Catalytic valorization of CO₂ by hydrogenation: current status and future trends

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Abstract

Terrestrial environmental and biological systems are being threatened by the tremendous amount of human carbon dioxide emissions. Therefore, is crucial to develop a sustainable energy system based on CO_2 as chemical feedstock. In this review an introduction to the CO_2 activation and transformation has been made, together with a more comprehensive study of the catalytical reduction of CO_2 to methane, methanol and formic acid, which are currently contemplated as chemical feedstocks and/or promising energy carriers and alternative fuels.

Keywords: CO_2; chemical valorization; catalyst, hydrogenation; reduction, methane; methanol; formaldehyde; formic acid

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1. Introduction

The increasing level on atmospheric CO_2 is an alarming fact nowadays. The emission of CO_2 is projected to exceed 600 ppm before 2050 as the world demand for energy climbs; and more coal, oil, and natural gas are consumed.[1] Although the complete set of impacts that will result from the increased CO_2 concentrations is not completely known; many observations have already correlated changes in temperature, precipitation, sea levels, ocean pH, and other climate-related parameters with these increased concentrations.[2-5] Therefore, the problem of thermodynamically efficient and scalable carbon capture[6] stands as one of the greatest challenges of our time.[6-8] The breakthrough of mitigating CO_2 emissions can potentially offer innovative solutions pertaining to global *"3E"* issues, namely: Energy-Environment-Economy challenges.[9] Thus, in the past decades, the control of CO_2 emission has been the subject of extensive research efforts. For the summary of recent progress on CO_2 capture and storage, several comprehensive reviews can be referred to.[10-12] As an important part of CCUS (carbon capture, utilization and storage), the utilization of CO_2 as a carbon source has attracted great attention worldwide, as a major advance in energy-efficient catalytic CO_2 conversion[13,14] (see **Figure 1**). Therefore, CO_2 hydrogenation to value-added products is one of the promising approaches for utilizing the abundant carbon source in CO_2, leading to the production of oxygenates (alcohols and dimethyl ether) and hydrocarbons (olefins, liquid hydrocarbons, and aromatics).

Carbon conversion pathways introduce alternative sets of reactions that produce hydrocarbons and other commercial chemicals. In this review, we will focus on the hydrogenation of CO_2. These reaction pathways, in consequence, compete with the conventional hydrocarbon production processes, known as the Fischer-Tropsch (FT) processes. Briefly, FT processes produce liquid hydrocarbons (paraffin, olefin, alcohol, carbonyl) via synthesis gas[15,16] which is in turn produced by reforming.[17] Due to the usage of methane in steam reforming, FT processes are heavily dependent on the steadily depleting oil reserves.[17] The involved reactions also include the water-gas shift (WGS) reaction, which can produce hydrogen, that is thereafter required for the production of hydrocarbons. Naturally, reaction selectivity towards paraffins, olefins, and alcohols is determined by the operating thermodynamic conditions.[15] Hydrogen is a very appreciated material and can be obtained with several reactions. Since over 90% of the US supply of hydrogen occurs via steam reforming,[18] steam reforming and Fischer-Tropsch plants continue to be widespread and more viable than carbon conversion plants. Nevertheless, due to the continuous generation of CO_2 emissions, today's research is shifting towards CCUS to mitigate the carbon footprint and satisfy the growing demand for commodity chemicals.
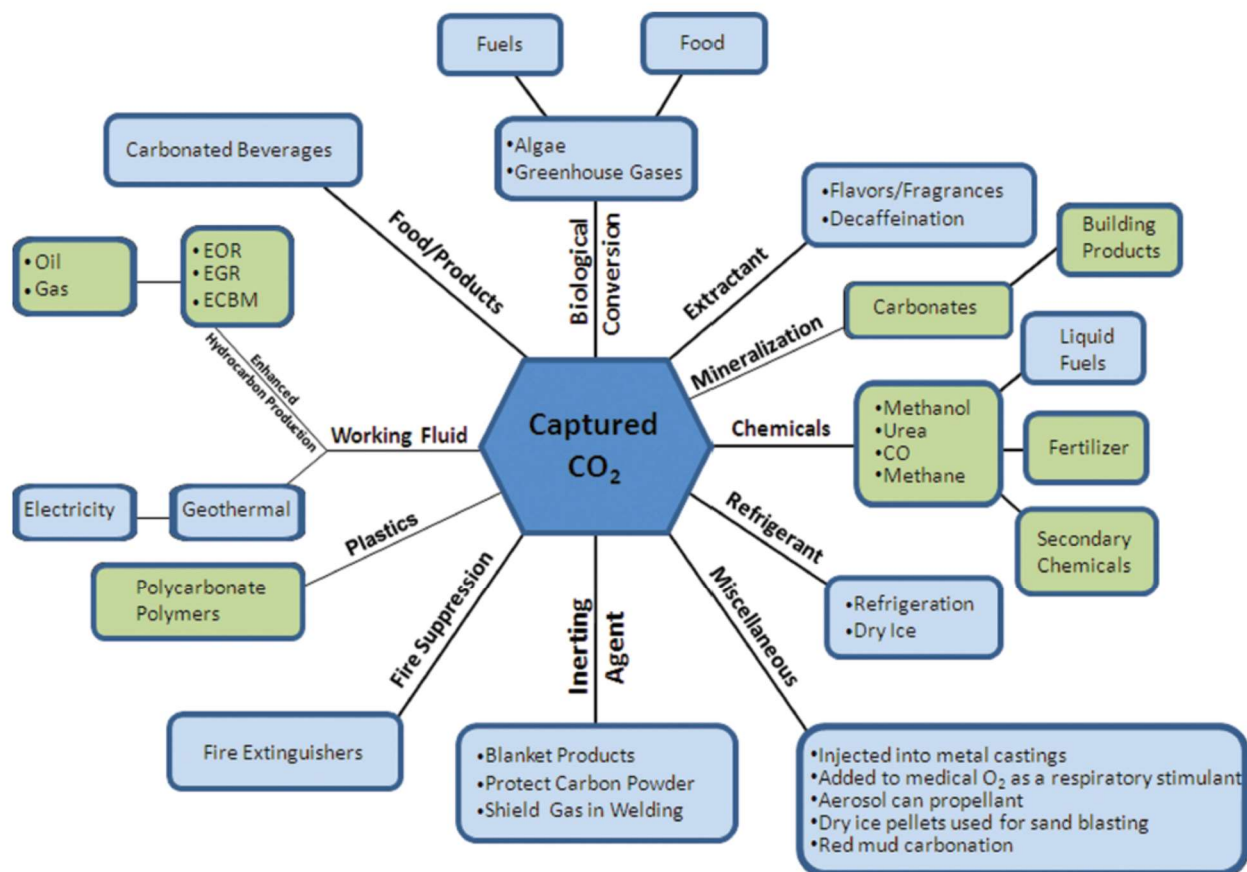
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Figure 1. Alternative pathways in the uses of CO_2 (Reproduced with permission from[14]).

While both FT and carbon conversion processes could yield C_n hydrocarbon chains,[15,19] the reactions herein, are limited to the production of molecules with a carbon atom. As a result, the considered pathways yield (1) methanol, (2) methane, (3) carbon monoxide (and thus part of syngas), and (4) formaldehyde. These products were selected due to their high global demand, as shown in **Table 1**. The specific reactions and conditions associated with the production of each of these commodity chemicals are highlighted in further sections. The catalytic hydrogenation of CO_2 to methane, methanol, and formic acid, formate and derivatives both with heterogeneous and homogeneous catalysts will be highlighted bellow.

Table 1. The annual global demand of commodity chemicals as converted from various sources.[14]

Chemical	Annual global production	Reference
Methane	3500 million tons	[20]
Carbon monoxide	595 million tons	[21]
Methanol	65 million tons	[22]
Formaldehyde	43 million tons	[23]

1.1. Thermodynamics of CO₂ hydrogenation

The hydrogenation reaction of CO_2 is one of the most studied thermal catalytic CO_2 conversions, and takes place at relatively low temperatures (≤ 250 °C) to produce useful fuels such as CO, methane, and methanol, among others.[13] Since CO_2 molecule is thermodynamically and chemically stable, large amounts of energy are required if CO_2 is the only reactant. The introduction of other substances with higher Gibbs free energy (such as H_2) as the co-reactant will make the thermodynamic process more favorable.[10] Thermodynamic calculation of chemical reactions is proven to be helpful for understanding and predicting the complicated catalytic process taking place in CO_2 hydrogenation[24] as it provides preliminary information in the chemical process; The thermodynamics stability of desired chemical species, the yield and selectivity of target product, the reaction heat as well as the impact of reaction parameters such as temperature, pressure, and reactant ratio. Hence, a combination of thermodynamics calculation and experimental validation is a useful tool to understand the intrinsic process in CO_2 hydrogenation reaction.[25]

The equilibrium distribution of a product mixture can be established by minimizing the Gibbs free energy function, which is subject to the mass balance constraints if only reactants and products are given in the first place. Jia *et al.*[26] presented a study in which systematic thermodynamics analyses of CO_2 hydrogenation reactions were conducted and compared with experimental catalytic studies to provide a rounded picture on the reaction processes towards CO_2 hydrogenation. Hydrogenation of CO_2 to CO via reverse water-gas shift reaction (RWGS, reaction 1 in **Table 2**) has been recognized as one of the most promising processes for CO_2 utilization, because CO can be used in downstream FT reaction and methanol synthesis, etc. Moreover, the RWGS reaction exists as a side reaction of the CO_2 methanation, both in laboratory scale and industrial process. The selectivity studies on CH_4 and CO indicate that CH_4 is the main product below 600 °C; further increase in the temperature leads to the larger percentage of CO because the amount of CH_4 produced reduces rapidly. The 100% selectivity to CO can be seen at 750 °C, implying that the exothermic CO_2 to CH_4 reaction

dominates at the temperatures below 600 °C, whereas the RWGS reaction is the predominate one above 600 °C.

Table 2. Gibbs free energy, enthalpy changes and equilibrium constant for the hydrogenation of CO_2 to various substances.[24-28]

No.	Reaction name	Reaction formula[*]	$\Delta G^{(-)}$ (25 ºC) (kJ/mol)	$\Delta H^{(-)}$ (25 ºC) (kJ/mol)	$K^{(-)}$ (25 ºC)
1	RWGS	$CO_2 + H_2 \rightleftarrows CO + H_2O$	28.6	41.2	$9.67\ 10^{-6}$
2	Hydrogenation to methane	$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$	−113.5	−165.0	7.79×10^{19}
3	Hydrogenation to methanol	$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$	3.5	−49.3	2.45×10^{-1}
4	Hydrogenation to ethanol	$2CO_2 + 3H_2 \rightleftarrows 1/2C_2H_5OH + 3/2H_2O$	−32.4	−86.7	4.70×10^5
5	Hydrogenation to formic acid	$CO_2 + H_2 \rightleftarrows HCOOH$	43.5	14.9	2.43×10^8

* All the components involved in the reaction formulas are specified as gas state.

The hydrogenation of CO_2 to alcohols has attracted wide scientific attention since alcohols are good energy carriers.[27] Hence it is important to study the hydrogenation of CO_2 to methanol, ethanol, and other higher alcohols. The hydrogenation process of CO_2 to methanol has the $\Delta G^{(-)}$ of 3.5 kJ/mol, corresponding to an equilibrium constant of $2.45 \cdot 10^{-1}$ at 25 ºC (as shown in **Table 2**). Moreover, the equilibrium conversion of CO_2 decreases regularly as the temperature increases, because of the exothermic reaction characteristic. ($\Delta H^{(-)}$ of -49.3 kJ/mol). Higher pressure leads to higher CO_2 conversion at the same reaction temperature as the reaction is a volume reducing reaction. Under the atmosphere condition, CO_2 can be hardly converted (conversion < 1%) in the whole temperature range. However, the CO_2 conversion of ~100% can be achieved under 50 atm at 100 °C. When calculating the free Gibbs energy of CO to methanol reaction, similar trends as for CO_2 to methanol process are found. The hydrogenation of CO_2 to methanol is not without byproducts, most commonly dimethyl ether (DME) and CO are also present in this reaction.[28-30] When calculated the %CO_2 conversion at several pressures and temperatures, together with the %selectivity to each of the products this is found to be a pressure sensitive process. Particularly, a high pressure greatly accelerates the CO_2 conversion and tends to enhance the selectivity for CH_3OH and CH_3OCH_3 but not for CO. The maximum point of CH_3OH selectivity moves to higher temperature direction with

the increasing pressure, as the methanol formation is a volume reducing and exothermic reaction. Therefore, it is recommended that typical CO_2 hydrogenation to CH_3OH proceeds at lower temperatures (< 300 ºC) and relatively high pressure (> 30 atm). Direct CO_2 hydrogenation to formic acid or formaldehyde (**Table 2**, reaction 5) is thermodynamically limited unless being tampered with additives.[31]

2. Recent developments in CO_2 hydrogenation to CH_4

CO_2 hydrogenation to value-added products is one of the promising approaches to combat the CO_2-induced climate change. However, currently uses of renewable energy sources are limited by their inherent intermittency, and require scalable means of storage.[32] Therefore, the production of synthetic natural gas or liquid fuels is the most feasible and convenient way to store large amounts of intermittent energy produced from renewable sources for long periods.[33] This has been tested in a large scale; in Copenhagen, where a commercial scale operation for methane production with 1.0 MW capacity was running successfully using transformation of the energy system toward a sustainable system in 2016.[34] Moreover, from 2009 to 2013, there were five projects in Germany involving CO_2 methanation at a pilot plant with capacity ranging from 25 kW to 6300 kW.[35]

2.1. Hydrogenation of CO_2 to CH_4 via heterogeneous catalysis

Carbon dioxide methanation has been studied extensively using various catalysts with several metals, supports and novel catalysts. Ni, Ru, Rh, Pt, Pd, Co and Fe,[36] have been reported suitable for carbon dioxide methanation. The support plays an extensive role in the catalyst performance, therefore various supports such as Al_2O_3, TiO_2, SiO_2, ZrO_2 and CeO_2 have been used in CO_2 methanation studies. Lastly, various novel catalysts such as structured catalysts, and metal organic frameworks (MOF) also have been gaining interest and used for carbon dioxide methanation. The active metals and supports have been classified as shown in **Figure 2**. To the active metal used for the hydrogenation is usually attributed the activity and selectivity of the reaction. For this reaction various noble (Ru, Rh) and non-noble metals (Ni, Co) have been extensively investigated. Other than that, numerous metals in group 8-10 such as Fe, Pd and Pt have also shown activity for CO_2 methanation processes.[35] When roughly analyzing the literature on the topic, the activity of the metal can be arranged as: Ru > Rh > Ni > Fe > Co > Os > Pt > Ir > Mo > Pd.[35] The selectivity of various metals is also ranked as Pd > Pt > Ir > Ni > Rh > Co > Fe > Ru > Mo.[34] In addition to its high activity, Ru has other positive characteristics such as high CH_4 selectivity, also at low temperatures, and high resistance to oxidizing atmospheres.[37-40] The main drawback is its cost, which makes its application

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not so useful for the industry. Fe is also an active catalyst for CO_2 methanation and it is very cheap,[41] however, it has low CH_4 selectivity.[35] Ni is the most common metal used for the CO_2 methanation. It has high activity, high CH_4 selectivity, and a low price. The main disadvantage of Ni is its high tendency to oxidize as the other non-noble metals Fe and Co.[41] Furthermore, nickel carbonyl, which is very toxic to the human organism, can be easily formed in these reactions.[42]
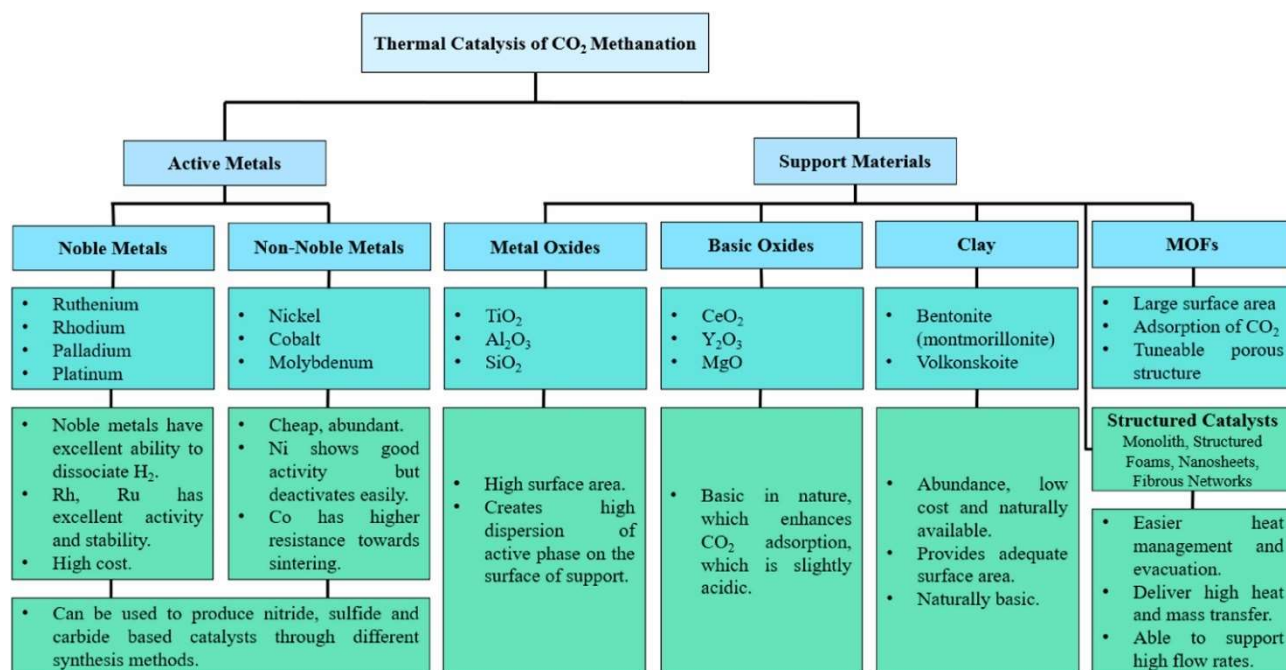

Figure 2. Overview of active metals and supports used for CO_2 methanation (Reproduced with permission from[36]).

Moreover, the catalytic performance of the catalyst is heavily affected by the carrier material. Selecting the right carrier material is thus an important factor for an efficient methanation of CO_2. Aluminum oxide,[43] silicium oxide,[44] zirconium oxide,[45] cerium oxide,[46] lanthanum oxide,[47] magnesium oxide,[48] titanium dioxide,[49] carbon materials,[50] zeolites[41] and MOF are the most used carrier materials for the above-mentioned catalysts. The active metals used for the heterogeneous catalytic conversion of CO_2 to CH_4 over the years have been summarized in **Table 3**.

2.1.1. Promoted, modified or mediated heterogeneous catalysts with noble metals

Ruthenium catalysts: Ruthenium is a Group VIII active metal that shows excellent activity for CO_2 methanation despite using a low loading or at low temperature. Moreover, Ru as active metal contributes to high CH_4 selectivity as well as presenting high resistance to oxidizing atmospheres. Ru

is also a suitable metal due to its proficiency at dissociation of hydrogen which reacts with adsorbed CO_2 at its reduced state.[52] Recently, Siudyga et al.[53] presented a novel system that enables the low temperature methanation of CO_2. Usually, a low temperature in the literature relates to 300 - 400 °C. But they show a novel system of nano-Ru, which was supported on nano-wired Ni, reactive for the methanation of CO_2 at temperatures as low as 130 - 179 °C (**Table 3**, entry 1). A comparison of nano-Pd and nano-Ru, supported on Ni-nanowires, proved that oxidized surface metals are highly important for the high activity of the investigated nano-Ru and nano wired-Ni. Moreover, the authors reported that the Ni nanowires (with a higher specific surface area than the standard metal surface) significantly enhances the performance of the Ru-Ni catalytic system. The importance of exposed crystal facets of underlying support was investigated thoroughly using 2.5 wt.% Ru supported on TiO_2 with exposed (001) and (101) facets.[54] The TiO_2 nanocrystals with different exposed facets were prepared using solvothermal hydrolysis. The catalyst with higher number of (001) facets have also been reported to display a higher number of surface oxygen vacancies.[55] It is shown that the nature of the catalyst support of Ru/TiO_2 strongly affected the dispersion of Ru species and the synergistic effect between Ru and underlying TiO_2 supporting materials due to the strong metal-support interaction, and thus affected their capability to activate CO_2 determining the catalytic activity for CO_2 methanation. Thus, the abundance of active sites and strong metal-support interaction of Ru supported on TiO_2 (001) facets ultimately leads to high catalytic activity (**Table 3**, entry 2).[54] Quindimil et al.[56] carried out a comparative study between Ni and Ru catalysts supported on alumina for CO_2 methanation. The catalysts were synthesized with various metal loadings (between 4 and 20 wt% Ni, and between 1 and 5 wt.% Ru) using wetness incipient impregnation method. Their study shows that an increase in Ni and Ru loading leads to formation of new basic sites, which suggests that both active phases can adsorb CO_2. For Ru supported on alumina, an increased in calcination temperature results in lower metal dispersion as they tend to grow and agglomerate into larger particles. There is no change observed for Ni dispersion when calcination temperature increases, but it will form higher interaction between nickel phases and alumina. Moreover, 4 wt.% Ru/Al_2O_3 exhibits highest CO_2 conversion of 85% at 375 °C (**Table 3**, entry 3), as compared to 12 wt.% Ni/Al_2O_3 with conversion of 80% at 425 °C. As Ru is more efficient in H_2 dissociation/adsorption, the TOF value for Ru/Al_2O_3 was observed to be higher than Ni/Al_2O_3 catalyst at low temperature.[56]

Table 3. Heterogeneous catalyst for CO_2 hydrogenation to methane.

Entry	Catalyst	H_2/CO_2 ratio	P (atm)	T (°C)	TOF[a]	Space velocity[b]	CO_2 conv. (%)	Selec. (%)	Ref.
1	1.0wt.% Ru/Ni NW	4:1	1	179	2479		100	100	[53]
2	2.5 wt.% Ru/TiO$_2$	4:1	1	150-400	7.24 10^{-2}		90	99	[54]
3	4 wt.% Ru/Al$_2$O$_3$	H$_2$: CO$_2$: He 5:1:1.5	1	375	4.14		85	100	[56]
4	1 wt.% Rh/FSA	4:1	1	500	-	(G) 15	83.6	100	[57]
5	Rh/CeO$_2$	4:1	1	352	-	-	46	41	[60]
6	Rh/ ACZ	4:1	0.98	402		(W) 93600	46	50	[61]
7	6wt.% Pd/UiO-66	4:1	39.4	340	-	(G) 15000	56	97.3	[63]
8	5wt.% Pd/Al$_2$O$_3$	4:1	1	240	8.6 10^{-3}	(G) 45000		40	[64]
9	Pd-Mg/SiO$_2$	4:1	1	450	-	-	59	95.3	[65]
10	10wt.% Ni-Al$_2$O$_3$	4:1		360	-	(G) 6000	83	98	[68]
11	27wt.% Ni/ MgO	5:1	1	325	-	-	91.2	99	[69]
12	20wt.% Ni/TiO$_2$	H$_2$: CO$_2$: He 24: 6: 10	1	400	-	(G) 48000	52	100	[70]
13	Ni/ZrO$_2$-P	4:1	1	350	-	(G) 60000	79	100	[71]
14	12Ni 4.5Ce/CNT	4:1	1	400	-	(G)30200	83.8	100	[72]
15	Ni/MgO/ SiO$_2$	4:1	1	350	-	(G) 15000	67	98	[73]
16	Ni-20 wt.% CeO$_2$/MCM-41	4:1	1	380	-	(G) 9000	85.6	99.8	[74]
17	2 wt.% Co/ZrO$_2$	4:1	29.6	400	1116	-	85	99	[76]
18	15 wt.% Co/Al$_2$O$_3$	4:1	1	400	-	(G) 16000	82	80	[77]

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19	Co NR	4:1	1	325	-	(G) 18000	80	98	[78]
20	Ni-Co/CeO$_2$-ZrO$_2$	4:1	1	300	-	(W) 12000	61	97	[82]
21	1.71Mn-Ni/Al$_2$O$_3$	H$_2$: CO$_2$: N$_2$ 39:9:5	1	500	-	(W) 48000	80	99	[83]
22	15wt.%Ni-5wt.%Fe/AC	4:1	1	430	-	(W) 60000	77	98	[84]
23	1Ru-15Ni/ Al$_2$O$_3$	5:1	1	400	-	(G) 5835	88	82	[85]
24	30Ni-7Fe/Al$_2$O$_3$	4:1	1	350	-	-	77.9	98.9	[85]
25	20Co$_4$N/γ-Al$_2$O$_3$	4:1	14.8	300		(G) 5000	98	98	[88]
26	MoS$_2$-1/G	3:1	9.9	600	17.6	-	50	90	[89]
27	ICNP supported on RuSiRAlO$_x$	4:1	1				88	99	[90]
28	Co$_2$C/γ-Al$_2$O$_3$	4:1	3	300	-	(G) 60000	89	99	[92]
29	MO-0.4Y	4:1	1	200	-	-	81	99	[102]
30	LDH 20Fe1.5Ni	4:1	1	250	-	-	72	99	[103]

a) TOF moles of product per mole of the catalyst per unit time and its value is usually expressed in h^{-1}

b) (W) = WHSV = mass flow rate/catalyst mass, mL/g$_{cat}$·h, (G) = GHSV = volume flow rate/bed volume, h^{-1}

Rhodium catalysts: Supported Rhodium catalysts are widely used for CO$_2$ methanation reaction as they are chemically active and stable.[57] Moreover, consequent to the flexible product selectivity, Rh catalysts can be tuned by adjusting the element doping, metal particle size and nanoparticle environment controlling associated with Rh content.[58] Rh supported on dendritic fibrous silica alumina (FSA) was studied intensively on the CO$_2$ methanation reaction using a fixed-bed quartz reactor at atmospheric pressure. It was detected that the basicity of catalysts increased with the Rh loading, whereas 1.5 wt.% Rh shows the highest basicity (**Table 3**, entry 4). Oxygen vacancies and basicity of FSA are closely associated with dendrimeric silica fibers and surface defect.[59] Thus, unpaired electrons will be generated due to the formation of oxygen vacancies, creating a strong Lewis basicity on catalyst surface. Oxygen vacancy sites and basicity of catalysts are proven to enhance the adsorption of CO$_2$ for the hydrogenation reaction. 1 wt.% Rh/FSA shows the best activity

due to its medium basic sites and appropriate metal-support interaction. This is because the 1.5 wt.% of Rh loading has the highest basicity strength, causing the adsorbed CO_2 molecules to bind strongly on the catalyst surface.[57] CO_2 methanation over Rh and Ni supported on cerium was carried out at atmospheric pressure conditions. Rh/CeO_2 catalyst exhibited a slightly enhanced activity when compared to Ni/CeO_2 in terms of higher CO_2 conversion and CH_4 production with a low CO production (**Table 3**, entry 5). Martin et al.[60] proposed in the study the cerium phase to be partially reduced during the CO_2 methanation, Ce^{3+} species seem to facilitate activation of CO_2 molecules. The activated CO_2 molecules would react with atomic hydrogen provided from H_2 dissociation on Rh and Ni sites to form formate species. For the most active catalyst (Rh/CeO_2), transmission electron microscopy measurements show that the Rh nanoparticles are small (average 4 nm, but with a long tail towards smaller particles) due to a strong interaction between Rh particles and the ceria phase. In contrast, larger nanoparticles were observed for the Ni/CeO_2 catalyst (average 6 nm) suggesting a weaker interaction with the ceria phase. The higher selectivity towards methane of Rh/CeO_2 is proposed to be due to the stronger metal–support interaction.[60] In a recent study conducted by Botzolaki et al.[61] the effect of support oxygen storage capacity (OSC) and Rh particle size was investigated on CO_2 methanation with Rh nanoparticles supported on various materials, γ-Al_2O_3, alumina-ceria-zirconia (ACZ) and ceria-zirconia (CZ). The support's OSC of the catalysts were arranged as follows: Rh/γ-Al_2O_3 < Rh/ACZ < Rh/CZ. They concluded that the activity of the catalysts was dependent on the surface OSC and the Rh particle size. The Rh/ACZ (**Table 3**, entry 6) catalysts shows the highest activity for CO_2 methanation.[61]

Palladium catalysts: Due to the capability to dissociate H_2 and distribute H atoms, Pd catalysts have also been used for the CO_2 methanation reaction.[52] However, the high cost and lower activity of Pd when compared to other noble metals can present some disadvantages.[62] A high catalytic activity for the CO_2 methanation was attributed to the synergetic effect of the Pd nanoparticle and UiO-66 (**Table 3**, entry 7). UiO-66 is a Zr-based MOF that exhibited high thermal stability as well as strong basicity.[63] The basicity of UiO-66 resulted in high CO_2 adsorption and activation as the CO_2 is mildly acidic in nature. These properties are usually displayed by MOF, making them an attractive support material for catalytic CO_2 methanation. The role of Pd nanoparticle is to provide H atoms for the hydrogenation reaction. Wang et al.[64] studied the methanation of CO_2 using two different Pd loading (0.5 and 5 wt.%) supported on Al_2O_3 in a packed bed tubular reactor (**Table 3**, entry 8). 5 wt.% Pd/Al_2O_3 catalyst has a larger average particle size and displayed a higher TOF for CH_4 formation and CH_4 selectivity when compared to 0.5 wt.% Pd/Al_2O_3. 5 wt.% Pd loading with larger Pd particles

has a higher population of terrace sites which makes it easier to form multi bound CO and dissociated H is bound in the vicinity of CO, showing a stronger CO interaction (**Figure 3**). These stable CO species in multi-bound forms are the direct intermediates to CH_4. In contrast, 0.5 wt.% Pd/Al_2O_3 catalyst has smaller Pd particles which hardly retain CO surface species formed from formate, thus exhibiting a higher selectivity to the CO product.[64] A $Pd-Mg/SiO_2$ catalyst (**Table 3**, entry 9) was found to be active and stable for the methanation of CO_2.[65] The catalyst presents the highest CH_4 selectivity (95.3%), yield (56.4%) and CO_2 conversion (59.2%) at 450 °C. This could be due to the greater contact between Pd-containing nanoparticles and Mg-containing oxide at this temperature. The oxidized Mg is proposed to react with CO_2 to form a carbonate which is stable in the absence of atomic hydrogen. The Pd then adsorbs H_2 to provide atomic hydrogen to hydrogenate the carbonates to form CH_4. After CH_4 is desorbed, the carbonate is reformed by gas phase CO_2, as shown in **Figure 4**.
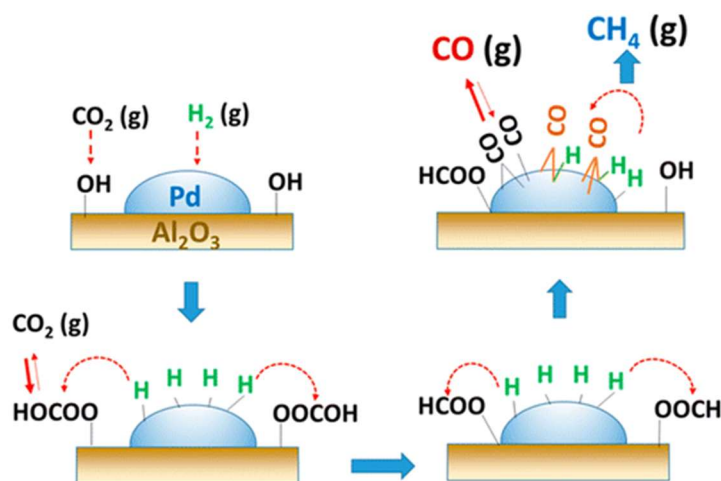

Figure 3. Mechanism of CO_2 hydrogenation on Pd/Al_2O_3 catalysts (Reproduced with permission from[64]).
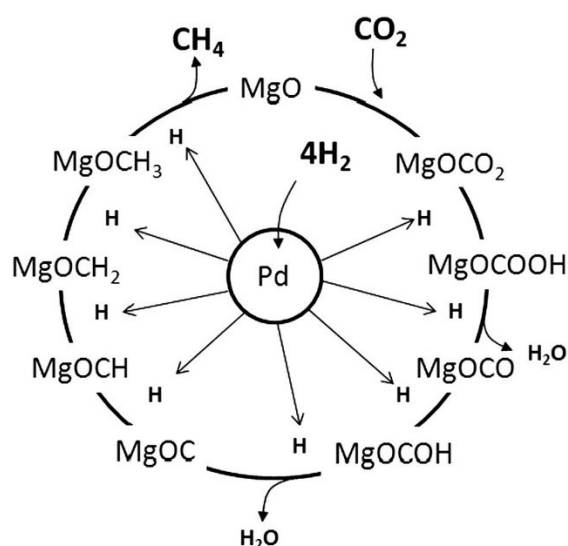
Figure 4. A potential bifunctional mechanism for Pd–Mg/SiO$_2$ whereby spillover of atomic hydrogen from Pd in intimate contact with Mg carbonate sequentially hydrogenates carbon until the product methane desorbs (Reproduced with permission from[65]).

2.1.2. Promoted, modified or mediated heterogeneous catalysts with non-noble metals

Nickel catalysts: Nickel based catalysts are the most used catalyst for hydrogenation of CO$_2$ into methane. Ni provides satisfactory catalytic performance in terms of activity, selectivity and stability.[34] Besides, Ni can be easily obtained due to its abundance and relatively low cost.[66] However, the main disadvantage of Ni is that they are prone to catalysts deactivation due to sintering of Ni particles, Ni(CO)$_4$ formation, coke formation and sulfur poisoning.[40,52,67] A parametric study of CO$_2$ methanation was carried out by Jaffar et al.[68] with varying temperature, reactant feed ratio, type of active metal used, support material used and reactant gases hourly space velocity (RGHSV). The best results were observed for 10 wt.% Ni-Al$_2$O$_3$ at 360 °C (**Table 3**, entry 10). The catalyst activity was tested on three support, Al$_2$O$_3$, SiO$_2$ and MCM-41, where the Al$_2$O$_3$ support shows the best results with CO$_2$ conversion of 83%, CH$_4$ yield of 81% and CH$_4$ selectivity of 98%. This is mainly due to the evenly distribution of Ni on Al$_2$O$_3$ support and its good resistance to sintering.[68] In another study, Loder et al.[69] investigated the hydrogenation of CO$_2$ using Ni/MgO catalyst (**Table 3**, entry 11). It was observed that when 27 % of Ni is used, a methane selectivity of 99% and CO$_2$ conversion of 91.2% is obtained at optimum temperature of 325 °C. A higher hydrogen concentration in the feed stream gas (H$_2$: CO$_2$ feed ratio of 5:1) also leads to a higher CO$_2$ conversion. Moreover, MgO resulted also in better yields than dolomite ore (which contains CaO and MgO). Unwiset et

al.[70] investigated the effect of Ni loading (3, 6, 12 and 20 wt.%) on TiO_2 support synthesized via sol-gel method. In their study it was observed that the addition of Ni causes a shifting of CO_2 conversion towards lower temperatures. Moreover, high reaction temperature will cause sintering of Ni particles and formation of coke on catalyst surface, and the increasing Ni loading can reduce the crystalline sizes of TiO_2, thus preventing its crystalline growth. Meanwhile, the addition of Ni existed in two forms, which are the dispersion of NiO onto the TiO_2 surface and incorporation of Ni ions into the TiO_2 lattice. When Ni^{2+} ions replaced the Ti^{4+} ions in the lattice, oxygen vacancies are formed which leads to the distortion of TiO_2. These oxygen vacancies act as an active site for the CO_2 adsorption. Therefore, reduction of the dispersed NiO to Ni^0 acts as active site for H_2 adsorption. 20 wt.% Ni/TiO_2 (**Table 3**, entry 12) is the best catalyst in terms of stability and activity from this study as it contains oxygen vacancies and NiO which promotes appropriate adsorption of both H_2 and CO_2.[70] The structural effect of Ni/ZrO_2 was thoroughly studied by Jia et al.[71] on the CO_2 methanation reaction. This Ni/ZrO_2-P catalyst was prepared using plasma decomposition of nickel nitrate. There are various factors contributing to Ni/ZrO_2-P (**Table 3**, entry 13) showing a good catalytic activity at optimum temperature of 350 °C. Firstly, plasma decomposition can prevent the blockage of pores on the support by inhibiting Ni diffusion and aggregation. Second, XRD results showed no NiO peaks on Ni/ZrO_2-P catalyst, suggesting that plasma decomposition improved Ni dispersion and reduced Ni particle size. Lastly, plasma decomposition forms oxygen vacancies on Ni/ZrO_2 interfacial sites, further improving the catalyst's activity.

Several studies were conducted where basic oxides have been used as promoters. Wang *et al.*[72] proposed a catalyst in which Nickel-based catalysts supported on multi-walled carbon nanotubes (CNT) were promoted with cerium. Their results indicated that the properties of CNT together with the accession of cerium enhanced the dispersion of metallic nickel, supported the reduction of metal oxides, and intensified the activation of CO_2. Moreover, the CNT constraint effect and the promotion effect of cerium could efficiently prevent the migration and sintering of the active species and restrict the carbon deposition reaction. Catalytic performances exhibited that 12Ni-4.5Ce/CNT (**Table 3**, entry 14) catalyst possessed the highest activity with 83.8% conversion of CO_2 and almost 100% selectivity of CH_4. Couple of years before, 10 wt.% Ni/SiO_2 catalyst was promoted with 1 wt.% MgO via co-impregnation method, leading to superior catalytic activity and stability.[73] The promotion of MgO improved the activation and adsorption of CO_2. In addition, the synergetic effect of both Ni and Mg improved the catalyst's resistance towards Ni sintering and oxidation (**Table 3**, entry 15). In another study, 20 wt.% CeO_2 promoted on Ni/MCM-41 (**Table 3**, entry 16) improved the activity and stability of the catalyst. The promoted catalyst showed higher CO_2 adsorption sites as well as

improved Ni dispersion and metal-support interaction, which are credited to the synergistic effect among Ni active sites, CeO_2 and MCM-41.[74]

Cobalt catalysts: Cobalt is also one of the metals that has been widely selected for catalyst development. There has been various studies indicating that among the Group VIII metals, Co is within the most active metals for hydrogenation reaction.[75] Li et al.[76] described the preparation of a highly dispersed Co/ZrO_2 catalysts for CO_2 methanation assisted by organic acid (**Table 3**, entry 17). They observed that organic acids were effective as low-cost complexing agent improving the dispersion of Co. Citric acid assisted 2 wt.% $Co-ZrO_2$ catalyst results in high CO_2 conversion (85%) and CH_4 selectivity (99%). Cobalt citrate complex as Co precursor enables better dispersion on the support, which improves the strength of the $Co-ZrO_2$ interaction (**Figure 5**). Thus, an appropriate cobalt metal and ZrO_2 support interaction contributes to more reduced active sites and oxygen vacancies, which promotes CO_2 adsorption and high catalytic activity. In another study, CO_2 methanation was researched to investigate the effect of coordination between metal and support with an alumina supported catalyst using Ni and Co. Liang et al.[77] sowed that 15 wt.% Co/Al_2O_3 (**Table 3**, entry 18) is the optimal metal loading as it gives superior activity and stability when compared to Ni/Al_2O_3. In the same study the authors also found out that Co/Al_2O_3 catalyst presents a higher resistance towards coke formation than the nickel one. The combination of Co and alumina also yields higher activity because the reaction intermediates formed from monometallic cobalt and pure alumina were similar (bicarbonate, carbonate and formate species), thus facilitating the conversions of these intermediates effectively. Jimenez et al.[78] proposed the use of nanorods (NR) as a way to increase the activity of Co catalyst for the CO_2 methanation. The Co NR with exposed (110)/(001) surface facet and Co NP with (111)/(001) were compared in terms of their catalytic activity. Co NR displayed a higher catalytic activity in terms of TOF and CH_4 selectivity due to the exposure of (110) family of facets at the surface (**Table 3**, entry 19). Co^{2+} and Co^{3+} were present on the (110) facet, whereas (001) facet does not possess exposed Co^{3+} cations. The Co NR with exposed (110) surface facets are reported to suppress site-blocking formate species, thus further enhancing its catalytic activity. Moreover, NR preserve the metallic cobalt phase during methanation reaction due to its resistance to oxidation, leading to improved catalytic activity.

Figure 5. Proposed mechanism for the organic acid assisted methanation of CO_2 (Reproduced with permission from[76]).

Bimetallic catalysts: A bimetallic catalyst is a type of metal catalyst where a second metal is integrated through alloying, which tends to alter and improve the geometric structures, activity and stability when compared to their parent metals.[79,80] In **Figure 6**(a) the five available structures for bimetallic catalysts are represented, which include crown-jewel structure, allow, core-shell, heterostructure and hollow structure.[81] As reported before, Ni-based catalysts are prone to catalyst deactivation due to the exothermic methanation reaction, which causes sintering of Ni particles.[66] Thus, bimetallic catalyst has been proven to be effective in enhancing the performance of catalyst for the methanation reaction, with Co as second. Bimetallic catalyst Ni-Co/CeO_2-ZrO_2 (**Table 3**, entry 20) yields CH_4 selectivity of 98% and CO_2 conversion of 78% at optimal temperature of 350 °C.[82] This is due to the redox properties of Co, which reduces the coke deposition and sintering of metal particles. This study also discussed the effect of methane in the reactant stream on catalytic performance. It was stated that the presence of methane promotes the catalytic performance due to low temperature reforming reactions occurring concurrently to methanation reactions.[82] Zhao et al.[83] presented a series of Mn-promoted 15 wt.% Ni/Al_2O_3 catalysts by wetness impregnation method. The effect of the Mn content on the activity of the Ni/Al_2O_3 catalysts for CO_2 methanation and the co-methanation of CO and CO_2 in a fixed-bed reactor was investigated. They suggest that the presence of Mn increased the number of CO_2 adsorption sites and inhibited Ni particle agglomeration due to improved Ni dispersion, as it weakened interactions between the nickel species and the support. The Mn-

promoted 15 wt.% Ni/Al_2O_3 catalysts improved CO_2 methanation activity especially at low temperatures (250 to 400 °C). The Mn content was varied from 0.86 to 2.54 wt.% and the best CO_2 conversion was achieved with the 1.71Mn-Ni/Al$_2$O$_3$ catalyst (**Table 3**, entry 21). The co-methanation tests on the 1.71Mn-Ni/Al$_2$O$_3$ catalyst indicated that adding Mn markedly enhanced the CO_2 methanation activity especially at low temperatures, but it had little influence on the CO methanation performance. The comparison of the Co and Mn as second metal for the hydrogenation reaction is illustrated in **Figure 6**(b).
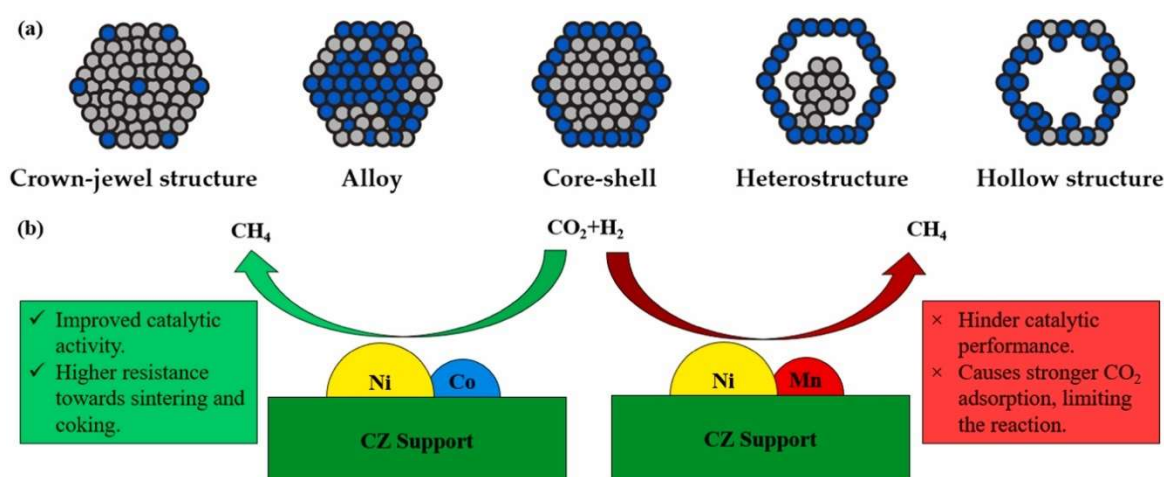
Figure 6. (a) Illustration of bimetallic catalysts with different structures (b) comparative scheme of Co and Mn as second metal for Ni/CeO_2-ZrO_2 (Ni/CZ) catalyst (Reproduced with permission from[36]).

In a recent study conducted by Gonçalves *et al.*[84] it is shown that bimetallic nickel and iron (15 wt.% and 5 wt.%, respectively) supported on activated carbon (AC) with increased Lewis basic sites (Ni-Fe/AC-R) yields a promising catalytic activity for the CO_2 methanation (**Table 3**, entry 22). The performance of the catalyst was mainly attributed to the good metal dispersion and higher metallic surface area due to a higher amount of oxygen-free Lewis basic sites on graphene layers resonating with π-electrons of carbon aromatic rings, which attracts protons and ultimately improves dispersion of the nickel nanoparticles. The enhanced catalytic activity is also due to the higher basicity exhibited by the catalyst due to the presence of many carbonyl-quinone groups and O-free Lewis basic sites. A higher basicity enables gradients of CO_2 concentration close to nickel active sites, which

enhances the adsorption capacity of CO_2 on the catalyst. Fe promotion further improve catalytic activity by reducing the temperature of methanation. Addition of Fe to the catalyst affects positively to the catalyst stability by preventing sintering of nickel nanoparticles. Chein and Wang[85] conducted a study to investigate the methanation of CO_2 using Ru-Ni/Al_2O_3 bimetallic catalyst (**Table 3**, entry 23). The experiments were carried out using a fixed bed reactor at atmospheric pressure with a H_2/CO_2 ratio of 5 and space velocity of 5835 h^{-1}. It was observed that at 400 °C, the monometallic Ru/Al_2O_3, Ni/Al_2O_3 catalysts and Ru-Ni/Al_2O_3 bimetallic catalysts yields the best results. Hence, 1 wt.% Ru-Ni/Al_2O_3 shows the best results in terms of CO_2 conversion, H_2 efficiency and CH_4 yield at 400 °C. The bimetallic catalyst also displayed good thermal stability after 74 h. The deterioration of the catalyst activity was inferred due to the oxidization of Ni to NiO and Ru to RuO_2 by CO_2. As shown above, conventional nickel-alumina catalyst is widely applied in the catalytic hydrogenation of CO_2. However, the strong interaction between Ni and Al_2O_3 promotes the formation of nickel aluminate species which are hard to reduce. Thus, introduction of a second metal could lead to adjust the interaction of Ni and support, which changes the chemical composition of the catalyst surface, contributing to enhanced activity. CO_2 hydrogenation to CH_4 was investigated using various promoters on Ni-M/Al_2O_3 bimetallic catalysts, where M = Fe, Co, Zr, La and Cu. The addition of Fe was presented to improve the catalytic performance by enhancing the H_2 adsorption and CO_2 dissociation. After carrying out comparison and optimization of the seconds metals, it was noticed that 30Ni-7Fe/Al_2O_3 (**Table 3**, entry 24) yields the best catalytic activity and stability. This is due to the higher surface area for Ni dispersion and the formation of new active sites which improves hydrogen adsorption.

2.1.3. Nitride, sulfide and carbide-based catalysts

As discussed above, several noble and non-noble metals can be employed as active metals for the CO_2 methanation reaction. However, nitride, sulfide and carbide-based catalysts have been also reported through the years as an alternative for replacing noble and non-noble metals. For instance, nitride-based catalysts have displayed excellent catalytic activity in various reactions.[86,87] Razzaq *et al.*[88] reported the use of γ-Al_2O_3 supported cobalt nitride (**Table 3**, entry 25) for the methanation reaction of CO_2. It was observed that cobalt nitride has a higher CO_2 methanation activity when compared to its cobalt counterpart. Co_4N/γ-Al_2O_3 exhibited excellent resistance towards deactivation such as coking and metal sintering. The enhanced activity and stability of the catalyst is mainly attributed to the strong-metal support interactions due to the formation of Co_4N phase. The

introduction of nitrides also formed nitrogen vacancies and increased the surface basicity, which enhances the adsorption of CO_2 and H_2.

Sulfide based catalysts have also been used for the thermal hydrogenation of CO_2 into CH_4. The most obvious one being the use of molybdenum, as it is usually in a sulfidic state in operation.[35] Additionally, Mo has shown an excellent sulfur tolerance, compared to other active metals discussed in this review. Several loadings of MoS_2 nanoplatelets were supported on layers of graphene, which were then tested to observe its activity on CO_2 methanation.[89] Compared with bulk MoS_2, supported MoS_2 on graphene (MoS_2/G) showed a drastic increase in CH_4 (**Table 3**, entry 26). It was revealed that the graphene plays an important role as well in altering the product selectivity from CO (major product for bulk MoS_2) to CH_4. Moreover, highest TOF was achieved over 1 wt.% MoS_2 at 600 °C. This is because a balance of two opposing factors was achieved, an increase in loading will increase number of active sites and also increase the particle size.

In the same way, carbide-based catalysts are also reported to show good catalytic performance for the hydrogenation of CO_2 to CH_4. In a study by Bordet et al.[90] Iron carbide nanoparticles (ICNP) are synthesized via carbidization, and then supported on Ru-doped $SiRAlO_x$ to investigate its effectiveness in CO_2 methanation reaction (**Table 3**, entry 27). The experimental runs were carried out in a continuous-flow reactor at atmospheric pressure, where a high CH_4 yield, and selectivity were obtained. The ICNP function as heating agents, where the heat released can be used to activate the Ru NP for the Sabatier reaction to proceed. This result is in accordance with a study conducted by Song et al.,[91] where the subsequent carbonization treatment of iron oxide (Fe_3O_4) to iron carbide (Fe_3C) shows a higher activity. The apparent activation energy for the Fe_3C is much lower than the one for Fe_3O_4, which facilitates the methanation reaction. Moreover, the formation of supported alumina with cobalt carbides through carburization of $CoO_x/\gamma-Al_2O_3$ (**Table 3**, entry 28) on the CO_2 methanation reaction has also been investigated.[92] In this study the cobalt carbide exhibited much better catalytic activity compared to the corresponding oxides, as expected from its high CO_2 conversion and CH_4 selectivity.

2.1.4. Metal-oxides based catalysts

The hydrotalcite-like compounds (HT) also known as layered double hydroxides (LDH) are natural and/or synthetic clays consisting of highly ordered two-dimensional hydroxide sheets $\left[M^{2+}_{1-x}M^{3+}(OH)_2\right]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ (whereas M^{2+} M^{3+} and A^{n-} are divalent and trivalent cations and the interlayer anions of valence n, respectively), and are promising candidates as a catalyst

precursor, as the LDH-based process leads to uniform dispersion of metal cations. In regard, the resultant catalysts feature high stability against sintering, high specific surface area and stronger basic properties. Such metal oxides are proven to be good catalysts, as they tune the metal dispersion, among other features.[93-95] It has also been reported in the literature a wide range of cations that maybe incorporated into the hydrotalcites structure, e.g., Li^+, Ti^{4+}, Sn^{4+} or Zr^{4+}.[96] The calcination of such materials leads to the formation of mixed nano-oxides with periclase-like structure, which show very interesting features.[66,97,98] Redox or acid-base properties may be tailored to some extent by controlling hydrotalcite composition as shown for dry reforming of methane, among other reactions[99] Another advantage of LDH is that the incorporated cations are usually homogenously distributed due to their random arrangement in the brucite-like layers. Moreover, such materials exhibit basic properties, which are of great interest when used as catalysts for the reaction of CO_2 methanation.[99-101] Sun *et al.*[102] presented a study in which Ni-containing mixed oxides (MO) derived from LDH with various amounts of yttrium were synthesized, characterized and proved useful catalysts for the methanation of CO_2 at atmospheric pressure. The obtained results confirmed the formation of nano-sized mixed oxides after the thermal decomposition of hydrotalcites. The introduction of yttrium to Ni/Mg/Al LDH led to a stronger interaction between nickel species and the matrix support and decreased nickel particle size as compared to the yttrium-free catalyst. The modification with Y (0.4 and 2 wt.%) had a positive effect on the catalytic performance in the moderate temperature region (250-300 °C), with CO_2 conversion increasing from 16% for MO-0Y to 81% for MO-0.4Y (**Table 3**, entry 29) and 40% MO-2.0Y at 250 °C. The improved activity may be correlated with the increase of percentage of medium-strength basic sites, the stronger metal-support interaction, as well as decreased crystallite size of metallic nickel. High selectivity towards methane of 99% formation at 250 °C was registered for all the catalysts. Wierzbicki *et al.*[103] obtained mixed nano-oxides with nickel and iron into the layers of LDH 20Fe1.5Ni (**Table 3**, entry 30). They proved that the introduction of Fe into the layered double hydroxides changed the interaction between Ni and supports matrix. Moreover, the introduction of low amount of iron influenced positively the catalytic activity in CO_2 methanation at 250 °C, with CO_2 conversion increasing from 21% to 72% and CH_4 selectivity ranging from 97 to 99%.

2.2. Hydrogenation of CO_2 to CH_4 via homogeneous catalysis

As well as many examples of heterogeneous hydrogenation of CO_2 to CH_4 can be found in literature, not so many are presented in which the same reaction takes place within a solvent. CO_2 and H_2 have been reported to react with various nucleophiles to produce methyl and formyl

derivatives,[104,105] which are a bit above the scope of this review and would therefore, not be highlighted here. Another homogeneous hydrogenation pathway usually involves a reductor molecule other than H_2, as silanes or boranes, some examples of which are listed below.

2.2.1. Direct homogeneous catalysis

Song *et al.*[106] presented a ruthenium-cobalt catalyst, Ru-Co$_3$O$_4$ (**Table 4**, entry 1) capable to activate the hydrogenation of CO_2 into CH_4 in liquid phase. The authors founded that, solvents including H_2O, n-butanol, 1,4-butyrolactone, DMF, n-nonane, decalin, cyclohexane and isooctane have significant solvent effects on the catalytic performance. The catalyst showed higher activity and selectivity when decalin and isooctane was applied as solvent. At 200 °C and H_2/CO_2=3:1 (v/v, 4 MPa) and with decalin as solvent, the conversion of CO_2 and the selectivity of CH_4 reached 45.6% and 97%, respectively. The isotope labeling experiments, and in-situ diffuse reflectance infrared spectra showed that the hydrogen atoms of the tertiary carbon in decalin and isooctane were active for CO_2 hydrogenation reaction, thus improving the catalytic peroformance. Decades before, ruthenium catalysts such as Ru(CO)$_{12}$ (**Table 4**, entry 2) have been investigated as viable catalysts for the hydrogenation of CO_2. Tominaga *et al.*[107] described a system in which the carbonyl ruthenium catalyst can generate CO, CH_4 and CH_3OH.

Table 4. Homogeneous catalyst for CO_2 hydrogenation to methane.

Entry	catalyst precursor	solvent	Additives	P (H$_2$,CO$_2$) atm	T (ºC)	T (h)	TON[a]	Ref.
1	Ru-Co$_3$O$_4$	Decalin	-	118:39	200	-	-	[106]
2	Ru(CO)$_{12}$	NMP	KBr	3:1	240	3		[107]
3	(POCOP)Ir(H)(HSiR$_3$)	C$_6$H$_5$Cl	Me$_2$PhSiH	(silanes)	60	72	8300	[108]
4	[TMPH]$^+$[HB(C$_6$F$_5$)$_3$]$^-$	C$_6$D$_5$Br	Et$_3$SiH					[109]
5	[Li$_2$[1,2-C$_6$H$_4$(BH$_3$)$_2$H]$^+$ [HB(C$_6$F$_5$)$_3$]$^-$	C$_6$D$_5$Br	Et$_3$SiH	(silanes)	50	21		[111]
6	(*L3*) Zr(CH$_2$Ph)$_2$ B(C$_6$F$_5$)$_3$	benzene-d6	R$_3$SiH		Room temperature	1.5	225	[112]

7	Ir(ppy)$_3$ Fe-p-TMA			(TDA)	102	79	[113,114]
8	Al(C$_6$F$_5$)$_3$ B(C$_6$F$_5$)$_3$	toluene	HSiEt$_3$	(silanes)	80	5	39	[115]

2.2.2. Indirect homogeneous catalysis

Park et al.[108] proposed that cationic silane complexes can catalyze hydrosilylations of CO_2. With silanes such as Me$_2$EtSiH or Me$_2$PhSiH a rapid formation of CH_4 and siloxane with no detection of bis(silyl)acetal and methyl silyl ether intermediates was observed (**Table 4**, entry 3). The catalyst system is long-lived, and 8300 turnovers can be achieved using Me$_2$PhSiH with a 0.0077 mol % loading of Ir. The proposed mechanism for the conversion of CO_2 to CH_4 involves initial formation of the unobserved HCOOSiR$_3$. This formate ester is then reduced sequentially to R$_3$SiOCH$_2$OSiR$_3$, then R$_3$SiOCH$_3$, and finally to R$_3$SiOSiR$_3$ and CH_4 (**Figure 7**). Bekerfeld et al.[109] proposed the formation of a frustrated Lewis pair (FLP) with 2 equiv. of 2,2,6,6-tetramethylpiperidine (TMP) and tris (pentafluorophenyl) borane [B(C$_6$F$_5$)$_3$] to generate [TMPH]$^+$[HB(C$_6$F$_5$)$_3$]$^-$ FLP species in the presence of hydrosilanes and an additional amount of B(C$_6$F$_5$)$_3$ (**Table 4**, entry 4). This FLP species was reported to be active for CO_2 hydrosilylation to CH_4.[110] The same catalyst, with various reducing reagents, has been shown to reduce CO_2 to several products. Lu et al.[111] reported the use of lithium o-phenyl bisborate (**Table 4**, entry 5) as a catalyst for CO_2 reduction. CO_2 was transformed into CH_4 in the presence of Et$_3$SiH, while with HBpin methanol was obtained as the final product. During their research on the hydrosilylation of CO_2 to CH_4 (**Table 4**, entry 6) using in situ generated zirconium-borane complex, Matsuo and Kawaguchi[112] studied the coproduct siloxane in more detail. Initially, they found that less bulky hydrosilanes reacted faster when using tertiary silanes and gave various siloxane products in 64-93% yields. Interestingly, when primary and secondary silanes were applied, oligomers and polymers were obtained. For example, the reaction with diethylsilane produced a mixture of cyclic and linear siloxane oligomers (Et$_2$SiO)$_n$ (n = 3-11); on the other hand, phenylsilane was transformed into a silsequioxane polymer (PhSiO$_{1.5}$)n.
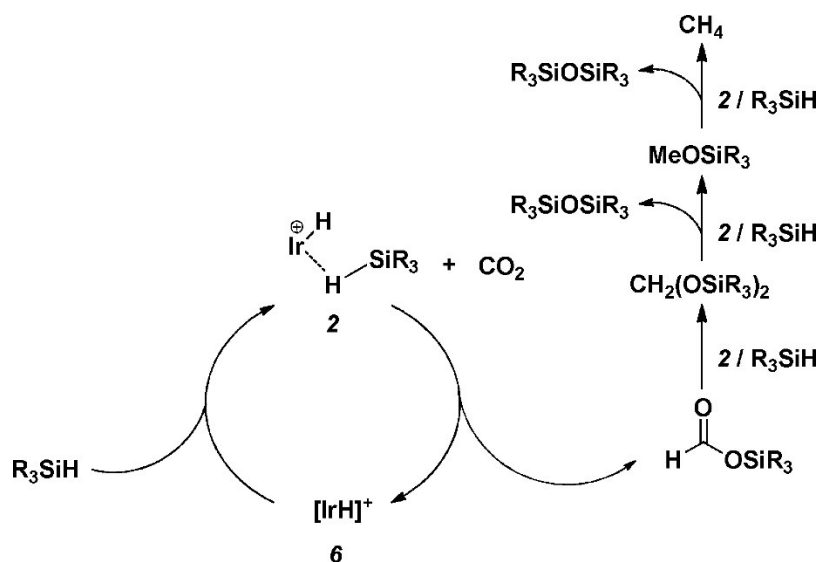
Figure 7. Proposed catalytic cycle for the CO_2 reduction to CH_4 via R_3SiH (Reproduced with permission from[108]).

2.2.3. Cascade catalysis

In a recent publication, Rao *et al.*[113] reported the first homogeneous photocatalytic system for the generation of CH_4 from CO_2 with visible light (**Table 4**, entry 7). This system comprises an iron(III) tetraphenylporphyrin complex functionalized with trimethylammonium moieties as the CO_2 reduction catalyst, the cyclometalated iridium complex [Ir(ppy)$_3$] (ppy = 2-phenylpyridine) as the photosensitizer, and triethylamine (TEA) as the sacrificial electron donor and proton source (**Figure 8**). Starting from either CO_2 or CO, turnover numbers (TON) of 79 and 159 for CH_4 were achieved over 102 h of stable operation. The combination of $Al(C_6F_5)_3$ and $B(C_6F_5)_3$ for the hydrosilylation of CO_2 to CH_4 was reported by Chen *et al.* (**Table 4**, entry 8).[115] Comprehensive mechanistic studies disclosed that in this tandem sequence $Al(C_6F_5)_3$ worked for the fixation of CO_2 to $HCOOSiEt_3$ via the LA-mediated C=O activation, while $B(C_6F_5)_3$ was responsible for further reduction through the FLP-type Si–H activation. It is to be noted that when $Al(C_6F_5)_3$ or $B(C_6F_5)_3$ were used individually the reaction was much less effective.
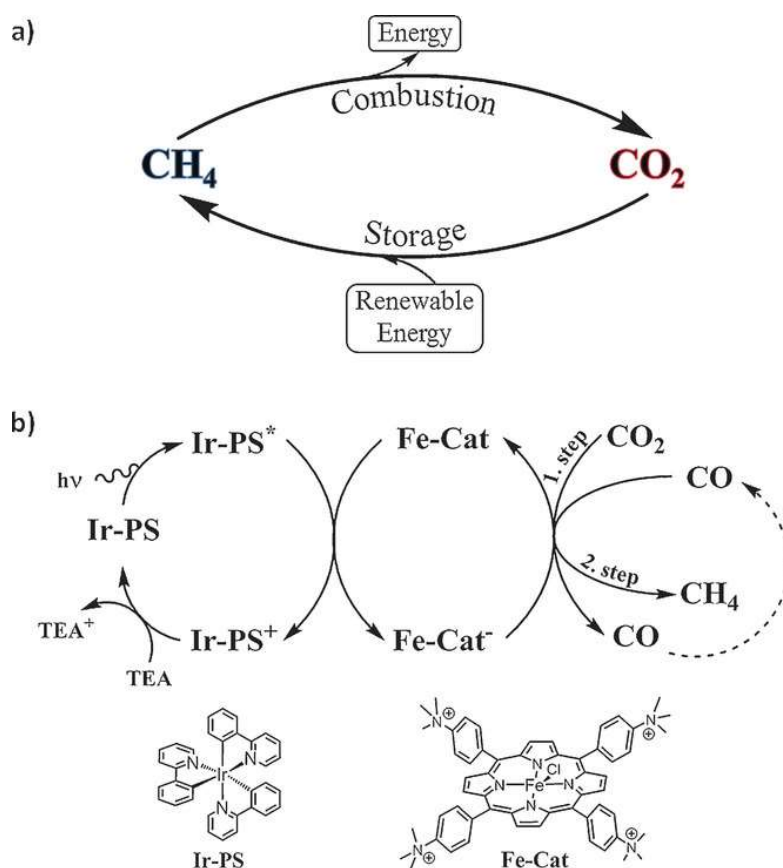
Figure 8. a) Energy storage cycle based on the direct conversion of CO_2 into methane (SNG) using renewable energy. b) Simplified mechanism for the homogeneous, photocatalytic reduction of CO_2 to CH_4 using Fe-p-TMA as the catalyst (Cat), [Ir(ppy)$_3$]as the photosensitizer (PS), and TEA as the sacrificial electron donor (SD). In the first step, CO_2 is converted into CO, which is further reduced to methane in the second step (Reproduced with permission from[114]).

3. Recent developments in CO_2 hydrogenation to methanol

With a global demand of approximately 65 million metric tons, methanol is a primary product in the chemical industry, both as an intermediate and a solvent.[116-119] It can be used to produce several interesting chemicals as formaldehyde, methyl *t*-butyl ether and acetic acid. Moreover, it is an alternative fuel suitable for internal combustion engine because of its high-octane number.[120] The industrial production of methanol is from syngas using heterogeneous catalysts at high temperature (200 – 300 $^{\circ}$C) and high pressure (5 – 20 MPa). To use CO_2 as a feedstock instead of CO attracted increasing attention since it contributes greatly to carbon recycling in methanol economy. Furthermore, the reaction using CO_2 is thermodynamically more favorable than using CO due to the

generation of H_2O. Meanwhile more H_2 is consumed. This reaction can be environmentally meaningful if H_2 is stemmed from renewables. There are multiple examples in literature of the reaction of CO_2 and H_2 to CH_3OH over a partially reduced oxide surface (e.g., Cu,[121] In,[122] and Zn) or noble metals via a CO or formate pathway.

3.1. Hydrogenation of CO_2 to methanol via heterogeneous catalysis

The most straightforward ways to produce methanol and dimethyl ether (DME) from CO_2 is by catalytic hydrogenation with H_2. The reaction of CO_2 and H_2 to methanol, is widely known,[123] some of the earliest methanol plants operating in the 1920 and 1930 in the U.S. were in fact commonly using CO_2 and H_2 for methanol production.[124,125] Both homogeneous and heterogeneous catalysts have been studied for the hydrogenation of CO_2 to methanol. The latter is however preferable in terms of cost, stability, separation, handling, and reuse of the catalyst as well as reactor design, furthermore it happens to be the one used in the industrial production of methanol from syngas.

Efficient heterogeneous catalysts based on metals and their oxides, notably copper and zinc, have been widely developed for the conversion of CO_2 to methanol.[126,127] These catalysts are very similar to those used presently in the industry for methanol production via fossil fuel-based syngas based on $Cu/ZnO/Al_2O_3$. Several reviews have been dealing with the various aspects of the production of methanol from syngas including catalyst design, catalyst preparation, reaction kinetics, catalyst deactivation, reactor design, etc.[128-130] In this review will focus only on the synthesis of methanol from CO_2 and H_2.[131] Cu-based catalysts have been extensively studied for CO_2 to methanol conversion via thermocatalysis, and the innovation continues. Major efforts are devoted to identifying the active sites; developing the catalytic structure-activity relationship, and improving the understanding of reaction mechanisms. In addition, reactor design and optimization are also explored to alleviate H_2O-induced catalyst sintering, increase methanol selectivity, and reduce energy consumption.[132] As the number and variability in catalyst has exponentially increased through the years, in this review we will only describe those catalysts with a CO_2 conversion greater than 20%. For a more comprehensive list of available catalysts for the hydrogenation of CO_2 to methanol see also reference[132] and those cited therein.

3.1.1. Promoted, modified or mediated heterogeneous Cu catalysts

There are plenty of promoters/modifiers for Cu catalysts, but commonly alkali and alkaline-earth metals,[133] rare earth metals,[134] transition metals[135] and main group metals[136] are used. Their performance in CO_2 hydrogenation to methanol helps to improve the Cu dispersion surface area,

conveys support in the adjustment of the adsorption properties and the surface H/C ratios, assist in the interaction between Cu and metal oxide for H_2 spillover and adjust the support material with desired single metal sites at the periphery of Cu NP. Some nonmetal materials, such as graphene oxide (GO) and C_3N_4 also present good features as catalyst modifiers.[137]

Metal-modified Cu catalysts: Lurgi AG, a leader in methanol synthesis process technology, in collaboration with Süd-Chemie, developed and thoroughly tested a strong catalyst C79-05-GL, based on Cu/ZnO (**Table 5**, entry 1) for methanol production from CO_2 and H_2.[138-141] Operating at a temperature around 260 ºC, slightly higher than the one used for conventional methanol synthesis catalysts, the selectivity in methanol was excellent. The performance of this catalyst decreased at about the same rate as the activity of commercial catalysts currently used in methanol synthesis plants, so it became a measuring point to further CO_2 hydrogenation to methanol catalysts. Ban et al.[134] have examined the effect of various rare-earth elements on the performance of Cu/Zn/Zr catalyst for CH_3OH synthesis. They found that lanthanum and cerium favor the production of CH_3OH (**Table 5**, entry 2). The better catalytic performance of La- and Ce- promoted catalysts is attributed to their stronger interaction with the catalyst components, benefiting CH_3OH synthesis via H_2 spillover. Arena et al.[142,143] have systemically studied the correlation between the oxide supports with catalytic properties over Cu-ZnO catalysts. Al_2O_3, ZrO_2, and CeO_2, three commonly used support materials, are chosen for the comparative assessment. In **Table 5**, entry 3 we only show the CuZnZr catalyst, but the performance of the studied ones decreases in the following order: CuZnZr > CuZnAl > CuZnCe. Considering the largest surface area, the biggest pore volume, and the smallest decay upon reduction, ZrO_2 is identified as the most effective textural promoter for Cu-ZnO catalysts. Shi et al.[144] developed a method for $CuO-ZnO-CeO_2$ dispersion on one-dimensional TiO_2 nanotubes surface (TNT).[144] The addition of the TNT support shows a promoting effect on the $CuO-ZnO-CeO_2$ system, which not only promotes CuO reducibility and improves the metallic Cu dispersion and specific surface area, but also enhances CO_2 adsorption and increases the proportion of basic sites. In **Table 5**, entry 4 we have listed $Cu/ZnO/CeO_2/TNT$ (or CZC/10TNT as labeled by Shi et al.[144]) and it shows a high CO_2 conversion and good CH_3OH selectivity.

Table 5. Heterogeneous catalyst for CO_2 hydrogenation to methanol.[138]

Entry	catalyst	Ratio (H$_2$:CO$_2$)	P (atm)	T (ºC)	Space velocity[a]	CO$_2$ conv. (%)	selec. (%)	Ref.
1	Cu/ZnO/Al$_2$O$_3$ (C79-05-GL)	3:1	29.6	260	(G) 8100	-	ca. 90	[139]
2	CuZnZrLa	3:1	29.6	230	(W) 10	20.5	49.8	[135]
	CuZnZrCe	3:1	29.6	230	(W) 10	22.8	53.0	
3	CuO/ZnO/ZrO$_2$	3:1	49.3	240	(W) 2.3	22.4	64.0	[142]
4	Cu/ZnO/CeO$_2$/TNTs	3:1	29.6	260	(W) 2.99	23.3	59.8	[144]
5	CuZn/NrGOae-U	3:1	14.8	250	(G) 2444 /(W) 1.40	24.16	-	[145]
6	CHT-AMn[1]	3:1	49.3	250	(W) 1.87	22.3	43.0	[146]
7	CHT-Y0.1	3:1	49.3	230	(W) 2.24	20.2	69.3	[147]
8	CHT0.24-F	3:1	49.3	250	(G) 4000	21.1	53.5	[148]
9	CuZnAlZr-FA-650	3:1	29.6	250	(G) 4000	25.88	49.2	[149]
10	CuZnAlZr-USP	3:1	29.6	230	(G) 10000	22.5	22.6	[150]
11	30CuZn-Z$_{pH}$	3.9:1	49.3	280	(G) 10000	22.2	34	[151]
	30CuZn-Z$_M$	3.9:1	49.3	280	(G) 10000	21.0	34	
12	CuZnZr	3:1	49.3	250	(W) 7.47	26.7	55.2	[152]

[1] There are a couple of CHT.based catalysts described in the same study all with %CO$_2$ conversion > 20%

Entry	catalyst	Ratio (H$_2$:CO$_2$)	P (atm)	T (°C)	Space velocity[a]	CO$_2$ conv. (%)	selec. (%)	Ref.
	CuZnZr (TPABr)	3:1	49.3	250	(W) 7.47	11.4	92.7	
13	CuZnAlZr-573	3:1	49.3	270	(G) 4600	24.5	57.6	[153]
14	Cu/SiO$_2$-AE	4:1	29.6	320	(W) 1.40	ca. 28	21.3	[154]
15	CuZnAl-400	3:1	39.5	240	(W) 25.6	59.5	73.4	[155]
16	CuZnAlZr-5Al	3:1	49.3	250	(W) 5.6	25.2	60.6	[156]
17	Pd/In$_2$O$_3$	4:1	49.3	300	(W) 1.1	20	70	[166]
18	Pt/film/In$_2$O$_3$	3:1	9.9	30	(W) 4.67	37	62.6	[167]
19	Cu@ZIF-8	3:1	44.4	260	(G) 21600	ca. 22	ca. 54	[176]
20	CuZnBTC	3:1	39.5	250	(W) 14.9	20.9	58.5	[177]
21	20 Cu/Al$_2$O$_3$ ‑ OG	3:1	9.8	30	-	92	99	[178]

a (W) = WHSV = mass flow rate/catalyst mass, mL/g$_{cat}$·h, (G) = GHSV = volume flow rate/bed volume, h^{-1}

Nonmetal-modified Cu catalysts: Graphene oxide (GO) has been also introduced in the preparation of CuO-ZnO-ZrO$_2$ as a surface. Witoon et al.[93] describe the preparation of the catalyst via reverse coprecipitation method. An appropriate amount of GO is proven to result into a higher CO$_2$ conversion. The addition of GO can also serve as a bridge between mixed metal oxides, through which the H$_2$ spillover is facilitated form the Cu surface to the carbon species adsorbed on the isolated metal oxide particles (**Table 5**, entry 5).

3.1.2 Metal-oxides based catalysts

The hydrotalcite-like compounds, present strong features in the hydrogenation of CO$_2$. In this regard, the resultant catalysts exhibit high stability against sintering, high specific surface area and stronger basic properties.[93-95] In **Table 5**, entries 6-8 we depict catalysts with modifiers into the

preparation of HTC-derived Cu/Zn/Al catalysts (HTC-Metal), including Mn, Zr, and rare-earth metals La, Ce, and Y.[146] In this study, Gao et al.[147] reported an increase in the CH_3OH selectivity as follows: Cu/Zn/Al < Cu/Zn/Al/Mn < Cu/Zn/Al/La < Cu/Zn/Al/Ce < Cu/Zn/Al/Zr < Cu/Zn/Al/Y. A linear relationship can be observed between the CH_3OH selectivity and the surface basic sites, as well as between CO_2 conversion and Cu surface area. Hence, it results clear that the modifier tune Cu surface area and surface basicity of the catalyst. The best performance has been shown by the Cu/Zn/Al/Y catalyst, the activity appears to correlate with the loading amount of Y and maximizes at $Y^{3+}/(Y^{3+}+ Al^{3+}) = 0.1$ (**Table 5**, entry 7). The preparation of the catalyst via precipitation allows higher metal loadings but comes with the price of control loss in the growth of Cu particle size and increase the surface area. Recently Hou et al.[149] have employed formaldehyde into the precipitate slurries of CuZnAlZr catalysts as a weak reducing agent. The results indicate that after calcination the copper components existed in state of Cu_2O, which could provide highly dispersed active Cu^0 particles with a weak interaction between metal and supports. Moreover, formaldehyde pre-activation gave rise to more crystallized semiconductor ZnO phase, after calcination with N_2 at higher temperatures. The synergy between these two factors leads to heightened catalytic performance as shown in **Table 5**, entry 9. Zahiruddin Ramli et al.[150] have prepared CuZnAlZr catalysts vie the ultrasonic spray precipitation technique (USP) in order to obtain finer Cu crystallites with better particle uniformity than via conventional precipitation (CP) techniques. In terms of reactivity, USP-prepared catalyst outperformed CP catalyst for CO_2 conversion by 20.9% whilst improving methanol selectivity and yield by 2.7 and 27%, respectively (**Table 5**, entry 10). The improved surface basicity of USP catalyst, which has a great influence on reaction pathways of intermediate species, contributed significantly to the enhanced catalytic performance, and hence justify the superiority of this new preparation technique over the conventional ones.

The microfluidic continuous coprecipitation method have been employed by Angelo et al.[151] as a tool to prepare Cu-ZnO-ZrO_2 catalysts, an example of the performance of such catalysts can be seen in **Table 5** entry 11. When compared with a batch coprecipitation technique, it was found that the continuous micro-fluidic coprecipitation provides a much more homogeneous and repeatable catalyst leading to better metallic copper surface area directly correlated to a better reactivity observed for the catalytic hydrogenation of CO_2 into methanol. This method can tune the Cu surface area by varying several parameters during preparation: including pH, temperature, molar ratio of carbonate/metal cations, speed of flow, and droplet size. The best methanol productivity was obtained for 30CuZn-ZM catalyst, with 15.19 compared to 10.18 (mol/(kg$_{cat}$ h)) for the catalyst of identical composition prepared by batch coprecipitation.

In order to modify surface structure Chen et al.[152] have introduced vapor-phase treatment to prepare CuZnZr catalyst by using tetrapropylammonium bromide (TPABr) and H_2O as treatment reagents. As shown in **Table 5** entry 12, the TPABr treated catalyst significantly improves CH_3OH selectivity. The post treatment results in the increase of particle sizes (CuO, ZnO and ZrO_2), the formation of rod-like structures, and the modification of the surface properties such as enriching Zn, Zr, and oxygen vacancies on the surface. Such TPABr induced variations lead both to high CH_3OH selectivity and significant suppression of CO formation. Another alternative to form small Cu particles with highly reduced states is the liquid reduction method. In order to achieve it, Dong et al.[153] have prepared CuZnAlZr catalyst using $NaBH_4$ as a reducing agent. The results show that a large, exposed Cu surface area promotes catalytic CO_2 conversion and a close correlation between the Cu^+/Cu^0 ratio and the selectivity for methanol is shown. A calcination temperature of 300 ºC was found to produce a Cu/Zn/Al/Zr catalyst exhibiting the maximum activity during the synthesis of methanol, which is listed as the entry 13 in **Table 5**. To control the composition evolution of the catalyst during its preparation, Wang et al.[154] have prepared Cu/SiO_2 catalyst by ammonia evaporation (AE) method. This method allows to tune the $Cu^+/(Cu^+ + Cu^0)$ ratios on the surface. A high exposed Cu surface area evidently favors CO_2 catalytic conversion while a high value of Cu^+/Cu^0 resulting from the use of an optimal calcination temperature is evidently helpful during the synthesis of methanol, as shows in **Table 5**, entry 14.

Inspired by the mutual replacement of cations between solid-phase materials during the mechanical-force-driven ball-milling process, Wu et al.[155] have prepared Cu/Zn/Al catalysts. With the increasing of milling speed during ball-milling, the ion exchange between Cu^{2+} and Zn^{2+} in catalyst precursors is enhanced. After calcination, CuO nanoparticles are neighboring to ZnO nanoparticles which serve as spacers to prevent the agglomeration of CuO nanoparticles, leading to a cross-distribution of CuO and ZnO in catalysts. The resulting catalyst (CuZnAl-400, **Table 5**, entry 15) exhibits comparable CO_2 conversion and CH_3OH selectivity as the commercial CuZnAl catalyst under the same reaction conditions (**Figure 9**). The catalytic performance can be attributed to both the cross-distribution of CuO and ZnO nanoparticles caused by solid-state ion exchange and the promotion of reversible CO_2 hydrogenation reaction toward methanol synthesis by the internal cooling system. Zhang et al.[156] tested a series of microspherical CuZnAlZr catalysts with the addition of various weight percentages of binder alumina sol from 0 to 20 wt.% for CO_2 hydrogenation to methanol. When the added alumina sol is below 10 wt.%, the CO_2 conversion is close to the equilibrium conversion of CO_2. Further increase of alumina sol content decreases the activity due to the decreased Cu surface area and weakened interaction among Cu and ZnO. When

used in slurry bed, the attrition resistance of catalysts plays an important role to determine the final catalytic performance. The catalyst without addition of alumina sol possesses low attrition resistance, which leads to catalyst loss and deactivation during reaction process. The introduction of suitable amount of alumina sol can enhance the attrition resistance of the catalysts markedly, and the catalytic activity can be still maintained at a high value. The spray-dried $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst with addition of 10 wt.% alumina sol exhibits the best performance with high activity and high stability as marked in **Table 5**, entry 16.
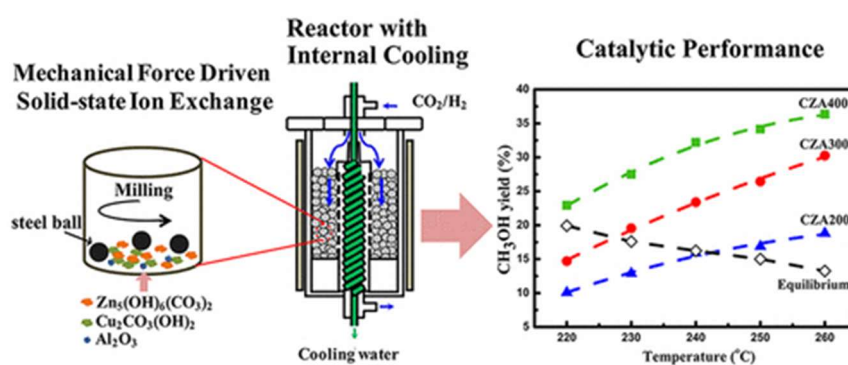
Figure 9. Ball milling catalyst generation (Reproduced with permission from[155]).

3.1.3. Precious metal-based catalysts (Pd and Pt)

Supported catalysts of precious metals such as Pd and Pt have been reported to be active for methanol via CO_2 hydrogenation at low temperatures.[157] Pd catalysts supported on La_2O_3,[158] Nd_2O_5[158] and CeO_2[159] can selectively convert CO_2 to methanol at around 170 ºC. With these results at hand, it can be thought that the precious metal catalysts should be able to perform CO_2 hydrogenation to methanol at low temperature. Such catalysts are not listed in the table above as they do not meet our selection criteria of % CO_2 conversion, but they are expected to present better yields.[160-163]

3.1.4 In₂O₃ catalysts

Recently, the catalytic property of In_2O_3 has been recognized.[164] The basic functionality of In_2O_3 is analogous to the dual-site mechanism, wherein these two types of active sites are thermally induced with oxygen vacancies and H-induced metals, behaving as active sites for adsorption and

activation of CO_2 and H_2, respectively. This unique pathway can significantly suppress RWGS, leading to a high selectivity to methanol over CO. To further improve the activity of In_2O_3 catalysts, a major strategy is to introduce dopants to improve the dissociative adsorption of H_2 and provide interfacial sites for CO_2 adsorption and hydrogenation. Ye *et al.*[165] have conducted DFT calculations and microkinetic modeling to study the reaction mechanism on the model catalyst Pd_4/In_2O_3. The strong interaction between Pd and In_2O_3 leads to the formation of bimetallic species during reduction and alteration of the nature of interfacial sites, which are detrimental to methanol synthesis. In order to avoid it, Rui *et al.*[166] used peptide templates in the preparation of the Pd/In_2O_3 catalysts, promoting certain control of the size and facet of the products under mild conditions. As a result, the Pd/In_2O_3 catalyst (**Table 5**, entry 17) exhibits high catalytic performance for CO_2 hydrogenation to methanol. Moreover, Men *et al.*[167] have incorporated In_2O_3 with highly dispersed Pt NP and applied the catalysts in methanol synthesis using a dielectric barrier discharge (DBD) plasma reactor. With the assistance of DBD plasma, the resulting catalysts present better activity and selectivity to methanol (CO_2 conversion, 37%; and methanol selectivity, 62.6 C-mol %, **Table 5**, entry 18), which outperforms the Pt/In_2O_3 and commercial CuZnAl catalysts for hydrogenation with H_2. Hence, with this catalyst, the high-energy electrons of the DBD plasma can trigger the CO_2 hydrogenation at nearly ambient conditions.

3.1.5. Ga-based intermetallic compounds

Several catalysts examples based on Ga intermetallic compounds are found in literature, none of them listed above, as they do not match the review criteria. Nevertheless, intermetallic compounds (IMC) have some advantages as: having a uniform bimetallic atomic ratio, being structurally stable due to the covalent nature of the metal-metal interactions, and providing a structure which makes feasible the modification of the electronic state of active metals. On such light, comparative studies have been performed on mixed metal Ni-Ga system because it comprises a series of stable intermetallic compounds.[168] Moreover, $Ni/\beta-Ga_2O_3$, among others, is found to be active for methanol synthesis via CO_2 hydrogenation.[169-172]

3.1.6. MOF/ZIF derived nanostructured catalysts

Defining the catalytic nanoscale structure with accurate control of the active sites remains a desirable task when developing highly efficient catalysts. In this regard, metal organic frameworks (MOF) exhibit excellent properties, as they are editable through large accessible surface areas, present tunable pore functionalities and reactive open metal sites.[173] It has been pointed out that the CO_2

hydrogenation to methanol is structure sensitive, and the catalytic performance closely relies on the composition and dimension of the metal/oxide interface.[174] Hence, MOF as supportrs could be of advantage, as they can be configured to present different nano size building units with diverse compositions. Moreover, the framework of MOF/ZIF (zeolitic imidazolate framework) habilitates the confinement effect of encapsulated metal NP, providing opportunities to preserve the catalysts from deactivation caused by aggregation or agglomeration.[175] Hu *et al.*[176] reported a synthesis of inverse ZnO/Cu catalysts by direct calcination of Cu@ZIF-8 (zeolitic imidazolate framework-8, **Table 5**, entry 19). The catalyst presented an excellent activity and TOF attributed to the inverse structure of Cu particles covered by sub 5 nm ZnO, which promotes the intimate Cu-ZnO interface with enhanced SMSI. Moreover, using another MOF preparation methodology, Zhang *et al.*[177] reported the preparation of a bimetallic CuZn-BTC (BTC: benzenetricarboxylic acid) coordination polymer through a new "acidic etching self-assembly" method by using ZIF-8 as a template. This approach based on CuZn-BTC precursor takes advantage of the structural feature of CuZn-BTC such as uniformly distributed bimetallic ions, preventing the aggregation of Cu and ZnO nanoparticles, and generating more stable Cu-ZnO interfacial sites. This catalyst (**Table 5**, entry 20) exhibits higher methanol formation rate than the standard $Cu/Zn/Al_2O_3$ catalyst with a methanol selectivity that remains constant at increased temperatures.

3.1.7. Indirect heterogeneous catalysts

Du *et al.*[178] reported the hydrogenation of alkyl formate to methanol over nanocomposite copper/alumina catalysts. The Cu/Al_2O_3 oxalate gel catalysts with several copper loadings (10-50 wt .%) were prepared by OG coprecipitation method (**Table 5**, entry 21). Then, the Cu/Al_2O_3 OG catalysts were used for the selective hydrogenation of a formate ester to methanol in the absence of solvent at 130 °C. The highest methanol yield was 92 % for a catalyst containing 20 wt. % Cu. The total TON based on three successive runs was as high as 1092, which is the highest TON value ever reported for the hydrogenation of methyl formate (MF) to methanol using heterogeneous catalysts.

3.2 Hydrogenation of CO_2 to methanol via homogeneous catalysis

The heterogeneous hydrogenation of CO_2 is usually carried out under harsh conditions (> 220 ºC) and shows low selectivity and activity, resulting in extensive energy consumption.[179] Catalyst stability and water tolerance at high temperature are strictly required to perform the reaction smoothly. Thus, rational tuning of catalytic performance and the product selectivity remains challenging.[180] Consequently, the possibility of homogeneous catalysts for hydrogenation of CO_2 to methanol has

been seriously considered. A transition metal can interact with a CO_2 molecule presumably leading to CO_2 activation.[181] In early studies, Ru[182] or Ni[107] carbonyl complexes could homogeneously catalyze the hydrogenation of CO to methanol, whereas Rh or Co[183] carbonyl complexes led to the formation of byproducts including ethanol and ethylene glycol besides methanol. In this context, homogeneous catalysis by transition metals for the synthesis of methanol via hydrogenation of CO_2 or its derivatives is summarized in **Table 6**. However, lots of catalysts generally remain limited by the requirement for other hydrogen sources such as boranes and hydrosilanes. To address these challenges, cascade catalysis has been exploited for the homogeneous catalytic reduction of CO_2 with H_2 to produce methanol.[184]

Table 6. Homogeneous hydrogenation of CO_2/CO derivatives to methanol.

Entry	catalyst precursor	solvent	Additives	Ratio (H_2:CO_2)	T (ºC)	t (h)	TON[a]	Ref.
1	$Ru_3(CO)_{12}$	NMP	KI	3:1	240	3	94.5	[185]
2	[(Triphos)Ru(TMM)]	THF/EtOH	$HNTf_2$	3:1	140	24	221	[187]
3	$Co(acac)_3$ triphos	THF/EtOH	$HNTf_2$	3.5:1	100	24	50	[189]
4	Ru(PNP)-C2	1,4Dioxane/THF	via carbonate	3:1	145	24	4400	[191]
5	Ru(II) PNP-C3	THF	t-BuOK	3:1	140	24	87000	[193]
6	Ru PNP-C11	THF	K_3PO_4/$NHMe_2$	2:1	155	36	220	[195]
7	Ru-MACHO	THF	Morpholine/t-BuOK	1:1/ 50 atm H_2	60	40		[199]
8	Ru-MACHO-BH	triglime	PEHA	3:1	135-155	55	1850	[200]
9	Mn-PNP C-13	THF	t-BuOK, RR´NH	1:1/H_2	110	24	128	[201]
10	[$RuCl_2$($Ph_2PCH_2CH_2NHMe$)$_2$]	Toluene	$EtONa$/R_2NH	3:1	180	20	8900	[202]
11	C-scorpionate Iron(II)	CH_3CN	PEHA	3:1	80	36	2387	[203]

Entry	catalyst precursor	solvent	Additives	Ratio (H$_2$:CO$_2$)	T (ºC)	t (h)	TON[a]	Ref.
12	Ru PNN	THF		3:1	110	12	93	[194]
13	(PMe$_3$)$_4$Ru(Cl)(OAc) Sc(OTf)$_3$ (PNN)Ru(CO)(H)	CD$_3$OH		3:1	135	16	2.5	[180]
14	Cu/Cr$_2$CuO$_4$ Cu/Mo$_2$C	1,4-dioxane n-decane		3:1	135	2	TOF:4.7 10^{-4}	[204]
15	[Cp*Co(bpy-Me)OH$_2$]$^{2+.}$ and relatives	computational						[206]

(a) (TON, turnover number) moles of desired product per mole of the homogeneous catalyst, and (TOF turnover frequency), moles of product per mole of the catalyst per unit time and its value is usually expressed in h^{-1}.

3.2.1 Direct homogeneous catalysis

The first homogenous metal catalyzed hydrogenation of CO$_2$ to methanol was performed by Tominaga et al.[185] using H$_2$, Ru$_3$(CO)$_{12}$ and potassium iodide in a N-methylpyrrolidone solution at 240 °C (**Table 6**, entry 1) under 79 atm of a 3 H$_2$:CO$_2$ mixture. In the absence of potassium iodide, Ru$_3$(CO)$_{12}$ decomposed to ruthenium metal causing methanation of CO$_2$. However, in the presence of an halide, CO$_2$ was first converted to CO (through the reverse water-gas shift reaction) at about 200 °C and then subsequent hydrogenation of CO formed methanol at about 240 °C. Below 160 °C, no trace of CO or methanol was observed and above 240 °C the formed methanol further hydrogenated to methane. A couple of years later the same group reported other transition metals complexes such as Rh$_3$(CO)$_{12}$, Ir$_4$(CO)$_{12}$, W(CO)$_6$, Mo(CO)$_6$, Fe$_2$(CO)$_9$, and Co$_2$(CO)$_8$ that presented no CO$_2$ hydrogenation products. Since then, multiple attempts to the homogeneous hydrogenation of CO$_2$ to methanol have been performed, mostly as an indirect reaction (**Figure 10**)[186] via carbonates, carbamates or formate esters, among others. Such reactions will be discussed below. Among the direct homogeneous hydrogenations of CO$_2$ to methanol we can count the one proposed by Wesselbaum et al. in 2012 and 2015.[187] They describe a ruthenium phosphine complex under relatively mild conditions (**Table 6** entry 2). A detailed mechanistic study on this catalytic transformation was published subsequently based on NMR experiments and DFT calculations.[187,188] The cationic formate complex [(Triphos)Ru(η$_2$-O$_2$CH)(S)]$^+$ (S = solvent) was identified as the essential intermediate, leading to the synthesis of the acetate complex as a robust and stable precursor for the catalytic transformation. The mechanism consists of a sequential series of hydride transfer and

protonolysis steps leading to methanol within the coordination sphere of a single Ru-Triphos-fragment (**Figure 11**). Schneidewind et al.[189] described the first homogeneous non noble metal catalyst for the hydrogenation of CO_2 to methanol. The catalyst is formed in situ from $Co(acac)_3$, Triphos, and $HNTf_2$ (**Table 6**, entry 3) and enables the reaction to be performed at 100 °C without a decrease in activity. In a similar system to the one described by Wesselbaum et al.,[190] $Co(acac)_3$, triphos and $HNTf_2$ were used as catalyst precursors.
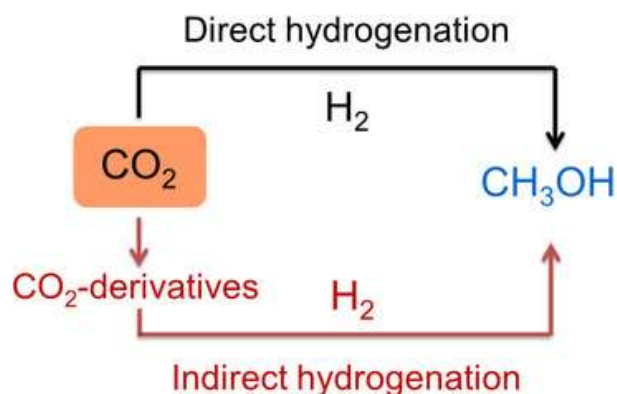
Figure 10. Direct and indirect hydrogenation of CO_2 to methanol.
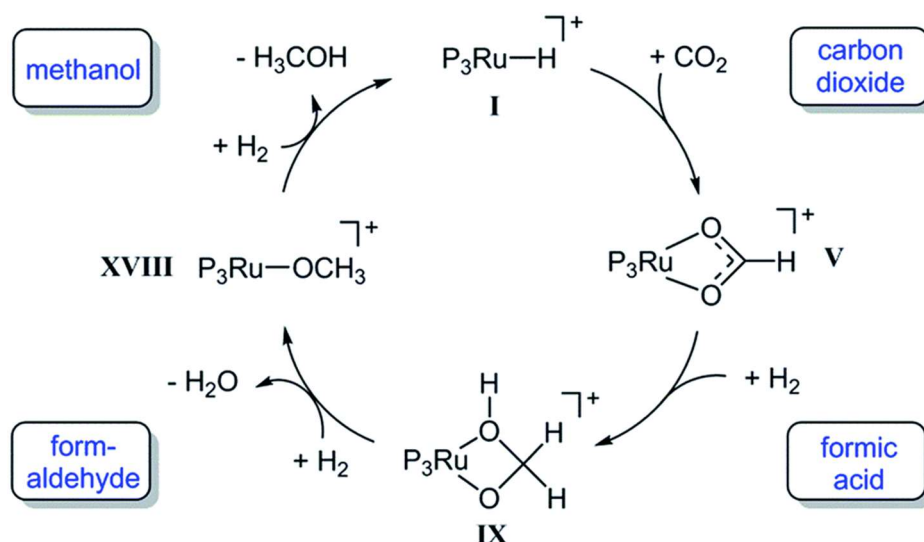
Figure 11. Basic catalytic cycle for the transformation of CO_2 to methanol at the Ru–Triphos fragment via the formic acid and formaldehyde stage through the key intermediates I, V, IX, XVIII.

P$_3$Ru denotes the Triphos–Ru(ii) fragment comprising additional ligands to fill the coordination sphere (Reproduced with permission from[190]).

3.2.2. Indirect homogeneous hydrogenation

Recently, various research groups intensively investigated the indirect hydrogenation of CO_2 to methanol, where easily available CO_2 derivatives, such as organic carbonates, carbamates, formates, cyclic carbonates, urea derivatives and dimethylformamide, can be used as substrates.[186,191-194] Then, these derivatives can be efficiently converted into methanol at relatively mild reaction conditions with a suitable catalyst. In this section we will outline the recent advances in the indirect hydrogenation of CO_2 to methanol.

Hydrogenation of CO_2 to methanol via organic carbonates, carbamates and formats: Balaraman et al.[191] developed an indirect approach from CO_2 to methanol through hydrogenation of CO_2 derived organic carbonates, carbamates and formates by using Ru-based homogeneous catalysts under mild conditions (**Figure 12, Table 6**, entry 4). In their experiments, the treatment of dimethyl carbonate (25 mmol) with H$_2$ (4 MPa) at 145 ºC for 3.5 h with a catalytic amount of **C-1** (0.01 mmol) resulted in complete conversion with selective formation of methanol and a turnover number (TON) of 2500. An even higher TON of 4400 was obtained using bipyridine-based pincer **C-2** as a catalyst with 49 atm of H$_2$. The ability of the Ruthenium complexes **C-1** and **C-2** to catalyze the hydrogenation reaction with molecular H$_2$ it is reported to come from their capacity to split hydrogen on a molecular level through metal-ligand cooperation (**Figure 13, Table 6**, entry 5). The monohydride complex **C-1** can react with molecular hydrogen to form the dihydride complex **C-1A**, the driving force for the reaction being supplied by the aromatization of the pyridine moiety of the ligand. Complex **C-1A** in turn can transfer the proton and hydride to a suitable acceptor molecule with carbonyl/imine functional groups, regenerating the complex **C-1** in the process. Thus, through metal ligand

cooperation and ligand aromatization and de-aromatization, complexes **C-1** and **C-2** can effectively hydrogenate organic molecules using H_2.
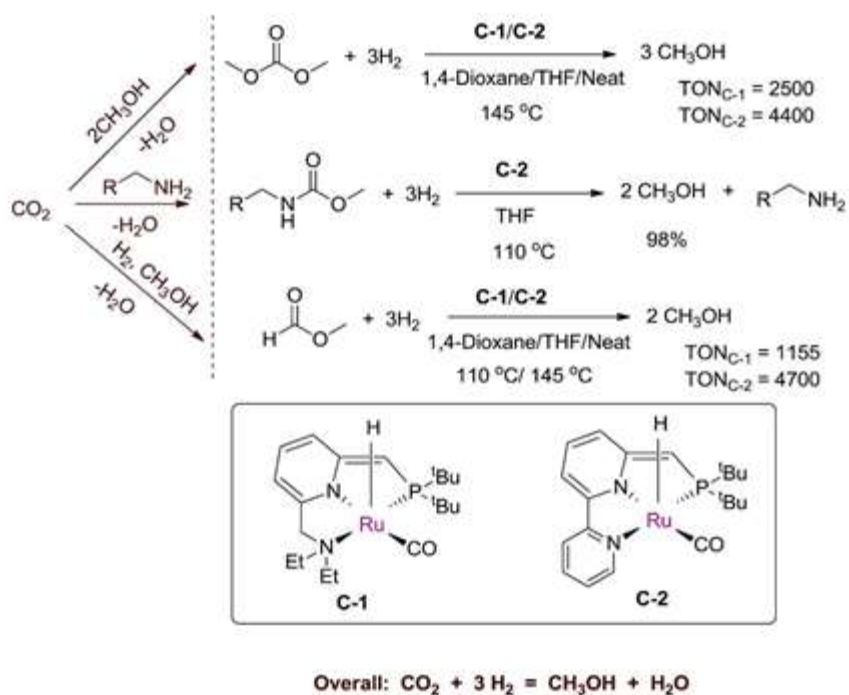

Figure 12. Indirect hydrogenation of CO_2 to methanol via carbonates, carbamates or formate esters (Reproduced with permission from[188]).
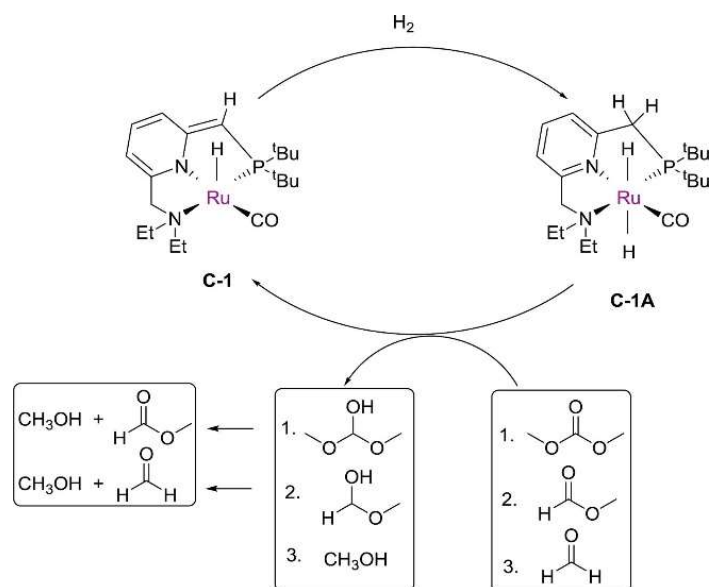
Figure 13. Favorable H_2 splitting by Ru complexes via metal-ligand cooperation (Reproduced with permission from[188]).

Rezayee *et al.*[195] were the first to achieve a CO_2 to methanol process under basic conditions. A combination of dimethylamine and Ru catalyst was used for this transformation (**Table 6**, entry 6). In the initial stage of this study, the abilities of the known hydrogenation catalysts **C-1**, **C-2** and **C-11** were screened for dimethylammonium dimethylcarbamate (DMC) hydrogenation, among which, the commercially available catalyst **C-11** along with K_3PO_4 was successful in producing methanol. Dimethylammonium formate (DMFA) and dimethylformamide (DMF) intermediates were also observed. The authors hypothesized two possible pathways for the reduction of DMC to methanol and Me_2NH. One involved the direct hydrogenation of the carbamate to formamide (path A). The other the reduction of free CO_2 generated in the reaction mixture upon heating DMC (path B). Among these, pathway B was found to be the most viable pathway based on careful investigation of the intermediate and product formation. Finally, the authors demonstrated that CO_2 can also be reduced to methanol by employing a similar strategy. The reaction was conducted at 95 °C for 18 h (to form DMFA and DMF intermediates from DMC) followed by 155 °C for 18 h (to form methanol from the DMFA and DMF intermediates), since the decomposition of the catalyst was observed when heated directly to 155 °C (**Figure 14**) 96% of CO_2 was converted to a mixture of methanol (22%) and DMF/DMFA (74%).
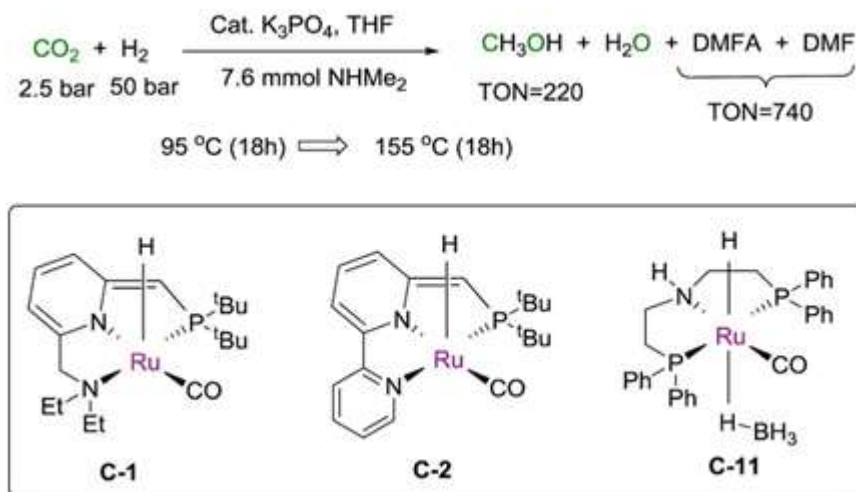
Figure 14. CO_2 hydrogenation to methanol under basic conditions (Reproduced with permission from[188]).

Hydrogenation of cyclic carbonates to methanol: The reaction of CO_2 and ethylene oxide to produce ethylene carbonate (EC) is a thermodynamically favorable process[196] which is developed as the key step in the "Omega process"for the industrial production of ethylene glycol (EG). In this context, Han et al.[193] reported in 2012 a novel CO_2 indirect conversion process by selective hydrogenation of cyclic carbonates to obtain methanol by using several ruthenium PNP pincer complexes (**C-3 - C-7**) under a moderate H_2 pressure of 49 atm (**Table 6**, entry 5). The cyclic carbonates can be industrially synthesized through the reaction of CO_2 with epoxides, which in turn can be prepared by controlled oxidation of ethylene, as in the first step of the Omega process developed by Shell Global Solutions. The hydrogenative products of the cyclic carbonates, methanol, and the diol, both hold commercial values and are important for the synthesis of value-added products. The authors screened several pincer catalysts for the hydrogenation and catalyst **C-3** (with t-BuOK) was found to be most efficient among them and a highest TON of 87000 was achieved. Catalyst **C-3** was also found to be able to hydrogenate polycarbonates along with cyclic carbonates. In a similar way as the Ru-PNP complexes used for the hydrogenation of CO_2 to methanol via organic carbonates, carbamates and formates **C-1** and **C-2**, complexes **C-3** to **C-7** can also split molecular H_2 through metal-ligand cooperation. Complex **C-3**, in the presence of a base such as t-BuOK, eliminates H^+ and Cl^- to form an imido complex **C-3A**. This imido complex can split H_2 to form the dihydride complex **C-3B**. Complex **C-3B** acts as the active species for the hydrogenation reaction as it transfers one proton and one hydride

to the substrate molecule, regenerating **C-3A** in the process. However, while discussing the involvement of PNP ligands on different hydrogenation reactions, it should be noted that the traditional idea of non-innocent ligands in pincer catalysts such as **C-3** to **C-7** has recently been questioned by Dub et al.,[197,198] who proposed an alternate mechanism based on transition state stabilization provided by N-H or N-Me functionality.

Hydrogenation of formamides and derivatives to methanol: Shortly after the report by the Sanford group for CO_2 hydrogenation to methanol under basic conditions (**Figure 15**), Zhang et al.[199] reported a sequential CO_2 reduction to methanol in one pot using Ru-MACHO catalyst [RuHClHN(CH$_2$CH$_2$PPh$_2$)$_2$CO; **C-3**] (**Table 6**, entry 7) in the presence of morpholine. In this study, which mainly focused on N-formylation utilizing CO_2 and H_2, the N-formylation reaction was first performed under 70 atm of 1:1 CO_2:H_2 at 120 °C to produce N-formylmorpholine. Consequently, the in situ formed N-formylmorpholine was reduced further in the same pot under 50 atm H_2 at 160 °C for 1 h to produce methanol with 36% yield. Kothandaraman et al.[200] presented a catalyzation approach in which the CO_2 was captured directly from air for the synthesis of fuels such as methanol (**Table 6**, entry 8). A polyamine with a low vapor pressure, pentaethylenehexamine (PEHA), was used to capture CO_2. The reduction proceeded through the formation of formamides intermediates. A series of catalysts based on Ru and Fe pincer complexes (**C-3** and **C-11** to **C-14**) were screened for the hydrogenation, out of which catalyst **C-11** (Ru-MACHO-BH) was found to be the most effective. Metal ligand coordination was reported to be crucial for this reduction. With a concentrated CO_2 source (3H$_2$: CO_2 = 75 atm), the authors were able to recycle catalyst **C-11** multiple times in triglyme, with a total TON of 1850 after the 5th cycle. The products, methanol and water were collected from the reaction mixture between each cycle by distillation. The scope of the system was extended in the same study, to direct CO_2 capture from air and its subsequent conversion to methanol. Resulting in the first example of direct CO_2 capture from air and subsequent conversion to methanol under homogeneous catalytic conditions. Kar et al.[201] reported the sequential hydrogenation of CO_2 to methanol via formamide in one pot using a Mn-PNP pincer complex **C-15** in the presence of amine (**Table 6**, entry 9). During the first step of this sequential reduction, N-formylation of the amine was performed in CO_2:H_2 (1:1) at a pressure of 60-70 atm in THF at 110 °C. The in situ formed formamide was then hydrogenated in the presence of high H_2 pressure (70–80 atm) at 150 °C to afford the desired product methanol with an 84% yield (with respect to amine). Everett and Wass[202] presented a system with non-pincer ruthenium complexes for the hydrogenation of CO_2 to methanol via the formation of formamides (**Table 6**, entry10). Metal ligand cooperation was identified as a key contributor for the

catalysis of the second hydrogenation step of formamide to methanol. Fundamental studies on the methanol yield with respect to the amine structure revealed that the methanol formation increases with increasing steric bulkiness of the employed secondary amine, whereas the amount of formamide intermediate decreased along with a decrease in total CO_2 conversion to methanol and formamide.
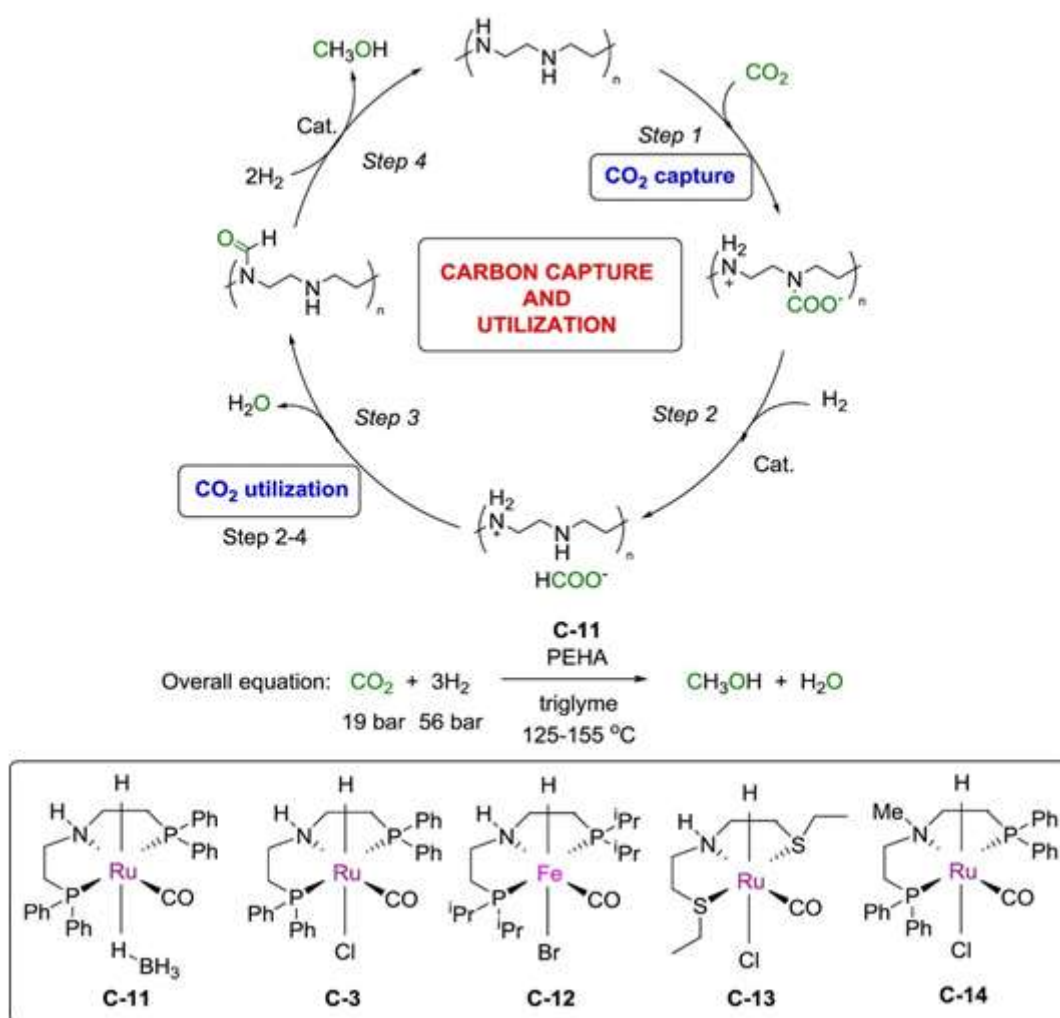

Figure 15. CO_2 capture with polyamines (Reproduced with permission from[188]).

Hydrogenation of formaldehyde to methanol: Ribeiro et al.[203] using a C-scorpionate iron(II) catalyst (**C-18**) reported an Iron-catalyzed hydrogenation of CO_2 to CH_3OH (**Table 6**, entry 11). The catalyst

[FeCl$_2$\{κ^3-HC(pz)$_3$\}] (C-18) was able to hydrogenate CO_2 at 80 °C with a total CO_2:H_2 (1:3) pressure of 74 atm. We decided to list this reaction as indirect hydrogenation as it was proposed to proceed via formic acid and formaldehyde intermediates but being a one pot reaction, it can also be found in literature as an example of direct homogeneous catalysis.

Hydrogenation of urea derivatives to methanol: The catalytic hydrogenation of urea derivatives to methanol is another example for the indirect hydrogenation of CO_2. Although urea derivatives are reported to be readily synthesized from CO_2 and amines using various catalysts, the catalytic hydrogenation of these compounds to methanol has never been reported before under homogeneous or heterogeneous conditions. The hydrogenation of urea derivatives to methanol was first reported by Balaraman et al. (**Table 6**, entry 12).[194] There, the selective formation of methanol using a bipyridine based tridentate PNN Ru(II) pincer complex occurs under neutral and mild conditions through the double cleavage of the C-N bond, with no generation of waste.

3.2.3. Cascade catalysis

The indirect hydrogenation of CO_2 with H_2 to produce methanol can also take place through cascade catalysis. Huff and Sanford presented a methodology with a one pot mechanism to directly synthesize methanol from CO_2 and H_2 under 40 atm of 3H_2: CO_2 mixture using three homogeneous catalysts, operating in sequence (**Figure 16**, **Table 6**, entry 13).[180] This cascade hydrogenation involved three steps:

a) Hydrogenation of CO_2 to formic acid (75 °C, catalyzed by (PMe$_3$)$_4$Ru(Cl)(OAc), **C-9**),

b) Esterification of formic acid to formate ester (75 °C, catalyzed by Sc(OTf)$_3$)

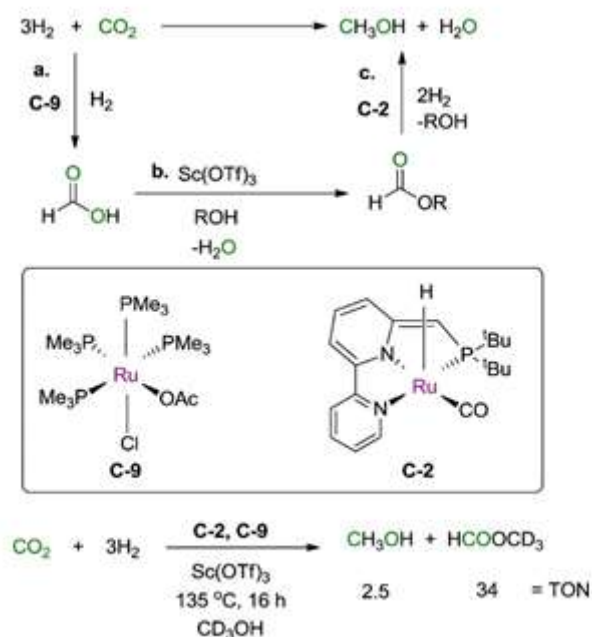c) Formate ester hydrogenation to methanol (135 °C, catalyzed by (PNN)Ru(CO)(H), **C-2**).

Figure 16. Cascade hydrogenation of CO_2 to methanol (Reproduced with permission from[188]).

However, due to the incompatibility of catalyst **C-2** with $Sc(OTf)_3$, methanol was formed with a very low TON of 2.5. The need to use three distinct catalysts is also a major drawback for this methodology. A challenge for Huff and Sanford's system was the incompatibility observed among some of the homogeneous catalysts and with the CO_2 reactant. Heterogeneous catalysts could achieve greater compatibility and easier separation from the reactant/product mixture. In this context, Thompson's group reported a novel heterogeneous cascade system for the hydrogenation of CO_2 to methanol through a formate intermediate (**Table 6**, entry 14).[204] This system consisted of a copper chromite catalyst (CO_2 hydrogenation to the formate) and Cu/Mo_2C catalyst (formate hydrogenation to methanol) and yielded a TOF of 4.7×10^{-4} s^{-1} for methanol production at 135 °C (**Figure 17**).
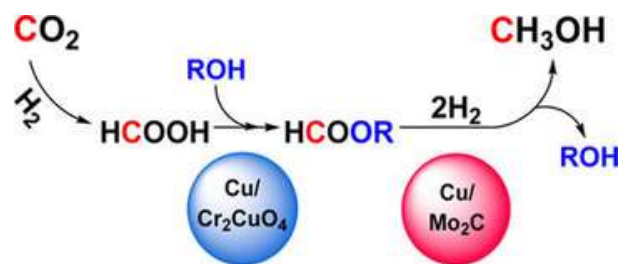
Figure 17. Schematic of proposed reaction pathway for the Cu–Cr and Cu/Mo$_2$C catalytic cascade system (Reproduced with permission from[205]).

Yan *et al.*[206] proposed a direct hydride transfer mechanism with three cascade cycles for the conversion of CO$_2$ and dihydrogen to methanol catalyzed by a half-sandwich cobalt complex [Cp*Co(bpyMe)OH$_2$]$^{2+}$ based on DFT calculations. The first cycle (**Figure 18, Table 6**, entry 15) transform CO$_2$ to formic acid. In the second cycle (**Figure 19**) they propose the formation of methanediol by formic acid hydrogenation (**C2-a**) and the formation of formaldehyde (**C2-b**) by methanol mediated proton transfer (Path 1, blue) and direct C-O bond cleavage after OH deprotonation (Path 2, green). The final mechanism for formaldehyde hydrogenation to methanol (Cycle 3) is shown in **Figure 20**.
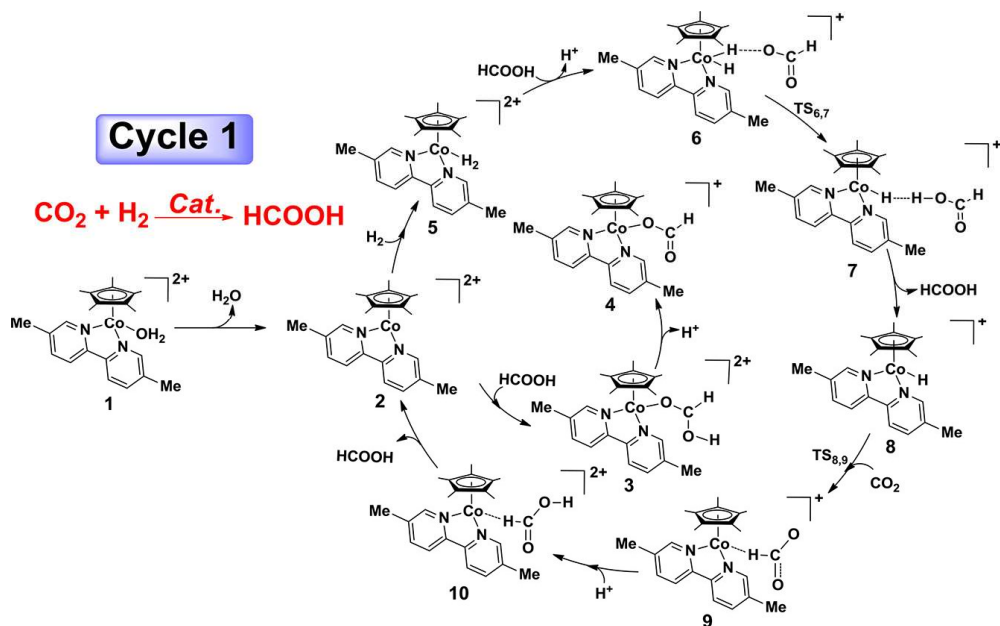
Figure 18. Proposed reaction cycle for the hydrogenation of CO_2 to formic acid catalyzed by 1:$[Cp*Co(bpy-Me)OH_2]^{2+}$ (Reproduced with permission from[206]).
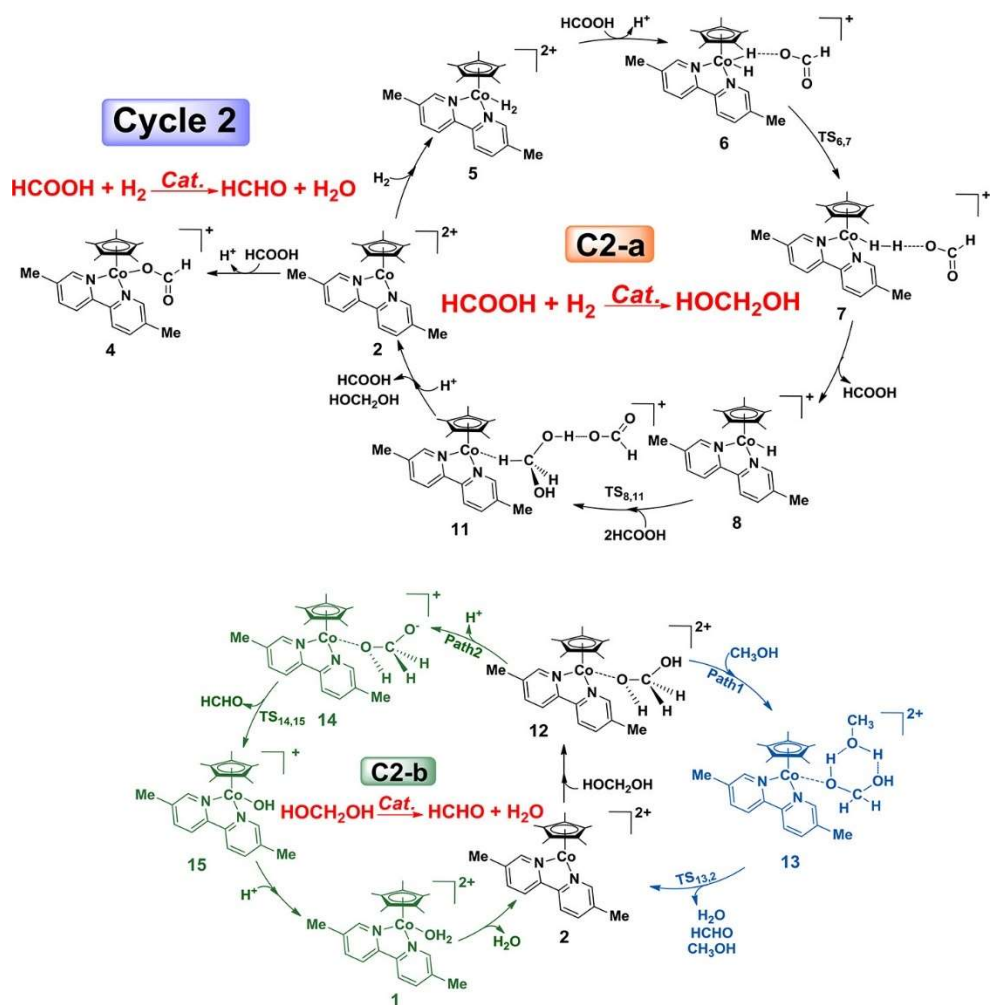
Figure 19. Predicted mechanism for the formation of formaldehyde with two consecutive cycles (Reproduced with permission from[206]).
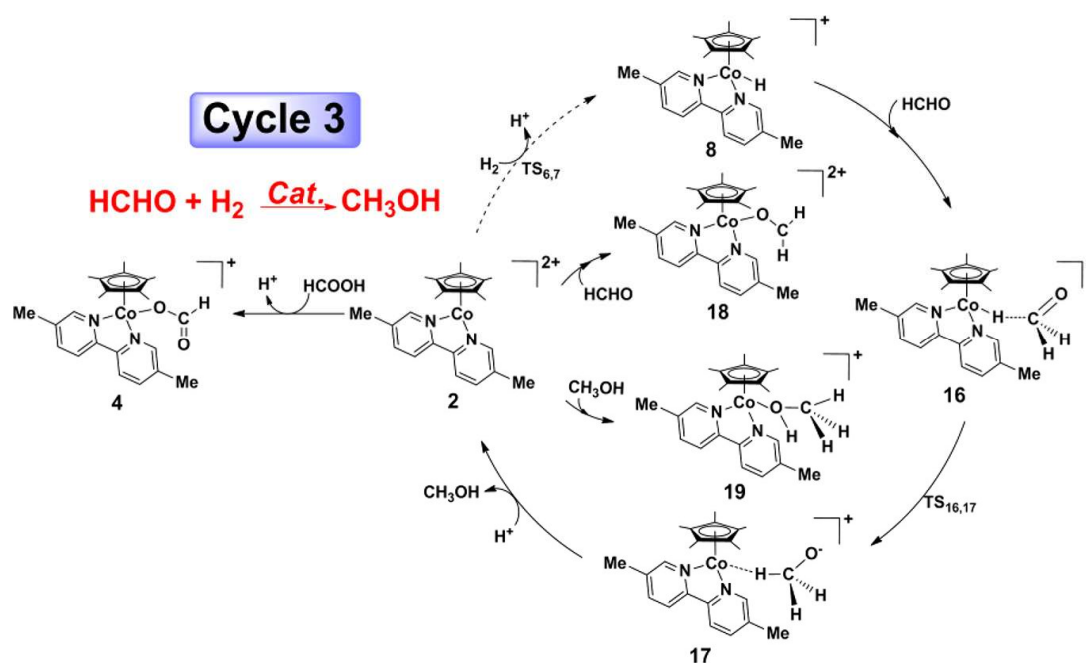
Figure 20. Predicted mechanism for the formation of methanol by hydrogenation of formaldehyde (Reproduced with permission from[206]).

4. Recent developments in CO₂ hydrogenation to formic acid, formaldehyde and derivatives

Formaldehyde is a widely used chemical, with an annual consumption of 30 million tons.[207] Although formaldehyde is obtained industrially by the partial oxidation of methanol, an alternative direct synthesis from CO_2 is an important objective from several perspectives, as aforementioned for the other hydrogenation processes. Formic acid is widely used as preservative, insecticide and industrial material for synthetic processes, and can be used directly in formic acid fuel cells to provide electricity. Most recently, it is recognized as one of the most promising hydrogen storage materials, especially for portable power application, because of its many advantages: it is nontoxic and biodegradable, liquid at ambient conditions, easy to store and transport, has relatively high hydrogen content (4.4 wt.%), and it is highly sustainable and renewable. Moreover, the interconversion of H_2/CO_2 and formic acid/formate occurs highly selectively under relatively mild conditions.

The first report on CO₂ hydrogenation to formic acid was by Farlow and Adkins in 1935 using Ni-Raney as catalyst.[208] This reaction took place in presence of amines and since then, several catalysts have been proven useful for this conversion. Recent studies[209-212] show that the CO_2 hydrogenation to formic acid may undergo two pathways which include formate as an intermediate

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and depend on the adsorption of the CO_2 molecule. The first pathway is depicted in **Figure 21** and displays the formation and reaction of monodentate formate with dissociated hydrogen. In the second pathway the bidentate formate is generated and then hydrogenated to produce formic acid. The direct catalyzed hydrogenation CO_2 to formic acid is thermodynamically disfavored and even under favorable conditions, namely H_2O solvent and low temperatures, very high CO_2/H_2 pressures must be used to reach a limited formic acid equilibrium concentration.[214] To make the hydrogenation more selective towards the formic acid formation the addition of base is usually employed. Inorganic base generates formate which is then converted to formic acid using a strong acid and organic base regenerating formic acid and shifting the reaction equilibrium towards higher selectivity to formic acid.[215] Alternatively, the use of buffers,[216] basic ionic liquids[217] and basic and coordinating solvents (DMSO)[218] is an interesting approach to generate free formic acid and avoid the need of stoichiometric amounts of amine or other strong bases as co-reagents.[216] Also reactive distillation is not necessary to form formic acid from formate adducts during product isolation.[217]
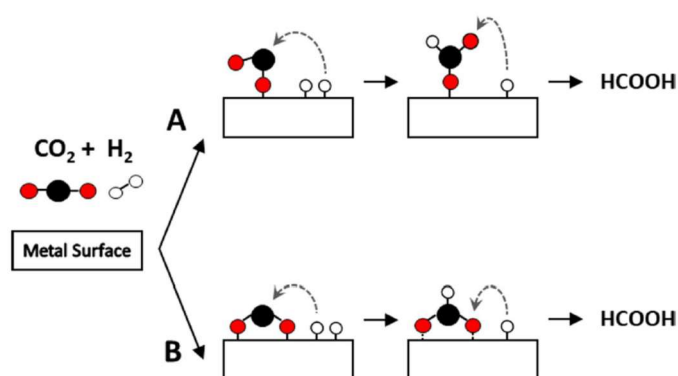

Figure 21. Synthesis of formic acid under basic conditions: a) formation of monodentate HCOO intermediate, b) formation of bidentate HCOO intermediate (Reproduced with permission from[213]).

4.1. Hydrogenation of CO_2 to formic acid and derivatives via homogeneous catalysis

In the last decades excellent reviews have summarized the field of homogeneously catalyzed hydrogenation of CO_2.[219-222] Since the beginning of the 1990 there has been an increasing interest in catalytic hydrogenations of CO_2 towards formic acid, alkyl formates and formic acid amides. Hence, improvements with respect to catalyst productivity and activity have been continuously accomplished. Compared to heterogeneously catalyzed reductions of CO_2,[223-226] hydrogenation towards formic acid

derivatives in the presence of organometallic complexes proceeds at comparably low temperature (< 100 ºC) and sometimes low pressure. As shown in **Table 7**, to date high turnover numbers (TON) have been achieved in the hydrogenation of CO_2 using transition-metal catalysts based on ruthenium,[227-229] rhodium,[230-232] and iridium[233,234] among others.

Table 7. Homogeneous catalyst for CO_2 hydrogenation to formic acid and derivatives.

Entry	catalyst precursor	solvent	additives	P (H_2/CO_2) atm	T (ºC)	t (h)	TON[a]	TOF (h^{-1})	Ref.
1	[RuH$_2$(H$_2$)$_2$(PCyp$_3$)$_2$]	C$_6$D$_6$	HBPin	(H from HBPin)	r.t.	24	-	-	[235]
2	[RuH$_2$(H$_2$)$_2$(PCyp$_3$)$_2$]	C$_6$D$_6$	HBpin	0.1	r.t.	0.5	--	--	[228]
3	RuH$_2$(PPh$_3$)$_4$	C$_6$H$_6$	NEt$_3$, H$_2$O	2.5/2.5	r.t.	20	87	4	[229]
4	RuCl(OAc)(PMe$_3$)$_4$	scCO$_2$	NEt$_3$/C$_6$F$_5$OH	7/12	50	0.3	31700	95000	[227]
5	RuH$_2$(PMe$_3$)$_4$	scCO$_2$	NEt$_3$, H$_2$O	8.5/12	50	20	1400	1400	[237]
6	[RuCl$_2$(tppms)$_2$]$_2$	H$_2$O	NaHCO$_3$	6/3.5	120	0.03	320	9600	[238]
7	Ru PNP-pincer	DMF	DBU	3/1	120			1100000	[241]
8	RhCl(PPh$_3$)$_3$	DMSO	Et$_3$N	2/4	25	20	2500	125	[231]
9	RhCl(tppts)$_3$	H$_2$O	NHMe$_2$	2/2	81	0.5	-	7260	[239]
10	RhCl(tppts)$_3$	H$_2$O	NHMe$_2$	20/20	r.t.	12	3439	287	[232]
11	Rh(NHC)	-	KHCO$_3$		100	72	3600	-	[243]
12	IrH$_3$(PNP)	H$_2$O/THF	KOH	1/1	120	48	3500000	150000	[233]
13	(PN^{Py}P)IrH$_3$	H$_2$O	KOH	1/1	185	24	348000	14500	[252]
14	[Cp*Ir(phen)Cl]Cl	H$_2$O	KOH	30/30	120	48	222000	33000	[234]
15	[Cp*Ir(N,N´)Cl]Cl	H$_2$O	-	1/1	120	-	10000	13000	[257]
16	Fe(BF$_4$)$_2$/PP$_3$	MeOH	NaHCO$_3$		80	20	610	30	[258]

17	(*t*Bu-PNP)Fe(H)$_2$(CO)	H$_2$O/THF	NaOH	0.67/0.33	80	5	788	156	[259]
18	Fe (PNP) hydride	EtOH	DBU	1/1	25	72	1032	-	[261]
19	Co(BF$_4$)$_2$/PP$_3$	MeOH	NaHCO3	6/0	120	20	3900	200	[262]
20	(^{iPr}PNP)CoCl	MeCN	-	1/1	45	16	29000	5700	[263]

(a) (TON, turnover number) moles of desired product per mole of the homogeneous catalyst, and (TOF turnover frequency), moles of product per mole of the catalyst per unit time and its value is usually expressed in h^{-1}.

4.1.1. Hydrogenation to formaldehyde

Bontemps *et al.*[228,235] reported the first unambiguous detection of formaldehyde from the pinacolborane reduction of CO$_2$ with a yield of 22% using the dihydride bis(dihydrogen) bis(tricyclopentylphosphine) hourglass ruthenium complex [RuH$_2$(H$_2$)$_2$(PCyp$_3$)$_2$] (Ru-1cyp) (**Table 7**, entry 1 and 2) as the catalyst precursor at room temperature in 24 h. Although the selectivity and yield of formaldehyde are not ideal enough, the controllable generation of formaldehyde by reducing CO$_2$ was still a significant breakthrough. Later, the mechanistical pathway of this reaction was investigated via DFT calculations by Dong *et al.*[236] in a study also integrating Fe and Os catalysts, elucidating the reaction mechanism.

4.1.2. Hydrogenation to formic acid and formate with noble metals

Ruthenium: The homogeneous hydrogenation of CO$_2$ to formic acid has been widely investigated and shows more promising results than the formaldehyde one. The first reported reaction date from 1976 by Inoue et al.[229] They carried out the reaction with phosphane complexes of group 8, 9, and 10 metals being ruthenium and Wilkinson catalyst the ones presenting the best results (**Table 7**, entry 3), in benzene in the presence of water and base. Munshi et al.[227] reported the use of supercritical carbon dioxide (scCO$_2$) to enhance the efficiency of RuII–phosphane complexes in the presence of amine. They obtained TOF up to 95000 h^{-1} by the use of pentafluorophenol as the additive (**Table 7**, entry 4). The properties of scCO$_2$, such as its high miscibility with H$_2$ and its good mass-transfer capability, accounted for those results. However, a scCO$_2$-soluble catalyst and a relatively high pressure are required for the reaction.

In a short review, Himeda[237] compares various ruthenium half-sandwich complexes with 4,4′-dihydroxy‐2,2′-bipyridine (dhbp) and 4,7-dihydroxy-1,10-phenanthroline (dhpt) ligands. An

exceptional catalytic performance with no waste generation was found, by tuning the catalytic activity through the acid-base equilibrium of the catalyst ligand (**Table 7**, entry 4, 5 and 6). As depicted in **Table 7**, the use of rhodium and ruthenium complexes with widely used water-soluble phosphane ligands (i.e., tppms, tppts and pta) have been investigated in detail.[231,232,238,239] The rate of hydrogenation strongly depends on the metal, the phosphane ligand, and the pH of the solution, as shown in those studies. A high TOF of 9600 h^{-1} was obtained by using [RuCl$_2$(tppms)$_2$]$_2$ at 9.5 MPa and 80 °C (**Table 7**, entry 6).[238] Himeda[237] states the significant features (high efficiency, catalyst recycling by self-precipitation, easy isolation of product, waste-free process, aqueous reaction, and prevention of reverse reaction) of the CO_2 conversion system that uses the half-sandwich complexes with dhbp and dhpt. Furthermore, the system overcomes almost all the problems occurring in the homogeneously catalyzed hydrogenation of CO_2 into formate. It should be noted that over a 1000-fold increase in catalytic activity was achieved because of the strong electron-donating ability of the oxyanion on the catalyst ligand. In addition, the three components (catalyst, product, and solvent) could be easily separated without waste generation.

Filonenko *et al.*[240] described the use of Ru-PNP pincer complexes 18 - 21 in the presence of DBU in THF for the catalytic CO_2 hydrogenation to formate. Complex 20 gave a high TOF of 14500 h^{-1} at 70 ºC under 40 bar H$_2$/CO$_2$, whereas complex 21 exhibited better performance with a TOF of 21500 h^{-1}. The authors disclosed the effect of metal-ligand cooperation in catalytic CO_2 hydrogenation by in situ NMR spectroscopy and DFT calculations. It was noted that complex 20 produced from ligand-assisted CO_2 activation remained in an inactive state and inhibited the catalytic reaction. The addition of water restored the catalytic activity by providing a pathway toward the formation of active species. Their group further investigated the reversible hydrogenation of CO_2 under mild conditions with Ru pincer complex 18.[241] Using DBU as a base, complex 18 provided an unprecedented TOF as high as 1100000 h^{-1} at 120 ºC under 39 atm H$_2$/CO$_2$ (3/1) in DMF (**Table 7**, entry 7). DFT calculations were made to elucidate the catalytic mechanism.[242]

Rhodium: More recently, Ezhova et al.[231] studied the hydrogenation by Wilkinson's catalyst in detail (**Table 7**, entry 8). They reported the need for phosphane L of the Rh catalyst, as the complex with bipyridine as a ligand was found to be inactive. Gassner and Leitner reported that the water-soluble analogue of Wilkinson's catalyst, [RhCl(tppts)$_3$] (**Table 7**, entries 9 and 10) serves as an effective catalyst in water.[232] In aqueous systems, an amine additive is also required, which determines the

final concentration of formic acid. In those cases, separating the base from the reaction medium remains a critical point for the reaction.

NHC ligands (*bis*-N-heterocyclic carbene) are also strong electron donors, which is a needed feature for CO_2 activation. Very recently, Jantke *et al.*[243] reported the hydrogenation of bicarbonate to formate using Rh NHC catalyst (**Table 7**, entry 11) with water-soluble bis-NHC ligand under mild reaction conditions. A high TON of 3600 was obtained with complex 32 under 50 atm H_2 in 2 mol/L $KHCO_3$ aqueous solution for 72 h at 100 ºC. $KHCO_3$ showed better catalytic performance than $NaHCO_3$ as bicarbonate source, because of the lower solubility of $NaHCO_3$ in water. The authors utilized DFT calculations to investigate the mechanism. The mechanism was divided into three steps: first, the chloride ligand was replaced by bicarbonate; subsequently, bicarbonate was reduced to formate by reducing agents; and finally, formate was exchanged by bicarbonate. The rate-limiting step could be the reduction of the carbon atom. The involvement of another catalyst molecule, which provided an external hydride for the reduction of bicarbonate was suggested.

To the best of our knowledge, most of the active catalysts for the hydrogenation of CO_2 to formic acid are rhodium- and ruthenium-based complexes with phosphane ligands. Recently the increase in the study of other metals (e.g., Ir,[229] Pd[244] and Ni[245]) and ligands (e.g., edta-H,[236] 6,6-dichloro-2,2-bipyridine[246]) is presenting several alternatives. Although an aqueous-phase catalyst might not be expected to be active based on mass-transfer rates, several active catalysts were also found from aqueous systems. In the same way, several active catalysts promote the decomposition of formic acid as a reverse process.[245] Therefore, the yield of formate is dependent on the equilibrium between CO_2 and formic acid. Furthermore, recovery and reusability of catalyst are serious concerns from the viewpoint of process cost, as highly active catalysts are restricted to the complexes of precious metals.[245] Several attempts have been made by Baiker and Ikariya to achieve reusability by immobilizing the catalyst for DMF synthesis under $scCO_2$.[247-249]

Iridium: Himeda et al.[234] have investigated the hydrogenation of CO_2 by using the half-sandwich bipyridine complexes in water. In their study, they present that the hydrogenation of CO_2 proceeded in aqueous solution without the use of amine additives. Interestingly, the hydrogenation can also proceed under neutral and acidic conditions, although these conditions are less suitable than basic conditions (**Table 7**). However, the decomposition of the formate as a reverse reaction occurred easily after pressure release, particularly in acidic solutions, which results a major drawback. It is noteworthy that the iridium complexes showed a catalytic activity like those of the rhodium and ruthenium complexes (**Table 7**, entry 14). Tanaka et al.,[233] presented the catalytic hydrogenation of

CO_2 in KOH by means of an isopropyl-substituted PNP-pincer iridium trihydride complex (**Table 7**, entry 12). In their study, a TON of $35 \cdot 10^5$ and a TOF: 150 000 h^{-1} was observed for the reaction to potassium formate, being both the best turnover values reported to date for this hydrogenation. The catalytic mechanisms of the PNP Ir complex were investigated with computational methods.[250,251] Tanaka et al.[250] carried out DFT calculations using pincer complex (**Table 7**, entry 12) as a catalyst. Two competing reaction pathways were identified, and the rate-determining steps (RDS) were shown to be de-protonative de-aromatization (via TS E/F) and hydrogenolysis (via TS I/A). The calculated free energy profiles provided an explanation for the effect of H$_2$ pressure, base, and solvent and were consistent with experimental data.

Schneider *et al.*[252] and co-workers developed another IrH$_3$(PNP) complex (**Table 7**, entry 13) bearing an N–H group, able to form an stable complex with CO_2. In their study it is shown that CO_2 insertion is facilitated by an N-H-O hydrogen bond through an outer sphere interaction. (PN^{Py}P)IrH$_3$ achieved a maximum TON of $348 \cdot 10^3$ and a high TOF of 14500 h^{-1}. Compared with the phosphine complexes, molecular complexes with N,N chelated ligands have attracted less attention for CO_2 hydrogenation.[253,254] Recently, Himeda *et al.*[255] have developed a series of N,N-chelated complexes [Cp*Ir(DHPT)(OH$_2$)]$^{2+}$, [Cp*Ir(nDHBP)(OH$_2$)]$^{2+}$, [(Cp*IrCl)$_2$(THBPM)]$^{2+}$, and [Cp*Ir(N$_n$)(OH$_2$)]$^{2+}$ (n = 1-14). Among these complexes, functionalized complex bearing OH group exhibited remarkable activity. The studies by Munshi *et al.*[227] indicated that complexes bearing strong electron-donating ligands have high activity in CO_2 hydrogenation. Later on, Himeda´s group, based on Munshi´s work, developed a series of half-sandwich Ir complexes [Cp*Ir(4,4´ R$_2$-bpy)Cl]$^+$ (R = OH, OMe, Me, H).[234,255,256] Aqua complexes can rapidly be formed by the hydrolyzation of the Cl ligand [Cp*Ir(4,4´-R$_2$-bpy)(OH$_2$)]$^{2+}$ in the presence of water (**Table 7**, entry 14).

Lu *et al.*[257] presented an iridium catalyst, [Cp*Ir(N,N´)Cl]Cl whereas, (N,N´ = 2,2´-bi-1,4,5,6-tetrahydropyrimidine), for the direct hydrogenation of CO_2 to formic acid in water in the absence of a base (**Table 7**, entry 15), achieving an initial TOF of over 13000 h^{-1} at 80 °C and 49 atm of H$_2$/CO$_2$ (1 : 1) and TON of over 10000 at 40 °C and 750 atm. The in situ ^{1}H NMR and reaction kinetics studies, show that the reaction is limited in terms of turnover by the CO_2 insertion step.

4.1.3. Hydrogenation to formic acid and formate with non-noble metals

Although noble metals, such as Ir, Rh, and Ru, are widely used for CO_2 hydrogenation to diverse molecules with great results, their high cost is one major drawback for their industrial application. Therefore, various non-precious metals, such as Ni, Fe, Co, and Mo, have been investigated over the

years. It is to expect that efficient ligands for noble metals-based complexes will also be capable to construct effective complexes of non-precious metals. However, some exceptions exist; for example, the Co analogues of the highly efficient Ir complexes $[Cp*Ir(_nDHBP)(OH_2)]^{2+}$ (n = 4 or 6) showed low activity because of their low stability.[258] Several phosphine and pincer ligands have been employed to develop efficient non-precious metal complexes.

Iron: Badiei et al.[258] reported the first hydrogenation of bicarbonate to formate with $Fe(BF_4)_2$ $6H_2O$ and $P(CH_2CH_2PPh_2)_3$ (**Table 7**, entry 16) which forms iron hydride complexes $[FeH(PP_3)]BF_4$ and $[FeH(H_2)(PP_3)]BF_4$ under the reaction conditions. The catalytic reaction under 60 atm H_2 at 80 °C provided sodium formate with an excellent yield of 88% and a TON of 610 for 20 h. The activity of the iron catalyst is comparable to that of a noble metal analogue $[\{RuCl_2(benzene)\}_2]/PP_3$ which exhibits a TON of 624. In **Figure 22** the proposed catalytic cycle for the hydrogenation of CO_2 using $Fe(BF_4)_2 \cdot 6 H_2O/PP_3$ is presented as elucidated by Langer et al.[259] reported an active pincer iron complex (tBu-PNP)$Fe(H)_2(CO)$ (**Table 7**, entry 17) which provided a TON of 788 and TOF of 156 h^{-1} under low pressure (6-10 atm) in H_2O/THF (10/1) at 80 ºC. The observed activity was comparable to known noble metal catalysts and highlighted the enormous potential of iron-based catalysts for industrial applications. The mechanism study suggested that the reaction proceeds through direct attack of the iron hydride to CO_2, followed by replacement of the resulting formate ligand by water. Rivada-Wheelaghan et al.[260] also developed pyrazine-based pincer Fe complex, which provided a moderate TON of 388 for CO_2 hydrogenation in H_2O/THF (10/1) under 10 atm H_2/CO_2 (6.3/3.3) for 16 h.

Kirchner and Gonsalvi among others,[261] prepared several iron pincer complexes which proved to be active catalysts for hydrogenation of CO_2 and $NaHCO_3$ to formate under mild conditions (**Table 7**, entry 18). The best hydrogenation result of $NaHCO_3$ to HCO_2Na with such complex proceeded with a TON of 856 after 21 h and 1032 after 72 h under an initial pressure of 80 atm in EtOH at 25 º C. A catalytic cycle with for this pincer complex was proposed based on the NMR study. A dihydrido intermediate was first formed from the PNP complex in the presence of H_2 and DBU. CO_2 insertion into the dydhidrido intermediate gave an hydrido formate complex. Further formate elimination and hydrogenolysis regenerated the intermediate with the assistance of DBU. DFT studies indicated an outer sphere mechanism with the hydrido formate complex as the catalyst resting state. Water molecule is involved in the catalytic process and stabilizes the reaction intermediates by forming hydrogen bond with the free formate ion. It facilitates formate elimination from the coordination

sphere of the metal, thereby promoting catalysis. The excess DBU enhances the overall reaction by acid base reaction with the formic acid product.
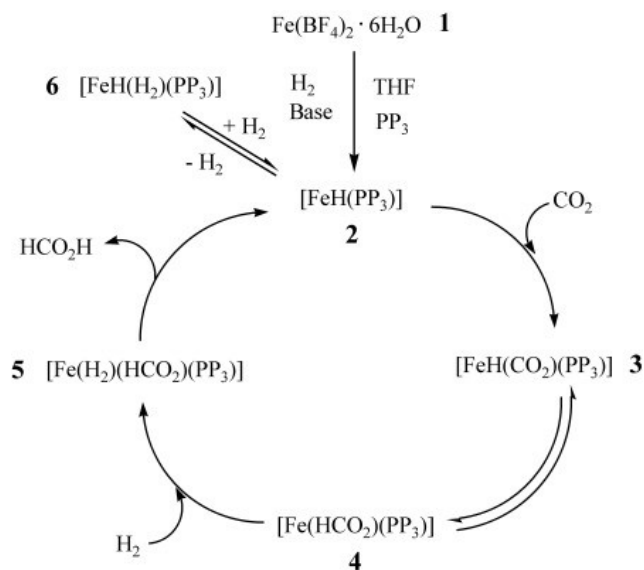

Figure 22. Proposed catalytic cycle for the hydrogenation of CO_2 using $Fe(BF_4)_2 \cdot 6\,H_2O/PP_3$.[205]

Cobalt: Following the results of the $Fe(BF_4)_2$ $6H_2O/(PP_3)$ catalyst, the cobalt analogue $Co(BF_4)_2$ $6H_2O$ and PP3 (**Table 7**, entry 19) was developed for hydrogenation of sodium bicarbonate.[262] A high TON of 3880 was obtained under 60 atm H_2 at 120 ºC with a yield of 71%. Spentzos et al.[263] developed a family of pincer cobalt complexes supported by PNP ligands containing a secondary or tertiary amine for hydrogenation of CO_2. Those catalyst were analogues to the previously reported by the same group using Fe as metal,[264] but presented some advantages in their catalytic performance. When paired with the Lewis acid lithium triflate, the pincer cobalt complex afforded a TON near $3 \cdot 10^4$ (**Table 7**, entry 20). Such an activity represents a notable improvement in the activity of cobalt catalysts.

4.2. Hydrogenation of CO_2 to formic acid and derivatives via heterogeneous catalysis

Since the discovery of phosphine-based Ru complexes by Inoue *et al.*[229] excellent progress has been achieved in the development of homogeneous catalysts.[220,265-267] In particular, extensive studies on homogeneous Ir, Ru, and Rh complexes have been reported, and recently, half-sandwich Ir derivatives and Ru/Ir-pincer complexes have shown tremendous catalytic activities, with a

maximum turnover number of $35 \cdot 10^5$ and a maximum turnover frequency of $11 \cdot 10^5$ h^{-1}.[234] Nevertheless, despite the homogeneous catalysts exhibiting excellent efficiency for the hydrogenation of CO_2 to formate, the difficulty in catalyst separation from the final reaction mixture makes them not so industrially desirable.[214] Moreover, these catalysts could also promote the decomposition of generated formate back into CO_2 and H_2 during the product separation steps, mostly when they take place in acidic medium.[218,268] Because of such limitations, diverse heterogeneous catalysts have been developed. Heterogeneous catalysts can be repeatedly reused due to their easily separation from the reaction mixture by filtration. They are environmentally friendly and can be operated in continuous processes, making them more industrially suitable. In addition, the use of heterogeneous catalysts in molecule transformation makes the product separation easier. Heterogeneous CO_2 hydrogenation to formate was first observed.[269] However, heterogeneous catalysts for formate or formic acid synthesis from CO_2 have only recently attracted renewed attention,[270] although many kinds of heterogeneous catalysts were prepared and used to reduce CO_2 to formic acid during the past decades. In this section, the most recent progress of CO_2 transformation to formic acid with heterogeneous catalysts will be presented,[205] and classified according to the different metal catalysts applied.

4.2.1 Direct catalysis

Nickel based catalysts: The synthesis of formic acid from CO_2 with a heterogeneous catalyst was reported in 1935 by Farlow and Adkins (**Table 8**, entry 1).[271] The reaction was carried out using Raney® nickel as catalyst in the presence various amines and under 200 - 400 atm overall hydrogen pressure, and 80 - 150 ºC. In addition, amine was added to shift the thermodynamic equilibrium toward product formation. There are also several works that present the reduction to formic acid from carbonic acid or carbonates as a CO_2 source.[272,273] Those works, as interesting as they result come abroad the scope of this review, so won`t be referred here.

Table 8. Heterogeneous catalyst for CO_2 hydrogenation to formic acid and derivatives.

Entry	catalyst	Ratio (H2,CO2)	P (atm)	T (ºC)	t (h)	Space velocity (h^{-1})	Conv. (%)	selec. (%)	Ref.
1	Raney-Ni	14:6	200-400	80	1		55	100	[271]
2	Ni-P/Al2O3	(NaBH4)	-	50	1		41.4	-	[274]

Entry	catalyst	Ratio (H_2,CO_2)	P (atm)	T (ºC)	t (h)	Space velocity (h^{-1})	Conv. (%)	selec. (%)	Ref.
3	Ru Si(CH_2)$_3$NH(CH_2)$_3$$CH_3$	12:4	-	80	1	1384	-	100	[275]
4	Si(CH_2)$_3$–NH_2–Ru	6:2	-	80	1	1481.5	-	-	[276]
5	Si(CH_2)$_3$NH($CSCH_3$)-RuCl$_3$PPh$_3$	1:1	8	60	2	103		100	[277]
6	Si(CH_2)$_3$NH($CSCH_3$)-RuCl$_3$PPh$_3$	1:1	89	80	2	920		100	[278]
7	Ru–DBU/Al_2O_3	9:6	148	80	1	239		100	[279]
8	Ru/MCM-41	1:1	395	80	5	17787	-	100	[280]
9	Ir-PN/SBA-15	1:1	39.5	120	2	1200	-	-	[281]
10	bpy-CTF-[IrCp*Cl]Cl	1:1	79	120	2	5300	-	-	[283]
11	Ir@CTF	1:1	19.7	90		800			[284]
12	Au/TiO_2	1:1	40	40					[285]
13	Au/Al_2O_3	1:1	39.5	70	20	215			[212]

Zhao *et al.*[274] developed a nickel-based catalyst Ni-P/Al_2O_3 for the reduction of CO_2 into HCO_2^- by using $NaBH_4$ as hydrogen source (**Table 8**, entry 2). The optimum preparation conditions for the Ni-P/Al_2O_3 catalyst were Ni to P ratio of 1:1, impregnation time of 12 h, and calcination temperature of 550 ºC. The Ni-P/Al_2O_3 catalyst obtained was used in industrial applications involving CO_2 reduction, and 41.37% of the average efficiency of CO_2 reduction was achieved under optimal conditions (addition amount of Ni–P/Al_2O_3 of 1%, $NaBH_4$ concentration of 0.175 mol/L, reaction temperature of 55 ºC). And 41.37% of the average efficiency of CO_2 reduction was reached. Ni_2P species distributed evenly on the Ni-P/Al_2O_3 catalyst were the active components for the reduction of CO_2 into HCO_2^-.

Ruthenium based catalysts: Zhang et al.[275] reported the preparation and application of amine-functionalized silica immobilized ruthenium catalysts for the hydrogenation of CO_2 to formic acid for the first time. The heterogeneous catalyst $RuSi(CH_2)_3NH(CH_2)_3CH_3$ exhibited higher catalytic activity than previously tried homogeneous catalysts. With this catalyst, formic acid was obtained with TOF of 1384 h^{-1} and selectivity of 100% when the hydrogenation reaction of CO_2 with H_2 was performed in ethanol under 158 atm and in the presence of PPh_3 and NEt_3 at 80 ºC for 1 h (**Table 8**, entry 3). Previously, they had investigated the effect of CO_2 pressure on the hydrogenation reaction. A TOF of 1482 h^{-1} for HCOOH generation was achieved on immobilized ruthenium catalyst $[Si(CH_2)_3–NH_2–Ru]$ under $scCO_2$ with H_2 pressure of 39 atm at reaction temperature of 80 ℃, and PPh_3/Ru molar ratio of 6:1 (**Table 8**, entry 4).[276] Zhang et al.[277] presented the first use of an ionic liquid (IL) as a base in the silica-immobilized ruthenium complex catalyzed hydrogenation of CO_2 to formic acid. The HCOOH had a TOF of 103 h^{-1} on the immobilized ruthenium catalyst $[Si(CH_2)_3NH(CSCH_3)RuCl_3PPh_3]$ under a total pressure of 18 atm (H_2:CO_2 =1) at a temperature of 60 ºC in the IL 1-(N,N-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethane-sulfonate ([mammim][TfO]) in aqueous solution (**Table 8**, entry 5). In a posterior study, they designed and prepared a novel IL 1,3-di(N,N-dimethylaminoethyl)-2-methylimidazolium ([DAMI][TFO]) for CO_2 hydrogenation promoted by ruthenium heterogeneous catalysts, which was used to improve the reaction efficiency. A maximum TOF of 920 h^{-1} was achieved in the presence of [DAMI][TFO] at 80 ºC under H_2 pressure of 89 atm (**Table 8**, entry 6).[278] The unique feature of this approach is that the formic acid can be recovered easily, and the IL and catalyst can be both reused after a simple separation process. Zhang et al.[279] synthesized a novel heterogeneous Ru–DBU/Al_2O_3 catalyst (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene) for the hydrogenation of CO_2 to formic acid (**Table 8**, entry 7). In the characterization of the Ru–DBU/Al_2O_3 an amorphous Ru(III)–DBU species was found. While using this catalyst, a maximum TOF of 239 h^{-1} was achieved at 80 ºC in a highly polar solvent DMSO in the presence of NEt_3 and KH_2PO_4 as Lewis organic base and protonic additive, respectively. The polar solvent improved the productivity of formic acid by promoting the insertion of CO_2 into the Ru-H bond, this CO_2 insertion resulting to be the rate-determining step of CO_2 hydrogenation.

Recently, Srivastava *et al.*[280] successfully synthesized air- and moisture-stable Ru/SiO_2 and Ru/MCM-41 catalysts for the selective hydrogenation of CO_2 to formic acid. The Ru/MCM-41 catalyst was found to be highly active in terms of formic acid quantity (**Table 8**, entry 8). To improve solubility of CO_2 and absorption of the formic acid produced during the reaction, they synthesized and screened a series of functionalized IL. They determined that [DAMI][$CF_3CF_2CF_2CF_2SO_3$] IL is

a promising reaction medium that can accommodate CO_2 at high concentrations. The highest TON value of 17787 for formic acid was reached using Ru/MCM-41 in a [DAMI] [$CF_3CF_2CF_2CF_2SO_3$] medium for the first catalyst round.

Iridium based catalysts: Xu et al.[281] reported that mesoporous silica-tethered iridium complex Ir-PN/SBA-15 (**Table 8**, entry 9) can be used as an effective catalyst for the synthesis of formic acid through CO_2 hydrogenation in aqueous solution in the presence of NEt$_3$ and under mild conditions [60 ºC, 39 atm total pressure (H_2:CO_2 = 1)]. The highest activity of the catalyst ($1.2 \cdot 10^3$ h^{-1}) was obtained at 120 ºC, 39 atm, and 2 h. The catalyst was highly recyclable and retained activity even after 10 cycles. The same group developed a new catalyst (PEI-PN/Ir) by modifying a branched polyethyleneimine (PEI) with an iminophosphine ligand coordinated to an Ir precatalyst.[282] By tuning the structure of the PEI-tethered materials, they were able to optimize CO_2 capture and the conversion abilities of these materials. Converting 65% of the available primary amines on PEI to PN/Ir active sites yielded the optimal balance between CO_2 capture and conversion, thereby achieving the highest formic acid yields. Park et al.[283] developed a novel heterogeneous catalyst (bpy-CTF-[IrCp*Cl]Cl) by immobilizing a {IrCp*} (**Table 8**, entry 10) unit onto a covalent triazine framework through coordination bonding. This catalyst exhibited excellent activities for the reduction of CO_2 to formate in aqueous solution under mild conditions [120 ºC, 79 atm total pressure (H_2:CO_2 = 1)]. A TON of 5000 and an initial TOF of 5300 h^{-1} were reached, which are the highest values reported to date for a heterogeneous catalytic system for CO_2 hydrogenation to formic acid. Bavykina et al.[284] developed a new stable heterogeneous catalyst by immobilizing IrCp* (**Table 8**, entry 11) through coordination within the covalent triazine framework (CTF) spheres. They found that the shaped catalysts, Ir@CTF spheres, are active for the direct hydrogenation of CO_2 into formic acid under mild reaction conditions (20 atm and 50-90 ºC). The highest TON (219) was reached at 90 ºC under 20 atm H_2:CO_2 (1). However, this TON is lower than that of Ir@meso-CTF catalyst. Nevertheless, the Ir@CTF sphere catalysts are easy to handle and recycle during the hydrogenation of CO_2 to formic acid, which makes then suitable candidates for industry purposes.

Gold based catalysts: In the last decade, Preti et al.[285] prepared a highly stable and robust titania-supported gold (Au/TiO$_2$) (**Table 8**, entry 12) for the formation of HCOOH/NEt$_3$ adducts through the hydrogenation of CO_2 in the presence of neat NEt$_3$. To recover HCOOH, they exploited an amine-exchange method, in which high-boiling tri-n-hexylamine was added to HCOOH/NEt$_3$ adduct with

acid/amine molar ratio (AAR) of 1.715 in a HCOOH/(n-C_6H_{13})$_3$N molar ratio of 2. A biphasic system was obtained and fractionated under reduced pressure (0,1 atm), and a liquid fraction consisting of pure NEt$_3$ (90% yield) was collected. At increased temperatures, a fraction consisting of 85 wt.% HCOOH contaminated by NEt$_3$ (11.5 wt.%) and (n-C_6H_{13})$_3$N (3.5 wt%) was recovered. Furthermore, pure anhydrous HCOOH was obtained by redistilling the high-boiling fraction at atmospheric pressure. Overall, HCOOH was recovered from the HCOOH/NEt$_3$ adduct with AAR of 1.715 in 83% yield. Filonenko et al.[212] investigated the hydrogenation of CO_2 to formate with several unsupported and supported gold nanoparticle catalysts. Among the examined catalysts, Au/Al_2O_3 was the most active catalyst. The catalytic activity depended strongly on the type of support. For example, TON of 110 was obtained using Au/TiO_2 as catalyst for CO_2 dehydrogenation, whereas nearly a twofold increase in TON (215) was observed when Au/Al_2O_3 was employed as catalyst under the same reaction conditions (3 mL EtOH, 0.5 mL NEt$_3$, 70 ºC, 40 atm H_2/CO_2, 20 h). The rate of formate formation, normalized per Au surface atom, was in the range of 118 - 123 h^{-1}. Based on the experimental results, the authors proposed that the reaction occurs at the interface of the Au^0 nanoparticles and alumina support (**Figure 23**). They also concluded that H_2 heterolytic dissociation occurs at the Au/support interface and then generates surface hydroxyl group and metal hydride. The reaction of surface OH with CO_2 affords bicarbonate, which can be reduced by hydride to produce formate. The key intermediates, surface formate, and bicarbonate were observed by FTIR.

4.2.2. Indirect catalysis

Palladium based catalysts: Palladium adsorbed on activated carbon (Pd/C) have been widely used for the generation of formic acid since 1982.[286] Nevertheless, it was not with CO_2 as reactant but with HCO$_3^-$, which is in equilibrium when CO_2 reacts with water.[287] Due to that, reactions involving HCO$_3^-$ will be discussed here. Klibanov et al.[286] have found that palladium adsorbed on activated carbon (Pd/C) not only can be used as a catalyst for formate decomposition but also as a catalyst for the synthesis of formate from H_2 and bicarbonate. They were able to obtain 13 mmol/L of formate by shaking 100 mg of catalyst in 5 mL of 0.3 mol/L sodium bicarbonate for 20 h and under 1 atm of H_2 and room temperature. The heterogeneous catalysts Pd/C, Pd/γ-Al_2O_3, Pd/$BaSO_4$ and [W/(PQ$^{2+/+/0}$)$_n$/Pd] (a polymer-supported palladium catalyst) were investigated by Stalder et al.[288] The Pd-based catalysts equilibrated the H_2/NaCO$_3$H(aq)/NaHCO$_2$(aq) system at 25 ºC to a formate to bicarbonate ratios of ~1:1 to ~1.5:1 under 1–1.7 atm of H_2. Owing to the chemical equilibrium between carbonate and formate, the reaction was incomplete. Similar observation was also reported

by Wiener et al.[289] They were able to reduce alkali metal bicarbonates to their respective formate salts over a Pd/C catalyst under mild temperature and pressure conditions. A strong influence of carbonate and hydrogen concentration on the initial reaction rates was then observed. The rate increased at elevated H_2 pressure in accordance with the Langmuir isotherm law. At increased HCO_3^- concentrations, the rate passed through a maximum. Measurements of the equilibrium at 35 ºC indicated a Gibbs free energy change of approximately -2.2 kcal/mol. The highest concentration of HCO_2^- obtained at 6 atm H_2 was limited by the common ion effect to 5.8 mol/L.
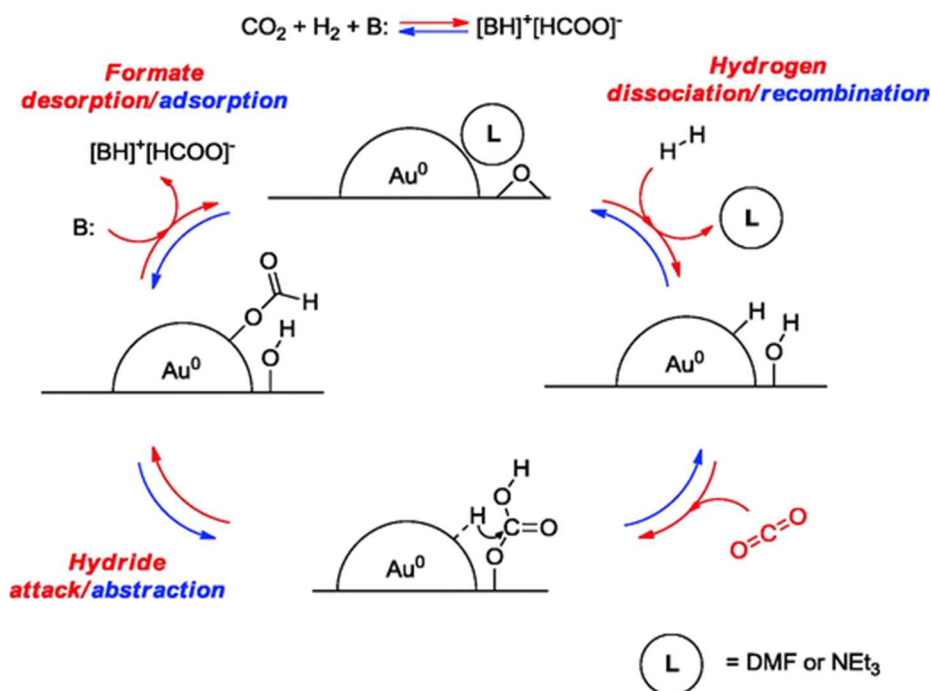
Figure 23. Proposed mechanism for CO_2 hydrogenation over Au/Al_2O_3 catalyst.[205]

5. Summary and future perspectives

In the present review, the recent progresses in CO_2 hydrogenation to energy-related products, specifically formate/formic acid methanol and methane using homogeneous and heterogeneous catalysts are outlined. The exceptional achievements contribute significantly to understanding the mechanism of CO_2 transformation and realizing the possibility of a methanol or hydrogen economy.

To activate the steady CO_2 molecule, chemists have employed various strategies, including optimization of hydrogen sources, solvents, additives and the design of catalysts. For the reduction of CO_2 to the molecules portrayed here not only H_2 have been used, but also other hydrogen sources

such as boranes and hydrosilanes which have an enormous interest in the homogeneous catalysis. Both present several interesting features in the reduction of CO_2 and the elucidation of the reaction mechanism. However, their industrial application is limited by their cost and sensitivity to pressure and temperature. To became industrially desirable, highly robust, cheap and renewable boranes and hydrosilanes are yet to be found. Hence, H_2 remains the most favorable and easily available hydrogen source. For a global green process the H_2 source must also be considered. Most H_2 is currently generated from the industrial reforming of natural gas. A better approach when targeting an environmentally friendly process in which the CO_2 footprint is reduced should encounter the production of H_2 via electrolysis of water with excess electricity, water photolysis or dry reforming of methane.

For the homogeneous catalysis, polar solvents, such as DMSO, DMF, water and ionic liquid, are found to be effective for CO_2 reduction. Water is particularly attractive because it is uniquely cheap and naturally eco-friendly. However, water-soluble, or water-compatible catalysts are required, which can be a difficulty. Further to this, the application of ionic liquids with high boiling point as solvents is proven to facilitate the evaporation of the product which eases the purification process.

For the CO_2 methanation Ni based catalysts results to be very effective due to the presence of easily transferable electrons in the frontier d orbitals and therefore are the most efficient and active catalytic system together with alumina as a support that may be applied on industrial scale. Even when Ru catalysts present better yields, Ru is about 120 times more expensive than Ni. Nickel catalysts have a short lifetime, because of carbon deposition which blocks pores and consequently deactivates the catalyst. A rational design of Ni based methanation catalysts with high activity at low temperatures, good redox properties, and better stability at reaction temperatures could lead to a better option for industrial applications of CO_2 hydrogenation to methane.

Basic additives including carbonate, bicarbonate and organic amines promote CO_2 reduction to formate. Although stoichiometric strong base, such as Verkade's base, is favorable in elaborating the reaction rate, high cost prevents its industrial application. When an inorganic base is used, additional acid must be added to neutralize formate. Therefore, the separation of formic acid from their amine salt and recycling of amine is a problem that is still to solve.

For the development of efficient homogeneous catalysts, various phosphine ligands, C,C-chelated ligands, N,N-chelated ligands and pincer ligands have been explored. The non-innocent ligand effects of pincer ligands endow the pincer complexes with high efficiency of H_2 or CO_2 activation via unique aromatization/ de-aromatization and/or hydrogen-bonding interactions. The hydroxy-substituted aromatic N-heterocyclic ligands construct bio-inspired proton-responsive

complexes, which exhibit extraordinary activity for CO_2 hydrogenation in aqueous solutions under mild conditions. The synergistic electronic effects and pendant base effects of such ligands substantially improve catalytic activities. The unique property of facilitating proton transfer through the second coordination sphere like those of hydrogenase demonstrates the remarkable success of enzyme mimicking.

As shown above, homogeneous catalysts are more effective for CO_2 reduction to formic acid than CO_2 reduction to methane and methanol. Important progress has been made in CO_2 transformation to methanol with various homogeneous catalysts through indirect approaches and cascade catalysis, such as disproportionation of formic acid, multistep synthesis, and most recently reported direct CO_2 hydrogenation, hydroboration, and hydrosilylation.

Although precious metals exhibit high efficiency, catalysts with earth-abundant metals, such as Fe, Co, and Ni, were also developed with considerable success. Boron-containing metal complexes, even metal-free organocatalysts, such as FLP are highly efficient for CO_2 activation and/or reduction with appropriate hydrogen sources under mild conditions. The developments of bio-inspired catalysts with earth-abundant metals and organocatalysts are important subjects for future research.

Contrary to homogeneous catalysts, controlling the selectivity of heterogeneous catalysts in CO_2 reduction is rather difficult. Several heterogeneous catalysts were prepared by immobilizing homogeneous catalysts, which are efficient for CO_2 hydrogenation to formate or formic acid. In addition, various heterogeneous catalysts based on Ni, Pd, Ru, Ir and Au were also prepared by sintering with an appropriate support and used to reduce CO_2 to different products. The Ni nanowired catalyst has recently been reported to be highly effective and selective for the hydrogenation of carbonate to methane. Nanoporous metal catalysts are promising for practical methane, and formic acid production from CO_2 and deserve more investigation.

Heterogeneous catalysts have been extensively investigated, and several excellent catalysts have been developed for CO_2 hydrogenation to methanol. Among the studied catalysts, Cu-based catalysts are considered to be the optimal choice for methanol synthesis due to their high activity. Furthermore, catalysts based on Pd, Ni, Ag, Au, In, and $AB_{1-x}B_xO_3$ perovskite are also effective for CO_2 reduction to methanol. A large surface area is proven to be crucial for high catalytic activity because it is favorable for better dispersion of active metal, thereby enhancing catalyst performance. In comparison with homogeneous catalysts, heterogeneous catalysts remain less active and selective for the hydrogenation of methanol and formic acid, not so for methane on the other hand. Therefore, the development of highly efficient, selective, and stable heterogeneous catalysts based on earth-abundant elements is desired.

Although important advancement has been recently achieved by CO_2 transformation to liquid fuels, such as formic acid and methanol, several problems, as above-mentioned, need to be solved before its industrial application. Given that numerous scientists are devoted in researching CO_2 transformations, significant progress could be expected in the next years.

Acknowledgments

Abbreviations

AC	activated carbon
Acac	acetylacetone
ACZ	alumina-ceria-zirconia
AE	ammonia evaporation (method)
BTC	benzenetricarboxylic acid
CCUS	carbon capture, utilization and storage
CP	conventional precipitation
CTF	covalent triazine framework
DAMI-TFO	1,3-di(N,N-dimethylaminoethyl)-2-methylimidazolium
DBD	dielectric barrier discharge
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
nDHBP	n,n′-dihydroxy-2,2′-bipyridine, n = 3, 4, 5, 6
DHPT	4,7-dihydroxy-1,10-phenanthroline
DMC	dimethylammonium dimethylcarbamate
DME	dimethoxyethane
DMF	dimethylformamide
DMFA	dimethylammonium formate
DMSO	dimethyl sulfoxide
CNT	carbon nanotube
EC	ethylene carbonate
FLP	frustrated Lewis pair

FSA	fibrous silica alumina
FT	Fischer Tropsch
GO	graphene oxide
HNTf$_2$	bis(trifluoromethane)sulfonimide
HT	hydrotalcite
HTC	hydrotalcite-like compound
ICNP	iron carbide nanoparticles
IL	ionic liquid
IMC	intermetallic compounds
LA	lewis acid
LDH	layered double hydroxyde
MCM-41	mobil composition of matter No. 41
MF	methyl formate
MO	mixed oxide
MOF	metal organic frameworks
NHC	*bis*-N-heterocyclic carbene
NMP	N-methylpyrrolidone
N,N´	2,2´-bi-1,4,5,6-tetrahydropyrimidine
NP	nano particle
NR	nanorod
NW	nanowired
OG	oxalate gel
OSC	oxygen storage capacity
PEHA	pentaethylenehexamine
PEI	polyethyleneimine
PN^{Py}P	2,6-C$_6$H$_3$(CH$_2$PMe$_2$)2
POCOP	2,6-[OP(tBu)$_2$]$_2$C$_6$H$_3$
PP$_3$	Tris[2-(diphenylphosphino)ethyl]phosphine
PZ	1H-pyrazol-1-yl
RGHSV	reactant gases hourly space velocity
RWGS	reverse water gas shift
SMSI	strong metal support interaction

TEA	triethylamine
THBPM	4,4´,6,6´-tetrahydroxy-2,2´-bipyrimidine
TMP	tetramethylpiperidine
TNT	titanium nanotubes
TOF	Turnover frequency
TON	turnover number
TPABr	tetrapropylammonium bromide
USP	ultrasonic spray precipitation technique
WGS	water gas shift
ZIF	zeolitic imidazolate framework

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