Hydrogenation of CO_2 or CO_2 Derivatives to Methanol under Molecular Catalysis: A Review

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Abstract: The atmospheric CO_2 concentration has been continuously increasing due to fossil fuel combustion. The transformations of CO_2 and CO_2 derivatives into high value-added chemicals such as alcohols are ideal routes to mitigate greenhouse gas emissions. Among alcohol products, methanol is very promising as it fulfills the carbon neutral cycle and can be used for direct methanol fuel cells. Herein, we summarize the recent progress in the hydrogenation of CO_2 or CO_2 derivatives to methanol, and focus on those systems with homogeneous catalysts and molecular hydrogen as the reductant. Discussions on the catalytic systems, efficiencies, and future outlooks will be given.

Keywords: CO_2 hydrogenation; transition metal; pincer complexes; methanol; homogeneous catalysis

1. Introduction

Global warming has been a growing problem for our ecological environment during the last several decades, due to the continuous combustion of fossil fuels and CO_2 emissions [1]. The atmospheric CO_2 concentration has increased to 415 ppm; therefore, CO_2 capture and utilization is not only important to academic research, but to the whole environment and ecosystem on Earth [2–4].

Transforming CO_2 into high value-added chemicals or alcohols, which can then be used as biofuel, is an efficient and profitable way to fulfil a carbon-neutral cycle. Nobel Laureate Prof. George A. Olah proposed the concept of the "methanol economy" [5–7], which advocated for the catalytic conversion of CO_2 to methanol by reducing the greenhouse gas in order to produce methanol for energy applications such as direct methanol fuel cells (DMFC), as well as raw materials for the synthesis of olefins and other hydrocarbons. In addition, methanol can act as a hydrogen energy carrier since it contains 12.6 wt% of hydrogen and can be easily stored, transported, and distributed using existing pipelines because of its liquid nature [8,9]. Under this concept, methanol is used as a liquid organic hydrogen carrier (LOHC) which can reversibly store and release molecular hydrogen whenever and wherever it is in demand [10–15].

Practical methods of CO_2 hydrogenation to methanol were usually based on heterogeneous catalysis, and these reactions were traditionally carried out at high temperatures (200–300 °C) [16–20]. Studies showing homogeneous catalytic CO_2 hydrogenation under relatively mild conditions (<150 °C) are of great significance, and considerable efforts have been made in the last decade to achieve this [21–28].

Among the homogeneous catalytic reactions of CO_2 hydrogenation to methanol, the major catalytic systems are transition-metal catalysts [21–29], frustrated Lewis-pairs (FLPs) [30–33] or N-heterocyclic carbenes (NHC) [34–36], and reductants such as H_2 [22,29], silanes [34,35], or boranes [37,38] are often employed. As a result of its atom efficiency and low cost, molecular hydrogen is used in CO_2 hydrogenation more often. Consequently,

this review will focus on the hydrogenation of CO_2 and CO_2 derivatives with H_2 as the reductant for molecular catalysis, and especially on those systems that have employed transition-metal pincer complexes and metal–ligand cooperation over the past ten years.

2. Hydrogenation of CO_2 or CO_2 Derivatives

2.1. Ru-Based Catalysts

The first homogeneous CO_2 hydrogenation to methanol was reported by Sasaki and coworkers in 1993 (Figure 1) [39]. In this report, methanol was observed to be an intermediate during the hydrogenation of CO_2 to methane. The reaction was carried out using a 1:3 CO_2/H_2 mixture with an initial pressure of 80 atm, which was gradually heated to 240 °C. The catalytic system consisted of $Ru_3(CO)_{12}$ and KI, which produced methanol with a TON of 32 based on a ruthenium atom. However, the selectivity was poor, different components such as carbon monoxide, methane, and ethane were generated, and the ratio was hard to control. In 1995, the same group studied the detailed mechanisms of this reaction [40]. Under 240 °C, the trinuclear Ru precursor $Ru_3(CO)_{12}$ was transformed into the tetranuclear species $[H_2Ru_4(CO)_{12}]^{2-}$ and $[H_3Ru_4(CO)_{12}]^{-}$, which were the catalytic active species.

$$CO_2 \ + \ H_2 \quad \xrightarrow[\substack{\text{NMP, 240 °C, 3 h} \\ \text{80 atm}}]{\text{Ru}_3\text{(CO)}_{12}\text{-KI}} \quad MeOH \ + \ CO \ + \ CH_4 \ + \ C_2H_6$$
$$1:3$$
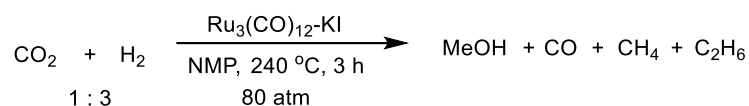
Figure 1. Hydrogenation of CO_2 using $Ru_3(CO)_{12}$.

This $Ru_3(CO)_{12}$–KI catalytic system demonstrated the feasibility of gaseous CO_2 hydrogenation to methanol; however, some limitations such as high temperature and pressure, low turnover efficiency, and poor selectivity have to be considered. Therefore, developing CO_2 hydrogenation under relatively mild conditions is urgent and of great significance, though great improvements have been made in the last ten years.

A cascade synthesis of methanol from CO_2 was reported by the Sanford group in 2011 (Figure 2) [41]. Three different homogeneous catalysts were employed, including $(PMe_3)_4Ru(Cl)(OAc)$ (**[Ru]-1**), $Sc(OTf)_3$, and $(PNN)Ru(CO)(H)$ (**[Ru]-2**). The three-step cascade reaction was realized in one reaction apparatus with an inner and outer vessel, without isolating the corresponding intermediates. The first and second steps were carried out in the inner vessel, and the hydrogenation of CO_2 to formic acid with **[Ru]-1** and $Sc(OTf)_3$- catalyzed esterification to generate methyl formate. The reaction temperature was then increased to 135 °C, and the formate was transferred to the outer vessel automatically. The last step was a ruthenium–pincer complex; **[Ru]-2** catalyzed hydrogenation of the formate ester to methanol. The inner–outer vessel transfer approach also enhanced the overall turnover number of the reaction significantly, with a turnover number of 21, which is eight times greater than the reaction carried out in one pot without an inner–outer vessel. The difference in catalytic efficiency was ascribed to the deactivation of the **[Ru]-2** catalyst in the first and second steps. A similar protocol was also developed by Goldberg and coworkers in 2019, with a combination of $Ru(H)_2[P(CH_2CH_2PPh_2)_3]/Sc(OTf)_3/Ir-(tBuPCP)(CO)$, and an overall TON of 428 was obtained [42].

The above approach, developed by the Sanford group, opened a new way for CO_2 hydrogenation to methanol, and used structurally well-defined metal–ligand complexes as a catalyst. However, the combination of three different catalysts was complicated. A one-pot CO_2 hydrogenation to methanol with a single catalyst was still desirable.

In 2012, Klankermayer, Leitner, and others presented a single ruthenium–phosphine complex that catalyzed the CO_2 hydrogenation to methanol with high efficiency (Figure 3) [43]. Two catalytic systems, $[Ru(acac)_3]/Triphos$ and $[(Triphos)Ru-(TMM)]_2$ (**[Ru]-3**), were able to promote formate hydrogenation to methanol independently. Acid additives were reported to have facilitated the generation of active ruthenium species from Ru precursors, thus, $[Ru(acac)_3]/Triphos/MSA/EtOH$ or **[Ru]-3**$/HNTf_2/EtOH$ were tested for direct CO_2 hydrogenation in one pot, respectively. These two multifunctional catalysts worked on

CO$_2$ hydrogenation to formic acid, and hydrogenation of formate ester to methanol. The highest TONs were 135 with [Ru(acac)$_3$] and 221 with **[Ru]-3** under 140 °C, with 20 bar CO$_2$ and 60 bar H$_2$. These results clearly demonstrate that CO$_2$ hydrogenation to methanol can be realized with a single catalyst in one pot, and that they exhibit comparable turnover numbers. The metal triphos system was further expanded by Klankermayer and others in 2020; a tridentate tdppcy (*cis,cis*-1,3,5-tris-(diphenylphosphino)cyclohexane) ligand was introduced as a structurally tailored ligand, in combination with a ruthenium precursor (cod)Ru(methallyl)$_2$. The TON of CO$_2$ hydrogenation was around 1100, and switching the solvent from THF to EtOH resulted in an unprecedented TON up to 2100 [44].
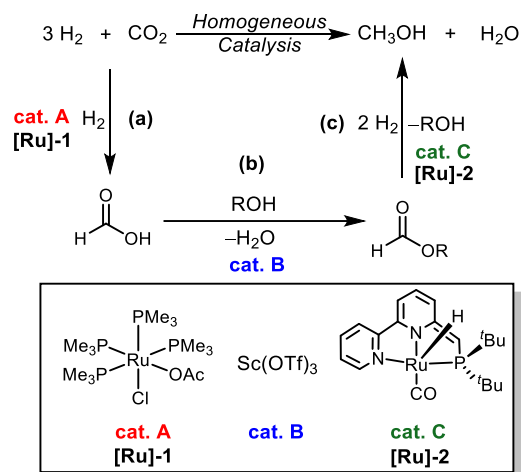

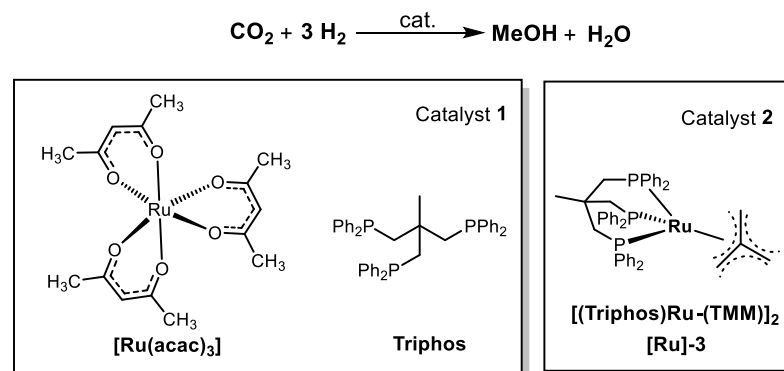**Figure 2.** A tandem CO$_2$ hydrogenation to methanol.

Figure 3. CO$_2$ hydrogenation to methanol by a single ruthenium phosphine complex.

The Sanford group also disclosed another elegant approach of tandem CO$_2$ hydrogenation to methanol in 2015, by using a single ruthenium catalyst **[Ru]-4** (Figure 4) [45]. The key to success was introducing a CO$_2$ capture process to generate carbamate intermediates, which underwent an additional hydrogenation step to produce methanol. In this report, dimethylamine was used as a CO$_2$ capture reagent for dimethylammonium dimethylcarbamate (DMC), which was tested as a model substrate for methanol synthesis. The optimal conditions for DMC hydrogenation were found to be Ru-MACHO-BH (**[Ru]-4**), with K$_3$PO$_4$ as base under 50 bar H$_2$ at 155 °C, and a TON of 19 was observed. Two possible mechanistic routes were suggested; the first was DMC hydrogenation to DMF, the other was a CO$_2$ release from DMC and subsequent CO$_2$ hydrogenation to formic acid, followed by an amidation reaction to generate DMF. Notably, this method was able to occur under 2.5 bar CO$_2$, which was a greatly reduced pressure compared with others. Under the optimal conditions, CO$_2$ (2.5 bar)/H$_2$ (50 bar) was heated at 95 °C to form DMF, after which, the temperature was increased to 155 °C in order to enable the hydrogenation of

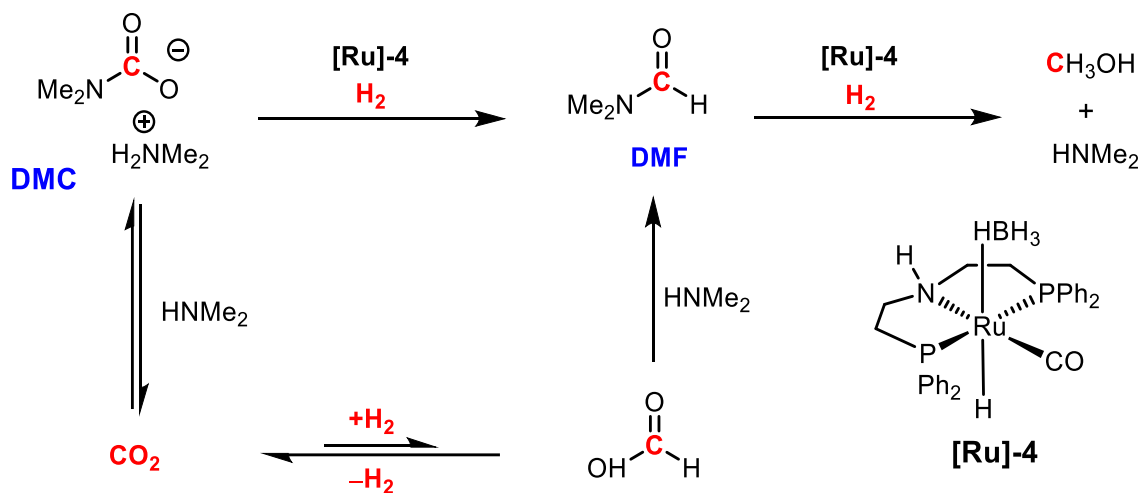DMF to methanol. The highest TON of 550 was achieved, and the conversion of CO_2 was as high as 96%.

Figure 4. Amine assisted Ru-catalyzed hydrogenation of CO_2.

Meanwhile, Milstein and coworkers developed a combined CO_2 capture/utilization protocol for methanol synthesis (Figure 5) [46]. They focused their efforts on the tandem reaction of CO_2 to oxazolidinone and oxazolidinone hydrogenation, and a variety of amino alcohols were used as CO_2 capture reagents. Valinol was found to be an ideal reagent to give higher yields and to shorten reaction time. The second step took place under Ru complex ([**Ru]-5**) and *t*BuOK, and methanol was obtained in 92% yield at 135 °C. In this work, they also showcased a one-pot reaction of CO_2 capture/hydrogenation, where 1–3 bar of CO_2 was transformed into oxazolidinone, and underwent the hydrogenation step without isolation, using a [**Ru]-5** catalyst to obtain methanol in 53% yield.
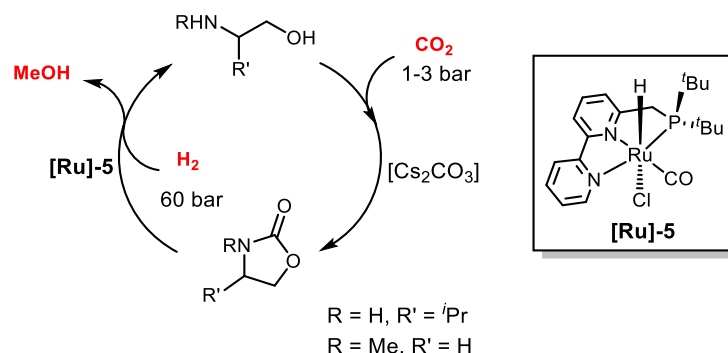

Figure 5. Amino alcohol involved Ru-catalyzed hydrogenation of CO_2.

In 2015, Ding and coworkers developed elegant examples of ruthenium catalyzed by *N*-formylation reactions of morpholine with H_2/CO_2 to generate formamide, which was able to undergo a second step of hydrogenation, which produced methanol with high efficiency (Figure 6) [47]. The highest turnover number achieved for the *N*-formylation reaction was 1,940,000, with a 0.00005 mol% [**Ru]-6** catalyst. A one-pot, two-step CO_2 hydrogenation to methanol was realized under 35 atm CO_2 and 35 atm H_2 at 120 °C in THF with a [**Ru]-7** catalyst, and then 50 atm H_2 at 160 °C to produce methanol in 36% yield. Notably, another Ru-catalyzed amine-assisted CO_2 hydrogenation to methanol via formamide was later reported by Prakash [48].
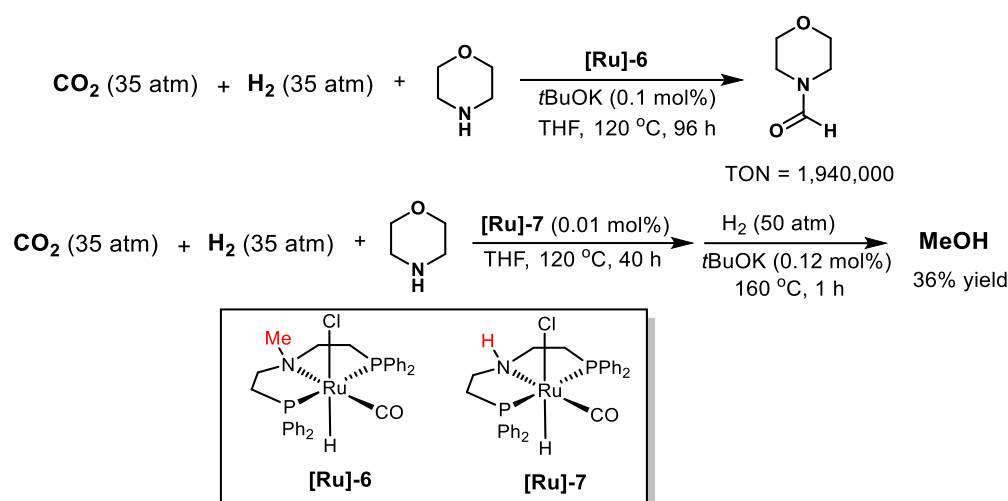
Figure 6. Ru-catalyzed hydrogenation of CO_2 with morpholine as the amine source.

These three methods developed by Sanford [45], Milstein [46], and Ding [47] provided a new way for CO_2 capture and utilization (CCU) using a homogeneous ruthenium catalyst and an amine as a capture reagent. In early 2016, the Olah and Prakash group reported a similar strategy (Figure 7) [49]. CO_2 was captured by pentaethylenehexamine (PEHA), which has low volatility, is a highly basic reagent, and showed good solubility in THF. A variety of ruthenium pincer catalysts were examined for this CO_2 hydrogenation to methanol with PEHA as an amine and K_3PO_4 as an additive at 75 bar CO_2/H_2 (1:3). It was found that a significantly higher TON (1060) was obtained when employing Ru-MACHO-BH (**[Ru]-4**) as a catalyst, and keeping the reaction temperature at 155 °C consistently resulted in a 23% CO_2 conversion to CH_3OH. The catalyst was recycled and reused by a simple distillation of the mixture after the reaction; five more cycles were performed and a total TON of 1850 was reached. By increasing the CO_2/H_2 ratio from 1:3 to 1:9, methanol was formed in 65% NMR yield. Remarkably, direct CO_2 capture from an ambient atmosphere, with PEHA and in situ hydrogenation, was achieved with up to 79% yield of methanol. This work was a significant step forward in terms of capturing CO_2 from an ambient atmosphere in order to transform it into methanol.

Based on this work, the Prakash group further demonstrated a recyclable system for a CO_2 capture/in situ hydrogenation system [50]. Methanol was generated in a biphasic 2-methyl THF/water system, which allows for regeneration and an easy separation of catalyst (**[Ru]-4**) and amine (PEHA). The catalytic system was recycled at least three times without significant loss of activity. CO_2 from the air can also be transformed into methanol under this protocol.

Very recently, Prakash and coworkers introduced an alkaline, hydroxide-based system for CO_2 capture and hydrogenation to methanol (Figure 8) [51]. Inexpensive inorganic bases such as NaOH, KOH, $Ca(OH)_2$ were combined with ethylene glycol for the CO_2 capture process. The in situ formed bicarbonate and formate were hydrogenated to methanol with a high yield; the inorganic base and ethylene glycol were regenerated, along with a methanol formation. The optimal catalytic system was found to be 0.5 mol% Ru-MaCHO-BH (**[Ru]-4**) under 70 bar H_2 at 140 °C, the NMR yield of methanol reached up to 100%, and TON reached up to 480 with 0.1 mol%. In an integrated one-pot system, CO_2 capture from ambient air and subsequent hydrogenation was realized to give a 100% NMR yield of methanol based on captured CO_2 [52].
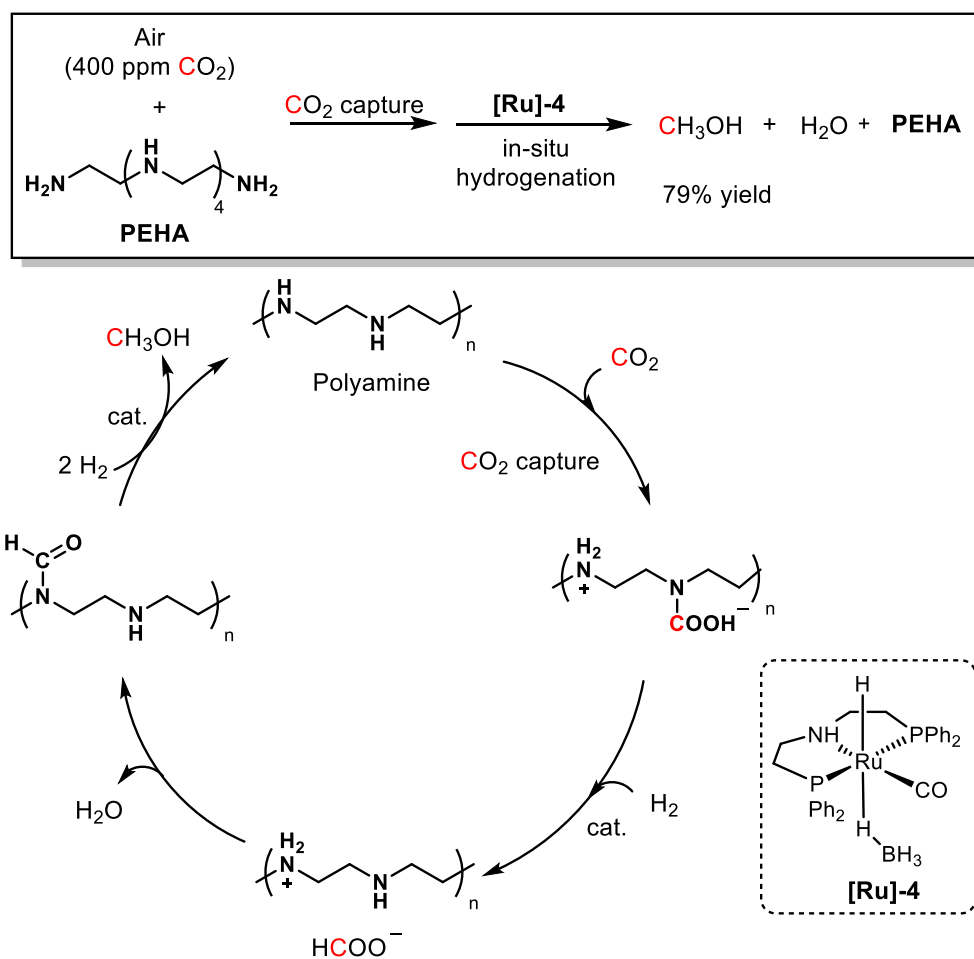
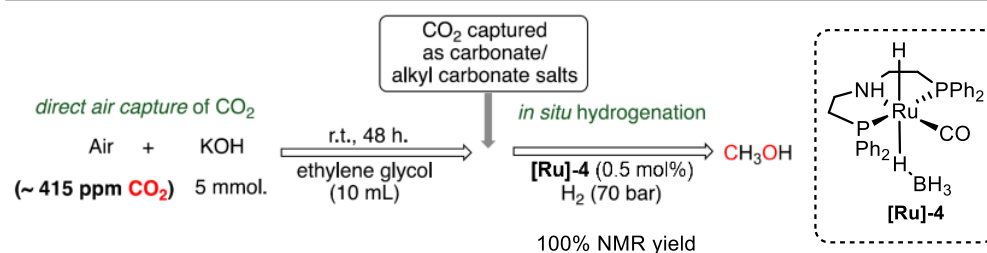**Figure 7.** PEHA as capture reagent for CO_2 hydrogenation from air.
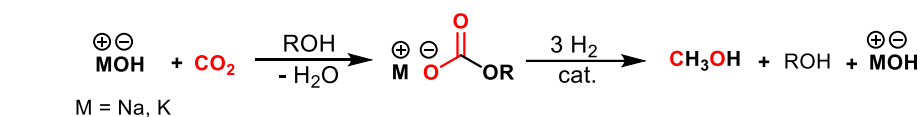
Figure 8. Inorganic base aided Ru-catalyzed hydrogenation of CO_2.

Another amine-assisted CO_2 hydrogenation to methanol without a tridentate pincer-type ligand was reported by the Wass group in 2017 (Figure 9) [53]. Several new catalyst systems containing ruthenium and amine auxiliaries were investigated, and an exceptional TON of 8900 and TOF of 4500 h^{-1} were obtained by employing [RuCl$_2$(Ph$_2$PCH$_2$CH$_2$NHMe)$_2$] (**[Ru]-8**) and diisopropylamine under 100 °C in 2 h.

Figure 9. Ruthenium and amine auxiliaries catalyzed hydrogenation of CO_2.
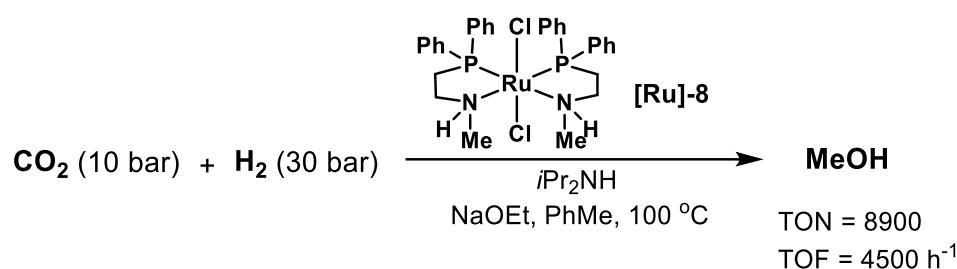
In addition to small molecular organic amines and inorganic bases promoting CO_2 hydrogenation, polymeric amines with a molecular weight ranging from 600 to 250,000 were investigated by Kayaki and their coworkers in 2019 [54]. Branched and linear poly(ethyleneimine)s (PEIs) were used as an amine source to be formylated, with the **[Ru]-4** catalyst at 100 °C in THF. The formamide group that was attached to the polymer backbones were hydrogenated to recover the PEI and obtain methanol. A one-pot protocol was also used so that methanol could be easily separated from the mixture. The highest TON was 689 under 20 bar CO_2 and 60 bar H_2 at 150 °C.

From the examples above, it is evident that the direct CO_2 hydrogenation to methanol is still demanding, and requires additional components, such as an organic amine or an inorganic base to promote the CO_2 fixation and transformation, which is due to the high activation barrier of CO_2. Cascade CO_2 hydrogenation, or one-pot two-step hydrogenation, were subsequently investigated. Alternatively, employing CO_2 derivatives as a substrate will significantly lower the activation barrier. One can use a different capture reagent to react with CO_2 in order to make a number of CO_2 derivatives, such as ureas, formates, carbamates, and carbonates; these derivatives then undergo hydrogenation to obtain methanol under transition metal catalysts.

Based on this conception, in 2011, the Milstein group hydrogenated various CO_2 derivatives, including formates, carbamates, and carbonates (Figure 10) [55]. When applying dimethyl carbonate as a substrate, the hydrogenation was achieved with **[Ru]-2** at 145 °C, 60 bar H_2, resulting in a TOF of 2500 h^{-1}, and with **[Ru]-9** at 110 °C, 50 bar H_2, a TOF of 314 h^{-1} was given. For methyl formate, **[Ru]-2** showed the highest efficiency and lead to a TON of 4700 at 50 bar H_2. A variety of substituted methyl carbamates as substrates were also able to be hydrogenated with **[Ru]-2** under 10 bar H_2 at 110 °C in THF, to deliver methanol in 94–98% yield.
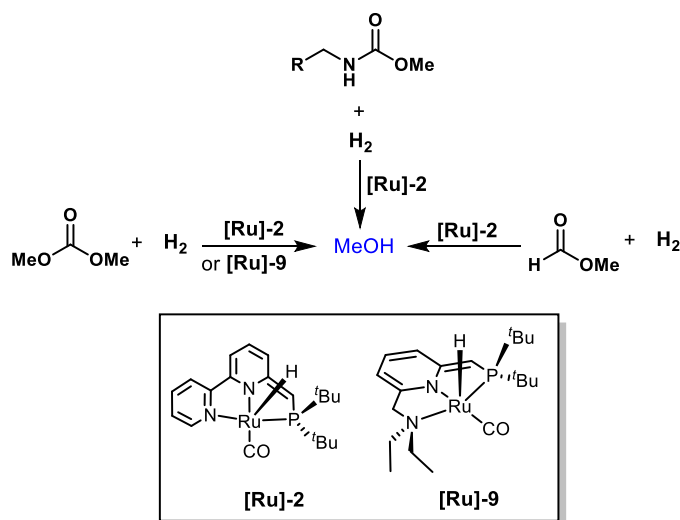

Figure 10. Hydrogenation of carbonates, carbamates and formates under Ru catalysis.

Shortly afterwards, the hydrogenation of another important CO_2 derivative, urea to methanol, was developed by Milstein and coworkers in the same year (Figure 11) [56]. **[Ru]-2** was found to be the most effective for urea hydrogenation, with 2 mol% **[Ru]-2** under 13.6 atm of H_2, and urea derivatives were successfully transformed into methanol with a 46–94% yield. Preliminary mechanism studies showed that the reaction first proceeded with the hydrogenolysis of urea to obtain formamide and amine, then the formamide was hydrogenated to deliver methanol.
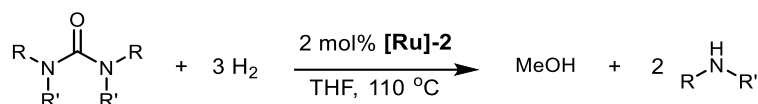
Figure 11. Hydrogenation of urea using a ruthenium pincer catalyst.

Another key intermediate in the chemical industry, ethylene carbonate, has been used for ethylene glycol synthesis as a key step in Shell's omega process. In 2012, the Ding group reported that a PNP pincer ruthenium complex catalyzed the hydrogenation of ethylene carbonate and other cyclic carbonates (Figure 12) [57]. Specifically, Ru-MACHO (**[Ru]-7**) was found to be the most efficient, and a remarkable TON of 87,000 was achieved by employing only 0.001 mol% **[Ru]-7** under 60 atm H_2 at 140 °C, which produced methanol in 84% yield. A number of substituted cyclic carbonates were hydrogenated to methanol with a high yield.
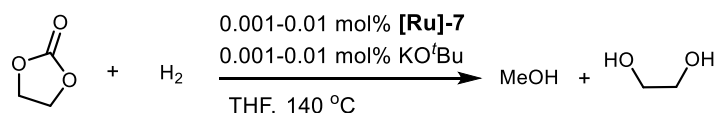
Figure 12. Ruthenium catalyzed hydrogenation of cyclic carbonates.

2.2. Co-Based Catalysts

The aforementioned CO_2 hydrogenation reactions were realized by ruthenium catalysts; in sharp contrast, the first-row transition metals are less developed for this transformation, and their high abundance, low cost, and low toxicity have also drawn much attention in the past five years [58–60].

Homogeneous CO_2 hydrogenation to methanol by non-pincer-type base metal catalysis was first discovered by Beller and coworkers in 2017 (Figure 13) [61]. The active catalytic species contains $Co(acac)_3$, triphos, and $HNTf_2$, with 20 bar of CO_2 and 60 bar of H_2 at 140 °C, which achieved a TON of 31. The continued increase in H_2 pressure to 70 bar, in addition to more Brønsted acid, improved the TON to 50, even with the lower temperature of 100 °C, which is one of the lowest temperatures to be recorded during a successful CO_2 hydrogenation to methanol reaction.
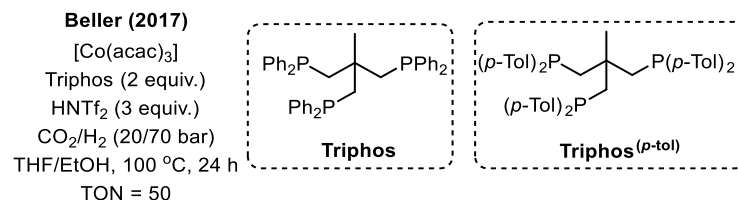
Figure 13. The non-noble cobalt catalysts for direct CO_2 hydrogenation.

Two years later, the Beller group modified the aforementioned molecularly defined cobalt catalyst system, and a TON of up to 125 was reached, which was more than twofold greater than the TON reached in the previous reaction [62]. The key to the increase was the modification of triphos by adding substituents on the phenyl ring of the ligand. Triphos$^{(p\text{-tol})}$ (Figure 13) was found to be the most efficient, which was attributed to the

increased electron density on phosphorus, which made the cobalt center more electron-rich to activate H_2. The additive, $HNTf_2$, could also be removed by using $Co(NTf_2)_2$ as the catalyst instead of $Co(acac)_2$.

2.3. Mn-Based Catalysts

Prakash and their colleagues discovered a Mn(I)–PNP pincer complex (**[Mn]-1**) that catalyzed a one-pot CO_2 hydrogenation in 2017 (Figure 14) [63]. Similar to previous works catalyzed by ruthenium catalysts, this procedure also contained two steps: (1) *N*-formylation of amines by CO_2 and H_2; and (2) formamide hydrogenation to methanol under H_2. In this work, a well-defined Mn–PNP catalyst (**[Mn]-1**) exhibited good activity in both steps. Morpholine and benzylamines were better amine sources than amines with a long alkyl chain, such as amylamine. The optimal conditions were found to be benzylamine under CO_2 (30 bar) and H_2 (30 bar) with 2 mol% **[Mn]-1** catalyst at 110 °C in THF, which gave the *N*-formylation product, and then an increase in the total pressure to 80 bar with another 36 h to obtain methanol in 84% yield. However, the turnover number and turnover efficiency were not able to be compared with noble metal catalysts. This study demonstrates the feasibility of using base-metal pincer catalysts in homogeneous CO_2 hydrogenation to methanol reactions.
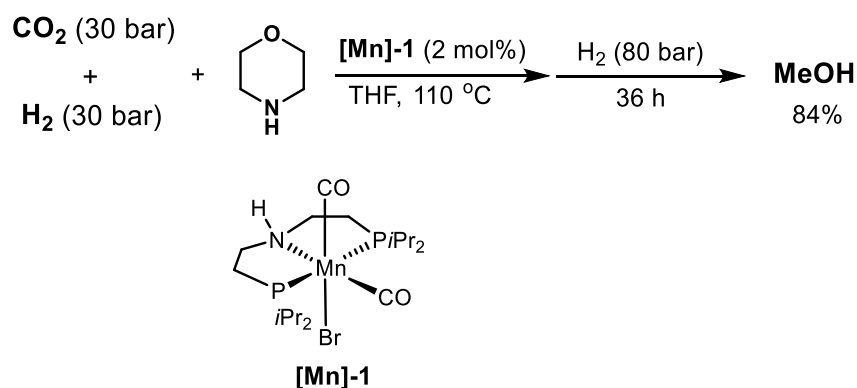

Figure 14. Manganese complexes catalyzed hydrogenation of CO_2.

In 2018, the groups of Milstein, Rueping, and Leitner independently reported the manganese-catalyzed hydrogenation of carbonates (Figure 15) [64–66]. In Milstein's report, a PNN pincer manganese complex (**[Mn]-2**) was chosen as the optimal catalyst at under 30–50 bar of H_2 at 110 °C, and a wide range of cyclic and acyclic carbonates were hydrogenated to methanol smoothly. Unsymmetrical acyclic carbonates were also suitable substrates for this transformation, although they achieved lower yields. Moreover, poly(propylene carbonate) from waste plastic was able to undergo depolymerization and hydrogenation to afford methanol in 59% yield [64]. Rueping and others mainly focused on cyclic carbonates as substrates, with a 0.25 mol% PNN pincer manganese complex(**[Mn]-3**) and KO*t*Bu as a base under 50 bar of H_2 at 140 °C. Ethylene carbonate was hydrogenated to >99% ethylene glycol and 92% methanol, and poly(propylene carbonate) was hydrogenated with a catalyst **[Mn]-3** to produce methanol in 84% yield, which also provides new avenues for plastic degradation. Density functional theory also confirmed the heterolytic cleavage of the dihydrogen molecule. [65] The Leitner group made use of the PNP pincer manganese complex **[Mn]-1** and NaO*t*Bu as a base under 30 bar H_2, to obtain methanol in 41–94% yields from different cyclic carbonates. These reports demonstrate the feasibility of using non-noble metal pincer-type catalysts in the hydrogenation of carbonates, which, combined with CO_2 fixation, could complete the CO_2 hydrogenation to methanol [66].
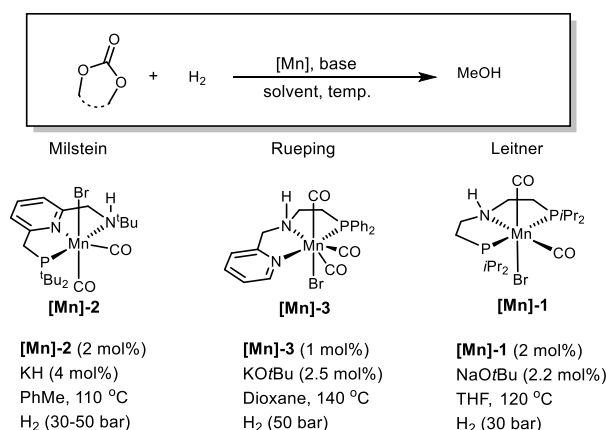
Figure 15. Manganese catalysts developed for hydrogenation of carbonates.

The hydrogenation tendency of polar unsaturated chemical bonds depends on their polarity. Compared to carbonate, carbamates, and ureas, they are more challenging carbonyls in terms of hydrogenation. As common products that result from the reaction of CO_2 with amines, or with amines and alcohols, the hydrogenation of carbamates and ureas is highly attractive, and will provide milder conditions for an indirect CO_2 hydrogenation to methanol (Figure 16) [67]. The conditions for the hydrogenation of carbamates developed by Milstein were 2 mol% **[Mn]-4**, 3 mol%, *t*BuOK under 20 bar, H_2 at 130 °C, which led to a series of aryl amine- and alkyl amine-derived carbamates to be hydrogenated in excellent yields. Under similar conditions, the most challenging urea derivatives were hydrogenated, obtaining both amines and methanol successfully.
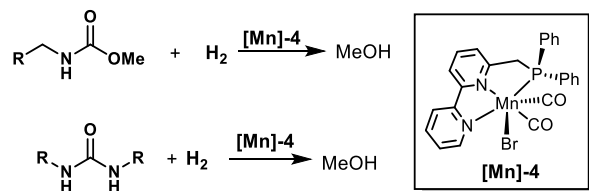
Figure 16. Mn-catalyzed hydrogenation of carbamates and ureas.

2.4. Fe-Based Catalysts

Recently, Bernskoetter and coworkers represented a homogeneous Fe–PNP complex (**[Fe]-1**), which catalyzed CO_2 hydrogenation to methanol in a two-step fashion (Figure 17) [68]. The reaction was attempted in a single batch and was found to be inefficient due to catalyst poisoning by CO_2 during the formamide hydrogenation step. More specifically, the catalyst formed a stable iron(II) formate complex under the CO_2 atmosphere and was not active anymore. By switching the conditions to a two-step procedure, a net TON of 590 was achieved, which was superior to the base-metal catalysts reported for this reaction.

Figure 17. Iron complexes catalyzed hydrogenation of CO_2.

3. Conclusions

As previously discussed, using CO_2 and CO_2 derivatives for hydrogenation is indicative of state-of-the-art research in this field (see Tables 1 and 2). The homogeneous catalytic systems show benefits such as relatively mild conditions, low catalyst loadings and clear reaction mech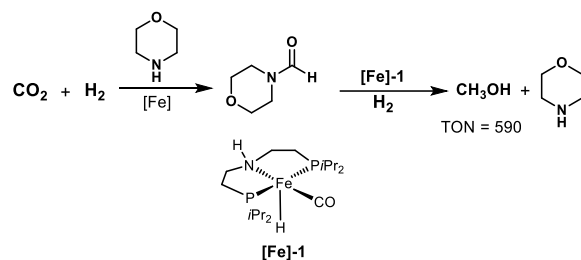anistic pathways. However, there is still a long way to go in order for these systems to be practical; the highest TONs achieved so far are around 9000 with ruthenium catalysis, and therefore the identification of new catalytic conditions, especially the development of non-noble catalysts with high catalytic efficiencies, is of great significance to this realm. Furthermore, the advantages shown by the homogeneous systems can be explored in more detail; given that the reaction is expected to occur under 100 °C or even lower temperatures, the catalyst loadings still have room to be decreased, which in turn may promote an increase in TONs. Finally, the direct capture of CO_2 from the flue gas of coal combustion or from an ambient atmosphere is important to the carbon neutral cycle and has been seen in a few examples.

Table 1. Molecular catalysts for CO_2 hydrogenation to methanol.

Catalyst	Auxiliary	T (°C)	P (bar)	Solvent	Time (h)	TON	Ref.
$Ru_3(CO)_{12}$	KI	240	80	NMP	3	32	[39]
[Ru]-1/[Ru]-3	$Sc(OTf)_3$	135	40	Dioxane	16	21	[41]
$Ru(H)_2[P(CH_2CH_2PPh_2)_3]$ Ir-(tBuPCP)(CO)	$Sc(OTf)_3$	90	62	Dioxane EtOH	16	428	[42]
$[Ru(acac)_3]$	Triphos MSA	140	80	EtOH	24	135	[43]
[Ru]-3	$HNTf_2$	140	80	EtOH	24	221	[43]
(cod)Ru(methallyl)$_2$	Tdppcy Al(OTf)$_3$	120	120	THF	20	1100	[44]
(cod)Ru(methallyl)$_2$	Tdppcy Al(OTf)$_3$	120	120	EtOH	20	2100	[44]
Ru-MACHO-BH	Dimethylamine	95~155	50	THF	54	550	[45]
[Ru]-5	Valinol	135	60	DMSO/THF	19	322	[46]
[Ru]-6	Morpholine	120	70	THF	96	1,940,000	[47]
[Ru]-4	PEHA	155	70	THF	40	1060	[49]
[Ru]-4	PEHA	145	70	2-MeTHF/H_2O	72	520	[50]
[Ru]-4	Ethylene glycol	140	70	THF	72	480	[51]
[Ru]-8	Amine	100	40	Toluene	20	8900	[53]
[Ru]-4	PEIs	150	80	THF	20	689	[54]
$Co(acac)_3$	Triphos $HNTf_2$	140	80	THF/EtOH	24	31	[61]
$Co(acac)_3$	Triphos	110	90	THF/EtOH	24	50	[61]
$Co(NTf_2)_2$	Triphos$^{(p\text{-tol})}$	100	90	THF/EtOH	24	125	[62]
[Mn]-1	Morpholine	110	80	THF	36	840	[63]
[Fe]-1	Morpholine	120	69	Dioxane	16	590	[68]

Table 2. Molecular catalysts for CO_2 derivatives hydrogenation to methanol.

Catalyst	CO_2 derivatives	T (°C)	P (bar)	Solvent	Time (h)	TON	Ref.
[Ru]-2	Dimethyl carbonate	145	60	Dioxane	1	2500	[55]
[Ru]-9	Dimethyl carbonate	110	50	THF	14	4400	[55]
[Ru]-2	Methyl formate	110	50	THF	14	4700	[55]
[Ru]-2	Urea	100	13.6	THF	72	202	[56]
[Ru]-7	Ethylene carbonate	140	60	THF	48	87,000	[57]
[Mn]-2	Carbonates	110	50	PhMe	30	390	[64]
[Mn]-3	Cyclic carbonates	140	50	Dioxane	16	920	[65]
[Mn]-1	Cyclic carbonates	120	30	THF	40	175	[66]
[Mn]-4	Carbamates, urea	130	20	Toluene	48	50	[67]

As is evident, regardless of whether a noble or non-noble metal is employed, the majority of the catalysts are tridentate pincer-type complexes, which demonstrates the superiority of pincer complexes for this transformation. In this regard, the modification of the pincer ligand to achieve higher TONs and TOFs is desired, so that the heteroatoms and substituents on the pincer ligand can be tuned based on their electronic and steric effects, or so that new tridentate coordinating skeletons can be developed for hydrogen activation in milder conditions. In terms of practical applications for CO_2 capture and utilization, the recyclability and stability of the catalysts should be considered. Prakash's biphasic system offers new routes for homogeneous catalysts to recycle in CO_2 hydrogenation reactions [50]. We believe that as the community has focused more on reducing CO_2 emissions and developing routes for CO_2 utilization, the homogeneous CO_2 hydrogenation will still be popular in the next decade or so, which will promote the realization of the carbon neutral cycle.

Author Contributions: W.X. and C.T. co-wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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