

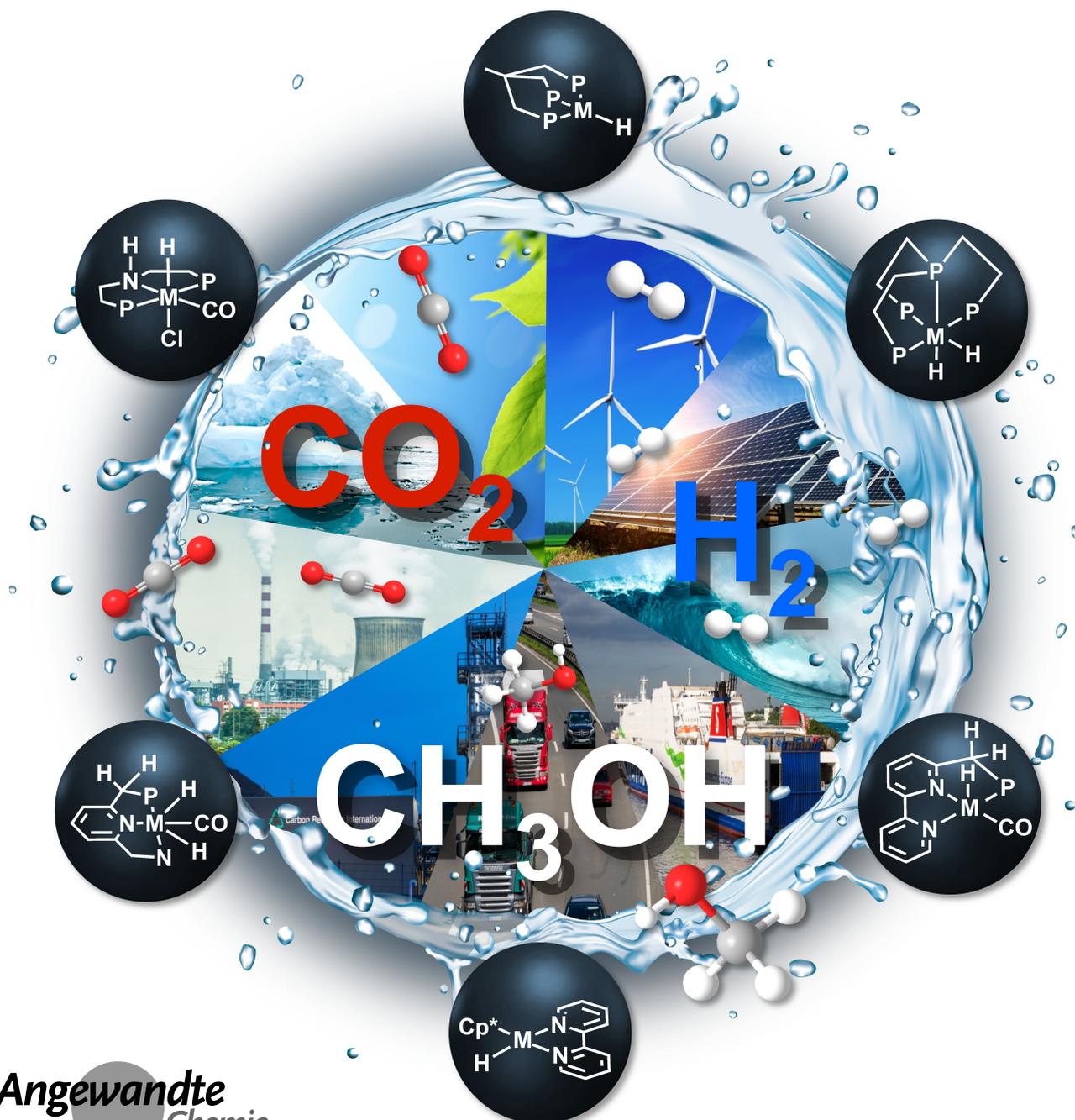
Methanol Economy

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Homogeneous Hydrogenation of CO₂ and CO to Methanol: The Renaissance of Low-Temperature Catalysis in the Context of the Methanol Economy

*Raktim Sen, Alain Goepfert, and G. K. Surya Prakash***In memory of Professor George A. Olah*

Abstract: The traditional economy based on carbon-intensive fuels and materials has led to an exponential rise in anthropogenic CO₂ emissions. Outpacing the natural carbon cycle, atmospheric CO₂ levels increased by 50 % since the pre-industrial age and can be directly linked to global warming. Being at the core of the proposed methanol economy pioneered by the late George A. Olah, the chemical recycling of CO₂ to produce methanol, a green fuel and feedstock, is a prime channel to achieve carbon neutrality. In this direction, homogeneous catalytic systems have lately been a major focus for methanol synthesis from CO₂, CO and their derivatives as potential low-temperature alternatives to the commercial processes. This Review provides an account of this rapidly growing field over the past decade, since its resurgence in 2011. Based on the critical assessment of the progress thus far, the present key challenges in this field have been highlighted and potential directions have been suggested for practically viable applications.

1. Introduction

Since the 19th century, we have witnessed unparalleled industrial and technological progress. Concurrently, the world population has grown rapidly, and so has the demand for energy, which has increased by at least a factor of ten over the past century. These energy requirements have come at the expense of exploiting our natural reserves of fossilized sunshine (fossil fuels) in an unaccountable fashion.^[1] As a natural consequence, this has been followed by the inevitable and unchecked emissions of CO₂, among other greenhouse gases (GHGs), to the atmosphere, outpacing the natural carbon cycle.^[2] Early signs of these repercussions include rise in average global temperatures by $\approx 0.8^\circ\text{C}$ over the past century, more unpredictable and extreme climate changes, rising of sea levels, ocean acidification, increasing wildfires and ongoing loss of biodiversity.^[3–5] In response, there have been increasing efforts towards a more sustainable approach to development and adoption of a *circular economy* model.^[6–9] These ongoing efforts range from policymaking, government regulations and incentives, to industrial implementation of greener technologies and academic research worldwide.^[10–13]

Within this broad framework, one of the key goals is to gradually substitute conventional feedstocks and processes with more sustainable and greener alternatives.^[13–16] In this context, technologies such as Power-to-Liquid (PtL) and Carbon Capture and Utilization (CCU) have emerged with growing interests (Figure 1).^[17–22] In such processes, renewable liquid hydrocarbons such as methanol, oxymethylene ethers (OME) and Fischer–Tropsch products can be produced using renewable electricity and feedstocks, mainly CO₂ and water.^[23–27] Methanol is one of the most attractive and fastest growing primary chemicals, which has been revolutionizing the chemical and energy sectors over the

past several decades.^[28] Methanol, when produced renewably, can cut CO₂ emissions by up to 95 % compared to conventional fuels.^[29] Sustainable production of methanol, preferably from renewable sources, is at the crux of the *Methanol Economy*, envisioned by the late Nobel Laureate Prof. G. A. Olah, and our group.^[30,31] Many aspects of this framework have been described in a monograph co-authored by Olah, Goeppert and Prakash.^[32] Renewable methanol (green methanol), in due course, has the potential to liberate us from our long-standing dependence on the finite reserves of fossil fuels and address the carbon conundrum facing humankind.^[33]

Catalysis holds a central role in the roadmap to achieve a circular economy and sustainable manufacturing.^[34–36] Industrial processes powered by catalytic technologies have allowed rapid and mass production of chemicals and materials with increased reaction rates and energy efficiencies. Parallely, catalysis is an important tool for renewable energy production, storage and utilization, for instance, in PtL and CCU processes. In this context, hydrogenation catalysts are of special interest as they offer direct routes to infuse renewable energy (in form of hydrogen atoms) into chemicals to produce value-added fuels and feedstocks.^[36] The stored renewable energy can later be utilized directly via combustion or by release of the stored hydrogen content (dehydrogenation).^[13,37] Catalytic hydrogenation is practiced in several industrial processes for production of both fine and bulk chemicals, using heterogeneous as well as molecular catalysts.^[38,39]

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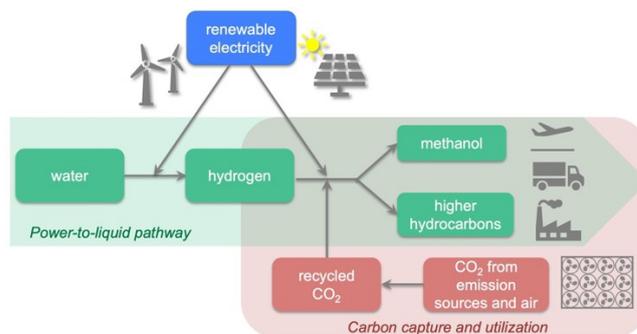


Figure 1. Sustainable production based on Power-to-Liquid (PtL) and Carbon Capture and Utilization (CCU).

1.1. Methanol: The Versatile Fuel and Feedstock

Methanol or methyl alcohol (CH_3OH) is the simplest member among alcohols. It is a colorless liquid at room temperature (b.p. 64.6°C) that is easy to store, transport and dispense. Methanol is water-soluble and readily biodegradable. It is one of the most critical building blocks in the chemical industry. The annual global demand has already reached about 107 million tonnes (Mt), almost doubling over the past decade largely driven by the expansion of the methanol-to-olefin (MTO) process and emerging energy applications (Figure 2).^[29,31,40]

Methanol is a primary feedstock and carbon source which is used to produce a myriad of chemicals, polymers, paints, adhesives, construction materials, pharmaceuticals and others.^[32] Production of formaldehyde, another key platform chemical, accounts for one of the largest shares ($\approx 23\%$) of the current methanol demand. Other chemical derivatives of methanol include acetic acid, methyl-*tert*-butyl ether, methyl methacrylate, dimethyl ether, etc. Methanol can also be catalytically converted to a variety of olefins such as ethylene and propylene as well as gasoline. The methanol-to-olefin (MTO) process has witnessed a tremendous growth as a substitute to the more traditional petrochemical routes. From almost no production in 2010, the MTO industry now accounts for about 31% of the global methanol usage.^[29,42]

Apart from its application as a feedstock, methanol is an attractive fuel and energy carrier. It is a direct drop-in fuel for internal combustion engines (ICE) and direct methanol fuel cells (DMFC).^[32] Methanol's role has grown rapidly in the energy sector, currently accounting for around 28% of its consumption.^[29] As an alternate and clean fuel, it is being widely adopted by a number of countries as gasoline and diesel fuel substitute (M100) or as gasoline blend (M15, M85) for vehicles, ships, boilers as well as cooking.^[30] Lately, methanol has also been recognized as a promising liquid organic hydrogen carrier (LOHC). Methanol's significant H_2 content of 12.6 wt% can be extracted through catalytic reforming and utilized in hydrogen fuel cells.^[13,43–49]

2. Methanol from Fossil and Renewable Sources

Methanol can be found naturally in fruits, vegetables, beverages, the atmosphere and even in space. Until the 1920s, methanol was manufactured solely from wood via destructive distillation, hence it is historically referred to as wood alcohol. Since then, methanol has been predominantly derived from fossil fuels, mainly from natural gas (65%) and coal (35%) at present.^[29] Worldwide, over 100 million tonnes of methanol are produced yearly in over 90 methanol plants.^[50]



Raktim Sen received his B.Sc. (Honors) in 2015 from St. Stephen's College, University of Delhi and M.Sc. in 2017 from Indian Institute of Technology (IIT) Delhi. He was a S. N. Bose Fellow in the summer of 2016 with Prof. G. K. Surya Prakash at the University of Southern California (USC). In 2017, he joined USC as a Ph.D. student in the group of Prof. Prakash. His research focuses on novel techniques and catalysis for CO_2 capture, conversion to methanol and H_2 generation. He is the recipient of 2022 Hancock Memorial Award from ACS Green

Chemistry Institute.



Alain Goepfert obtained his Ph.D. in 2002 from the University of Strasbourg. He is currently a Research Scientist in the Prakash group at the Loker Hydrocarbon Research Institute, USC. His research focuses on methane and CO_2 activation and catalytic transformation to value-added products, including methanol, methyl formate, formic acid, and dimethyl ether. He is also involved in the catalytic decomposition of formic acid to hydrogen and CO_2 as well as the development of regenerative sorbents for CO_2 separation and capture from

various sources, including air. He is a coauthor, with G. A. Olah and G. K. S. Prakash, of the book *Beyond Oil and Gas: The Methanol Economy*.



G. K. Surya Prakash received his B.Sc. (Honors) in 1972 from Bangalore University, his M.Sc. in 1974 from IIT Madras, and his Ph.D. in 1978 from USC under the tutelage of late Prof. G. A. Olah. He joined the USC faculty in 1981 and is currently a Professor in the Department of Chemistry and Director of the Loker Hydrocarbon Research Institute, holding the Olah Nobel Laureate Chair in Hydrocarbon Chemistry. His research interests include fluorination and synthetic methods, mechanistic studies, superacid chemistry, electrochemistry, and the

methanol economy. He is a prolific author with 830 publications, 115 issued patents and 14 books. He has received three ACS national awards. He is a co-proponent of the methanol economy concept with the late Prof. Olah, for which he shared with Prof. Olah the 2013 Eric and Sheila Samson Prime Minister's Prize for Alternative Fuels for Transportation from the State of Israel.

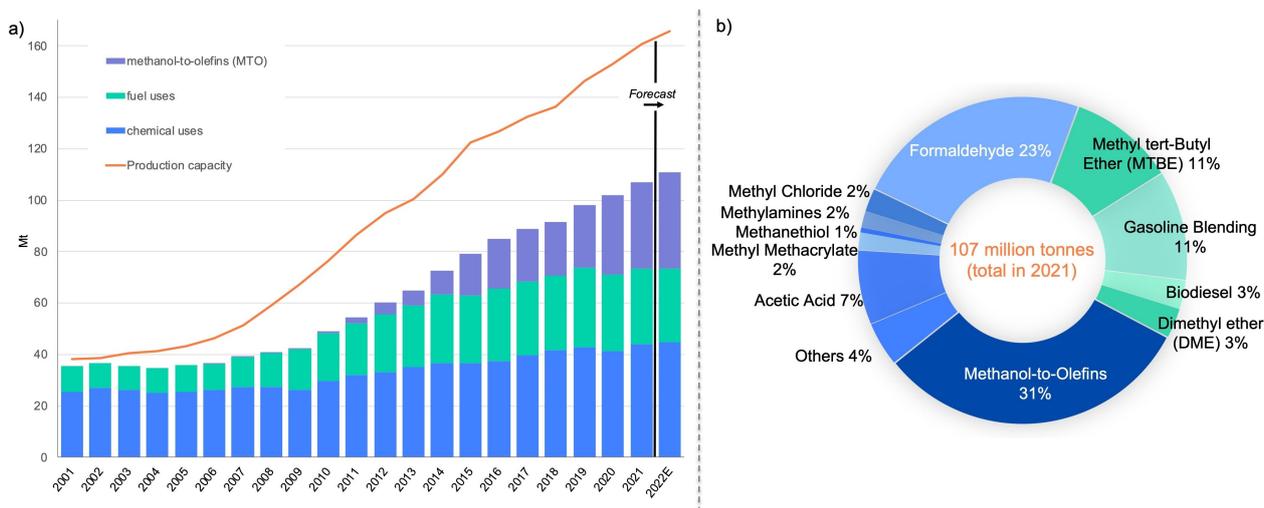
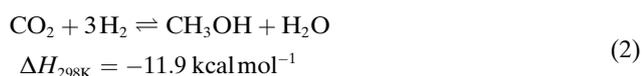
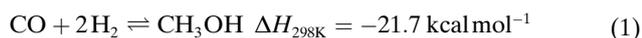


Figure 2. a) Global methanol demand and production capacity and b) methanol usage by industrial sectors. Based on data from MMSA.^[29,41]

2.1. Traditional Methanol Synthesis from Syngas

In conventional commercial processes, methanol is produced from a feed gas mixture, referred to as synthesis gas or syngas, that typically comprises carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen (H₂).^[51] Syngas is mainly obtained via coal gasification and natural gas (or shale gas) reforming; and the produced methanol is tagged accordingly as “brown” or “gray”. In comparison to the typical methane reforming routes (steam/dry/tri-reforming), steam and dry reforming, when combined as bi-reforming, results in an exclusive 1:2 ratio for CO/H₂, coined as *metgas* by Olah and Prakash, that is well suited for methanol synthesis.^[52–54] After conditioning and purification, syngas is subjected to catalytic conversion at elevated temperatures of 200–300 °C and pressures of 50–100 bar. The obtained crude methanol is distilled to remove the formed water and other minor by-products. The commercial catalyst is generally based on copper, zinc oxide and alumina (Cu/ZnO/Al₂O₃).^[55,56] Hydrogenation of CO and CO₂ to methanol is exothermic [Eqs. (1), (2)]. Hence, syngas to methanol proceeds with a thermodynamic conversion limit of about 30 % per cycle at such high operating temperatures. The unreacted syngas needs to be recycled continuously over the catalyst to enhance the overall conversion. It is widely agreed that the syngas-to-methanol process proceeds significantly through the transformation of CO to CO₂ via the water gas shift (WGS) reaction [Eq. (3)].



2.2. Renewable and Low Carbon Methanol

With the rapidly growing demand for methanol projected to surpass 120 Mt by 2025 and 500 Mt by 2050, the production capacity is also rising sharply worldwide.^[29] Given the high fossil dependency and carbon emissions associated with the methanol production at present, there is a growing urge to decarbonize this industry. Steps in this direction include the use of power and feedstocks (H₂ and carbon) that are generated with reduced carbon footprint and, preferably, using renewable resources.^[21,57–59]

In parallel, low carbon methanol (LCM) can be achieved through recycling of the CO₂, which would be emitted to the atmosphere otherwise, to synthesize methanol.^[18,60] Waste CO₂ is produced at various stages within the methanol industry, for instance, during coal gasification, syngas conditioning, and heat generation.^[61,62] CO₂ from these and other emission sources can be fed back into the methanol synthesis loop to produce low carbon methanol (LCM). Further, carbon from renewable sources, such as geothermal vents, biomass and air, can be recycled to afford net carbon-neutral methanol (e-methanol and bio-methanol).^[29] Air-to-methanol, in particular, is a distinct proposition, given that air has no geopolitical constraints, and is a near inexhaustible source of renewable carbon.^[63,64]

3. Hydrogenation of CO₂ to Methanol

Similar to hydrogenation of CO to methanol (refer to Section 2.1), CO₂ can be activated by the same class of copper-based commercial catalysts for its hydrogenation to methanol under comparable reaction conditions (230–300 °C and 50–75 bar).^[65] The catalyst activities decrease gradually due to water-induced sintering and deactivation of active sites. High reaction temperatures favor the reverse water gas shift (RWGS) reaction resulting in formation of water. CO₂ hydrogenation proceeds with a high selectivity of

>99% for methanol using the standard Cu/ZnO/Al₂O₃ catalysts.^[66] However, the CO₂ conversion is severely limited by thermodynamics similar to the syngas-to-methanol process. Over the past few years, significant research has taken place to develop improved heterogeneous catalytic systems with higher conversions and stability, and operating under milder conditions. These include diverse modifications of the Cu/ZnO/Al₂O₃ catalyst, as well as designing entirely new compositions such as Ni–Ga, Pd, Pt, Re, and In₂O₃ based catalysts, among others.^[56,67,68]

During 1993–95, a series of reports of CO₂ hydrogenation to methanol via reverse water gas shift reaction were presented by Tominaga and co-workers.^[69,70] A Ru₃-(CO)₁₂ complex was shown to catalyze the hydrogenation with KI as an additive in *N*-methylpyrrolidone (NMP) solvent. Methanol formation was observed at high temperatures (160–240 °C) and a net pressure of 80 bar (CO₂:3H₂). It was proposed that CO₂ initially converts to CO via the reverse water gas shift reaction, which undergoes further reduction to methanol. CO and CH₄ were observed as side products, whose formation increased significantly at temperatures above 240 °C. The addition of an iodide was crucial to stabilize the in situ formed Ru carbonyl clusters, which act as the active catalytic species for hydrogenation. Although the system demonstrated the first examples of a homogeneous CO₂-to-methanol process, this method suffered from significant challenges including low yields, poor selectivity and high operating temperatures, comparable to existing heterogeneous conditions. Following this work, the field of homogeneous catalysis for CO₂ hydrogenation to methanol remained mostly unexplored for almost two decades.

3.1. Low-Temperature Methanol Synthesis using Homogeneous Catalysts

Since CO₂ hydrogenation to methanol is exothermic in nature [Eq. (2), $\Delta H_{298\text{K}} = -11.9 \text{ kcal mol}^{-1}$], the reaction would be thermodynamically favored at lower temperatures. Similarly, milder operating temperatures can significantly reduce the overall energy and capital inputs. Despite the exoergicity, a minimum temperature threshold is often required to maintain activity of the catalyst and enhance the overall kinetics of the reaction. Along these lines, parallel to the exploration in the field of heterogeneous catalysis, there has been a continuous search for alternate catalytic systems that offer selective routes to methanol, especially at lower temperatures.^[56] In general, the design of novel catalysts should take into account desirable features such as being robust, relatively inexpensive, the ease of separation and recycling, among others. Additionally, high catalytic activity in combination with exclusive selectivity for the desired product is ideal for development of a viable methanol synthesis technology.

In this context, molecular metal complexes are a promising class of catalysts which can activate CO₂ and H₂ for methanol synthesis under relatively mild conditions.^[35,71] Operating at relatively low temperatures and in liquid phase, such catalysts also offer high selectivity for methanol by

inhibiting side reactions. Additionally, homogeneous systems provide significant opportunity for a better understanding of the reaction pathways and catalytic mechanisms at a molecular level. Based on such mechanistic insights as well as computational predictions, the catalytic frameworks can be rationally tuned to improve the efficiency and selectivity of the reaction.^[72] Desirable homogeneous catalysts should exhibit enhanced robustness and thermal stability over long runs under operating conditions along with substantial turnovers (both TONs and TOFs).

Most of the molecular catalysts initially selected for CO₂ hydrogenation were strongly inspired by their abilities to hydrogenate other carbonyl-based substrates and carboxylic acid derivatives such as amides, esters, ketones and others.^[73–78] While several of these catalysts are successful in the hydrogenation of CO₂, the reduction is often arrested at the formic acid/formate stage.^[8,79–85] While thermodynamically favored, further hydrogenation to methanol is kinetically challenging, primarily due to the lower electrophilicity (hydride affinity) of the carbonyl moiety in these molecules. Hence, catalysts which form metal hydrides with higher hydricity (or ease of hydride transfer) are required for methanol synthesis reactions, compared to other carbonyl hydrogenation reactions. Additionally, formate species act as strong ligands to the metal center, blocking the active site for further hydrogenation.^[80] Hence, a mediating component such as an alcohol or amine is often required to detach the formate species and stabilize it in the form of formate esters or formamides, enhancing the rates of hydrogenation further towards methanol.

For methanol synthesis from CO₂, homogeneous catalysts should be able to split H₂ for its insertion into CO₂ to afford formate species, and have a high enough hydricity to reduce formate to methanol.^[73,78,86] In addition, these catalysts should retain activity and be compatible to any additive, reaction pH and side products such as CO. Some of the first and most widely explored catalysts for such transformations include metal–pincer PNN and PNP complexes including pyridine-based complexes developed in Milstein's group as well as the PN(H)P type catalysts which can split H₂ via metal–ligand cooperation (MLC) to afford the hydrogenation of a carbonyl moiety (Figure 3).^[72] On the other hand, notable catalysts including ones bearing tripodal phosphine and bipyridine based ligands performing under acidic–neutral conditions have also gained special significance in the field of CO₂ hydrogenation. The early examples of CO₂-to-methanol homogeneous catalysts are based on precious transition metals, mostly with ruthenium and a few with iridium. Lately, analogues of these catalysts with earth-abundant metals, namely iron, manganese and cobalt, are being developed as well. Many of these state-of-the-art catalysts as well as the ligand frameworks are becoming commercially available with increasing demand and research interests due to the rapid growth in the overall homogeneous hydrogenation and dehydrogenation catalysis fields.^[38,87–97]

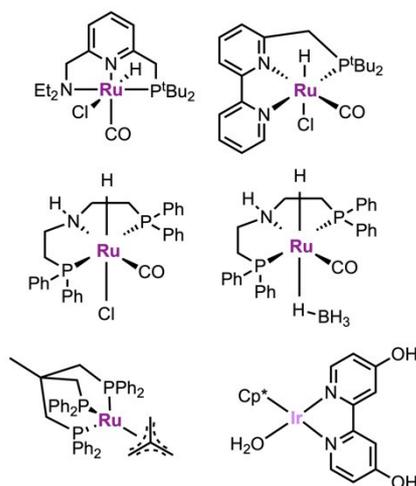


Figure 3. Selected examples of the first-generation homogeneous catalysts instrumental in developing CO₂ hydrogenation to methanol.

3.2. Hydrogenative Routes for CO₂ to Methanol

Hydrogenation of CO₂ to methanol with H₂ can proceed through various intermediates and derivatives of CO₂.^[98] In the direct hydrogenation of CO₂, the reaction may proceed through a HCOOH intermediate as in the cases of additive-free systems. Additionally, other favorable intermediates such as formate esters and formamides observed in presence of an alcohol and amine additive, respectively, have been shown to facilitate the hydrogenation of CO₂ and CO to methanol. Invariably, formaldehyde or dihydroxymethane is the immediate species hypothesized to precede methanol formation. However, the high reactivity poses challenges in detection or isolation of such species. Further, CO₂ hydrogenation may proceed through CO in a reverse water gas shift reaction. However, it is a minor route under mild homogeneous conditions.^[99]

Parallely, methanol can be accessed via hydrogenation of various derivatives of CO₂ or carbonic acid as well as ionic capture products of CO₂.^[72] The derivative or intermediate formed is also governed by the pH of the system: acidic, neutral or alkaline. Organic derivatives including organic carbonates (acyclic and cyclic), urea and carbamate derivatives can be readily obtained from CO₂ via known processes without any reduction step. On the other hand, CO₂, which is a weak acid, can be chemically captured in presence of a base under ambient conditions. In alkaline medium, amines or alkali metal hydroxides react with CO₂ to form ammonium or metal salts of carbamate, bicarbonate or carbonates.^[100,101] Such molecules can be catalytically hydrogenated to obtain methanol with three equivalents of H₂. While reduction of CO₂ to methanol has also been achieved using other hydrogen sources including metal hydrides, boranes, silanes, water and others, molecular H₂ stands out as the most efficient, atom-economical, cost-effective and industrially viable reductant, provided that appropriate infrastructure is available to handle H₂ under high pressures (Figure 4). In addition, H₂ is also a direct and

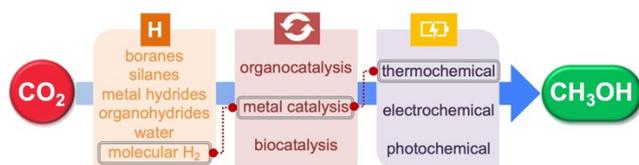


Figure 4. CO₂ reduction to methanol: selected categories of H-source, catalysis and process covered by this Review (framed).

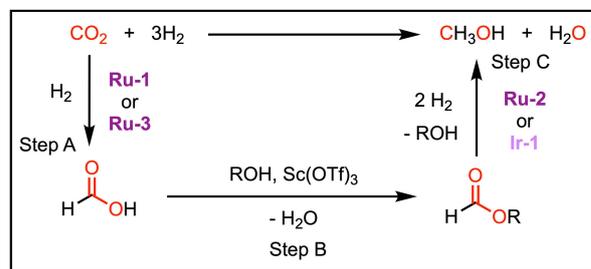
green carrier of renewable energy. In parallel to the thermocatalytic processes for CO₂ hydrogenation, there have been significant advances in achieving such transformations through alternate routes involving photocatalysis, electrocatalysis, organocatalysis and biocatalysis. However, these subjects are outside the focus and scope of this Review.^[102–115]

4. Direct CO₂ to Methanol Using Molecular Catalysts

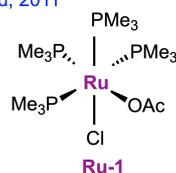
4.1. Precious Metal Based Catalytic Systems

4.1.1. Cascade Route for CO₂ to Methanol

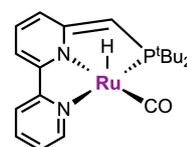
In 2011, Sanford and co-workers achieved a breakthrough in synthesizing methanol directly from CO₂ with homogeneous catalysts at low temperatures (Figure 5).^[116] Using a cascade



Sanford, 2011

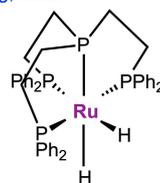


Ru-1

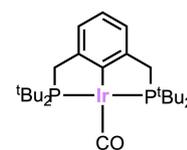


Ru-2

Goldberg, 2020



Ru-3



Ir-1

Figure 5. Cascade catalysis of CO₂ to methanol. Based on ref. [116] and ref. [117].

of three different catalysts, the reaction proceeded through the sequence: Step A) CO₂ hydrogenation to formic acid with a Ru–phosphine catalyst (**Ru-1**); Step B) esterification with CD₃OH in presence of Sc(OTf)₃, a Lewis acid catalyst to generate methyl formate; and Step C) hydrogenation of formate ester to methanol using a Ru–PNN catalyst (**Ru-2**). The broad class of Ru–PNN catalysts had been developed previously by the group of Milstein and have been utilized extensively for numerous (de)hydrogenation transformations. When the tri-catalytic hydrogenation was attempted with a 1:3 CO₂:H₂ mixture (40 bar) in one-pot at 135 °C, methanol was formed, albeit with a very low TON of 2.5. Possible deactivation of the **Ru-2** by Sc(OTf)₃ was suggested to be a key challenge. To circumvent the catalyst decomposition, the cross-reactive catalysts were physically compartmentalized within the reactor, which enhanced the catalytic activities significantly with a TON of 21 for methanol over 16 h. While the turnovers were modest for the cascade catalysis, this approach served as one of the primary reports in the development of homogeneous catalysis for direct hydrogenation of CO₂ to methanol.

Goldberg and co-workers further evaluated the individual steps in the cascade catalysis previously reported by Sanford and modified the system accordingly (Figure 5).^[117] Using ethanol (EtOH) as the solvent, the rationally selected catalyst triad involving **Ru-3**, Sc(OTf)₃ and **Ir-1** showed considerable improvement in the net catalytic efficiency. A notable TON_{MeOH} of 428 over 40 h was achieved partly due to the use of higher reaction temperatures (155 °C) and more active Ir metal. **Ir-1** was also more stable than the previously employed **Ru-2** by Sanford under high temperature and acidic conditions. Additionally, it was noted that **Ru-3** required preactivation with H⁺ in step A, which is generated in situ by the triflate salt. Interestingly, a substantial amount of diethyl ether was also observed due to self-condensation of EtOH under acidic conditions. A notable limitation of this system is the generation of CO as a side product due to ethyl formate decomposition, which inhibited the catalytic activities of both the **Ru-3** and **Ir-1** catalysts.

4.1.2. Tripodal Phosphine Based Catalytic Systems

In 2012, Leitner, Klankermayer and co-workers developed a single molecular catalyst for hydrogenation of CO₂ to methanol (Figure 6).^[118] The catalyst was based on ruthenium metal decorated with a tripodal and tridentate phosphine ligand, commonly abbreviated as Triphos (1,1,1-tris(diphenylphosphinomethyl)ethane). The hydrogenation catalysis required the presence of an organic acid co-catalyst such as methanesulfonic acid (MSA) or bis(trifluoromethane)sulfonimide (HNTf₂). Similar to the catalysis reported by Sanford and Goldberg, the present reaction was also assisted by an alcohol additive. The metal–triphos complex was either formed in situ from the precursors Ru(acac)₃ and Triphos ligand (**Ru-5**); or was introduced as the isolated Ru–triphos species (**Ru-4**). Using ethanol and **Ru-5**, the authors achieved a TON of 221 for methanol

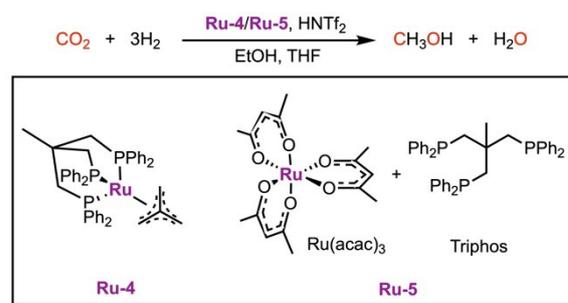


Figure 6. Ruthenium–triphos catalysis for CO₂ to methanol. Based on ref. [118].

under the optimized reaction conditions (CO₂:3H₂=80 bar, 140 °C, 24 h).

Continuing on their initial findings, the same group of authors later demonstrated the catalytic hydrogenation even in the absence of an alcohol additive.^[119] Using **Ru-4** in combination with HNTf₂ in THF, a promising TON of 603 was reported over 48 h. The catalysis was active for methanol even at low temperatures (80–100 °C) albeit with lower activities. Further, a biphasic system (2-MeTHF and water) was developed for efficient catalyst separation and recycling. After four cycles, a TON of 769 was achieved and about half of the initial catalytic activity was retained (Figure 7).

In a 2020 report, Klankermayer and co-workers tuned the original catalytic system by introducing a tdppcy (1,3,5-tris(diphenylphosphino)cyclohexane) ligand in place of the triphos ligand (Figure 8).^[120] The Ru–tdppcy (**Ru-6**) showed up to four-fold enhancement in the TON for hydrogenation of CO₂ to methanol compared to Ru–triphos (**Ru-4**), even under additive-free conditions. In presence of ethanol, a remarkable TON of 2148 was achieved with **Ru-6** and Al(OTf)₃ as a cocatalyst. The authors suggested that the increased activity was possibly due to higher rigidity of the tdppcy ligand with a cyclohexyl ring structure when compared to the more flexible triphos ligand.

Around the same time, another modification to the Ru–triphos system was reported by Wiedner et al. by modulating the bridgehead moiety of the tripodal ligand (Figure 9).^[121] N-triphos (**Ru-7**) and cationic ^{Me}N-triphos (**Ru-8**) complexes were studied in comparison to the previously explored C-triphos complex (**Ru-4**). The authors were able to study the reaction profile via operando ¹H NMR spectroscopy. While

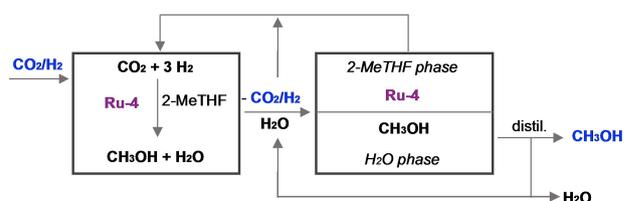


Figure 7. Biphasic system to separate methanol and catalyst. Adapted from ref. [119] with permission from the Royal Society of Chemistry.

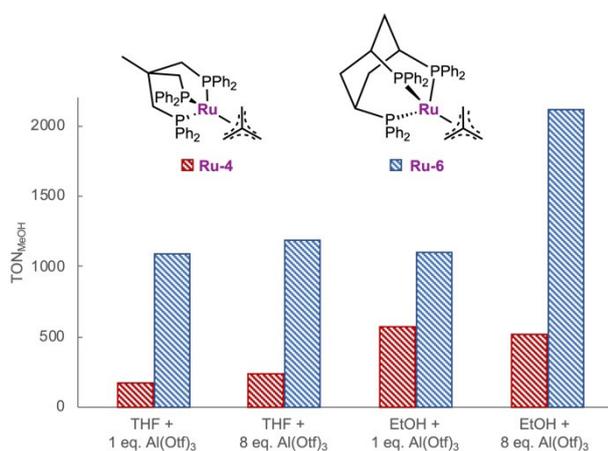


Figure 8. Comparative performances of **Ru-4** and **Ru-6**. Adapted from ref. [120] with permission from the American Chemical Society.



Figure 9. Comparison of Ru catalysts based on neutral C-triphos, N-triphos and cationic ^{Me}N-triphos.

the formation rates of formate ester were similar for all the studied catalysts, the corresponding methanol production was in the order **Ru-8** (^{Me}N-triphos) < **Ru-7** (N-triphos) < **Ru-4** (C-triphos) in ethanol. The relative rate constants showed that **Ru-8** displayed a 12-fold enhancement compared to **Ru-4** in rate of methanol formation from the transient formaldehyde intermediate. The relative electron deficiency of the N-triphos ligand was suggested to make the catalyst more active towards methanol than the formaldehyde acetal (dialoxymethane).

4.1.3. Amine-Assisted Catalysis

The catalytic systems described previously in Sections 4.1.1 and 4.1.2 operated in neutral or slightly acidic medium. In parallel to such pathways under alcohol-assisted or additive-free conditions, there has been significant progress in CO₂ reduction in basic medium. In 2015, Sanford and co-workers reported an amine-promoted approach for the transformation of CO₂ to methanol (Figure 10).^[122] In the amine-assisted route, CO₂ reacts with an amine moiety to form the corresponding ammonium carbamate. The carbamate species can directly undergo hydrogenation to formamides and then further to methanol. Alternatively, the carbamate adduct can reversibly release CO₂ gas at mild operating temperatures. The free CO₂ can be catalytically hydrogenated to ammonium formate. This is followed by the formation of the key formamide intermediate via condensation, for subsequent reduction to methanol. Based on these

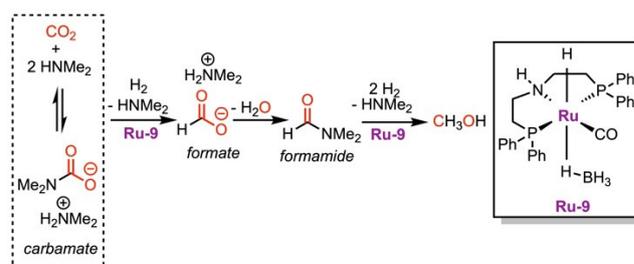


Figure 10. Amine-assisted one-pot CO₂-to-methanol system.

hypotheses and other preliminary investigations, authors demonstrated a one-pot temperature ramp strategy (95 °C to 155 °C) to hydrogenate a gaseous mixture of CO₂ (2.5 bar) and H₂ (50 bar) to methanol with a TON of 550 after 54 h. A ruthenium metal complex with PNP-based pincer ligand, trademarked as Ru-Macho-BH (**Ru-9**) was found promising to catalyze this transformation efficiently in presence of dimethylamine, a model amine additive.

Shortly after, Ding and co-workers accomplished a sequential route to synthesize methanol from CO₂ as an application of the N-formylation of amines developed in the same report (Figure 11).^[123] In the first step of the one-pot sequence, a 1:1 mixture of CO₂ and H₂ at 70 bar was reacted at 120 °C for 40 h in presence of Ru-Macho catalyst (**Ru-10**) and morpholine, a model amine, to afford the corresponding formamides. In the subsequent step, the resulting crude reaction mixture containing the active catalyst was subjected to 50 bar of H₂ at a higher temperature of 160 °C to obtain methanol in 36 % yield within 1 h.

It is also worth highlighting here that the preliminary reports by Sanford and Ding provided key insights into the amine-assisted CO₂-to-methanol sequence: a) while CO₂ hydrogenation with one equivalent of H₂ to formate/formamides proceeds at relatively low temperatures, further hydrogenation to methanol (with two equivalents of H₂) required elevated temperatures indicating that this step is more challenging; b) identification of the Ru-Macho-based catalysts, a family of metal-PNP pincer complexes effectively catalyzing the CO₂-to-methanol process under basic conditions. These molecular catalysts had previously been explored for related (de)hydrogenative transformations.^[8,75]

In 2015, another sequential approach for conversion of CO₂ under near-ambient pressures to methanol was demonstrated by Milstein et al. using aminoalcohols (Figure 12).^[124]

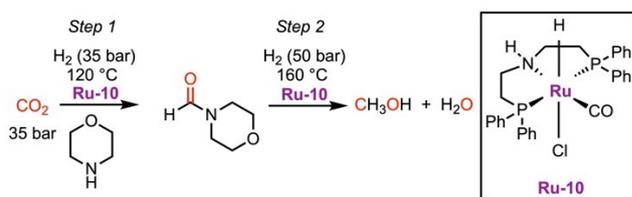


Figure 11. Amine-assisted sequential methanol synthesis from CO₂ via N-formylation.

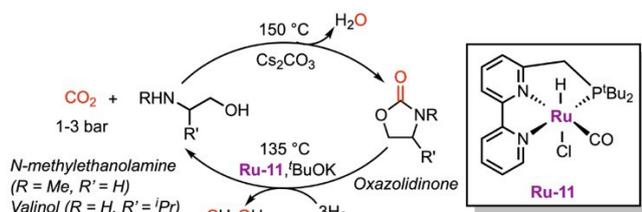


Figure 12. Low-pressure CO₂-to-methanol route via oxazolidinone. Based on ref. [124].

First, CO₂ (1–3 bar) was heated to 150 °C in presence of an aminoalcohol (*N*-methylethanolamine or valinol) and Cs₂CO₃ catalyst in DMSO to form the corresponding oxazolidinone. Here, the higher operating temperatures and catalytic conditions allowed for a different reactive pathway between aminoalcohols and CO₂ in contrast to the formation of carbamate salts observed at lower temperature. In the second step, the Ru–PNN catalyst (**Ru-11**) and a co-catalyst *t*BuOK were introduced to the reaction mixture following evacuation of CO₂ and the mixture was subjected to hydrogenation at 135 °C with 60 bar of H₂ to produce methanol

with up to 53 % yield. Notably, the Ru–PNN catalyst (**Ru-11**) showed higher efficiency for the hydrogenation step as compared to Ru–Macho (**Ru-9**) under similar conditions. Additionally, small amounts of formate species were also detected as possible intermediates, though further hydrogenation to methanol could proceed through either formamides or formate esters.

During this period, Olah, Prakash and co-workers also reported a one-step methanol synthesis process directly from CO₂ using pentaethylenhexamine (PEHA), a commercially available and high-boiling polyamine (Figure 13).^[125] Among the pincer catalysts screened, Ru–Macho-BH (**Ru-9**) and Ru–Macho (**Ru-10**) showed the most promising activities. The hydrogenation was carried out with 75 bar of 1:9 CO₂:H₂ in presence of PEHA in triglyme solvent to afford methanol with high TONs of 1200 (CH₃OH yield=65 %) and 985 (CH₃OH yield=54 %) at temperatures of 145 °C and 125 °C, respectively, over an extended reaction time of 200 h. The reaction system was shown to be quite robust and stable allowing efficient recycling of the catalyst, amine and solvent over multiple cycles. The products formed (methanol and H₂O) were distilled out after each cycle, and a total TON of 2150 could be achieved

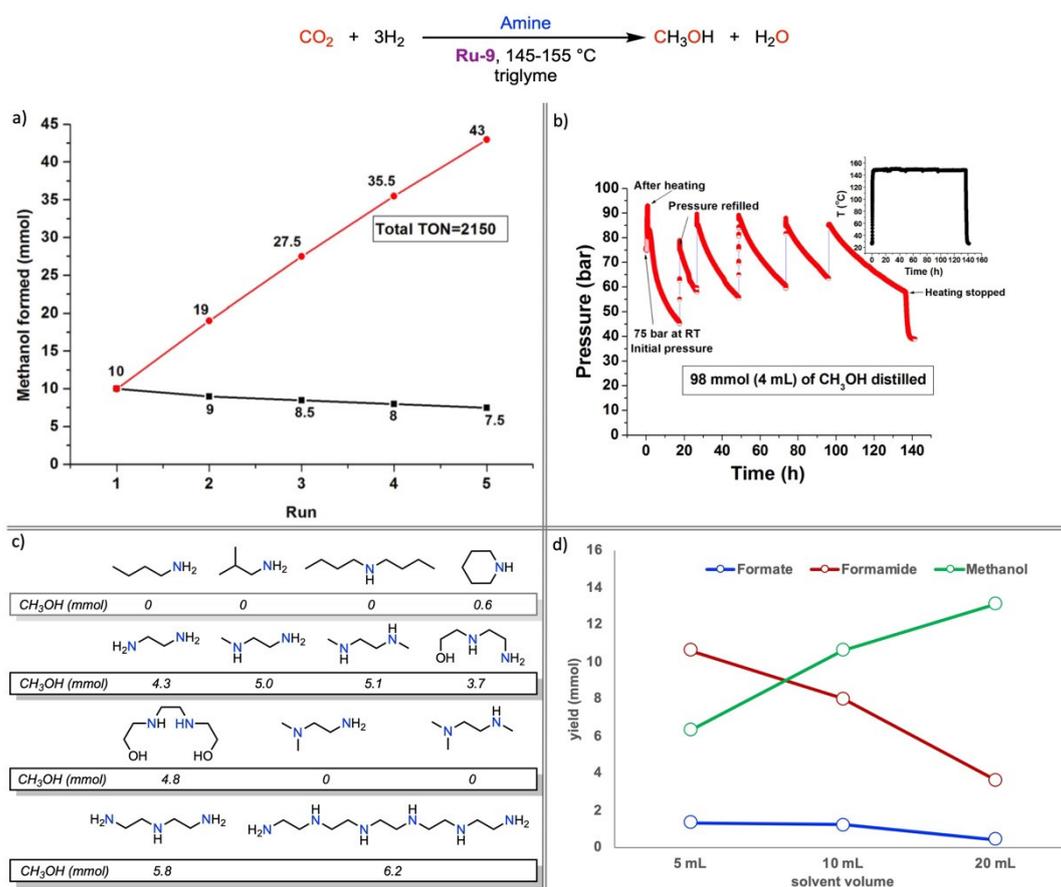


Figure 13. Amine-assisted CO₂ hydrogenation to methanol using Ru–Macho-BH (**Ru-9**). a) Recycling of reaction components with PEHA and CO₂:H₂ (1:9); b) Repeated pressure refill experiment with PEHA and CO₂:H₂ (1:3); c) Effect of amine molecular structures on methanol formation; and d) Effect of solvent volume on yields of methanol and intermediates with PEHA. Adapted from ref. [99] and ref. [125] with permission from the American Chemical Society.

after five hydrogenation cycles (Figure 13a). Similarly, a repeated pressure refill experiment led to an accumulation of 4 mL (98 mmol) of CH₃OH isolated via distillation (Figure 13b). Also, trace amounts of CO were detected in the unreacted gas mixture due to RWGS reaction and possible decomposition of formaldehyde, a transient intermediate species. Another key highlight of this study was the demonstration of methanol synthesis using air as the carbon source (discussed in Section 5.2).

Following up on their initial work, Prakash et al. reported a detailed and systematic investigation of the amine-assisted CO₂ hydrogenation to methanol.^[99] The effect of the amine's molecular structure was evaluated as amines play multiple key roles in the catalytic CO₂-to-methanol pathway (Figure 13c). Upon screening a library of amines with varied molecular structures, authors observed that monoamines afforded only trace methanol and mostly formate/formamide species, whereas diamines with primary and secondary amino groups were significantly active for methanol synthesis. Polyamines with higher N contents such as diethylenetriamine (DETA) or PEHA showed further enhancements. In contrast, presence of a tertiary amino group completely arrested the methanol formation. Additionally, the solvent volume had a notable effect, as the methanol yield doubled when the volume of triglyme was increased from 5 mL to 10 mL (Figure 13d). An opposite effect on the accumulation of formamide intermediate was observed, suggesting that increased amounts of solvent enhances the dissolution and hence, conversion of these intermediates. Finally, running the CO₂ hydrogenation for a prolonged time (10 days) led to a remarkable TON of 9900 using a combination of **Ru-9** as catalyst and PEHA as the amine at 145 °C. In a similar approach, Gademann demonstrated a CO₂-to-methanol system with pyrrolizidine-based diamine and **Ru-9** as the catalyst, although the selected amine demonstrated a modest promoting effect leading to a TON of 28 for methanol over 134 h (Figure 14).^[126]

In 2017, Everett and Wass studied a catalytic system with a series of Ru complexes bearing bidentate P–N ligands and relatively low-boiling amines (Figure 15).^[127] While the

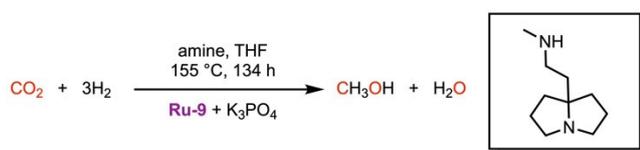


Figure 14. Pyrrolizidine-assisted CO₂ hydrogenation to methanol.

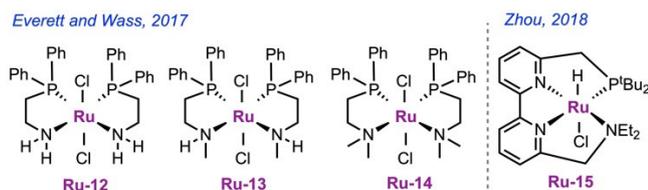


Figure 15. Ruthenium catalysts for amine-assisted CO₂ to methanol.

hydrogenation occurred under a relatively harsh temperature of 180 °C, the applied H₂ pressure was lower (30 bar). Increasing the steric bulk of the amine enhanced the rate and selectivity of the formamide-to-methanol step. Using diisopropylamine for instance, a much higher TON of 2300 was obtained as compared to that with dimethylamine (TON=110). Interestingly, modifying the N substituent on the catalyst had a profound effect on the methanol productivity. When the NH₂ moiety on the ligand (**Ru-12**) was mono-methylated (**Ru-13**), a higher TON of 4000 was achieved. However, further methylation (**Ru-14**) led to a complete loss of catalytic activity. This is strongly indicative of a metal–ligand cooperation involving the outer sphere. Finally, lowering the catalyst loading resulted in a notable TON of 8900 within 2 h.

Zhou and co-workers presented a novel tetradentate bipyridine based Ru catalyst (**Ru-15**) for the amine-assisted hydrogenation of CO₂ (Figure 15).^[128] Primarily, the catalysis was demonstrated separately involving two steps via formamides, similar to the prior study by Ding et al. Direct hydrogenation of CO₂ in the presence of excess H₂ (CO₂/H₂=2.5/50 bar) was also achieved using dimethylamine in 2-propanol solvent to realize a net CO₂ conversion of 84 % to CH₃OH with a TON of 2100.

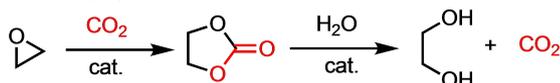
In the same direction, in 2019, Kayaki et al. carried out methanol synthesis in presence of high molecular weight polyethylenimines catalyzed by **Ru-9**.^[129] Increasing temperatures as well as decreasing the CO₂:H₂ ratio had an enhancing effect on methanol formation. Most linear and branched PEIs had comparable TONs for methanol (203–362) except for BPEI_{10K} (TON=102). The highlight of this report was the demonstration of the intended catalytic role of amines in the CO₂-to-methanol process as an amine turnover of 3 was achieved. A similar amine turnover was also achieved by Prakash and co-workers in a very recent study using PEHA over an extended period of 96 h.^[130]

4.1.4. Miscellaneous CO₂-to-Methanol Systems

4.1.4.1. Co-Production of Methanol and Glycol

In 2020, Kothandaraman and Heldebrant demonstrated a process for the co-production of methanol and glycol from CO₂, H₂ and an epoxide in an atom efficient approach converging the industrial OMEGA process and methanol synthesis under homogeneous hydrogenation conditions (Figure 16).^[131] At 140 °C in presence of an amine promoter (PEI₆₀₀), CO₂ (30 bar) and epoxide were reacted to form the corresponding cyclic carbonate. Next, the carbonates were hydrogenated with Ru–Macho (**Ru-10**) to co-produce methanol (yield=84 %) and glycol (yield > 99 %). Interestingly, the methanol formation was consistently lower as compared to the glycol, which could in part be explained by the detection of CO and CO₂ as unreacted species. However, the authors did not observe any formate or formamide intermediates. While attempts to carry out both processes in one step lowered the product yields, the sequential addition of CO₂ and H₂ to the reactor (containing amine, **Ru-10** and

Shell Omega process



Heldebrant, 2020

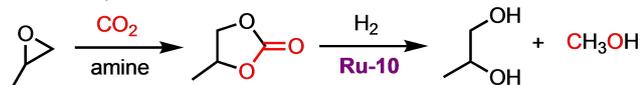


Figure 16. Co-production of glycol and methanol from epoxide and CO₂.

epoxide) successfully produced methanol and glycol in high yields. Overall, the proposed process avoided the formation of an equivalent amount of water, which would be produced in the conventional CO₂-to-methanol systems.

4.1.4.2. MOF-Encapsulated Molecular Catalysts

In a novel direction for CO₂-to-methanol processes, Byers, Tsung and co-workers disclosed in 2020 a highly recyclable MOF-encapsulated catalytic system (Figure 17).^[132] Inspired by the cascade pathway via formate ester previously reported by Sanford and Goldberg, authors identified two molecular catalysts: a Ru–PNP catalyst (**Ru-16**) for the CO₂

to formate step and a Ru–PNN complex (**Ru-11**) for the hydrogenation of formate ester. These complexes were encapsulated in a zirconium-based metal–organic framework, trademarked as UiO-66, selected based on a good fit of the catalyst into the pores of the MOF. Besides, the ZrO₂ nodes in the MOF acted as Lewis acid catalysts to promote the esterification step. Using trifluoroethanol (TFE) as the optimized alcohol additive, **Ru-16**@MOF and **Ru-11** catalysts, an impressive TON of 6600 was achieved for methanol within 16 h at a significantly mild temperature of 70 °C. Notably, the authors used a very low CO₂:H₂ ratio of about 1:12 in the feed gas at 40 bar. Upon interchanging the catalyst in the MOF, **Ru-11**@MOF with **Ru-16** gave a comparable TON of 5700. Using both catalysts in encapsulated form (**Ru-11**@MOF + **Ru-16**@MOF) or as co-encapsulated (**[Ru-11 + Ru-16]**@MOF) gave lower TONs of 3500 and 4300, respectively. However, when the catalytic components (**Ru-11**, **Ru-16** and UiO-66) were introduced together directly in solution without any prior encapsulation, no hydrogenation activity was observed. Authors believed that this could be a result of possible bimolecular decomposition pathways between catalysts **Ru-11** and **Ru-16** which establishes the importance of their mutual isolation in form of encapsulation. Overall, the catalytic setups demonstrated excellent recyclability over five cycles affording remarkable TONs of 17500 and 21000 for **Ru-11**@MOF + **Ru-16**@MOF and **[Ru-11 + Ru-16]**@MOF, respectively.

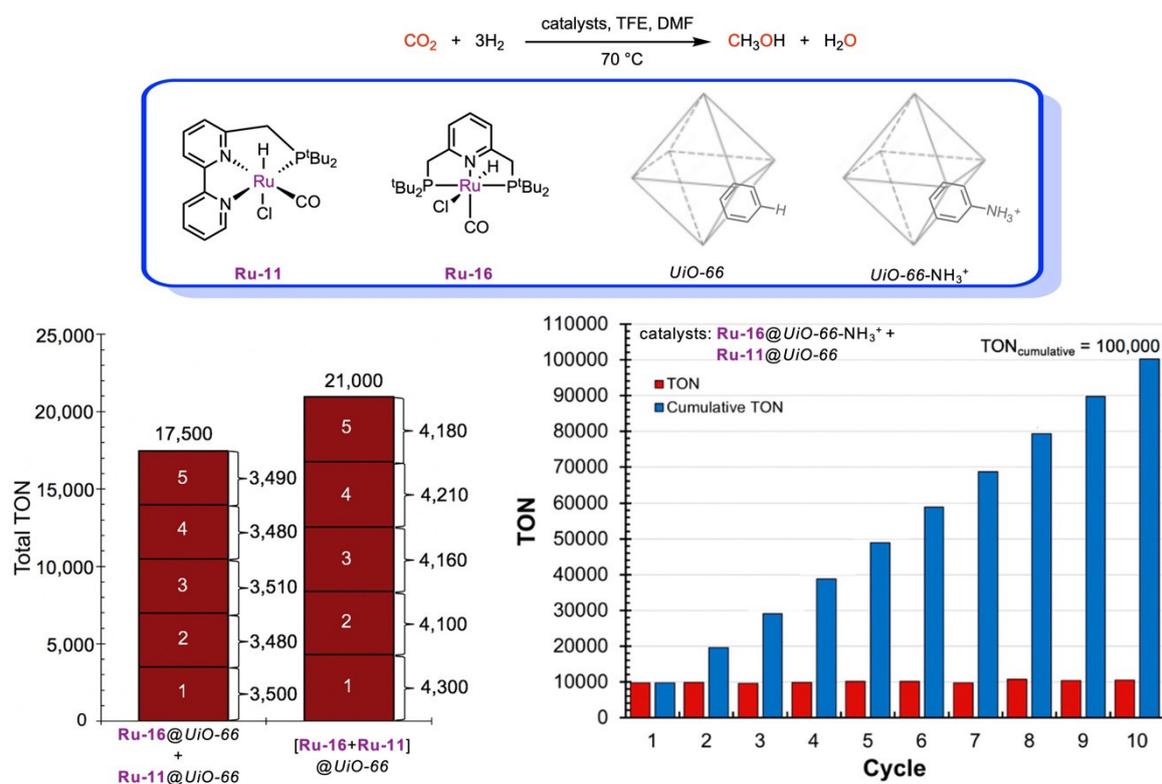


Figure 17. MOF-encapsulated catalysts for one-pot CO₂ to methanol. Adapted from ref. [132] and ref. [133] with permission from Elsevier Inc. and American Chemical Society.

The same group later studied the effect of systematically manipulating the functionality of the UiO-66 MOF and found that methanol productivity was significantly enhanced by a NH_3^+ functionality closely followed by NH_2 (Figure 17).^[133] Authors suggested that the ammonium group, when in close proximity to **Ru-16**, promoted the CO_2 to HCOOH reduction step by detaching the formate species from the metal center. Finally, recycling of the catalytic system (**[Ru-11]@MOF**) + (**[Ru-16]@MOF-NH₃⁺**) over ten runs led to a striking TON of 10^5 . *N,N*-dimethylformamide (DMF) was used as a solvent for hydrogenation and the authors confirmed via control experiments that DMF did not undergo hydrogenation to methanol under the reaction conditions.

4.1.4.3. Aqueous Phase Catalysis

CO_2 hydrogenation to methanol may proceed through formic acid that can undergo further hydrogenation without its derivatization to either formamides or formate ester. However, such a route has rarely been achieved in the domain of homogeneous catalysis. The field encompassing formic acid disproportionation under aqueous conditions to CH_3OH and CO_2 has been explored previously.^[134] In 2016, this concept was extended by Himeda, Laurency and co-workers to establish a novel CO_2 -to-methanol process using an iridium-based complex (**Ir-2**), which could catalyze both the hydrogenation (of CO_2) and disproportionation (of HCOOH) at a notably low temperature of 70°C (Figure 18).^[135] The transformation required highly acidic medium (2.5 M H_2SO_4) leading to a TON of about 8 for methanol after 50 h. With a wide scope for further improvement in the catalytic activities, the Ir-based system is the only viable neat aqueous process reported to date for CO_2 to methanol.

4.1.4.4. Solvent-Free Catalysis

Very recently, Onishi, Himeda and co-workers envisioned a gas–solid phase hydrogenation of CO_2 to methanol using molecular catalysts under solvent- and additive-free conditions (Figure 19).^[136] A series of dinuclear (**Ir-4/ortho**, **Ir-5/meta**, **Ir-6/para**) and trinuclear (**Ir-7**) complexes based on a monomeric picolinamide-based catalyst (**Ir-3**) were developed for this transformation. Among these catalysts, only the **Ir-5** and **Ir-7** catalysts were active for methanol synthesis

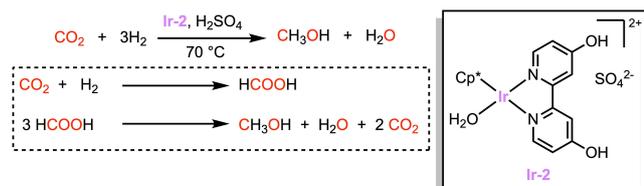


Figure 18. CO_2 to methanol via formic acid disproportionation.

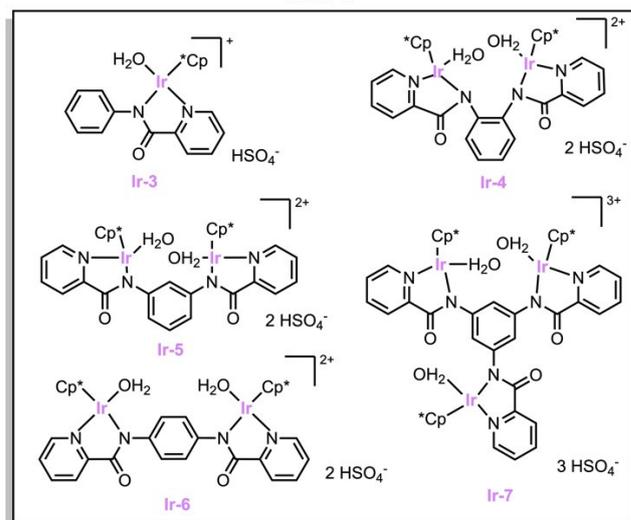
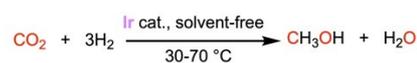


Figure 19. Multinuclear Ir complexes for gas–solid phase hydrogenation of CO_2 to methanol.

with similar TONs of 9 and 11, respectively, over 165 h using a 40 bar gas mixture of $\text{CO}_2:3\text{H}_2$. Further, the catalyst **Ir-5** was recycled over five hydrogenation cycles of 336 h to achieve a cumulative TON of 113. While the kinetics of the reaction were rather slow, it is worth noting that the system was active even at 30°C (TON=2). Authors proposed that the multinuclear template prevented the liberation of the formate species from the metal center, pushing towards a concerted reduction mechanism via multiple intramolecular hydride transfers on the catalyst.

4.1.4.5. Transfer Hydrogenation of CO_2 to Methanol

Catalytic transfer hydrogenation of CO_2 has been explored previously. The primary advantage of such systems is avoiding the use of high-pressure H_2 . Instead, abundant and renewable alcohols can act as the source of H_2 (H-source). However, these transformations have been mostly limited to afford formates from CO_2 . Further hydrogenation to methanol has been a major challenge in the absence of molecular hydrogen under pressure. In a rare example, Klankermayer and co-workers successfully demonstrated a transfer hydrogenation system for CO_2 -to-methanol in one step, using alcohols as the H-donor and Ru-catalysts with triphos ligand (**Ru-4**) and substituted equivalents (Figure 20).^[137] Although pressurized H_2 gas was avoided, the reactions were performed with a relatively high CO_2 pressure of 50 bar. Among the screened alcohols as H-source, ethanol performed most efficiently with TONs of 96–121 for CH_3OH at 160°C . Apart from CH_3OH , ethyl formate was obtained as a result of partial hydrogenation followed by condensation. H_2 was generated in situ by the dehydrogenation of ethanol to ethyl acetate. The reaction mixture, after transfer hydrogenation, was subjected to 80 bar H_2 to regenerate the H-

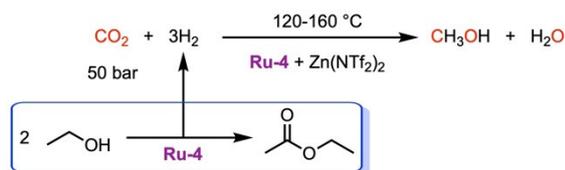


Figure 20. Transfer hydrogenation of CO₂ to methanol using ethanol as H-source.

source (ethanol) from its H-lean form (ethyl acetate). The catalyst showed comparable activity for a second cycle of methanol synthesis, indicating that the system could be promising in the development of a recyclable ethanol-based system for methanol synthesis.

4.1.4.6. CO₂-to-Methanol Using Solid-Supported Amines

As an alternative to liquid-based amine systems, solid-supported amines (SSAs) have also gained much interest as convenient and reusable matrix for varied purposes including CO₂ adsorption (Figure 21).^[138] Yet, their use as heterogeneous amine components in CO₂ hydrogenation systems remains limited. In a study by Prakash and co-workers in 2019,^[139] linear and branched polyethylenimines anchored (physically or covalently) on silica supports were screened for amine-assisted homogeneous CO₂ hydrogenation reactions with Ru-Macho-BH (**Ru-9**). Results indicated that most of the SSAs screened were able to assist in methanol formation with TONs up to 520. However, leaching of the amine moieties into the solvent still remains a major challenge, though chemically grafted SSAs suffered from much less degradation when compared to the physically impregnated adsorbents.

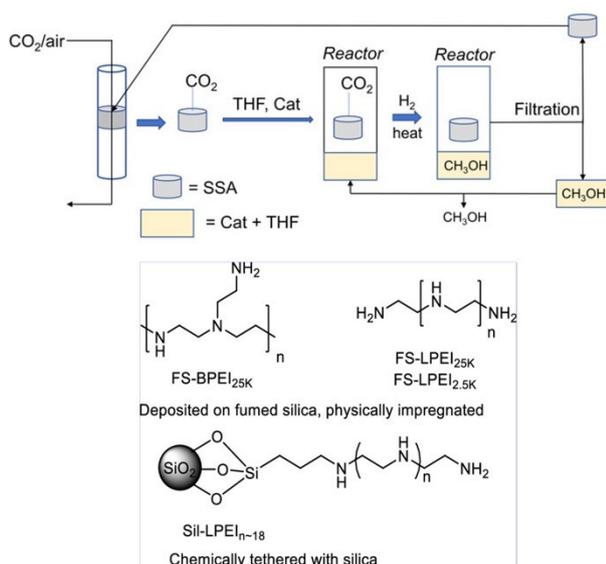


Figure 21. Solid supported amines for CO₂ hydrogenation to methanol. Reproduced from ref. [138] with permission from John Wiley and Sons.

4.2. Base Metal Based Catalytic Systems

4.2.1. Cobalt-Based Catalysts

In early 2017, Beller et al. developed the first example of a base metal based molecular catalyst for a homogeneous CO₂-to-methanol system (Figure 22).^[140] Extending on the previously studied ruthenium–triphos catalysts, this work involved Co(acac)₃ as the most active cobalt precursor along with the triphos ligand and HNTf₂ as the acid additive (**Co-1**). Interestingly, unlike the ruthenium-based analogues (**Ru-5**), the cobalt catalyst did not show a drop in activity when the reaction temperatures were reduced from 140 °C to 100 °C. The authors observed a marked induction period of 6–8 h during which only a trace amount of methanol was produced due to the slow formation of the active cationic cobalt–triphos species. In the presence of ethanol, a maximum TON of 78 for methanol was achieved with 20 bar of CO₂ and 70 bar of H₂ after 96 h at 100 °C.

Later, the same group was able to improve on their previously reported TONs by modifying the P-substituents on the tripodal phosphine–cobalt catalyst (**Co-2** to **Co-5**).^[141] When *o*-methyl- and *p*-methyl-substituted aryl groups (xylyl, tolyl, anisyl) were used in place of phenyl as in the parent triphos ligand, the TONs increased up to 125. Authors surmised that the effect could be due to a) increased electron density on the metal center accelerating the H₂ activation, and b) minimized Co-dimer formation. However, the *o*-tolyl substituent completely inhibited the catalytic activity indicating a strong steric effect. Additionally, other base metal based catalysts did not show any promising activity under the reported reaction conditions.

4.2.2. Manganese-Based Catalysts

The first manganese-based catalyst for CO₂-to-methanol conversion was developed in late 2017 by Prakash and co-workers (Figure 23).^[142] The Mn catalyst, decorated with a PNP^{iPr} ligand (**Mn-1**), was similar to the well-studied ruthenium analogues for (de)hydrogenation catalysis. In presence of morpholine as an amine additive, CO₂ reductively condensed to form *N*-formyl morpholine under 70 bar of 1:1 CO₂/H₂ mixture at 110 °C. Further hydrogenation to methanol was, however, ineffective. Rather, a sequential protocol similar to that developed by Ding et al. was found

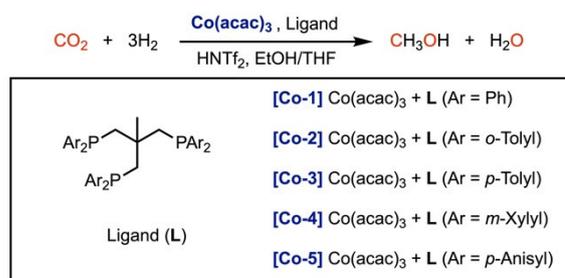


Figure 22. Cobalt-based catalysis with triphos-derived ligands.

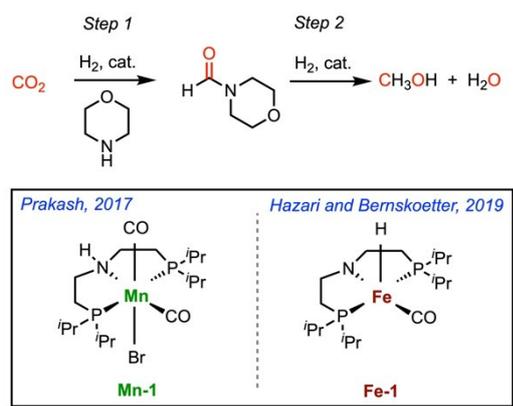


Figure 23. Sequential amine-assisted CO₂ to methanol using base metal catalysts.

productive wherein the in situ generated formamides were hydrogenated in the same pot containing the active catalyst in the presence of 80 bar H₂. At 150 °C, TONs of 840 and 36 were achieved for the formamide synthesis and methanol formation steps, respectively. Authors were able to detect a manganese–formate species as the resting state during the formylation step. The complex when isolated was active for hydrogenation of formamides to methanol only at high H₂ pressures. It was proposed that H₂ pressure enhances the conversion of the Mn–formate complex to form the catalytically active Mn–hydride species. On the other hand, the presence of CO₂ during the reaction favors the formation of the formate complex, which made a one-step CO₂-to-methanol system challenging under the reported reaction conditions.

Very recently, a potential route to the one-step CO₂-to-methanol reaction with a Mn catalyst was suggested by Leitner et al. (Figure 24).^[143] To unlock the Mn–formate resting state, the authors proposed that in place of an amine, a combination of alcohol and acid additives could detach the formate ligand via esterification and exchange it with the counter anion (from the acid additive). A Lewis acid, Ti(O^{*i*}Pr)₄ in the presence of ethanol, activated the Mn catalyst for a TON of 19 for methanol directly from CO₂ and H₂ in one step. Additionally, the authors noted that replacing the ^{*i*}Pr substituent on the catalyst (**Mn-1**) with

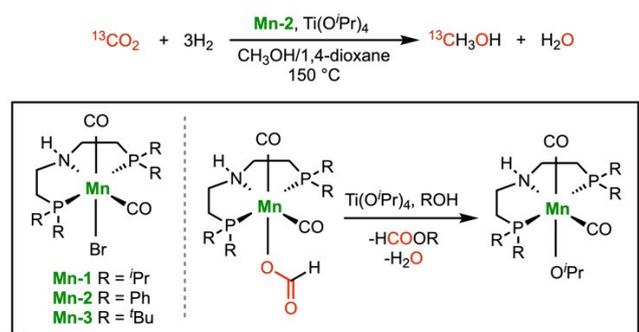


Figure 24. Mn-catalyzed direct hydrogenation of CO₂ to methanol.

phenyl (**Mn-2**) led to increased catalytic activity. Finally, using methanol as the alcohol, 5 bar of ¹³CO₂ and a significantly high pressure of H₂ (160 bar at rt), the reaction afforded a TON of 160 for methanol (¹³C-labeled).

4.2.3. Iron-Based Catalysts

Following the Mn–PNP catalyzed sequential hydrogenation system, Hazari, Bernskoetter et al. developed an Fe–PNP (**Fe-1**) based catalysis, proceeding via the formamide intermediate in the presence of an amine additive (Figure 23).^[144] Similar to the system developed by Prakash and co-workers previously, the catalyst was unable to turnover to produce methanol in the presence of CO₂ gas, owing to the formation of the Fe–formate resting state. However, in a two-step manner, a notable TON of 590 for methanol was achieved at 100 °C with CO₂:H₂ (250:1150 psi) and morpholine as a model amine. When the authors employed 3 Å molecular sieves during the formylation step and LiOTf and DBU in the methanol synthesis step, enhanced productivities were observed. Interestingly, the authors observed an increase in product yields for both steps by lowering the temperature from 120 to 100 °C.

Martins, Pombeiro et al. developed another example of iron-based homogeneous catalysts for hydrogenation of CO₂ to methanol (Figure 25).^[145] Distinct from the pincer or tripodal phosphine lead complexes documented for such transformations, this system involved a phosphine-free pyrazole-based Fe^{II}C–scorpionate complex, **Fe-2** [FeCl₂(κ³-HC(pz)₃)] (pz = pyrazol-1-yl). The hydrogenation reaction proceeded efficiently in the presence of an amine such as PEHA or tetramethylguanidine (TMG). However, an amine-free system was also demonstrated using acetonitrile solvent. Methanol was produced at a much lower temperature of 80 °C with a TON of 2335 at 75 bar of CO₂/3H₂ gas mixture. While the catalytic system presented a novel and highly promising CO₂-to-methanol process at low temperatures, there has yet to be any further development using this catalytic system, mostly due to the unusual and difficult to obtain Fe precursor (FeCl₂·2H₂O) needed to synthesize this complex.

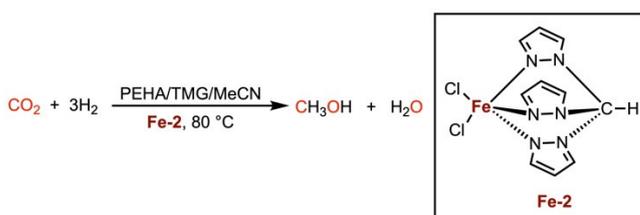


Figure 25. Fe–scorpionate catalysis for CO₂ to methanol.

5. Hydrogenation of CO₂ Derivatives to Methanol

5.1. Hydrogenation of Neutral Carbamic Acid Derivatives

In parallel to direct hydrogenation of CO₂ gas, reduction of various carbonic acid derivatives has also been developed over the years as indirect routes to access methanol from CO₂ (Figure 26). In 2011, Milstein and co-workers developed the first catalytic systems for efficient hydrogenation of organic carbonates, carbamates, and later, that of urea derivatives under relatively mild homogeneous conditions.^[146,147] At 110 °C, the hydrogenation of dimethyl carbonate proceeded effectively to afford TONs as high as 4400, whereas higher catalyst loadings of 1–2 mol% were needed to achieve high conversions for the relatively challenging carbamate (TON_{max} = 97) and urea derivatives (TON_{max} = 61). Since this report, this family of catalysts has contributed significantly to the further exploration of homogeneous hydrogenation chemistry, including direct CO₂-to-methanol systems, described in previous sections.

In a similar approach, Ding et al. demonstrated the hydrogenation of cyclic carbonates to methanol and corresponding diol in 2012.^[148] Using Ru–Macho catalysts (**Ru-9/Ru-10**), the hydrogenation of different cyclic carbonate substrates was achieved up to near quantitative yields and impressive TONs of up to 84000 for methanol were reported. Later, Leitner, Klankermayer and co-workers

used the Ru–triphos system (**Ru-4**) for methanol synthesis from organic carbonates and urea derivatives.^[149] Furthermore, the research groups of Cavallo, El-Sepelgy and Rueping,^[150] Leitner,^[151] Milstein,^[152,153] and Beller^[154] have independently reported different manganese- and cobalt-based catalytic systems as alternatives to the precious metal based catalysts, for the hydrogenation of carbonate, carbamate and urea derivatives with notable methanol yields (> 95 %) in the temperature range of 110–140 °C. Hydrogenation of oxazolidinones, another derivative of CO₂ was demonstrated by Milstein (refer to discussion in Section 4.1.3).^[155] Apart from the widely explored transformations using molecular H₂, Hong et al. reported the transfer hydrogenation of cyclic carbonates using **Ru-10** and 2-propanol (H-source) at 140 °C with up to 99 % methanol yield.^[156] It is worthwhile to note here that the reductive transformation of the organic derivatives of CO₂ is of significant conceptual and practical impact. While molecular catalysts were majorly instrumental in the discovery of these small molecule transformations, the catalytic systems further inspired the development of several hydrogenative depolymerization of polycarbonates, polyurethanes and polyurea derivatives to methanol and the co-monomers, demonstrating a green chemical process for waste upcycling.^[8, 148, 150, 157–160]

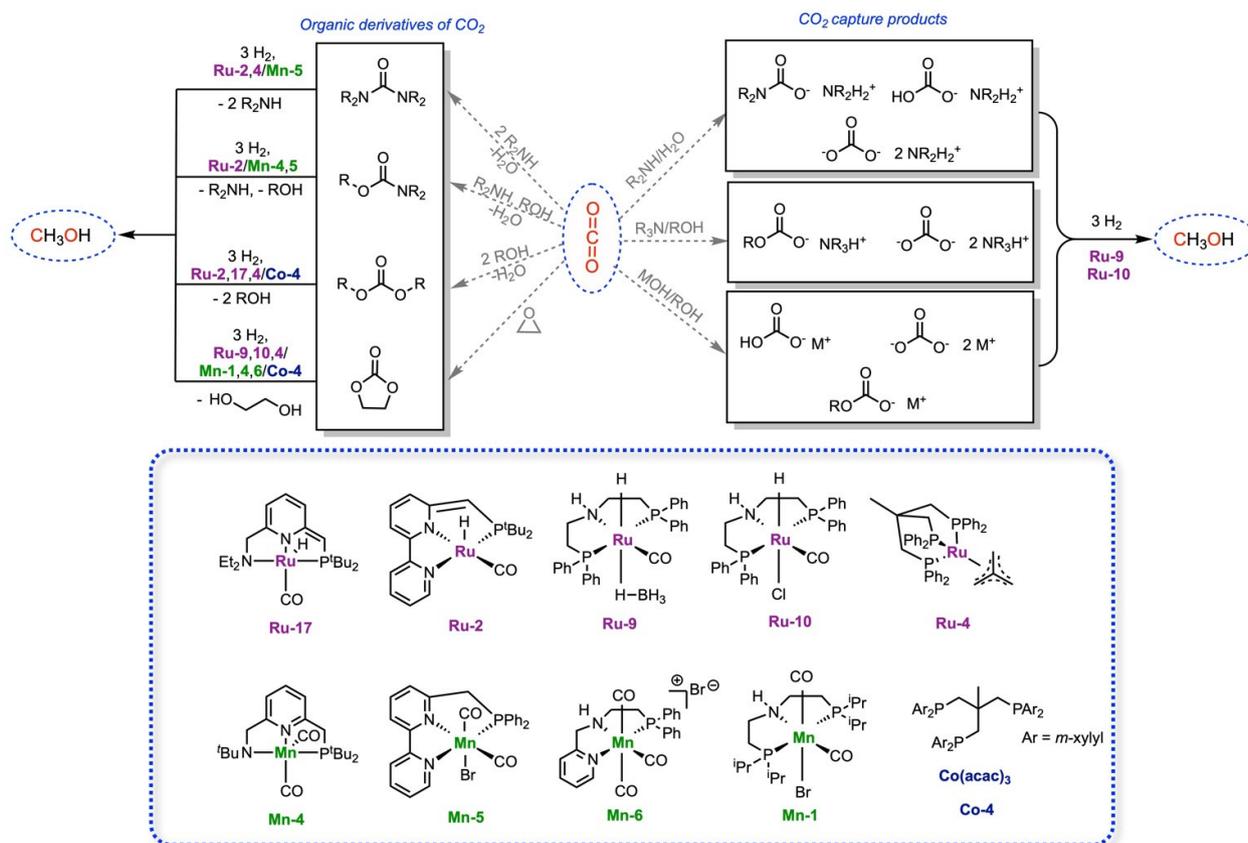


Figure 26. Indirect methanol synthesis from various derivatives and capture products of CO₂.

5.2. Hydrogenation of CO₂ Capture Products

In contrast to neutral organic derivatives of carbonic acids, CO₂ can also be derivatized as ionic molecules. This is achieved via the reaction between CO₂, a weak acid (pK_a of 6.37 in H₂O), with a basic moiety, most common being ammonia, amines, amino acids and metal hydroxides. These reactions are broadly referred to as CO₂ capture, and many of such capture processes are being practiced at industrial scales.^[161] When compared to the synthesis of organic carbamates, carbonates and urea derivatives from CO₂, which often require high temperatures or high CO₂ pressures (or both), the ionic salts of carbonic acids (carbamate/carbonate/bicarbonate) can be readily obtained at ambient pressures and temperatures by exposing CO₂ to a basic medium (Figure 27). Another major advantage is that many of these basic media are capable of chemically absorbing CO₂ from sources as dilute as ambient air (containing about 420 ppm CO₂).^[162] Direct air capture (DAC) is an emerging field over the past few years and is considered as a prime tool to counter growing anthropogenic CO₂ emissions.^[163–167]

In the context of chemical recycling of CO₂, a convergent system is desired wherein the CO₂ capture products are directly upgraded to products with added value, without any purification or separation (Figure 28).^[27,168,169] The highlight of such integrated carbon capture and utilization (CCU) processes is the elimination of the considerable energy and capital inputs for the desorption and compression steps

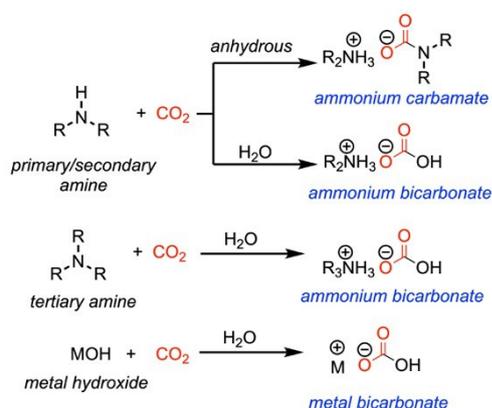


Figure 27. CO₂ capture with amines and metal hydroxides.

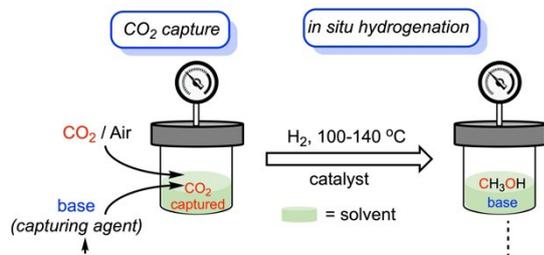


Figure 28. Integrated carbon capture and conversion to methanol. Based on ref. [179].

required to extract pure CO₂ in conventional processes.^[80] Hydrogenation of CO₂ capture products has been explored widely for the synthesis of formate salts. However, further hydrogenation to methanol is a significant challenge. To note, ICCU to methanol has been developed predominantly as solvent-based systems using homogeneous catalysts, in particular Ru–Macho catalysts (**Ru-9** and **Ru-10**), enabling the hydrogenation at relatively mild temperatures.^[80,98,125]

The initial work in the field of integrated capture and hydrogenation of methanol was inspired by the amine-assisted CO₂ hydrogenation systems. Amines are also attractive CO₂ capturing agents (Figure 27).^[170,171] Primary and secondary amine functionalities react with CO₂ to form the corresponding ammonium carbamates. In presence of water, they can also form ammonium bicarbonates and carbonates.^[172] In 2015, Sanford et al. demonstrated methanol synthesis from dimethylammonium dimethylcarbamate (obtained from the reaction between dimethyl amine and CO₂) using Ru–Macho–BH (**Ru-9**) and molecular H₂ as a novel approach to obtain methanol with 50 % yield and a TON of 306 at 155 °C.^[122] Later, Olah, Prakash and co-workers revealed an integrated process using polyamine solutions containing primary and secondary amino groups, into which CO₂ was captured to form the corresponding ammonium carbamates as well as ammonium bicarbonates in presence of water. These capture species were effectively hydrogenated in situ to afford high yields of methanol (up to 95 %). Further, using a biphasic water/2-MeTHF system, effective recycling of both the catalyst and the amine was demonstrated to achieve cumulative TONs of about 800.^[173] Methanol synthesis was also demonstrated by capturing CO₂ directly from air, which can be considered as a renewable carbon source.

In contrast to other forms of amine, tertiary amines capture CO₂ only in presence of water or a protic solvent (Figure 27). Prakash et al. recently developed a tertiary amine based integrated system wherein a series of tertiary amines and polyamines in the presence of an alcohol captured CO₂ to form ammonium alkyl carbonate and were further hydrogenated to methanol in the presence of H₂.^[174] While the amine–alcohol system was inefficient in capturing CO₂ from air, it was able to remove CO₂ from a simulated flue gas stream (10 % CO₂ in N₂) and the captured species were thereafter converted to methanol.

Instead of amines, CO₂ can also be captured with alkali metal hydroxide solution to form carbonates, bicarbonates, and alkyl carbonates.^[175–177] However, owing to the extremely low electrophilicity of these ions, their hydrogenation to methanol remains a major challenge.^[63,178] In a rare example, Prakash and co-workers recently studied a hydroxide-based integrated system in which CO₂ captured by alkali metal hydroxides was hydrogenated in situ to methanol in presence of ethylene glycol, which performed a dual role of solvent as well as an alcohol mediator.^[179] The hydrogenation was relatively fast with quantitative methanol yields within 20 h and the catalysis was found to be active at temperatures as low as 100 °C. It is important to note here that irrespective of the nature of the captured products (alkali- or ammonium-based), the corresponding formate

salts were found to be a key intermediate in the hydrogenation to methanol pathway.

6. Homogeneous Hydrogenation of CO to Methanol

Hydrogenation of CO over heterogeneous catalysts is one of the most developed processes to produce methanol.^[180] However, there has been relatively limited progress in the field of homogeneous catalysis. One of the primary challenges of using soluble metal salts or complexes is the high affinity of CO for metal centers as a ligand forming metal carbonyls and possibly inhibiting the catalysis.^[99] One of the first reports is by Bradley and co-workers from Exxon in 1979 using soluble $\text{Ru}(\text{acac})_3$ in THF, although at extremely high pressure (1300 bar) of CO and H_2 and a high temperature of 268 °C.^[181] The Ru precursor eventually coordinates with CO in solution to give different ruthenium carbonyl clusters, as detected by the authors. Shortly after, Dombek from Union Carbide Corp. demonstrated a similar approach directly using a Ru-carbonyl complex, $\text{Ru}_5(\text{CO})_{12}$, which afforded methanol under 240 bar of H_2 :CO.^[182] Later, a series of studies including those by the groups of Mahajan, Marchionna, Ohyama and Jiang independently presented the use of nickel salts in combination with alkoxide salts to activate CO and H_2 to methanol.^[183–186] While the operating conditions of 100–120 °C and 20–40 bar were significantly milder than in the preceding reports, the addition or in situ formation of highly toxic and flammable Ni carbonyl complexes posed a significant limitation. Alternatively, Cu acetate salts were employed by Li and Jens to catalyze the hydrogenation of CO to methanol, albeit in the presence of stoichiometric alkali metal hydride reagents.^[187,188]

Lately, there has been a resurgence in low-temperature CO-to-methanol studies, significantly aided by the development of robust homogeneous catalysts for the similar CO_2 -to-methanol routes (Figure 29). To note, CO is also an

intermediate in CO_2 hydrogenation and often detected in trace quantities in the homogeneous CO_2 hydrogenation systems. With this background, Prakash et al. utilized the amine-assisted route to access CH_3OH from CO.^[189] Using a high-boiling amine diethylenetriamine (DETA), the reaction proceeded at 140–145 °C in two steps: 1) K_3PO_4 -catalyzed anchoring of CO onto the amine as formamide; and 2) hydrogenation of formamides to CH_3OH in the presence of H_2 and Ru-PNP catalyst (**Ru-9/Ru-10**). The reaction steps were efficiently demonstrated as a two-step sequential process as well as a one-pot direct process in a toluene/ethanol solvent system. Using a CO: H_2 mix (10:70 bar) and Ru-Macho-BH (**Ru-9**), a TON of 539 for methanol was achieved over 168 h.

Shortly after, Beller, Checinski and co-workers reported a similar methanol synthesis system using Mn-PNP catalyst (**Mn-1**), K_3PO_4 and a N-promoter.^[190] Among the N-promoters screened, pyrrole-based N-heterocycles were found to be the most promising with TONs of 546 (indole), 3170 (Scatole) and 2550 (pyrrole). The catalytic nature of the amines was also highlighted in the report. While the reaction pathway proceeded via N-formyl intermediates, authors also observed the formation of methyl formate suggesting autocatalysis by the methanol product. In 2021, Leitner et al. also presented a Mn-PNP (**Mn-1**) catalyzed system via an alternate alcohol-assisted pathway.^[191] Interestingly, using ethanol under the reaction conditions of CO: H_2 (5:50 bar) at 150 °C, authors observed similar activities with **Ru-9**, **Ru-10** and **Mn-1** catalysts, although the P-substituents in the PNP ligands were not identical. High TONs of >4000 for methanol were achieved upon condition optimizations. Finally, the reaction was also demonstrated as a potential “autocatalytic” system using methanol as the solvent and ^{13}C -labeled CO.

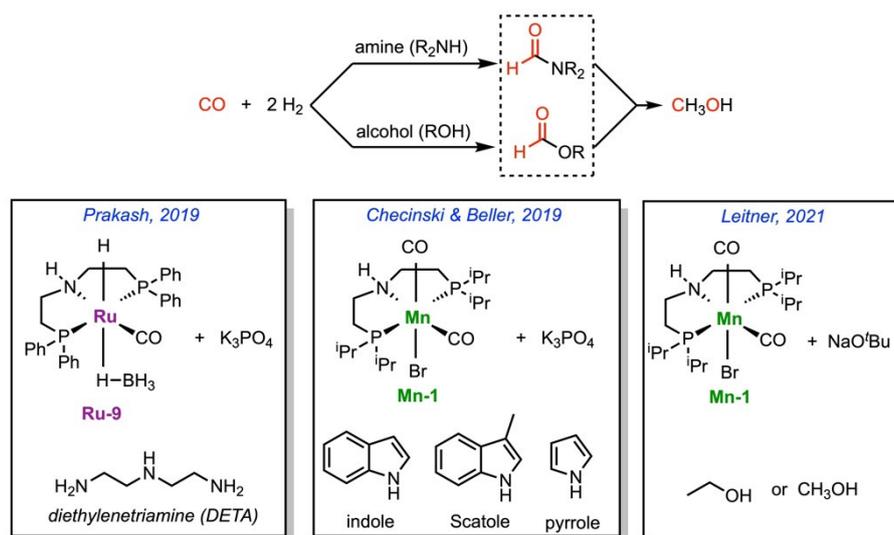


Figure 29. Homogeneous catalytic systems for hydrogenation of CO to methanol.

7. Mechanistic Insights into the Catalysis

7.1. Catalysts with Bifunctional PN(H)P Pincer Ligands

As shown in the previous sections, molecular catalysts with tridentate pincer ligands having a non-innocent -NH moiety (Noyori-type catalysts) have been employed extensively for the transformation of CO₂ as well as its derivatives to

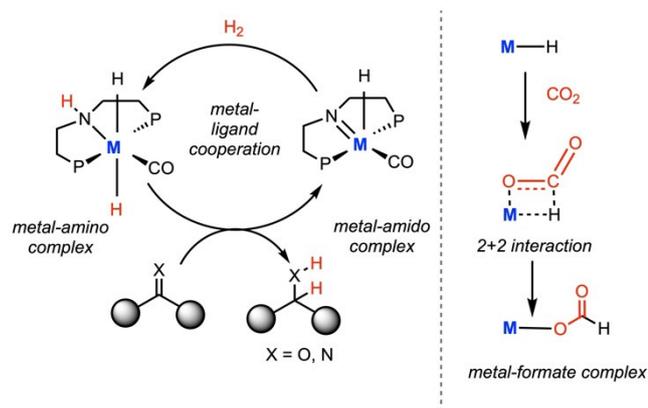


Figure 30. Modes of bond activation by metal-PN(H)P complexes.

methanol. Broadly, two modes of bond activation have been proposed for this group of catalysts.^[73] First, they can operate through an amino/amido-based metal–ligand cooperation (MLC) for heterolytic H₂ activation and hydride/proton transfer to an acceptor molecule (Figure 30). This is the primary catalytic pathway assigned to addition of H₂ across a carbonyl bond for reduction of CO₂-derived molecules including carbamate, urea, carbonate, formate, formamide, formaldehyde. In addition to that, direct activation of CO₂ is also possible via a proposed inner-sphere mechanism involving insertion of CO₂ to a metal–hydride (M–H) bond as a “2+2 interaction”, resulting in a metal–formate complex.

Based on a series of control experiments and trapping of catalytic species, a catalytic cycle was proposed by Prakash et al. (Figure 31),^[99] wherein: 1) the formation of Ru–dihydride via H₂ cleavage is followed by the insertion of CO₂ to generate Ru–formate species; 2) the formate is detached from the metal by an amine as the corresponding ammonium formate and further condensed to formamides; 3) formamide is hydrogenated to hemiaminal via a reversible amino–amido cycle based on a MLC mechanism; and 4) hemiaminal dissociates to formaldehyde (HCHO), which is reduced to methanol by another amino–amido cycle. As a side reaction, a small amount of HCHO decomposes to

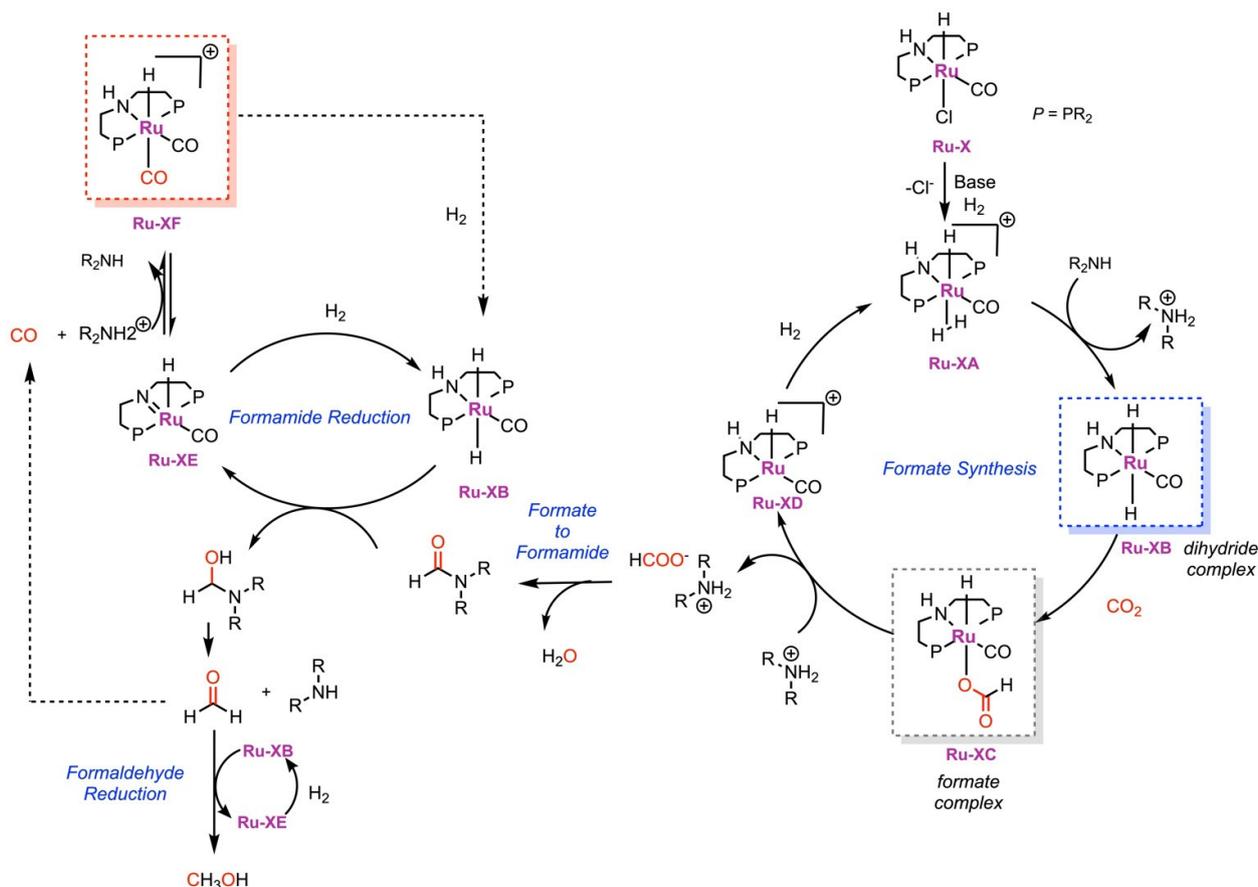


Figure 31. Proposed catalytic route with Ru–PN(H)P catalysts for amine-assisted CO₂ hydrogenation to methanol. Adapted from ref. [179] with permission from the American Chemical Society.

produce CO. The role of the amine additive was also found to be crucial in the catalysis. In addition to increasing availability of CO₂ in solution, amine assists in cleaving the metal–formate bond, a key step to move the catalyst from the resting state. In the absence of an amine, the hydrogenation of CO₂ is completely arrested, even to formate. Moreover, amine with an -NH proton is required to afford a formamide, which is necessary for methanol formation.

Among the PN(H)P catalysts, the Macho type **Ru-9** and **Ru-10** have been found to be most effective in the hydrogenation of CO₂ and derived molecules to methanol. Consequently, Prakash et al. carried out an in-depth investigation to gain insights into the catalysis of the amine-assisted CO₂ hydrogenation (Figure 32). First, the effect of varying the ligand functionalities in the catalyst was studied.

Replacing the CO spectator ligand by an N-heterocyclic carbene moiety resulted in comparable activities. In contrast, as the P-substituents were swapped from Ph (phenyl) to ^tPr (isopropyl), Cy (cyclohexyl) and ^tBu (*tert*-butyl), the CO₂ hydrogenation reaction produced only marginal amounts of methanol. This trend in catalyst activity could be attributed to the in situ formation of deactivating Ru-biscarbonyl complexes during the reaction, which were detected and characterized by the authors. The biscarbonyl complex could be converted to the active dihydride species, the rate of which indirectly correlated to the nature of the P-substituents. In case of electron-rich phosphines (^tPr, Cy, ^tBu), the electron density on the metal center was enhanced, which further strengthened the back-bonding between the axial CO and metal. Consequently, the rate of reversal of

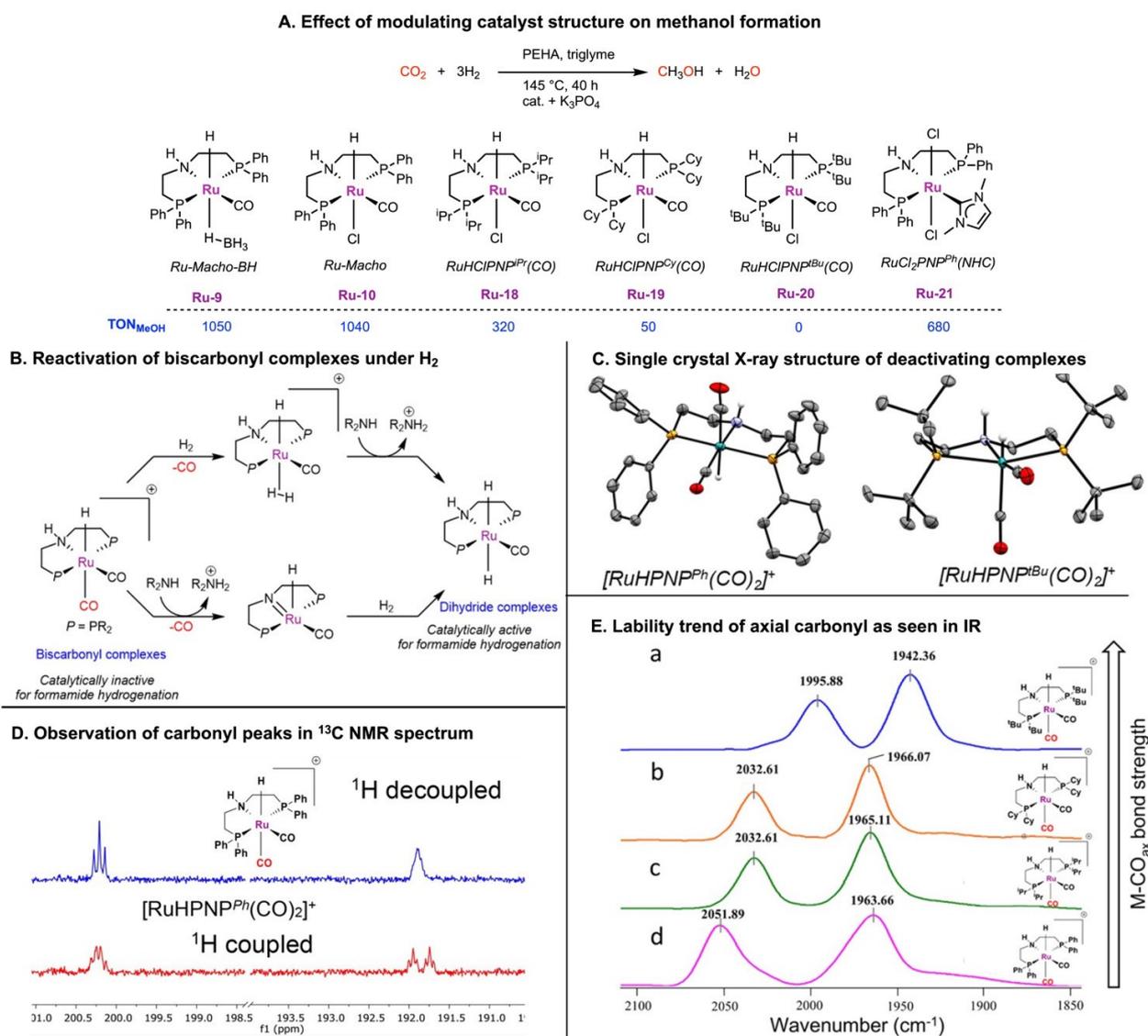


Figure 32. Mechanistic insights into the role of catalyst molecular structure on methanol formation, B) Reactivation of biscarbonyl complexes under H₂, C) Single crystal X-ray structure of deactivating complexes, D) Observation of carbonyl peaks in ¹³C NMR spectrum, E) Lability trend of axial carbonyl as seen in IR. Adapted from ref. [80] and ref. [99] with permission from the American Chemical Society.

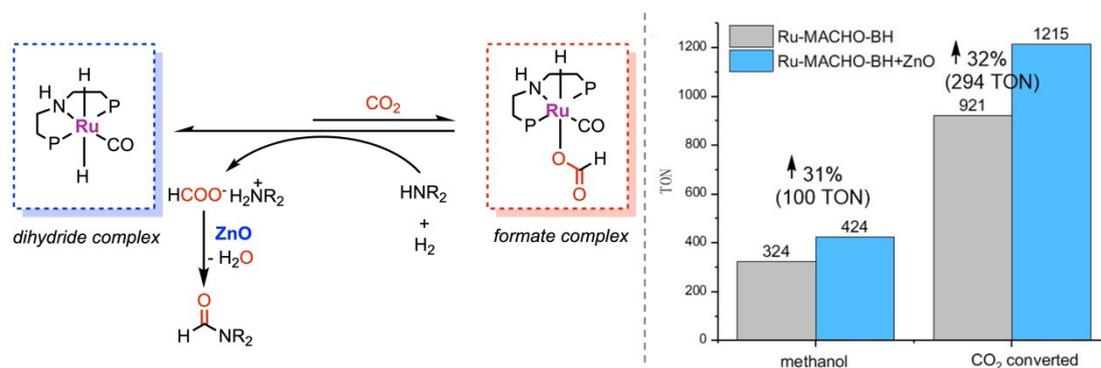


Figure 33. Addition of heterogeneous Lewis acid (ZnO) to enhance CO₂ hydrogenation to methanol. Adapted from ref. [192] with permission from the American Chemical Society.

the Ru–carbonyl species was lower. On the other hand, phenyl as the P-substituent enhances the lability of the CO ligand and hence the reversibility to the catalytically active dihydride species. Hence, Ru-Macho-BH (**Ru-9**) and Ru-Macho (**Ru-10**) were the most active catalysts for one-step hydrogenation of CO₂ to CH₃OH.

In order to suppress the formation of dormant metal–formate complexes, Bai, Sels et al. suggested the addition of a Lewis acid co-catalyst to accelerate the formate-to-formamide step and increase the amount of the active metal–dihydride species.^[192] Among various Lewis acid promoters, ZnO was found to enhance both CO₂ conversion and methanol yields by additional TONs of about 300 and 100, respectively (Figure 33). Operando IR studies showed that the formation of Ru–formate complex gradually disappeared upon addition of ZnO. Similarly, recent efforts on investigating the catalytic species of these PNP complexes and their possible degradation as well as further stabilization have been performed by several groups, including those by Schaub, Keith and Chianese.^[193–195]

There has also been some progress on the front of computational modeling of the catalytic pathways.^[196] Pathak and co-workers presented several DFT studies supporting the previously proposed reaction pathways for morpholine-assisted CO₂ to methanol.^[197,198] Authors highlighted the high exergonicity of the N-formylation step (−10.4 kcal mol^{−1} for morpholine), which enhances the overall reactivity. Two parallel pathways were modeled for formamide to methanol, based on the priority in C=O and C–N bond hydrogenation, although both the routes afforded a comparable free energy barrier. The energy barrier for the CO₂-to-HCOOH step was found highest for Mn–PNP, followed by that of Fe and Ru. The energy for the hydride transfer also followed the same trend. However, the amide hydrogenation step was energetically similar for the different metal complexes. Further, Yang et al. performed calculations focusing on the role of N–H in the PN(H)P catalysts.^[199] Notably, the authors found the hydrogenation of the carbamic acids with corresponding amines to be more favorable than direct CO₂ insertion. Moreover, the proposed reaction sequences in the report departed significantly from the otherwise proposed mechanism. In particular, the N–H

functionality was suggested to be partly innocent in the hydrogenation sequence. This argument was also supported in a report by Gordon and co-workers suggesting an inner sphere mechanism, although it was shown for ketone hydrogenation.^[200]

7.2. Aromatized Metal–PNP Catalysts

One of the key classes of hydrogenation catalysts discussed in the previous sections includes metal–PNP or PNN complexes involving N-heterocycle-derived pincer ligands (Figure 34). Such catalysts operate via aromatization–dearomatization-based MLC.^[201] Heterolytic cleavage of H₂ occurs between the side arm C–H proton and the metal center to transform the enamide to the imine form reversibly and further activating an unsaturated bond. The N-heterocyclic backbone includes pyridine, bipyridine as well as acridine, providing added rigidity to the metal complex. The other ligand functionalities are different innocent ligands including phosphines and tertiary amines.^[73]

This broad group of catalysts was introduced by Milstein and co-workers for the hydrogenation of numerous CO₂-

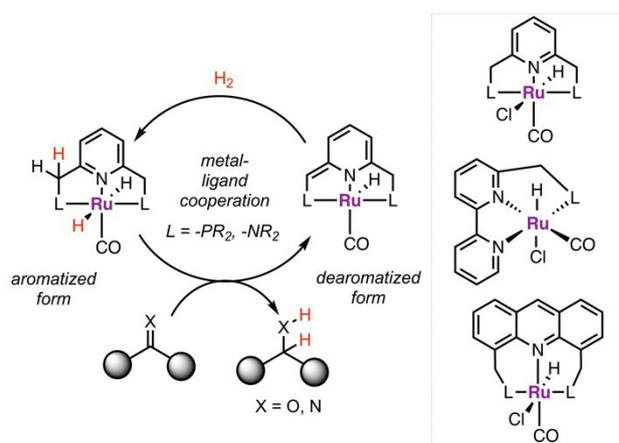


Figure 34. Modes of bond activation by aromatized Ru–PNP complexes.

derived carbonyl compounds, including organic carbamates, carbonates, urea and formates, as discussed in Section 5.1. Authors proposed a general catalytic cycle for the hydrogenation of these molecules (Figure 35a).^[146] First, the dearomatized complex activates H_2 and transforms into the aromatized dihydride form. Subsequently, the hydride is transferred to the carbonyl group of the carbonate/urea/carbamate substrate. This can occur directly via hydride attack on the carbonyl or by coordination of the carbonyl O to the metal center on the site vacated by the pyridyl arm. Next, one of the carbonyl substituents (alkoxy or amino group) leaves with one of the benzylic protons, and results in the dearomatized catalytic form bearing the formate/formamide ligand. Repetitions of a similar cycle lead to the formation of formaldehyde, and finally methanol while regenerating the pre-catalyst.

Apart from the carbamic acid and formic acid derivatives, these catalysts have been studied for direct CO_2 hydrogenation as well. The groups of Sanford^[79] and Pidko^[202] have independently investigated the activation of

CO_2 and H_2 using Milstein's pyridine-PNP and PNN catalysts under alkaline conditions, wherein the hydrogenation proceeded up to formate (Figure 35b).^[203] Later, Saouma et al. performed a detailed thermodynamic analysis of the catalytic process and its relation to the catalyst performance.^[204] Calculations showed that the Ru-formate resting state was favored by four orders of magnitude as compared to the active Ru-hydride form. To drive the hydrogenation forward, the authors used a sub-stoichiometric amount of a strong base such as $tBuOK$ or $LiDMC$ to produce methanol from dimethylammonium dimethylcarbamate, used as a CO_2 surrogate. A maximum turnover of 40 was achieved, and a catalyst deactivation pathway was suggested in presence of methanol and/or water. Among several computational studies relevant to this class of catalysts,^[205] Yang presented DFT calculations in support of the proposed mechanism for Ru-PN(Py)N-catalyzed dimethyl carbonate hydrogenation to methanol.^[206] The essential role of MLC with reversible gain/loss of aromaticity was also highlighted. In a similar study, Wang and co-

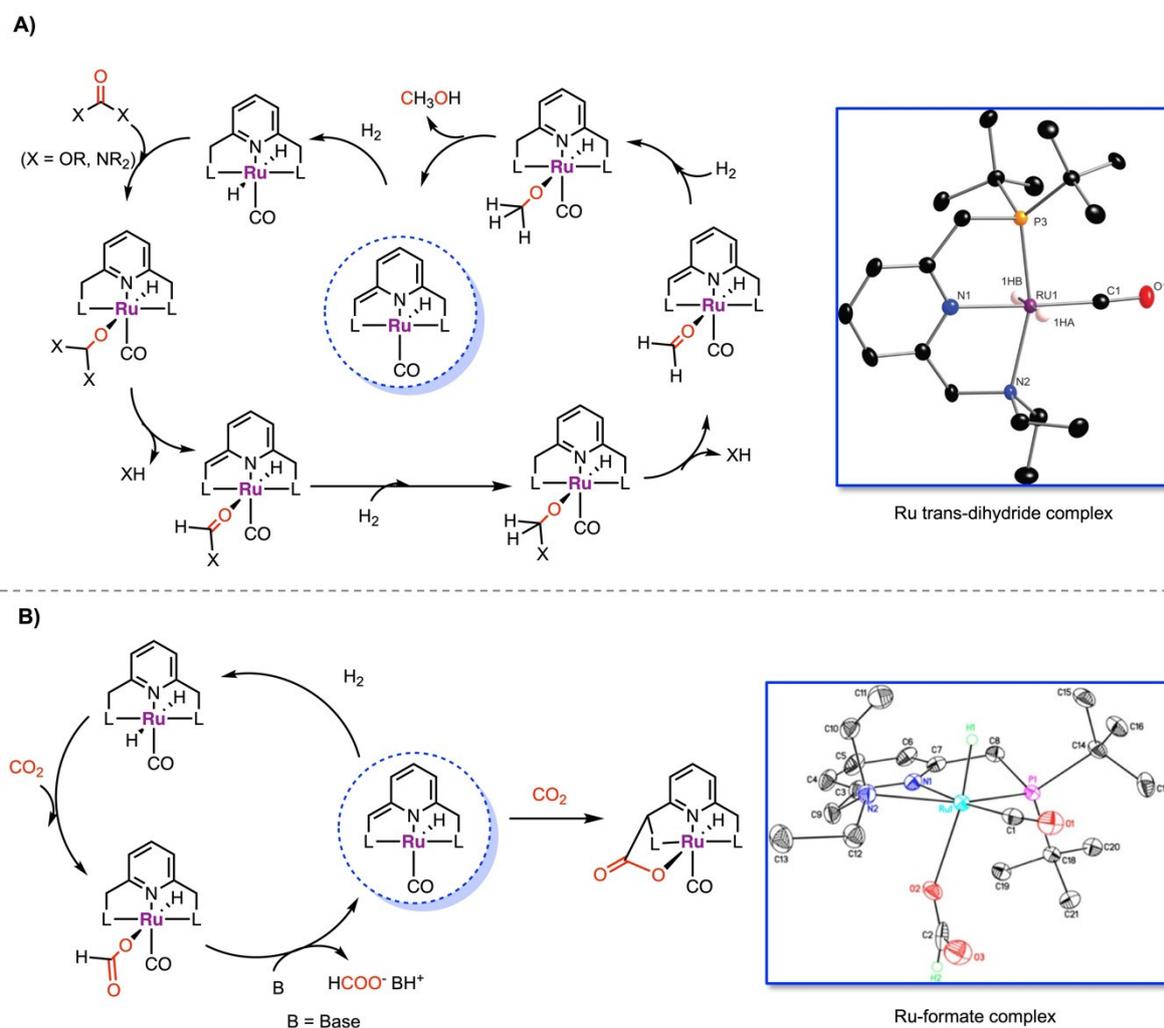


Figure 35. Catalytic cycle for aromatized Ru-PNP/PNN complexes for hydrogenation of A) carbamic acid derivatives and B) CO_2 . Adapted from ref. [146] and ref. [79] with permission from the Springer Nature and American Chemical Society.

workers noted that the hydrogenation route through carbonyl insertion into the Ru–H bond is energetically disfavored when comparing to a stepwise hydrogen-transfer route.^[207] Another pathway was suggested in the reports by Hasanayn et al. involving direct ion pair mediated metathesis.^[208,209] As per the proposed model, the reaction can proceed via a) hydride transfer from Ru–dihydride to dimethyl carbonate forming an ion pair of cationic metal complex and an anionic dimethyl orthoformate; b) rearrangement and coordination of a methoxy group to the metal followed by cleavage of the methoxy group from the carbonyl substrate to yield methyl formate and Ru–methoxy catalytic species.

7.3. Metal–Triphos and Related Catalysts

While the pincer-based metal catalysts discussed in Sections 7.1 and 7.2 have been exploited widely owing to their high activities in CO₂ hydrogenation reactions, these catalysts predominantly operate under neutral to alkaline conditions. In contrast, the triphos ligand based molecular catalytic systems developed by Leitner, Klankermayer and co-workers have been key in allowing CO₂ hydrogenation under neutral, and preferably, acidic conditions.^[118–120] The tridentate ligands in these catalysts are innocent and are not involved in MLC. Hence, these catalysts are monofunctional and H₂ activation and hydride transfer steps take place on the metal center through an inner sphere mechanism.

Leitner, Klankermayer et al. provided a comprehensive mechanistic investigation into the Ru–triphos-catalyzed CO₂-to-methanol system (Figure 36).^[119] The Ru–formate species with formate acting as a bidentate ligand was identified in solution and assigned to be the catalyst resting state. Since the formate complex could not be isolated in solid state, the analogous Ru–acetate complex was isolated which was able to catalyze the hydrogenation to produce methanol even in the absence of any acid or alcohol additive (TON=165). Hence, an additive-free pathway was achieved as an alternative to the route via formate ester, which proceeds via three stages; 1) formate/formic acid, followed by 2) hydroxymethanolate/formaldehyde and ultimately 3) methanolate/methanol species. These transformations were suggested to occur via multiple hydride transfer–protonolysis steps within the coordination sphere of a cationic Ru–triphos complex, enabled by the favorable facial coordination of the tripodal ligand. The proposed catalytic route and the hydride transfers were also supported by DFT calculations by the authors. Further, the barriers for proton transfer steps were significantly lowered in a protic solvent medium.

8. Status Quo

As described previously, the current production of methanol is almost exclusively based on syngas conversion. Even so, there has been a paradigm shift over the past decade,

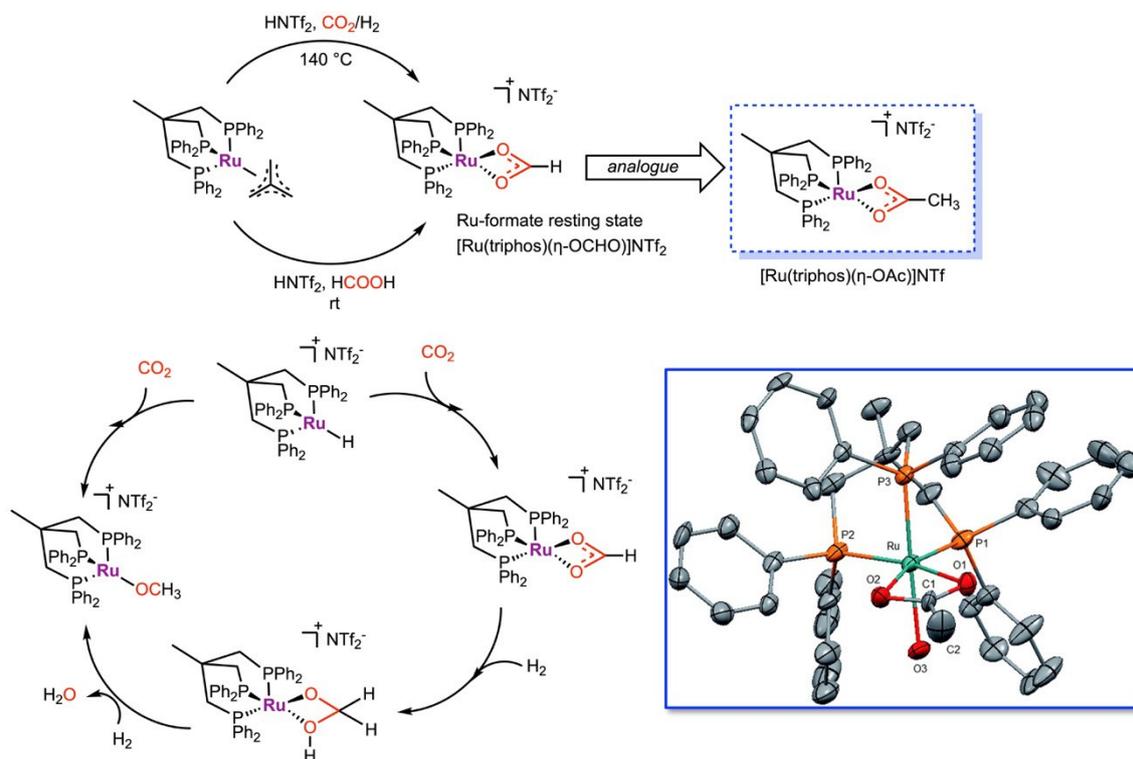


Figure 36. Mechanistic insights and catalytic cycle of Ru–triphos-based CO₂ to methanol. Adapted from ref. [119] with permission from the Royal Society of Chemistry.

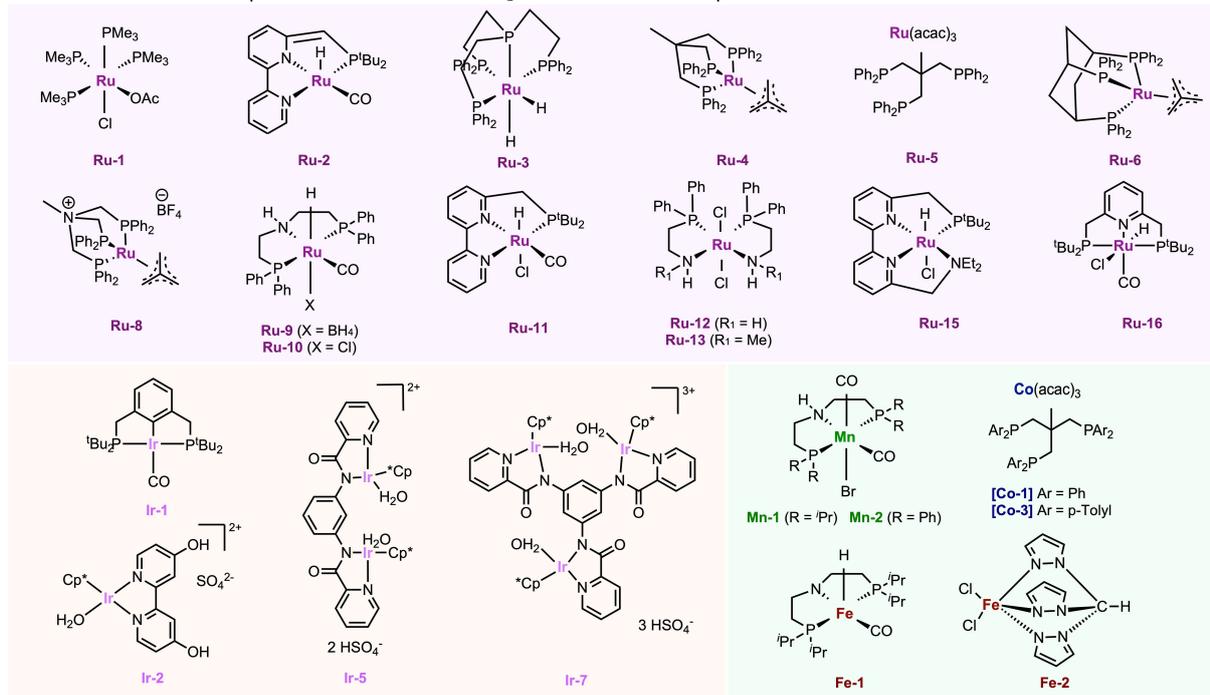
towards realizing CO₂-to-methanol processes at commercial scales.^[29] The first commercial CO₂-to-methanol plant was established in 2011, at the George Olah Renewable Methanol Plant in Svartsengi, Iceland by Carbon Recycling International (CRI).^[210] The plant holds an annual capacity of recycling 5500 Mt of CO₂ which is captured from the flue gases released by an adjacent geothermal powerplant. Parallely, the required H₂ is sourced through water electrolysis using local hydrothermal and geothermal energy sources. The renewable CO₂ and H₂ are subjected to direct hydrogenation to produce methanol, rather than converting them first to syngas via RWGS. The plant produces around 5 million liters of e-methanol per year, trademarked as Vulcanol. This brand of green methanol cuts CO₂ emissions by 90 % compared to gasoline or diesel, well to wheel. More recently, the Dalian Institute of Chemical Physics, China developed a demonstration plant for e-methanol with an annual capacity of 1000 tonnes. In addition, several commercial CO₂-to-methanol plants are being developed across the globe with capacities ranging from 8000 to 180 000 tonnes per year, with a projection that e-methanol, especially obtained via CO₂ recycling, can cater to a substantial fraction of the methanol demand in the foreseeable future.^[29]

Meanwhile, over the past decade, scientific research in homogeneous catalysis with the goal of developing low-temperature processes for methanol synthesis has progressed significantly (Table 1). Alcohol-assisted pathways operating under mild acidic to neutral conditions and enabled by the cooperation of three catalysts have been identified. The modest TONs achieved in the first report (TON = 21) for this route have been remarkably improved to TONs of up to 100 000 when the catalysts were caged inside MOFs.^[116, 133] Similarly, single-molecular catalysts decorated with tripodal ligands have not only demonstrated their ability to catalyze alcohol-assisted methanol synthesis, but have also shown the possibility of an additive-free hydrogenation pathway. In addition, reports of this family of catalysts support a fundamental lesson: rational tweaking of the core ligand framework has considerable potential in enhancing catalytic activity. Overall, continued developments in catalysis for CO₂ hydrogenation under acidic conditions are crucial in the pursuit of a feasible low-temperature CO₂-to-methanol process. On the other hand, methanol synthesis under alkaline conditions, especially with amines, has gained momentum. To date, these transformations have been mostly enabled by a handful of Ru-PNP and Ru-PNN catalysts. While high TONs and efficiencies have proven the power of these catalysts, the development of catalysts for hydrogenation under highly alkaline conditions has been challenging. Furthermore, in the library of 30+ catalysts developed for CO₂ to methanol, examples of earth-abundant base metal catalysts remain extremely limited. Especially, development of Fe-based catalysts is worthwhile, as iron is significantly more abundant when compared to Mn and Co. Alongside, a highly active ligand framework will be required to achieve activities comparable to existing Ru-based catalysts. In-depth mechanistic inves-

tigations are also required in parallel to catalyst design for a broader understanding of this space.

Reasonably, the industrial methanol synthesis continues to utilize heterogeneous catalysts, which have gained much more maturity as compared to the homogeneous catalysts. To date, production of heterogeneous catalysts is less capital- and labor-intensive. Additionally, they offer simplified operating conditions in gas-solid phase under flow conditions, and ease of separation and recycling, making them more appealing to industrial setups. On the other hand, the field of molecular catalysis for methanol synthesis is still in an early stage of development. This provides a wide scope for identifying limitations in the present systems and proposing possible improvements and directions.

- (1) A majority of the molecular catalysts developed for CO₂-to-methanol are cost intensive as well as challenging to prepare and handle at an industrial scale when compared to heterogeneous catalysts. Along with the metal component, which is often a precious metal like Ru or Ir, the exotic and specialized ligands contribute substantially to the cost of these catalysts (Table 2). Hence, it is equally important to design ligands which are easy to synthesize, scalable, and stable to light, O₂ and water; as is to develop catalysts out of earth-abundant metals (such as iron, manganese, and cobalt). In this context, replacing the phosphine-based ligands with amine-based alternatives is a possible direction, especially given the fact that amines also facilitate CO₂ capture and conversion. Together, addressing these issues will potentially lead to the discovery of molecular catalysts which are efficient and sustainable as well as cost-effective and scalable.
- (2) The recycling ability of the catalysts plays a key role in process development as the life-cycle of the catalyst affect the cost of the overall process. Hence, studies focused on recycling, long term stability and understanding of possible deactivation pathways of the molecular catalysts are necessary.
- (3) While impressive TONs have been demonstrated using several catalysts, there is substantial opportunity to improve on the kinetics of the reactions and, hence, the TOFs. Similarly, in parallel to using TONs as a standard parameter to compare catalytic systems, it is also important to present the overall CO₂ conversions and methanol selectivities, which are often useful industrial standards.
- (4) A synergistic relationship between the realms of homogeneous and heterogeneous catalysis has been evolving over the past several years. Some properties of a heterogeneous catalyst can be mimicked using molecular catalysis via, for instance, tethering of the catalyst on a solid support or a fluidized bed, encapsulation of the catalyst inside insoluble frameworks, or design of polymeric ligand structures around the metal center.^[212-214] It is important that the active sites of the catalyst must remain unperturbed. The MOF-encapsulated catalysis developed by Tsung, Byers and co-workers for CO₂ hydrogenation provides a promising example in this direction.^[132] Conversely, lessons from

Table 1: Selected examples of CO₂-to-methanol processes with molecular catalysts.

Entry	Catalyst	CO ₂ :H ₂ [bar] ^[a]	T [°C] (time)	Solvent/additive	TON/yield	Ref.
<i>Precious metal catalysts (Ru, Ir)</i>						
1	Ru-1 + Ru-2 + Sc(Otf) ₃	10:30	75 (1 h)– 135 (15 h)	methanol, dioxane	21	[116]
2	Ru-3 + Ir-2 + Sc(Otf) ₃	10:80	155 (40 h)	ethanol	428	[117]
3	Ru-4 / Ru-5 + CH ₃ SO ₃ H/HNTf ₂	20:60	140 (24 h)	ethanol, THF	221	[118]
4	Ru-4 + HNTf ₂	20:60	140 (48 h)	THF	603	[119]
5	Ru-6 + Al(Otf) ₃	30:90	120 (20 h)	ethanol/THF	2148	[120]
6	Ru-8 + Al(Otf) ₃	15:45 ^[b]	90 (16 h)	ethanol, THF	240	[121]
7	Ru-9 + K ₃ PO ₄	2.5:50	95 (18 h)– 155 (36 h)	NHMe ₂ , THF	550	[122]
8	Ru-10 + KO ^t Bu	Step 1: 35:35, Step 2: n/a:50	Step 1: 120 (40 h), Step 2: 160 (1 h)	morpholine, THF	36 %	[123]
9	Step 1: Cs ₂ CO ₃ , Step 2: Ru-11 + KO ^t Bu	Step 1: 1:n/a, Step 2: n/a:60	Step 1: 150 (24 h), Step 2: 135 (72 h)	valinol, DMSO	45 %	[124]
10	Ru-9	19:57	145 (244 h)	PEHA, triglyme	9900	[125], [99]
11	Ru-12 / Ru-13 + NaOEt	10:30	180 (2 h)	ⁱ Pr ₂ NH, toluene	8900	[127]
12	Ru-15	2.5:50	90 (48 h)– 170 (72 h)	Me ₂ NH, ⁱ PrOH	2100	[128]
13	Ru-9	1:3 (80)	150 (20 h)	B-PEI _{10k} , toluene	362	[129]
14	Ru-10	Step 1: 20:n/a, Step 2: n/a:50	140 (16 h + 16 h)	B-PEI ₆₀₀ , PO, THF	82 %	[131]
15	Ru-11 @MOF + Ru-16 @MOF-NH ₃ ⁺	3:37	70 (16 h)	trifluoroethanol, M.S. (3 Å)	19000	[132], [133]
16	Ir-2	20:60	70 (50 h)	water, H ₂ SO ₄	≈ 8	[134]
17	Ir-5 / Ir-7	10:30	60 (336 h)	n/a	23	[136]
18	Ru-4 + Zn(NTf ₂) ₂	50:n/a	160 (22 h)	ethanol	96	[137]
19	Ru-9	20:60	145 (40 h)	THF, silica-supported LPEI _{25k}	520	[139]
<i>Base metal catalysts (Co, Mn, Fe)</i>						
20	Co-1 + HNTf ₂	20:70	100 (96 h)	THF, ethanol	78	[140]
21	Co-3 + HNTf ₂	20:70	100 (24 h)	THF, ethanol	125	[141]

Table 1: (Continued)

Entry	Catalyst	CO ₂ :H ₂ [bar] ^[a]	T [°C] (time)	Solvent/additive	TON/yield	Ref.
22	Mn-1 + KO ^t Bu	Step 1: 30:30, Step 2: n/a:80	Step 1: 110 (36 h), Step 2: 150 (36 h)	THF, morpholine	36	[142]
23	Mn-2 + Ti(O ⁱ Pr) ₄	5:160	150 (68 h)	methanol, 1,4-dioxane	160	[143]
24	Fe-1	Step 1: 17:78, Step 2: n/a:78	Step 1: 100(16 h), Step 2: 100 (16 h)	THF, morpholine	590	[144]
25	Fe-2 + K ₃ PO ₄	19:57	80 (24 h)	PEHA	2335	[145]

[a] Pressures at room temperature. [b] Pressures at reaction temperature. PEHA = pentaethylenehexamine, B-PEI = branched polyethylenimine, PO = propylene oxide.

Table 2: Selling prices of selected molecular catalysts and ligands.^[a]

Entry	Catalyst	Catalyst price [USD]	Ligand price [USD]	Ligand [wt. %]
1	Milstein's Ru-PNN (Ru-16)	99 (100 mg)	83 (100 mg)	66
2	Ru-Macho-BH (Ru-9)	53 (250 mg)	50 (500 mg)	75

[a] Prices in the US catalogue of Strem Chemicals.^[211]

homogeneous catalytic systems have aided developments in the field of heterogeneous catalysts. For example, the indirect CO₂-to-methanol systems demonstrated using molecular catalysts have been successfully translated with heterogeneous catalysts. Recent studies, independently by the groups of Heldebrant and Prakash, showed that amine- and alcohol-mediated processes can enable hydrogenation of CO₂ as well as its derivatives to methanol using the commercial Cu/ZnO/Al₂O₃ catalyst at much lower temperatures (140–200 °C) with up to 90% conversion, which is rarely accomplished under conventional heterogeneous setups.^[215–219] Hence, homogeneous catalysis has long-term value as a go-to tool to discover and test novel processes for methanol synthesis rapidly at small scales using easy-to-operate setups.

- (5) To date, all the homogeneous methanol synthesis investigations have been studied under batch conditions and at extremely small scales. While batch processes are practiced at industrial scale, continuous flow processes offer significant advantages for the massive production scale of methanol.^[38] Hence, engineering of flow systems using homogeneous catalysts geared towards a pilot demonstration is desired. One of the plausible ways is to opt for solvent-free conditions as demonstrated by the preliminary report by Onishi and Himeda by converting a mononuclear molecular catalyst to its multinuclear forms.^[136] Alternatively, liquid-phase methanol synthesis (LPMEOH) processes can also be operated as a flow process. In fact, such a process was developed by the Air Products and Chemicals in association with the US Department of Energy in a demonstration plant.^[220] Overall, such demonstrations will require collaborative efforts which include system modeling, reactor engineering, process intensification,

heat and mass transport analysis, techno-economic and life-cycle analysis, among others.

- (6) Although methanol synthesis is exothermic per se, the overall processes are significantly energy-intensive to operate. First, energy is required to recycle CO₂ from waste sources, and for the production of H₂. Next, circulation of these gases under high pressure and heating the reactor to high temperatures require energy inputs. The required energy comes at a considerable cost, both in terms of capital as well as carbon footprint. Hence, there is a paradigm shift towards use of low-carbon and renewable energy for such processes and for the production of H₂ via water electrolysis. Nevertheless, enhancing energy efficiency of the process is a long-term goal in the field of methanol synthesis.

9. Conclusion and Outlook

Within a short span of ten years, homogeneous catalysis has played a dominant role in deciphering novel routes to synthesize methanol from CO₂ and in achieving this at temperatures significantly lower than traditional heterogeneous catalysis. This has primarily been enabled by the highly active metal sites of molecular catalysts with rigid spatial and electronic environments leading to high activities and selectivities. Under solvent-assisted conditions, key alternate routes have been realized using alcohol and amine additives which offer energetically favorable pathways for CO₂ to methanol by forming adducts with the formate intermediate. These include early examples of Milstein's pioneering homogeneous catalysts for hydrogenation of various CO₂ derivatives, Sanford's amine- and alcohol-assisted routes and several other homogeneous systems that have shown excellent activities in the mild temperature range of 100–140 °C. A few catalysts have shown turnovers even at temperatures below 100 °C and as low as 60–70 °C. The challenging additive-free CO₂-to-methanol reaction has been achieved in rare cases (Leitner, Klankermayer et al.) and with water as a medium (Himeda et al.), in contrast to most commonly used organic solvents. These initial studies have been followed by extensive mechanistic investigations and DFT modeling to help understand the catalytic routes involved in the hydrogenation processes and have further led to rational tuning of the molecular catalysts. In recent

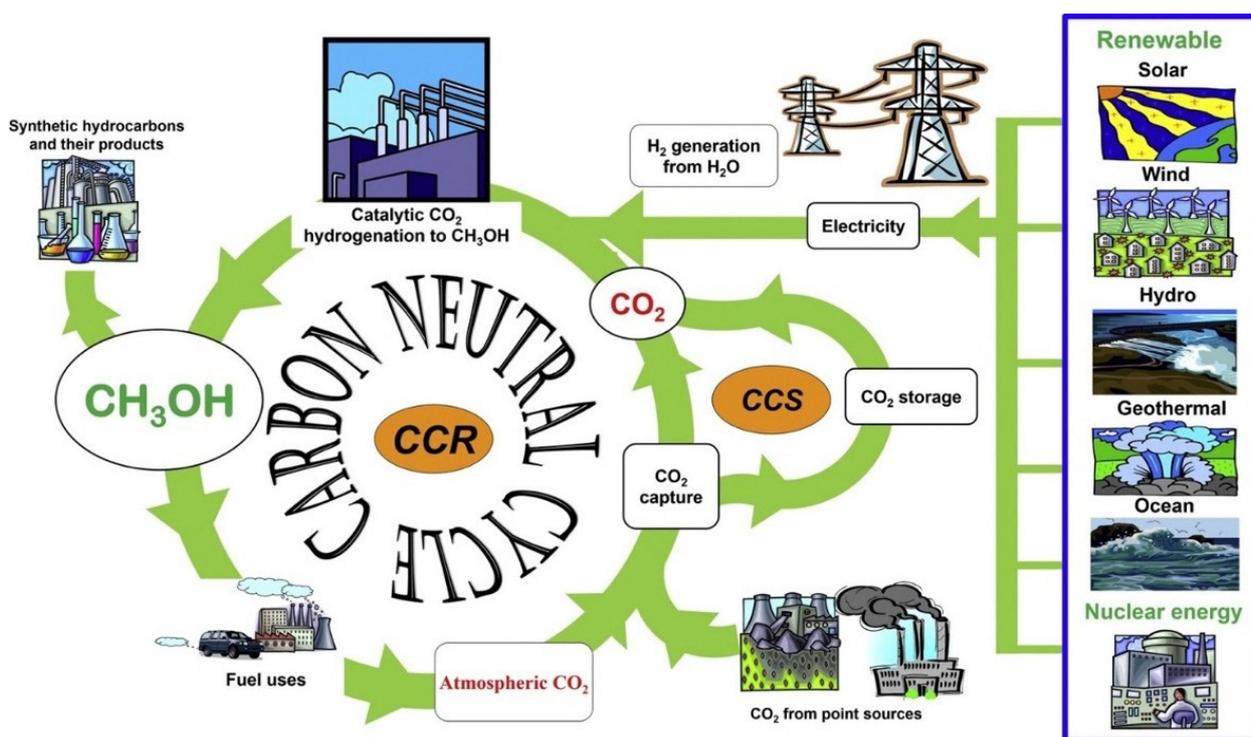


Figure 37. Anthropogenic carbon cycle in the context of a circular methanol economy. Reproduced from ref. [43] with permission from Springer Nature.

years, integrated CO_2 capture and utilization have been realized using homogeneous catalysts. Prakash et al. have demonstrated several amine-assisted capture and conversion systems to recycle CO_2 from air into carbon-neutral methanol. The first example of a hydroxide-based integrated system was also realized recently by the same group. In the broad context, homogeneous catalysis has led to key breakthroughs in green and energy-efficient transformations including that of CO_2 and CO to methanol; and will continue to play a vital role in realizing sustainable and green processes in a carbon-neutral framework (Figure 37).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO_2 recycling · carbon capture and utilization · homogeneous catalysis · hydrogenation · renewable methanol

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