

## CARBON SEQUESTRATION: HYDROGENATION OF CO<sub>2</sub> TO FORMIC ACID

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**Key words:** carbon sequestration, hydrogenation of CO<sub>2</sub>, formic acid

**Abstract.** The concentration CO<sub>2</sub> gas has become a great worldwide challenge because CO<sub>2</sub> is considered as an important counterpart of greenhouse gases. The tremendous increase in the concentration of CO<sub>2</sub> gas, elevated the worldwide temperature as well as it altered the climatic changes. Various physiochemical approaches have been reported to trap the CO<sub>2</sub> gas and the chemical conversion of CO<sub>2</sub> to useful chemicals is one of them. This review covers the conversion of CO<sub>2</sub> gas to formic acid. In this CO<sub>2</sub> hydrogenation reaction, both the homogeneous as well as heterogeneous catalytic systems were discussed along with the effect of solvent systems on reaction kinetics.

### Introduction

The increased release of carbon dioxide (CO<sub>2</sub>) due to the employment of carbon-rich fossil fuels like natural gas, oil and coal, have a drastic effect upon the binomial surrounding and human life. Hence, the rising temperature of the environment and prevailing psychological state changes, are the major concern of the scientists to overcome these problems [1]. The increased emission of CO<sub>2</sub> is not just by the use of carbon-rich fossil fuels, but also due to the advancement of the human development, created many critical problems related to the environment [2]. The emission of the greenhouse gases, especially CO<sub>2</sub> (due to its immense emission amount), contributes more than 60% of the global warming [4, 5]. Before the industrial revolution, the level of the CO<sub>2</sub> was about 280 p.p.m., which has significantly increased in the recent years. Now it is 400 ppm in 2015 and at the last stage throughout the century, which is further predicted to be near by 600 ppm [1, 3, 4]. Various attempts have been made by the researchers to seize CO<sub>2</sub> effectively [6, 7]. There are three possible systematic action plans to control CO<sub>2</sub> as,

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- a. Reduction of the quantity of CO<sub>2</sub> produced [3].
- b. Storage of CO<sub>2</sub> [8].
- c. Utilization of CO<sub>2</sub> [9].

CO<sub>2</sub> could be reduced successfully by applying less carbon intensive energy sources like hydrogen and use of renewable energy source instead of fossil fuel [8]. Capture and sequestration of CO<sub>2</sub> are somewhat well developed process for storage of CO<sub>2</sub>, but they involve the evolution of new technologies [3, 8, 10, 11]. CO<sub>2</sub> shows an attractive property as C1 building blocks, appropriate to the synthesis of the organic chemicals and carbohydrates, and turns out a frugal, renewable and secure carbon source [12]. Various opportunities for the catalytic industries have been generated to create new concepts and employment of the CO<sub>2</sub> as raw materials in the production of value added chemicals to aggravate the global warming caused by the increased CO<sub>2</sub> emissions [13]. To transform CO<sub>2</sub> into other chemicals, high-energy materials or electro-reductive operations are generally required because of high thermodynamic stability of CO<sub>2</sub> gas [14-16]. To convert CO<sub>2</sub> into the useful chemicals, hydrogen is considered as an important high energy material. We can classify the product formation of CO<sub>2</sub>, in two different classes, 1. Chemical products, 2. Fuels (Figure 1) [1].

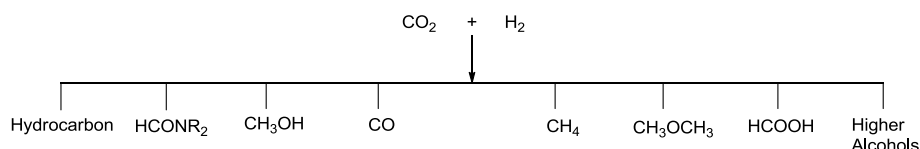


Figure 1. CO<sub>2</sub> Hydrogenation possible products

The non-fossil fuels are considered as an alternative to conventional fuels. The growing consumption with a decrease in the resources of the fossil fuels, non-fossil fuels gave an opportunity to burn them in the innermost combustion engines. Non-fossil fuels like methanol, dimethyl ether (DME) and hydrocarbons could be easily obtained from the CO<sub>2</sub> hydrogenation reaction. The advantages of this product are easy transportation, handling and storage. In a chemical industry methanol and formic acid are applied as platform chemicals in various processes not only as a reaction intermediate but also as raw material.

The active presence of the catalysis, biology, nanoscience, nanotechnology and environmental science, based on their principles and practical importance, the CO<sub>2</sub> hydrogenation has been more intensively investigated in recent years. The catalytic reduction or the hydrogenation of CO<sub>2</sub>, both heterogeneous and homogeneous catalysts were used under different reaction conditions for figuring out the problem of fuels and global warming.

The stability, separation, handling and reuse of heterogeneous catalyst is well documented over homogeneous catalysts as it suffers with problems like retrieval and regeneration catalysts, but surprisingly, they showed acceptable activity and selectivity during the CO<sub>2</sub> hydrogenation reaction.

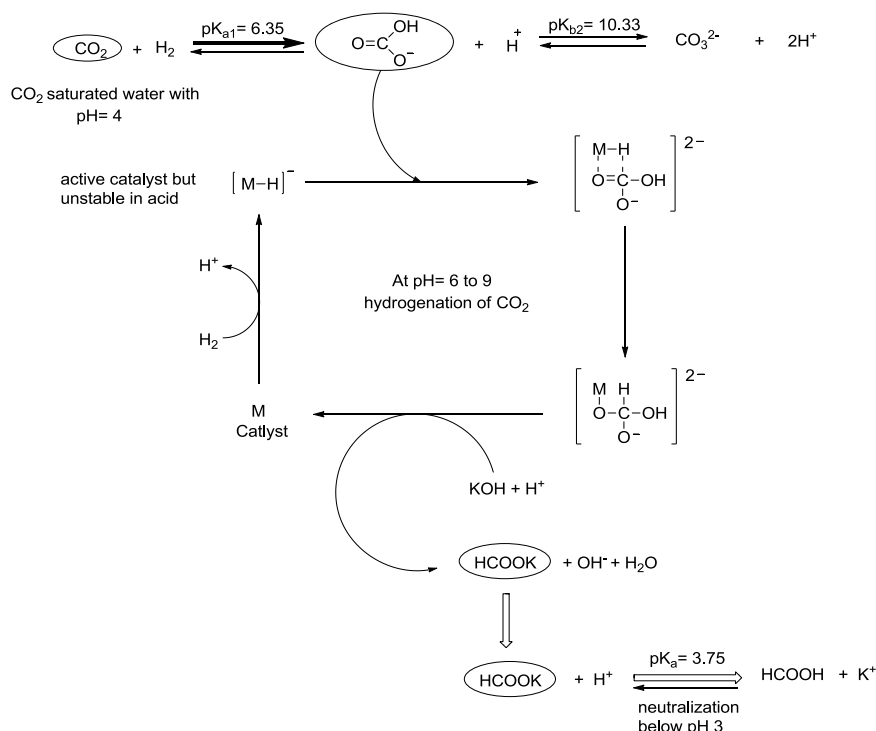
The review is mainly focused on the synthesis of formic acid and formates followed by hydrogenation reaction. The mechanism behind hydrogenation of the CO<sub>2</sub> is also broadly discussed in the review article. Moreover, we also discussed the use of ruthenium (Ru) catalyst in the CO<sub>2</sub> hydrogenation reaction. Therefore, this review attempts to provide an understanding of the catalytic reactivity and mechanism of the CO<sub>2</sub> hydrogenation reaction over several types of reported Ru based catalysts.

### Synthesis of formic acid and formates

In industries, for producing plentiful chemicals, formic acid was used as a feed stock [17] and mainly because of that at the start of 1990's, the keen interest for the CO<sub>2</sub> hydrogenation developed to synthesize formic acid and formates [18]. In a recent development, by combining CO<sub>2</sub> hydrogenation with the selective formic acid decomposition, it has been considered that the formic acid also used as a hydrogen storage material [18, 19]. The numerous efforts were made earlier based on the electrochemical or photochemical reduction under mild condition to reduce CO<sub>2</sub> with transition metal catalysts. The water is readily available, cheap, nonflammable, nontoxic in nature and also has immense property to dissolve CO<sub>2</sub> completely into it. Hence, in the recent advancement, researcher moved towards the study of CO<sub>2</sub> hydrogenation in the water solvent system. The water saturated with the CO<sub>2</sub> has pH 4 at 20°C [65]. Many transition metal hydride complexes are unstable in the acidic condition, were tried in water. In some of the previous reports, bases like KOH and NaOH were used to obtain the CO<sub>2</sub> hydrogenation product in the formate complex like HCOOK (Scheme 1) at the pH range 6-9 in water. In this type of hydrogenation, the water shows pH dependent equilibrium between HCO<sub>3</sub><sup>-</sup> with pK<sub>a1</sub> value 6.35 at 25°C and CO<sub>2</sub> with pK<sub>b2</sub> value 10.33. Hence, bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) is the real substrate not the CO<sub>2</sub> gas as it gets dissolved in the water. At the end of this reaction, the base was separated from the solution by neutralizing it below pH 3.0 to obtain formic acid (with pK<sub>a</sub> value 3.75 at 25°C).

In the synthesis of formic acid, it is very essential to add an inorganic or organic base in the reaction system in order to shift the reaction equilibrium [17] to make more selective towards formic acid formation. The formate is generated during the addition of an inorganic base, and converted to formic acid using strong acid. The recovery of formic acid is complicated by using

organic base as it is more volatile than inorganic base, hence more energy consuming [17].



Scheme 1. Synthesis of formic acid under basic condition [64]

### Active catalytic systems for CO<sub>2</sub> Hydrogenation reaction

The synthesis of formate and formic acid generally moves ahead with the organometallic complex in a homogeneous system at low temperatures as compared to the heterogeneous systems during the CO<sub>2</sub> hydrogenation [18]. In table 1, ruthenium (Ru), rhodium (Rh) and iridium (Ir) like transition metal based catalyst used for the CO<sub>2</sub> hydrogenation, shown a good increase in the turnover number (TON) value of formic acid.

In 1976, the CO<sub>2</sub> hydrogenation with the Wilkinson catalyst was introduced by Inoue, where the catalyst having transition metal rhodium in the organometallic complex, *i.e.* RhCl(PPh<sub>3</sub>)<sub>3</sub> [22]. Later, the CO<sub>2</sub> hydrogenation to formic acid formation was studied by Ezhova *et al.* with the help of Wilkinson catalyst and he reported that the phosphine ligand complex with Rh metal work effectively in the formic acid synthesis [23]. As per their study, the nature of solvents also decides the catalytic activity during the reaction. In

conclusion they recorded that polar solvents like DMSO and alcohol gives a high rate of CO<sub>2</sub> hydrogenation reaction.

Table 1. CO<sub>2</sub> hydrogenation catalyzed by transition metal to formate & formic acid

Entry No.	Catalyst	Solvent	Additives	$p(\text{H}_2)/p(\text{CO}_2)$ (atm)	T/°C	TON	TOF (h <sup>-1</sup> )	Ref.
1.	Si-(CH <sub>2</sub> ) <sub>3</sub> NH(CSCH <sub>3</sub> )-{RuCl <sub>3</sub> (PPh <sub>3</sub> )}	H <sub>2</sub> O	IL	88/88	80	1840	920	17
2.	[Ru(COD)(2-methylallyl) <sub>2</sub> ]	[DAMI][NTf <sub>2</sub> ]	H <sub>2</sub> O	20/20	100	1225	245	20
3.	Ru-MMT NPs(6 mM)	[DAMI][NTf <sub>2</sub> ]	Ethanol+PPh <sub>3</sub>	25/25	100	1620	324	21
4.	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	MeOH	PPh <sub>3</sub> , NEt <sub>3</sub>	20/40	25	2700	125	23
5.	Ru <sub>2</sub> (CO) <sub>5</sub> (dppm) <sub>2</sub>	acetone	NEt <sub>3</sub>	38/48	RT	207	207	24
6.	CpRu(CO)( <i>m</i> -dppm)Mo(CO) <sub>2</sub> Cp	C <sub>6</sub> H <sub>6</sub>	NEt <sub>3</sub>	30/30	120	43	1	26
7.	RuCl <sub>2</sub> (PMe <sub>3</sub> ) <sub>4</sub>	scCO <sub>2</sub>	NEt <sub>3</sub> , H <sub>2</sub> O	80/140	50	7200	153	27
8.	NiCl <sub>2</sub> (dcpe)	DMSO	DBU	40/160	50	4400	20	28
9.	TpRu(PPh <sub>3</sub> )(CH <sub>3</sub> CN)H	CF <sub>3</sub> CH <sub>2</sub> OH	NEt <sub>3</sub>	25/25	100	1815	113	29 b
10.	TpRu(PPh <sub>3</sub> )(CH <sub>3</sub> CN)H	THF	NEt <sub>3</sub> , H <sub>2</sub> O	25/25	100	760	48	30
11.	RuCl(OAc)(PMe <sub>3</sub> ) <sub>4</sub>	scCO <sub>2</sub>	NEt <sub>3</sub> /C <sub>6</sub> F <sub>5</sub> OH	70/120	50	31667	95000	31
12.	( $\eta^6$ -arene)Ru(oxinato)	H <sub>2</sub> O	NEt <sub>3</sub>	49/49	100	400	40	39
13.	( $\eta^6$ -arene)Ru( <i>bis</i> -NHC)	H <sub>2</sub> O	KOH	20/20	200	23000	306	40
14.	[Cp*Ir(phen)Cl]Cl	H <sub>2</sub> O	KOH	29/29	120	222000	33000	41
15.	PNP-Ir(III)	H <sub>2</sub> O	KOH, THF	29/29	120	3500000	73000	42
16.	Cp*Ir(NHC)	H <sub>2</sub> O	KOH	30/30	80	1600	88	43
17.	Si-(CH <sub>2</sub> ) <sub>3</sub> NH(CSCH <sub>3</sub> )-Ru	C <sub>2</sub> H <sub>5</sub> OH	PPh <sub>3</sub> , NEt <sub>3</sub>	39/117	80	1348	1384	51

The focus of CO<sub>2</sub> hydrogenation study was diverted towards ruthenium (Ru) complex more, as it was found most promising metal for the selective synthesis of formic acid synthesis [24]. In one of the study, followed by *in situ* catalyst formation, various phosphine and other ligands were compared understand their catalytic performance of Ru (II) catalyst [25] for the same reaction. Surprisingly, no proper correlation was established between the catalytic activity and basicity of monophosphines (PR<sub>3</sub>) ligand. The Bite angle effect and the unusual interplay of the electronic effects of ligands [25] were considered their crucial effect on the CO<sub>2</sub> hydrogenation reaction as while reducing the the bite angle of weak basic diphosphines like *bis*(diphenylphosphino) compounds, they start working as an extremely active hydrogenating catalyst and opposite trend were shown by strong basic diphosphines like *bis*(dicyclohexylphosphino) compounds [25].

Low activity for the hydrogenation of CO<sub>2</sub> exhibited by Ru/Mo heterobimetallic complex and directs to the active dihydride species because of the non-facile reaction of complex with H<sub>2</sub> [26]. A careful, systematic search of the water effect in a reaction process has been going on. An addition of minor amount of the water in the organic solvent results in accelerating effect in the reaction for the active systems like Pd, Rh and Ru etc., [22, 27, 29a]. In

some cases the cognitive process within the reaction system could not produce a more desirable change after adding a minimum amount of the water [58]. The highly effective catalytic system can be generated through the application of water during the reaction process as the water can act as an auxiliary ligand and to facilitate CO<sub>2</sub> insertion, which forms a hydrogen bond with the oxygen of the CO<sub>2</sub> gas (Figure 2A) [29a]. It was assumed that within the water molecule (H<sub>2</sub>O) and an oxygen atom of the CO<sub>2</sub>, hydrogen bonding interaction leads to carbon electrophilicity and it facilitates insertion within the metal-hydride bond [29a,30]. A reaction mechanism with the ruthenium complex TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>CN)H to account the water effect was established based on the theoretical calculations and high pressure nuclear magnetic resonance (NMR) [30] study. An aqua metal hydride species TpRu(PPh<sub>3</sub>)(H<sub>2</sub>O)H formed, which is the key intermediate in the catalytic cycle due to a ligand displacement reaction of the water molecule. Adding 20% water in the THF, catalyst TpRu (PPh<sub>3</sub>) (CH<sub>3</sub>CN) H [Tp =hydrotris (pyrazolyl) borate] gave an enhanced reaction rate [29b]. The mechanism of water effect in the CO<sub>2</sub> hydrogenation using TpRu (PPh<sub>3</sub>) (CH<sub>3</sub>CN) H can be understood by Figure 2B [29b], where during the hydrogenation of the CO<sub>2</sub>, the hydride and a proton continuously transferred by the intermediate to the CO<sub>2</sub> for the synthesis of formic acid. To regenerate TpRu (PPh<sub>3</sub>) (H<sub>2</sub>O) H, the intermediate was converted into a transient hydroxyl species by itself associating with H<sub>2</sub> molecule. As per calculation, the internalization of water could trigger the CO<sub>2</sub> molecule, and the reaction barrier in a significant manner can be reduced [30].

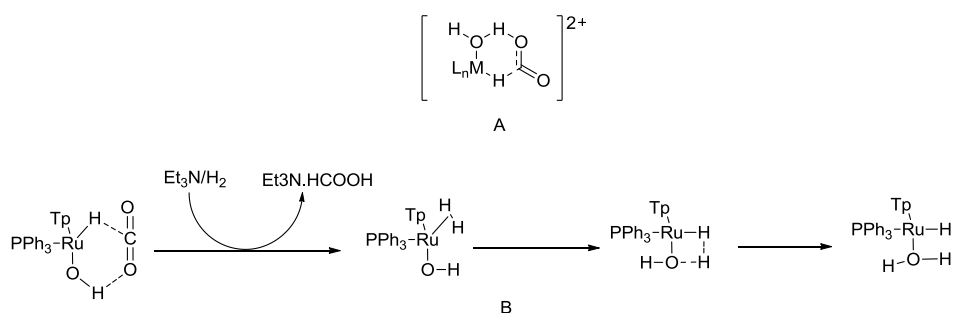
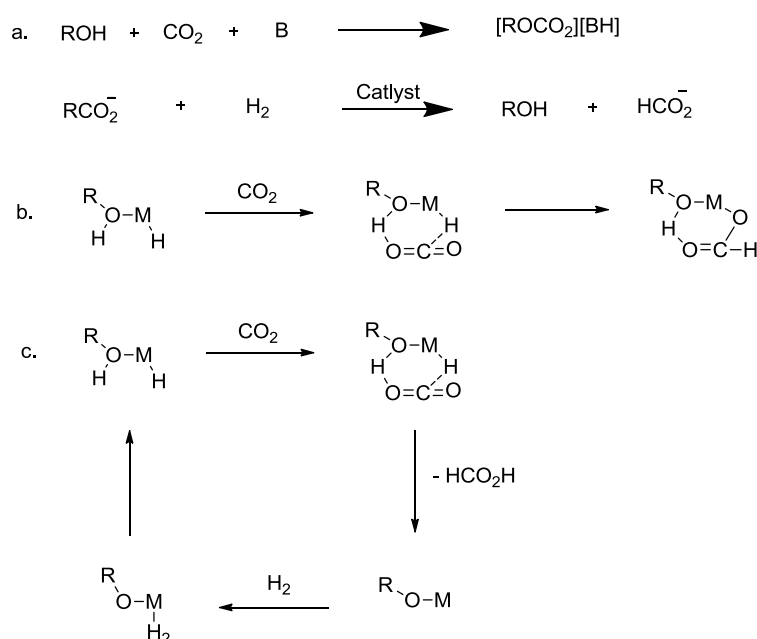


Figure 2. The technical aspects of the water effect in the CO<sub>2</sub> hydrogenation [29b]

Density functional theory (DFT) calculation was used to investigate the reaction mechanism and found that after the addition of one or two moles of the water, in a clearly noticeable manner, lowering in the reaction barrier seen as compared to that in gas phase [42]. Further study of the TpRu (PPh<sub>3</sub>) (CH<sub>3</sub>CN) H catalyst to analyze the consequence of the alcohol reveals that the intermediate of a catalytic process is the alcohol analogue of the aqua hydride

complex. An oxygen atom of the CO<sub>2</sub> and the highly acidic hydrogen in the intermediate create strong interaction between them and resulting the enhanced electrophilicity in the carbon atom of CO<sub>2</sub>, which helps to the pronounced promotion effect of the CF<sub>3</sub>CH<sub>2</sub>OH among the alcohols. Study of the mechanism of the CO<sub>2</sub> hydrogenation based upon the effect of the bases and alcohols was described in the details [31]. The affinity of 1,8-Diazabicyclo (DBU) compound to trap CO<sub>2</sub> makes a huge impact about the magnitude of the reactions and increase the rate of the reaction seen by replacing NEt<sub>3</sub> with DBU [32, 33]. Transformation of Ru-based precursor into a cationic complex was studied by *in situ* NMR spectroscopy, which revealed that the alcohol induces the precursor [31] in CO<sub>2</sub> hydrogenation reaction. The alcohol plays an important role in not just to generate carbonic acids or protonated amines in the solution, but it can facilitate to insert the CO<sub>2</sub> into the M–H bond as well as in a concerted ionic hydrogenation mechanism to hydrogenate CO<sub>2</sub> (Scheme 2) [35].



Scheme 2. The CO<sub>2</sub> hydrogenation with three possible explanations for involvement of alcohol [1, 35]

Since, super critical carbon dioxide (scCO<sub>2</sub>) hydrogenation develops interest [9] as scCO<sub>2</sub> can not only work as reactant, but also as a reaction

solvent during the process. Soluble  $\text{RuXY}(\text{PMe}_3)_4$  catalysts ( $\text{X}, \text{Y} = \text{H}, \text{Cl}, \text{or } \text{O}_2\text{CMe}$ ) in a  $\text{scCO}_2$  solution, prominent rates of hydrogenation were obtained along with the following merits such as improved mass and heat transfer properties, easy separation and high solubility [27, 36, 37]. Under experimental conditions, the reaction of the  $\text{scCO}_2$  hydrogenation follows 1<sup>st</sup> order reaction kinetics and the reaction rate mainly dependent upon the choice of the additive [37].

On the other hand, water-soluble ligands were tested for catalysis in water. Hydrogenation of the  $\text{CO}_2$  to the formic acid or formate, a series of Ru and Ir complexes have been developed to the greatest advantage in the aqueous alkaline solution [38-44]. The reaction can be accelerated, if the catalyst contains, the stronger electron donor ligands [38, 40]. Himeda, prepared Ir based complex catalyst and at the beginning of the reaction is homogeneous and highly reactive. However, at the final stage of the reaction, it turns into heterogeneous and get deactivated [38, 41, 44]. The conventional evaporation and filtration without generation of the waste, the solvent, product, and catalyst easily separated in this process. A catalytic cycle on account of the  $\text{CO}_2$  hydrogenation involves the formation of a hydrido complex by *in situ* process and as per its plausible mechanism (Figure 3) [39, 42, 43]  $\text{CO}_2$  inserts into the hydrido complex and gives formyl species and further turned into the formate anion after reacting with hydroxide [1].

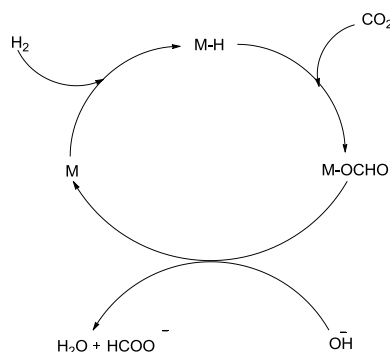


Figure 3.  $\text{CO}_2$  hydrogenation using Ru and Ir complexes via a plausible reaction mechanism [1].

The water-soluble ruthenium aqua complexes without any base in  $\text{H}_2\text{O}$  under acidic conditions (pH of 2.5–5.0) converted  $\text{CO}_2$  into formic acid has been followed by hydrogenation reaction at  $40^\circ\text{C}$  after 70 hours, bby TON value 55 [45]. Here, to afford the formate complex, the aqua complex reacts



with H<sub>2</sub> at pH of 2.5–5.0 to give hydride species, which further reacts with CO<sub>2</sub> (Figure 4) [45].

Investigating the non-platinum gatherings having dynamic components embodying metals are exceptionally restricted work inside of this area. Significant, CO<sub>2</sub> hydrogenation activity of formic acid was found in the combinations of FeCl<sub>3</sub>, NiCl<sub>2</sub>, or MoCl<sub>3</sub> with dcpe [28]. Towards CO<sub>2</sub> hydrogenation, Cubanes *et al.* reported remarkably, the discrete reactivity of

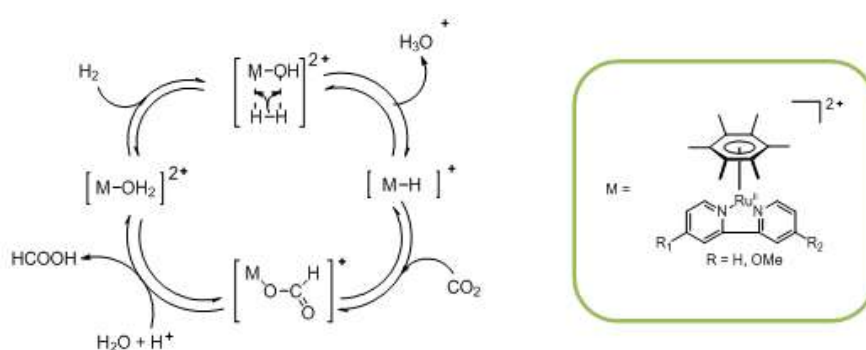


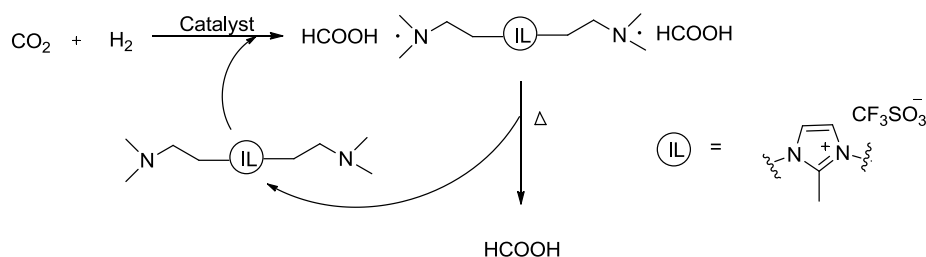
Figure 4. CO<sub>2</sub> hydrogenation through a plausible reaction scheme for aqueous under acidic conditions [45]

the hydrido zinc heterobimetallic [46]. The transfer of the hydride substantially accelerated in the presence of Li ions from Zn–H to CO<sub>2</sub> prompting the separate metal formate hydrate. The CO<sub>2</sub> hydrogenation in the alcohol solvents leads to the formation of the formic acid esters [47]. The scCO<sub>2</sub> hydrogenation in the methanol solvent over a ruthenium catalyst had efficiently synthesized methyl formate (MF) with TOF of 55 h<sup>-1</sup> at 80°C [27, 48]. Initially, formic acid formed, which further subsequently produced MF after reacting it with methanol. The formation of MF in the CO<sub>2</sub> hydrogenation is a solitary step process, completed with hydrogen in an excessive methanol with Pd/Cu/ZnO catalyst [49]. The CO<sub>2</sub> can be converted as MF, during the reaction with the high yield (>20%) and splendid selectivity (>96%). TOF value greatly influences by doping of noble metals like Au, Pd, and Ru [49], which promotes hydrogen activation at catalyst surface. However, Pd noble metal exhibits the best hydrogen spillover activity than other noble metal [50].

#### Formic acid synthesis of by immobilized ruthenium catalysts

The distinctive properties of ionic liquids (ILs), like impressive thermal stability, favorable solvation for the various material and wide liquid range [17] helps them to replace many organic solvents from the reaction process and become alternative to the conventional solvent system. In addition, properties

of ILs can be tuned as per need and they are non-toxic as well as non-flammable in nature. In hydrogenation of the  $\text{CO}_2$  to formic acid, the homogeneous catalysts efficiently proven their uniqueness, but they have certain limitations like catalysts recycling and product isolation. To improve the recyclability and stability of the catalyst, one can immobilize a metal complex onto a supporting material, which also enhances the separation of the product and catalyst after the completion of the reaction. *In-situ* synthetic approach was applied in the formic acid formation *via* hydrogenation of the  $\text{CO}_2$  catalyzed by immobilized Ru complex on amine functionalized silica [51]. This type of catalyst not only helped in order to achieve 100% selectivity but also exhibits high activity as well as easy detachment and recycling properties [51].  $\text{CO}_2$  hydrogenation to the formation of formic acid with acceptable activity and precise selectivity can be attained by the combination of a silica-supported Ru-complex in the presence of basic ILs (Scheme 3) [17, 52]. The moderate basicity and non-volatility of the ILs lead to the easy recovery of formic acid followed by simple distillation.



Scheme 3. The hydrogenation of  $\text{CO}_2$  promoted by [DAMI][TfO], [17]

In one of the recent report, Srivastava *et al.* developed *in situ* generated Ru nanoparticles (NPs) immobilized in the [DAMI][NTf<sub>2</sub>] functionalized ionic liquid and found extremely dynamic with respect to the formic acid synthesis [20]. During the  $\text{CO}_2$  hydrogenation, [DAMI][NTf<sub>2</sub>] ILs gave a better result compared to other ILs immobilized standing Ru NPs [20]. In the continuation, the catalytic activity of Ru-exchanged montmorillonite (MMT) clay with functionalized ILs for the specific  $\text{CO}_2$  hydrogenation to formic acid [21] also came from the same group. In this process Ru-exchanged MMT clay with distinct catalyst loading was well synthesized and provide for the selective  $\text{CO}_2$  hydrogenation to formic acid [21]. Most important points of the above mentioned two reports were low catalyst loading, easy product isolation step and catalyst recycling up to 5-7 times. Acid-base titration using phenolphthalein indicator and  $^1\text{H}$  NMR analysis was applied to estimate the amount of formic acid formed after the hydrogenation reaction [17, 20, 21].

### Mechanistic Understanding of CO<sub>2</sub> hydrogenation reaction

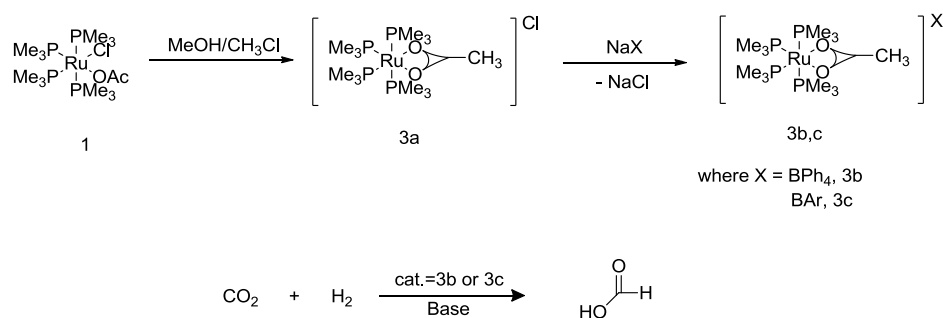
The theoretical reading and experimental observation for the formic acid synthesis are the major argument for the many years. In the experimental studies, CO<sub>2</sub> insertion into a Ru-hydride complex is a facile step, while according to theoretical understanding it is the rate determining step [53-56] (Scheme 4). A mechanistic investigation of the formic acid synthesis reveals that in the Ru complex catalyzed CO<sub>2</sub> hydrogenation, the foremost step of the reaction is CO<sub>2</sub> insertion in a hydrogen bond of the active species, *i.e.* [RhH<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup>, [57]. Two subsequent reaction routes are possible in the above condition. The primary subsequent reaction routes for the hydrogen activation rely on the insertion of the CO<sub>2</sub>, includes a sequence of oxidative and reductive elimination steps [58]. The other reaction rate is a formic acid formation, implies the hydrogen addition to the Rh-formate intermediate, which is obtained from CO<sub>2</sub> insertion [59]. The rate determining step in the above two reaction pathways are insertion of the CO<sub>2</sub> into the Rh (III) -H bond.

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The mechanism of CO<sub>2</sub> hydrogenation gives a clear idea behind the reaction process and selection of the better catalyst [59, 61]. Distinct features associated with the CO<sub>2</sub> hydrogenation are significant effect of the solvent and additive, dehydrogenation and CO<sub>2</sub> activation involving ligand as well as metal. Using ruthenium dihydride homogeneous catalysts, complete reaction routes relevant to hydrogenation of the CO<sub>2</sub> have been investigated experimentally and theoretically [56, 60]. The synthesis of the formate complexes is a rapid process due to the CO<sub>2</sub> insertion indicated by stimulation, with a relatively low activation barrier. The subsequent H<sub>2</sub> introductions into the Ru-formate complex is the rate determining step, leads to the formation of formic acid, which takes place *via* an intermediate [Ru( $\eta^2$ -H<sub>2</sub>)] complex [60]. *Cis*-isomer has higher activation energy as compared to *trans*-isomer in the insertion of H<sub>2</sub> [60]. The complex *cis*-(PMe<sub>3</sub>)<sub>4</sub>RuCl(OAc) shown favorable activity for the hydrogenation of CO<sub>2</sub> (table 1) [31]. The formic acid synthesis mechanism was investigated with the help of complex **1** and its derivatives **3b** and **3c** under high pressure NMR spectroscopy analysis (Scheme 4) [61]. As a dynamic component in the reaction, ruthenium complex [(PMe<sub>3</sub>)<sub>4</sub>RuH]<sup>+</sup> (indicated as B) has been projected, which is cationic and unsaturated in the nature [61]. The base plays a significant function to trap formic acid formed and also supports the transformation of **3b** and **3c** to B.

Basic condition was applied to study the mechanism of model catalyst Ir (III) reactivity with H<sub>2</sub> and CO<sub>2</sub>, in a detailed manner by Nozaki *et al.* (Figure 2) and Ahlquist *et al.* using DFT calculations [42, 62]. The two-step mechanism was found by the author for formate complex synthesis. The Ir (III)

trihydride intermediate regeneration is the rate determining step, and this experimental setup proved that the greatest concentration of the basicity yields to higher conversion rates [62]. The development of the iridium trihydride continues by means of an arrangement of a cationic  $\text{Ir}(\text{H})_2(\text{H}_2)$  complex and the dihydrogen ligand proton was abstracted by base [62].



Scheme 4:  $\text{CO}_2$  hydrogenation mechanism of formic acid with the help of complex 1 and its derivatives [61, 62]

The role of water in the  $\text{CO}_2$  hydrogenation into formic acid was investigated theoretically by Ohnishi *et al.* using Ru(II) catalyst (Figure 5) [55, 63]. In the presence or absence of the water, *cis*-Ru( $\text{H}$ )<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and *is*-Ru( $\text{H}$ )<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>) are respectively active species. Through  $\text{CO}_2$  insertion the Ru-(Z1-formate) intermediate is synthesized without H<sub>2</sub>O molecule, and the H-ligand nucleophilic attack on the  $\text{CO}_2$  occurs in the presence of the H<sub>2</sub>O molecule, which contribute to the acceleration of the reaction [63]. The reaction, performed in the presence of the H<sub>2</sub>O molecule, involves the metathesis as rate determining step, and with respect to  $\text{CO}_2$  insertion into the Ru-H bond, the activation barrier is very low in this process [63]. The main study of these two processes reveals that the H<sub>2</sub>O accelerates the nucleophilic attacks while alcohol and base also contribute the same kind of the nucleophilic attacks [63].

Without any base,  $\text{CO}_2$  hydrogenation to formic acid occurs at pH of 3.0 in the H<sub>2</sub>O, catalyzed by Ru or Ir complexes [45, 64]. Similarly, kinds of mechanisms are shown by both the complexes [Ru and Ir], only they differ by nature of the rate determining step. In a catalytic system based on the Ru complex for the hydrogenation of  $\text{CO}_2$ , the rate determining step is the reaction of the aqua complex with H<sub>2</sub>, and the catalyst based on the Ir complex, the reactivity of the hydride complex with the  $\text{CO}_2$  is the rate determining step [64]. As catalyst ruthenium aqua complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuII}(\text{L})(\text{OH}_2)]^{2+}$  {L = bpy (1) and 4,4'-OMe-bpy (2), bpy = 2,2'-

bipyridine, 4,4'-OMe-bpy = 4,4'-dimethoxy-2,2'-bipyridine recently reported for the CO<sub>2</sub> hydrogenation at pH 3.0 without any addition of the base. Under

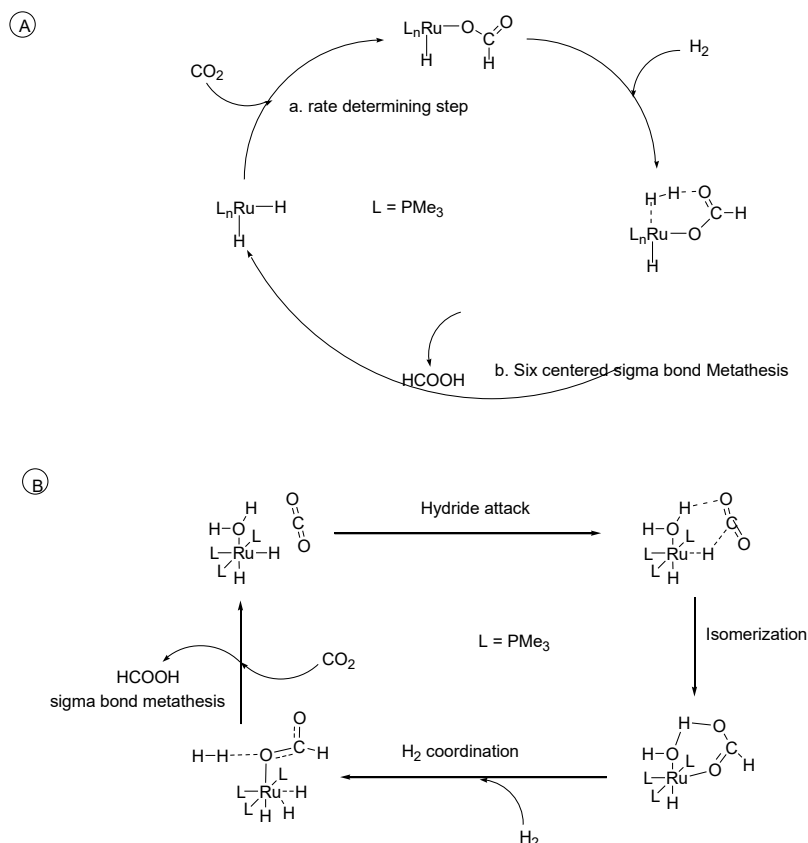


Figure 5. Formic acid synthesis mechanism in the water molecule's absence (A) and presence (B) through CO<sub>2</sub> hydrogenation [55, 56, 64]

acidic conditions, the hydride complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuII}(\text{L})(\text{H})]^+$   $\{\text{L} = \text{bpy}$  (3) and 4,4'-OMe-bpy (4) $\}$ , act as the active catalysts, still need to be isolated during the hydrogenation process of CO<sub>2</sub> (Figure 6) [64]. Under acidic conditions in the water, iridium aqua catalysts  $[\text{Cp}^*\text{IrIII}(\text{L})(\text{OH}_2)]^{2+}$   $\{\text{L} = \text{bpy}$  (5) and 4,4'-OMe-bpy (6) $\}$  was used in the CO<sub>2</sub> hydrogenation to isolate active iridium hydride catalysts  $[\text{Cp}^*\text{IrIII}(\text{L})(\text{H})]^+$   $\{\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{L} = \text{bpy}$  (7) and 4,4'-OMe-bpy (8), (Figure 6) [64]. During the catalytic hydrogenation of CO<sub>2</sub>, the change in the rate determining step was observed from the active

hydride catalyst's formation for both the catalyst (Ru and Ir) revealed by the kinetic studies [64].

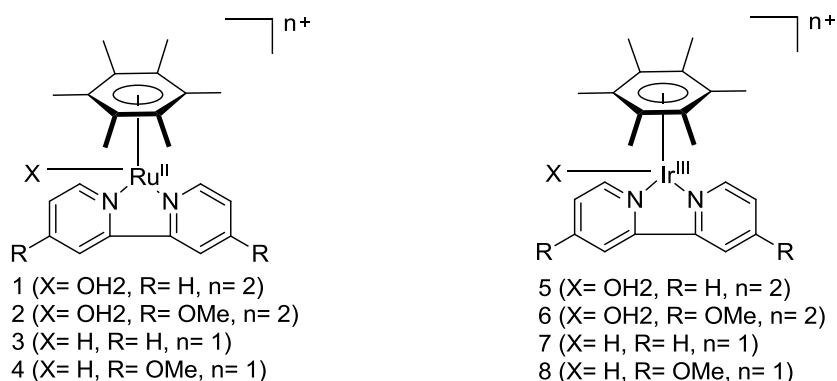


Figure 6. Ru and Ir complex as a catalyst for hydrogenation of CO<sub>2</sub> [64]

Let see the mechanism of Ru(II) and Ir(III) complex catalyzed CO<sub>2</sub> hydrogenation into formic acid. The pressure of the H<sub>2</sub> and CO<sub>2</sub> affects the rate of the CO<sub>2</sub> hydrogenation under acidic condition in the water, with the ruthenium aqua complexes 1(SO<sub>4</sub>) and 2(SO<sub>4</sub>) [64]. Hydrogenation of the CO<sub>2</sub>, turn over number (TON) was determined with the help of <sup>1</sup>H NMR and as internal standard 3-(trimethylsilyl) propionic-2,2,3,3-d<sub>4</sub> acid sodium salt (TSP)

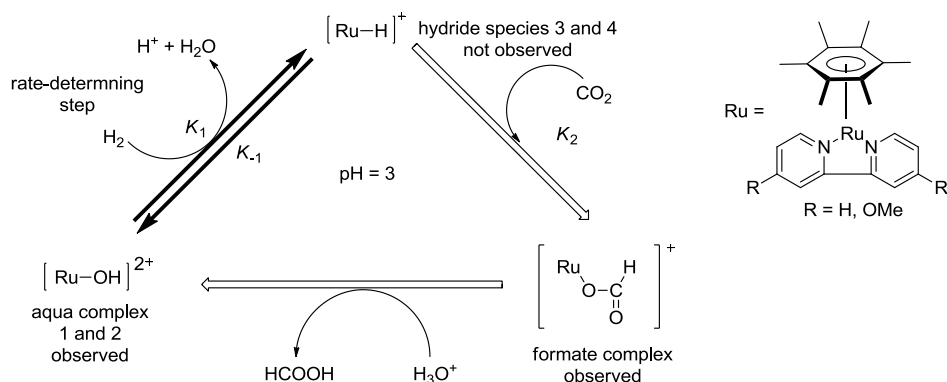


Figure 7. Hydrogenation of CO<sub>2</sub> catalyzed by the ruthenium complexes 1 and 2 [64].

was used [64]. Hydrogenation of the CO<sub>2</sub> by 2, the TON dependent on H<sub>2</sub> pressure without exhibiting any saturation behavior and there is an increase in the CO<sub>2</sub> at 2.5 MPa, at pH 3.0, at 40 °C for 3 hrs. [64]. In an opposite to this

hydrogenation of the CO<sub>2</sub> with 2, the TON dependent on CO<sub>2</sub> pressure shows a constant value after increasing the pressure of the CO<sub>2</sub>, the increase in pressure of H<sub>2</sub> observed at 5.5 MPa, at pH 3.0, at 40 °C for 3 hrs. [64]. The aqua and formate complexes were observed in the ruthenium complexes 1 and 2, for the hydrogenation of CO<sub>2</sub> but no indication of the active hydride species observed (Figure 7) [64]. The reactivity of the aqua complexes 1 and 2 with H<sub>2</sub> is the rate determining step for Ru based catalytic CO<sub>2</sub> hydrogenation [64].

The hydrogenation of the CO<sub>2</sub> catalyzed by Ir complex 6, the TON dependent on the H<sub>2</sub> pressure shows a constant value after the increase in H<sub>2</sub> pressure at 2.5 MPa, in a citric buffer solution of pH 3.0, at 40 °C for 0.5 hrs. [64]. The iridium catalyst 6 shows a saturation behavior of TON, which is a contrast to the ruthenium catalyst 2 with the linear dependence TON. The hydrogenation of the CO<sub>2</sub> catalyzed by Ir complex 6, the TON dependent on CO<sub>2</sub> pressure shows a linear increase through an increase in the pressure of the CO<sub>2</sub> without exhibiting any saturation behavior at 5.5 MPa, in a citric buffer solution of pH 3.0, at 40 °C for 0.5 hrs. [64].

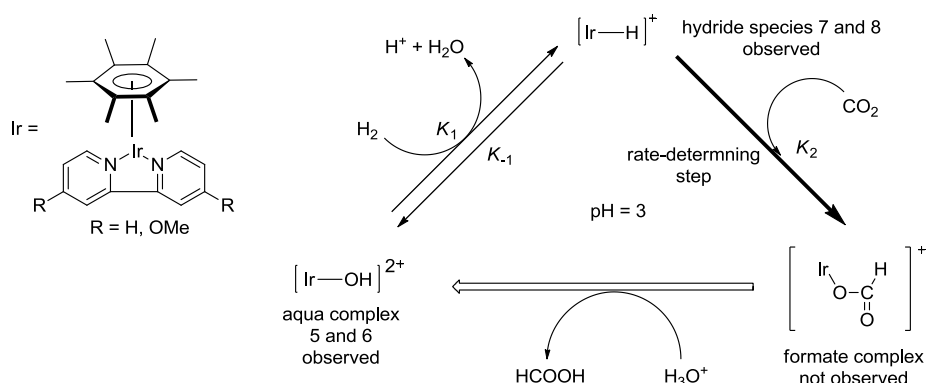


Figure 8. Hydrogenation of CO<sub>2</sub> catalyzed by the iridium complexes 5 and 6 [64]

In contrast to the ruthenium complex 1 or 2, formate complex could not be observed in the hydrogenation of CO<sub>2</sub> with the iridium complexes 5 or 6 [64]. Aqua complex and the active hydride species are observed (Figure 8) [64]. The reaction of the hydride complexes (7 or 8) with the CO<sub>2</sub> is the rate determining step for Ir based catalyzed CO<sub>2</sub> hydrogenation [64]. Hence, from above two mechanisms of hydrogenation of the CO<sub>2</sub> catalyzed by Ru or Ir complexes, shows two distinct rate determining step. In Ru catalyze hydrogenation of the CO<sub>2</sub>, formate complex observed, but not active hydride complex, while in Ir catalyze hydrogenation of the CO<sub>2</sub>, formate complex not observed but active hydride complex successfully isolated.

### Conclusion

The CO<sub>2</sub> concentration reduction becomes a worldwide focus of studies, as CO<sub>2</sub> is a major greenhouse gas increased tremendously in the recent years, which made a worldwide temperature alteration and climatic changes. CO<sub>2</sub> hydrogenation is an executable and powerful process to extenuate CO<sub>2</sub> increasing buildup. CO<sub>2</sub> can get converted to the fuels and chemicals, as well as ecofriendly and renewable source of carbon [1]. Chemical stability and thermodynamics are not encouraging nature of CO<sub>2</sub>. Conversion and the selectivity limitation can be eradicated by various technical utilization and rational designing of the catalyst with appropriate understanding of the reaction mechanism. In CO<sub>2</sub> hydrogenation, both the homogeneous and heterogeneous catalyst plays an essential role during the reaction process of the CO<sub>2</sub> hydrogenation. Ru, Rh and Ir based homogeneous catalyst function effectively for the synthesis of the formic acid and formate. In this review article, how an addition of solvents like water, alcohol and ILs effectively increases the reaction rates are discussed. Limitation associated with the homogeneous catalyst like catalyst separation process and recovery, etc., makes it unattempting for commercial application. Hence, the researchers are working efficiently on the active easy separation and recyclability of the catalyst. Fe, Cu and Ni based heterogeneous catalysts compared to a homogeneous catalyst are more effective for commercial applications [1]. The quick kinetics of the C-H bond formation results to low yield and unsatisfactory selectivity in the heterogeneous catalysis. CO<sub>2</sub> hydrogenation process related catalyst shows high activity, selectivity and long life span, if the catalyst has the largest surface area, extremely fine particles and more eminent metal diffusion [1]. The catalyst modulation and catalyst recyclability both are the advantages of the homogeneous and heterogeneous catalysis respectively, by combining these two, the more efficient catalytic system can be formed, and CO<sub>2</sub> hydrogenation can be made more economically executable. The combine advantages of the homogeneous and heterogeneous catalysis had been done with the support of the ILs, which created the scope with respect to reactivity, selectivity, recyclability of catalyst and easy separation in the hydrogenation of the CO<sub>2</sub> to formic acid [17, 20, 21].

The mechanism of hydrogenation of the CO<sub>2</sub> is disputed based on their experimental observation and theoretical analysis in the many reports [64]. Let say in the homogeneous systems the function of adding solvent at the molecular level is unclear, while in the heterogeneous catalysis, the predominant opinion reached by a group that the primary catalyst and promoter or the support works together to provide an active site [1]. Hence, it is still difficult to describe, active site nature and a reciprocal action between an



active component and promoter or the support, also the nature of the reaction mechanism. Hydrogenation of the CO<sub>2</sub> to formic acid and formate is elusive regarding first step of the hydrogenation. Therefore, the essential focus will be on the activation and interaction of the CO<sub>2</sub> with hydrogen or hydroxyl species, under various reaction conditions for both homogeneous and heterogeneous catalysts. More research should be done in the future on the rational design of catalysts based on the mechanism, so that the highly active, selective and recyclable catalyst can be developed for the conversion of the CO<sub>2</sub> to formic acid and formate, as well as to control CO<sub>2</sub> level in the atmosphere.

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