ru(PTA)_4Cl_2]$$

$+ H_2$ $- Cl^- ; - H^+$

$[HRu(PTA)_4Cl]$ $\xrightleftharpoons[- H^+ ; + Cl^-]{+ H_2 ; - H^+ ; - Cl^-}$ $[H_2Ru(PTA)_4]$

HCOOH

CO_2

H_2

Cl^-

$[(HCOO)Ru(PTA)_4Cl]$ $[HRu(PTA)_4(CO_2)]^+$

Cl^-

Figure 6. Catalytic cycle for CO_2 hydrogenation using [RuCl2(PTA)4] in DMSO.

This complex catalyzes the direct hydrogenation of CO_2 to formic acid in dimethyl sulfoxide (DMSO), which is highly stable and can be recycled without loss of activity, at significantly higher concentrations than other catalysts have shown, approximately 15 volume percent. Additionally, the separation of formic acid from the reaction mixture is much simpler without the need of a base [9].

Recent developments for the dehydrogenation of formic acid include complexes based on iron, a cheap and abundant element, such as the recently researched pincer-supported iron catalyst [10, 11]. Although the results with the first-row transition metals

are promising, they are still inferior to the results achieved with precious metal catalysts. It is also unclear what role the additives in the catalytic reaction is; an increased understanding of additives could lead to the enhancement of the catalysis of formic acid dehydrogenation by inexpensive iron-based catalysts [10].

Efficient catalysts capable of converting CO_2 directly into formic acid and selectively decomposing formic acid into H_2 and CO_2 may help to propel a hydrogen-based economy. The homogeneous ruthenium catalyst developed by Moret et al. that is considerably more sustainable than existing routes and the recent developments in inexpensive iron-based formic acid dehydrogenation catalysts will be imperative in the developing the use of formic acid as a renewable energy hydrogen carrier.

2.4 Methanol

Methanol has many potential uses due to its flexibility. It is a great fuel that can be blended with gasoline or used directly in fuel cells and is a key starting material for many industrial chemicals, such as acetic acid or formaldehyde. This versatility led to the idea of the, "methanol economy," proposed by George A. Olah [3]. In the methanol economy, an alternative to the previously discussed hydrogen economy, methanol replaces fossil fuels as a mean for energy storage, transportation, and raw materials for chemical production; in combination with CO_2 hydrogenation, the methanol economy is a possibility for sustainable production and development.

Methanol is synthesized industrially from gas mixtures of H_2, CO_2, and CO at elevated pressures and temperatures with $Cu/ZnO/Al_2O_3$ industrial catalysts [12].This catalytic system has also been proposed for the production of methanol via CO_2 hydrogenation as Cu/ZnO based catalysts have been studied extensively for the

catalysis of CO_2 hydrogenation to methanol. Generally, methanol synthesis by CO_2 hydrogenation contains three competing reactions. The first reaction is the direct synthesis of methanol from CO_2, as follows.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
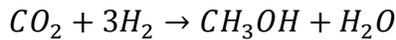
The second reaction is the hydrogenation of CO to methanol, as follows.
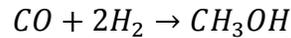
$$CO + 2H_2 \rightarrow CH_3OH$$

The third reaction is the endothermic reverse water gas shift reaction, which has been discussed above and is shown again.

$$CO_2 + H_2 \rightarrow CO + H_2O$$

In order to fully understand catalytic performance, the kinetics and thermodynamics of the three competing reactions must be considered. Reaction kinetics are largely influenced by the catalyst utilized and the residence time of the reactor, while the thermodynamics are influenced by the reactor conditions, such as temperature and pressure. Typical single pass CO_2 conversion through a fixed bed reactor are in the range of 20%-40%, with nearly complete CO_2 conversion and high methanol selectivity being achieved by recycling the unreacted components. However, it is advantageous to omit the recycling process; this can be accomplished through the development of an efficient catalyst that would achieve high single pass CO_2 conversion and methanol selectivity [3].

Palladium (Pd) supported over gallium oxide (Ga_2O_3) is a prominent catalyst for CO_2 hydrogenation to methanol because gallia polymorphs can be converted to a thermodynamically stable crystalline phase at high temperatures. This phase is called the β form in which the Pd-Ga intermetallic compound increases the catalytic

performance for CO_2 hydrogenation to methanol; the gallium oxide polymorphism and stability was studied by Roy et al. in 1952 and can be applied to Pd/Ga_2O_3 catalysts for methanol synthesis [13, 14].

A recent study was conducted by Oyola-Rivera et al. that utilized a Pd-Pd_2Ga catalyst supported over Ga_2O_3 polymorphs (α-Ga_2O_3, α-β-Ga_2O_3, β-Ga_2O_3). This research was conducted in order to better understand the role of Pd catalysts supported on Ga_2O_3 polymorphs in the conversion of CO_2 to methanol with a focus on CO_2 adsorption and characterization aspects [13]. Pd/Ga_2O_3 based catalysts are considered an alternative to Cu/ZnO catalysts for CO_2 hydrogenation to methanol.

The primary reaction product for CO_2 hydrogenation on a Pd/Ga_2O_3 catalysts at 543 K and 1.72 MPa is methanol, with trace amounts of dimethyl ether produced by methanol dehydration at the acid sites of Ga_2O_3. It was determined that the catalytic activity improves with an increase in the amount of Pd_2Ga intermetallic compound, and thus, less metallic Pd. This is advantageous as a reduction in metallic Pd allows for the catalysts to be produced with less cost. Although high selectivity can be achieved, figure 7 shows that the CO_2 conversion was relatively low for all Ga_2O_3 polymorphs. The maximum conversion achieved at 543 K and 1.71 MPa was approximately 16% on an α-Ga_2O_3 support.
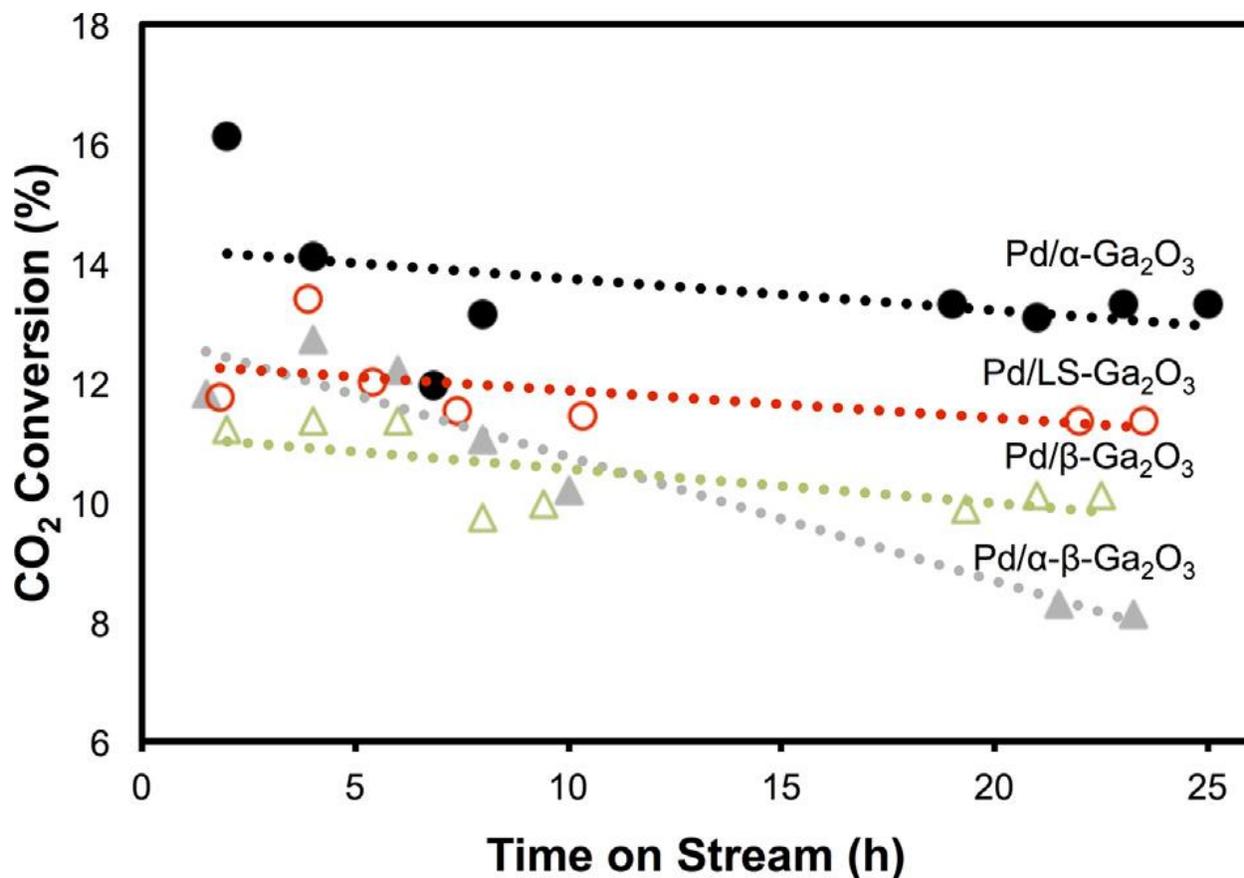
Figure 7. CO2 conversion as a function of TOS for Pd catalysts supported on Ga2O3 polymorphs at 543 K and 1.72 MPa.

Other major catalysts for CO_2 hydrogenation to methanol include Cu/ZnO based catalysts. A recent study has identified the active site for the activation of CO_2 during the synthesis of methanol on $Cu/ZnO/Al_2O_3$ industrial catalysts [12]. The active site consists of copper surface defects with zinc atoms present; because copper does not actively interact with CO_2, substitution of zinc into the copper surface defects strengthens the binding of intermediates and increases the activity of the catalysts [12, 15].

Because copper interacts very poorly with CO_2, and zinc is necessary to enhance binding of intermediates and accelerate conversion, Graciani et al. have provided theoretical evidence for an entirely different type of site for CO_2 activation [15]. They

have suggested the use of a Cu-ceria interface, which is highly active for the synthesis of methanol from CO_2, because the combination of metal and oxide centers in the Cu-ceria interface provides favorable reaction pathways that are not seen over a Cu-Zn alloy, such as $Cu/ZnO/Al_2O_3$ industrial catalysts. Specifically, the ceria component enhances the stability of CO_2 on the catalyst surface, allowing for efficient routes of methanol synthesis not seen on pure Cu or Cu/Zn alloys [15].

Understanding activation is an important approach to the conversion of CO_2 because it aids in overcoming the chemical inertness of CO_2. The research conducted by Graciani et al. is an important step in understanding CO_2 activation and can be used to overcome its kinetic limitations. This understanding can also be expanded to the production of dimethyl ether via CO_2 hydrogenation.

2.5 Dimethyl Ether

Dimethyl Ether (DME) is another attractive chemical as it is a potential substitute for diesel fuel with better combustion performance, usable as a chemical feedstock for production of oxygenates, olefins, and hydrocarbons, and an efficient H_2 carrier for fuel cells or other applications [3, 16]. DME can be synthesized from methanol via a dehydration reaction or via a one-step hydrogenation reaction of CO_2; typical production of DME utilizes a two-step process. In this two-step process, methanol is synthesized from syngas and then DME is produced from the dehydration of methanol. A two-step process allows methanol to be synthesized on a metallic catalysts and then dehydrated on an acid catalyst in separate reactors. However, a superior method integrates this two-step process into a single step in which methanol is synthesized and dehydrated in the same step utilizing a bifunctional catalyst, though only a few articles discuss the

direct synthesis of DME via CO_2 hydrogenation [17]. A single step process has an economic advantage over a two-step process, but the utilization of bifunctional catalysts requires that the catalysts efficiently catalyze both methanol synthesis and dehydration reactions. Regardless of which method of synthesis is chosen, a two-step or a single step process, three independent reactions are involved in DME synthesis. The first reaction is the direct synthesis of methanol from CO_2, as follows.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
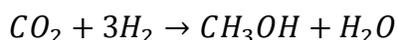
The second reaction is the dehydration of methanol to DME, as follows.
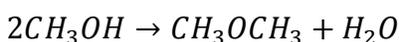
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

The third reaction is the endothermic reverse water gas shift reaction, which has been discussed above and is shown again.

$$CO_2 + H_2 \rightarrow CO + H_2O$$
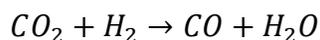
These three reactions are very similar to the methanol synthesis reactions discussed above. As a result, catalysts for the direct CO_2 to DME process must be able to efficiently catalyze both methanol synthesis and dehydration reactions, while minimizing the yield of CO produced via the RWGS reaction [13, 16, 17].

Oyola-Rivera and coworkers use of Pd-Pd$_2$Ga catalyst supported over Ga$_2$O$_3$ polymorphs, which was previously discussed, also examined the single step synthesis of DME via CO_2 hydrogenation. As mentioned above, DME was observed as a result of methanol dehydration at the acid sites of Ga$_2$O$_3$. It was determined that the selectivity to DME was not dependent on Pd$_2$Ga content, but instead was dependent on the catalyst acidity. By adding the highly acidic niobium oxide (Nb2O5) to the catalyst surface, Oyola-Rivera and coworkers were able to increase the selectivity for DME from mere

traces to approximately 53%; the disadvantages of adding niobium oxide to the surface include the reduction in catalytic surface area of about 30% [13]. This demonstrated that the selectivity to DME can be enhanced by the addition of an acidic species on the catalyst surface.

Other bifunctional catalysts for the single step conversion of CO_2 to DME include Cu-ZnO based compounds, such as a Cu-ZnO-ZrO2 catalysts studied by Bonura et al. [17]. In a recent study, Bonura et al. studied the influence of catalyst preparation on CO_2 activation at hydrogenation and dehydration reaction sites.

3. Conclusion

CO_2 is kinetically and thermodynamically stable. Because of this, CO_2 conversion reactions require efficient catalysts. These catalysts must have high CO_2 conversion, high selectivity to the desired product, and high stability.

Many promising fuels and chemicals can be produced via CO_2 hydrogenation, as shown, that are currently or potentially will be in high demand. Several of these chemicals can be utilized in order to generate sustainable development and processes. Though many developments in catalysis have been made since 2014 that enhance hydrogenation processes, further developments must be made in catalysis in order to achieve high enough CO_2 conversion, selectivity, and stability to develop sustainable industrial processes.

4. Acknowledgements

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