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From 'Gift' to gift: producing organic solvents from CO₂

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'Gift' means 'poison' in German, which fits the situation of CO₂ in our atmosphere from some points of view. Hence, the utilization and transformation of CO₂ into highly value-added chemicals are like going from 'Gift' to gift and have attracted considerable attention from the chemical community. In this review, the latest advances in the field of production of commonly used organic solvents from CO₂ are summarized and discussed.

1 Introduction

As one of the main components of greenhouse gases, the steady increase of CO₂ concentration has become the chief culprit of global climate change, which has caused serious social concerns. Contemporary chemists are obliged to face this severe challenge and seek suitable and sustainable methods to solve this problem. On the other hand, as an ideal and versatile C1 building block, much attention on the valorization of CO₂ has been attracted among chemists due to its abundance, easy availability, nontoxicity and renewability.^{1–8}

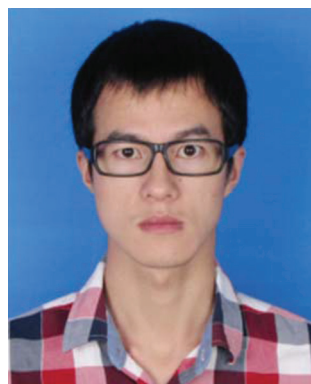
Recent years have witnessed the rapid development of chemical transformations of CO₂ into a variety of high value-added chemicals.^{9–18} Among these transformations, the production of various organic solvents from CO₂ is of prime significance, as organic solvents are widely used in academic research and are usually employed as raw materials in the chemical industry. In addition, the utilization of supercritical CO₂ (scCO₂) as a solvent in various chemical transformations has been flourishing in the past decades; these have found wide applications in a range of research fields due to the nontoxic and nonflammable properties of CO₂.^{19–23}

Considering the huge demand for organic solvents, the transformation of CO₂ into organic solvents has emerged as an attractive and promising research area, especially for industrial processes. However, CO₂ is a highly oxidized form of carbon and thermodynamically stable and/or kinetically inert; hence its activation and utilization typically require the involvement of reactive substances with high energy or severe reaction

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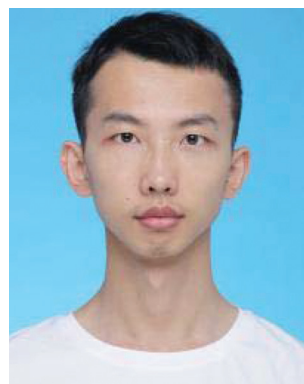
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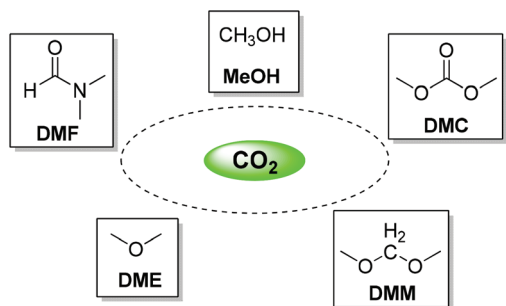
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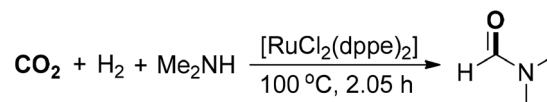


Scheme 1 Producing organic solvents from CO₂.

conditions,^{24,25} limiting the wide utility of CO₂ transformations at some extent. With respect to solvent synthesis from CO₂, relevant research progress mainly focuses on methanol, *N,N*-dimethylformamide (DMF), dimethyl carbonate (DMC), dimethyl ether (DME), and so on. Virtually, there are a large number of publications about methanol synthesis from CO₂ *via* diverse catalytic systems and there have been several excellent reviews on this subject during the past decades.^{4,7,26–28} Therefore, this review will emphatically introduce the preparation of DMF and DMC from CO₂ and select some of the mainstream studies about methanol synthesis, as well as the synthesis of some other useful solvents (Scheme 1).

2 Synthesis of DMF from CO₂

N,N-Dimethylformamide (DMF) is a frequently used polar solvent and extremely versatile chemical reagent in organic



Scheme 2 Ru-catalyzed DMF synthesis from CO₂.

synthesis.^{29,30} The conventional method for the construction of DMF is the reaction of dimethylamine with carbon monoxide in methanol, which was first reported by Haynes and co-workers in 1970.³¹ Afterwards, Kudo and co-workers developed a PdCl₂-catalyzed protocol for the synthesis of DMF with 40 bar of CO₂ and 80 bar of H₂ at 170 °C.³² Vaska's group optimized the reaction by testing diverse metal complexes and DMF could be produced in the presence of an active platinum-based catalyst ([Pt₂(μ-dppm)₃].^{33,34} Later, Noyori and co-workers achieved Ru-catalyzed production of DMF in supercritical CO₂ (130 bar) with a higher turnover number (TON) of up to 370 000.^{35,36} A well-defined homogeneous RuCl₂[P(CH₃)₃]₄ catalyst was the key factor for the reaction and scCO₂ was regarded as both reaction medium and reactant. In the reaction, ammonium formate salt was generated.

An improved protocol for the synthesis of DMF was demonstrated by Baiker and co-workers (Scheme 2).³⁷ A bidentate Ru/phosphine complex [RuCl₂(dppe)₂] was applied as a highly efficient catalyst to realize a TON of up to 740 000 and the reaction was conducted at 100 °C under 130 bar of CO₂ and 85 bar of H₂. The reaction could be scaled up to produce 530 kg of DMF within 2 hours by using 1 gram of ruthenium catalyst. Notably, the solvent methyl formate was formed under a similar catalytic system in the presence of methanol and tri-



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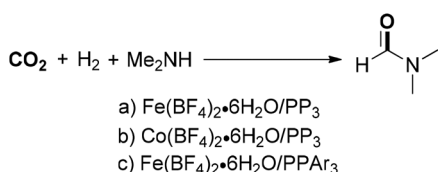
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Xiao-Feng Wu was born in China. He studied chemistry at Zhejiang Sci-Tech University (China), where he got his bachelor's degree in science (2007). In the same year, he went to Rennes 1 University (France) and earned his master's degree in 2009. Then he joined Matthias Beller's group at the Leibniz Institute for Catalysis (Germany), where he completed his PhD defense in January 2012. Subsequently he started his independent research at LIKAT and ZSTU where he was promoted to professor in 2013. In March 2017, Xiao-Feng defended his Habilitation successfully from Rennes 1 University (France). In 2020, he joined the Dalian Institute of Chemical Physics (DICP) and is leading a research group on practical synthesis. Xiao-Feng has authored >350 publications in international journals; meanwhile, he is also the editor or author of >10 books. In 2019, Xiao-Feng was invited to publish his Author Profile in *Angew. Chem., Int. Ed. (Angew. Chem., Int. Ed., 2019, 58, 8624)*.

methylamine. Then, a sol-gel-derived heterogeneous catalyst containing ruthenium complexes was synthesized and utilized for DMF synthesis with high turnover frequencies (up to $18\,400\text{ h}^{-1}$), which was completed by the group of Baiker.^{38–40} The serial positive results for DMF synthesis under ruthenium catalysis provide many insights for further intensive investigation upon industrialized application, such as developing soluble catalytic complexes in the supercritical system and suitable ligands.

Ito and co-workers designed a molybdenum complex, $\text{MoH}_3[\text{Si}(\text{Ph})[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\text{-}o]_2]$, and first applied it to catalytic DMF synthesis from CO_2 .⁴¹ The insertion of CO_2 into the Mo–H bond produced another formal molybdenum complex, which was identified as an active catalyst and the key intermediate in DMF synthesis. A cheap heterogeneous Cu–ZnO catalyst mediated synthesis of DMF from CO_2 , H_2 , and dimethylamine with high efficiency was disclosed by Han and co-workers.⁴² Dimethylammonium dimethylcarbamate (DIMCARB) was used as a safe and convenient source of dimethylamine. The low-toxic Cu and ZnO catalyst showed good synergistic effects and great potential for application in the solvent-free conditions for producing DMF. After four years, another heterogeneous *trans*-bis(glycinato)copper(II) complex was developed to catalyze DMF synthesis in a highly efficient manner, which was disclosed by Jain's group.⁴³ In 2018, Sadeghzadeh and co-workers reported a new class of copper(II) complex based on $\text{FeNi}_3/\text{KCC-1}$ for the *N*-formylation of amines *via* CO_2 reductive hydrogenation and DMF could be delivered in 91% yield.⁴⁴

Beller, Laurency and co-workers developed a series of non-precious metals to catalyze DMF synthesis from CO_2 . An active iron catalyst system was *in situ* generated from $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and the tetradentate ligand $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ for the hydrogenation of carbon dioxide (Scheme 3a).⁴⁵ Under the established catalytic system, DMF was produced in 75% yield with a TON of 727 with 30 bar of CO_2 and 60 bar of H_2 at $100\text{ }^\circ\text{C}$. Soon after, a novel cobalt dihydrogen complex ($\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}/\text{PP}_3$) was applied to DMF synthesis under similar conditions, showing an improved catalytic activity with a TON of 1308 (Scheme 3b).⁴⁶ Another efficient iron-based catalyst with a tetradentate phosphorus ligand [tris(2-(diphenylphosphino)phenyl)phosphine] could enable the production of DMF in good yield with higher TONs (5104) (Scheme 3c).⁴⁷ Similarly, diethylformamide could be obtained in moderate yield with a TON of 2114, which was substantially higher than that of a previously reported iron-catalyzed system. These well-defined iron- or cobalt-based catalyst systems achieved significantly

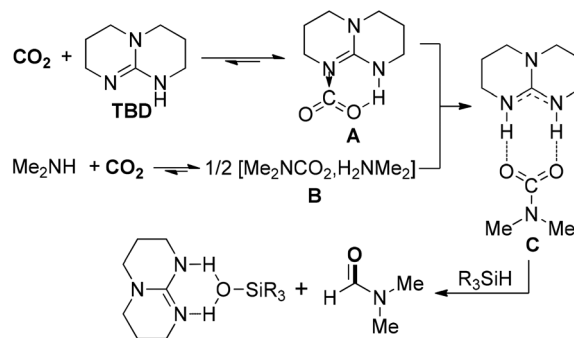


Scheme 3 Fe- or Co-catalyzed DMF synthesis from CO_2 .

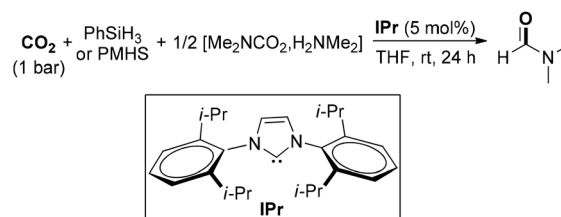
higher yields and TONs for CO_2 hydrogenation than those of other non-precious-metal-based catalysts and even superior to many known precious-metal catalytic systems.

Except for commonly used dihydrogen (H_2), other reductants with high activity were also explored for the hydrogenation of CO_2 , such as hydrosilanes ($\text{R}_3\text{Si-H}$) and hydroboranes ($\text{R}_2\text{B-H}$), due to active Si–H and B–H bonds. In 2011, Cantat and co-workers reported a diagonal transformation for the synthesis of formamides from CO_2 , in which organosilanes were chosen as cheap and nontoxic reducing agents (Scheme 4).⁴⁸ In the organocatalytic process, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was an effective catalyst to promote the insertion of CO_2 into N–H bonds to form the CO_2 adduct **A**. The carbamate $[\text{Me}_2\text{NCO}_2][\text{H}_2\text{NMe}_2]$ **B** reacted with **A** to give salt **C**, which was reduced by phenylsilane to lead to the DMF product and silanol by-product. The protocol exhibited several advantages over the previously established amine/ CO_2 / H_2 formylation system, including no use of metal catalyst, a lower pressure, solvent-free conditions and wide scope of amines. Considering the use of cheap and nontoxic silanes as reductants, the organocatalytic protocols for the formylation of amines with CO_2 perhaps have broader prospects on the way to industrialization.

Cantat and co-workers further explored the organocatalytic formylation of N–H bonds by using N-heterocyclic carbenes, which featured mild reaction conditions and the utilization of two abundant and nontoxic chemical wastes of CO_2 and polymethylhydrosiloxane (PMHS) (Scheme 5).⁴⁹ The combination of NHC and silane enabled the formation of DMF in high yield at room temperature under 1 bar of CO_2 starting from carba-



Scheme 4 TBD-catalyzed synthesis of DMF from CO_2 .



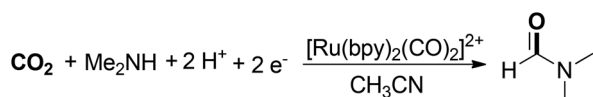
Scheme 5 N-Heterocyclic carbene (NHC)-catalyzed synthesis of DMF from CO_2 .

mate $[\text{Me}_2\text{NCO}_2][\text{H}_2\text{NMe}_2]$. The highly active organocatalytic system was also amendable for the formylation of various N–H bonds, including amines, anilines, imines, hydrazines, hydrazones and N-heterocycles. Under this efficient organocatalytic system, a large-scale CO_2 recycling process is expected to be achieved. Another reaction for the formylation of amines using CO_2 and PMHS was reported by Bhanage and Nale, who applied K_2CO_3 as the catalyst.⁵⁰

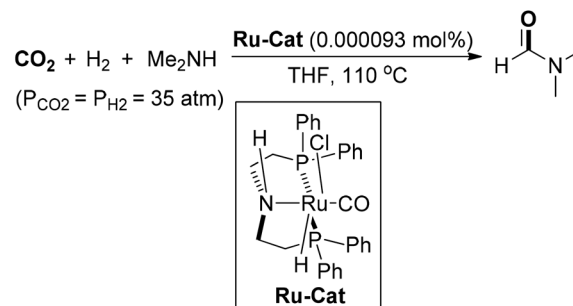
In 2014, Shi and co-workers prepared a heterogeneous $\text{Pd}/\text{Al}_2\text{O}_3\text{-NR-RD}$ catalyst and utilized it for the catalytic formylation of amines with $\text{CO}_2\text{-H}_2$ under mild conditions.⁵¹ High catalytic activity was observed for the production of DMF in 84% yield. In the same year, another heterogeneous catalytic reaction for exclusive DMF synthesis was described by Cao and co-workers.⁵² A bifunctional catalyst based on partially reduced iridium oxide supported on TiO_2 was created and found to show excellent activity for DMF synthesis through reductive activation of CO_2 under a H_2 atmosphere. The method directly employed available aqueous NHMe_2 as the amine source instead of previously reported expensive dimethylammonium dimethylcarbamate.

Tanaka and co-workers developed a photocatalytic CO_2 reduction reaction for the selective synthesis of DMF (Scheme 6).⁵³ In the transformation, a $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}/\text{Me}_2\text{NH}/\text{Me}_2\text{NH}_2^+$ system was established to enable photocatalytic CO_2 reduction. The nucleophilic attack of Me_2NH on $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ produced $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CONMe}_2)]^+$, which acted as the precursor of DMF.⁵⁴ Me_2NH and Me_2NH_2^+ were used as electron donor and proton source, respectively. It was also found that the presence of the Li^+ ion could greatly inhibit DMF production because Li^+ blocked the formation of the RuCO complex through its strong stabilization of the Ru-CO_2 scaffold.

In 2015, Ding and co-workers demonstrated a highly efficient catalytic system for N-formylation of amines with CO_2 and H_2 , which utilized ruthenium-pincer-type complexes as catalysts to produce diverse formamides with high efficiency and selectivity (Scheme 7).⁵⁵ With regard to DMF synthesis, the N-formylation of dimethylamine was achieved with the ruthenium catalyst at a loading of 0.000093 mol%, producing DMF in 56% yield with a TON value of up to 599 000. Noteworthy was that the ruthenium catalyst could be recycled for 12 runs for the preparation of DMF without significant loss of activity, which showed huge potential of practical utilization of this protocol. Gratifyingly, the industrial application of this cost-effective reaction of CO_2 hydrogenation for DMF production was successfully realized in 2019. It is the first kiloton pilot plant of DMF production in the world, which provides a useful and practical pathway for CO_2 utilization.



Scheme 6 Photocatalytic CO_2 reduction for the synthesis of DMF.

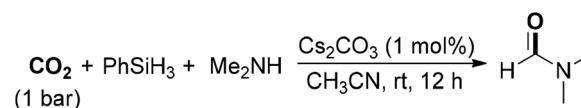


Scheme 7 Ruthenium-catalyzed DMF synthesis from CO_2 .

Fu, Lin and co-workers reported readily available alkali-metal carbonates especially a cesium carbonate catalyzed reaction for the formylation of amines with CO_2 and hydrosilanes (Scheme 8).⁵⁶ Under mild conditions (1 bar of CO_2 at room temperature), DMF could be delivered in 95% yield in the presence of PhSiH_3 as a reductant. In addition, methylation of amines could also be attained and the selectivity was readily controlled by tuning the reaction temperature and silane. An obvious “cesium effect” upon the catalytic activity of alkali-metal carbonates was observed in the reaction, which might originate from the increased solubility of the carbonate salt.

Jain and co-workers synthesized a graphene oxide (GO)-immobilized heteroleptic iridium complex and used it as the first heterogenized homogeneous catalyst for DMF preparation from CO_2 , H_2 and dimethylamine under solvent-free conditions.⁵⁷ The catalyst could be easily recovered and recycled six times without the loss of catalytic efficiency.

An amine-modified $\text{meso-Al}_2\text{O}_3@\text{MCM-41}$, developed by Bhanage and co-workers, was applied as a catalyst for the formylation of amines with CO_2 .⁵⁸ Under the developed heterogeneous catalytic system, DMF could be obtained in excellent 98% yield with dimethylamine borane (DMAB) as a green reducing source. Then, DMAB was applied to another heterogeneous catalytic N-formylation of amines for the synthesis of N-formamides and benzimidazole,⁵⁹ which employed ruthenium nanoparticles (Ru-NPs) supported on polymeric ionic liquids (PILs) as effective catalysts to give DMF in 89% yield with a TON of 296. Subsequently, the same authors discovered an N-heterocyclic olefin (NHO) organocatalyst promoted chemical fixation of CO_2 through the N-formylation of amines by using polymethylhydrosiloxane (PMHS) or 9-borabicyclo [3.3.1]nonane (9-BBN) as the reducing agent.⁶⁰ In the reaction, DMF could be produced in good yield under mild conditions. The *in situ* formed zwitterionic NHO-carboxylate (NHO-CO_2) adducts were the key factor for the activation of CO_2 . By the

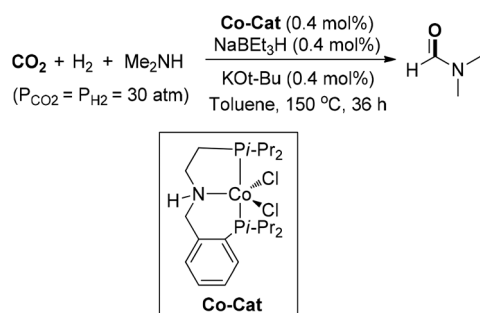


Scheme 8 Cesium carbonate catalyzed DMF synthesis from CO_2 .

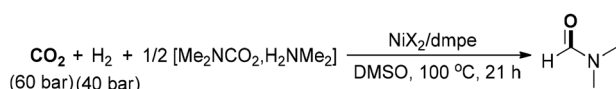
use of $B(C_6F_5)_3$ as an efficient organocatalyst and dimethylamine borane (Me_2NHBH_3) as a green hydrogen transfer source, N-formylation of amines *via* hydrogenation of CO_2 led to DMF in 89% yield with a TON of 1112.⁶¹ The interaction of bulky boron catalyst with amines could effectively activate CO_2 and Me_2NHBH_3 molecules. The abovementioned transformations all enable the production of DMF in high yields but with moderate TONs, which is seemingly far from industrial application.

An Earth-abundant cobalt-catalyzed N-formylation of various amines under CO_2 and H_2 pressure (30 bar each) was disclosed by Milstein and co-workers (Scheme 9).⁶² A Co-PNP pincer complex was synthesized and could be transformed into active species in the presence of catalytic $NaHBET_3$ and *t*-BuOK. For large-scale DMF synthesis, the lower catalyst loading (0.4 mol%) rendered the formation of DMF in 54% yield with a TON of 130 with the addition of 4 Å molecular sieves. Later, Tu and co-workers explored a series of NHC-Ir coordination assemblies as solid molecular catalysts for N-formylation of diverse amines.⁶³ Moderate yield of DMF was attained, even at 0.1 mol% catalyst loading, and the solid catalyst could be reused more than 10 runs.

Jessop and co-workers also developed an abundant-metal-catalyzed formylation of amines by catalytic hydrogenation of CO_2 to prepare formamides (Scheme 10).⁶⁴ Dimethylammonium dimethylcarbamate was adopted under the catalysis of Ni(II)-phosphine complexes for the synthesis of DMF with a high TON value. Several metal complexes showed catalytic activity and Ni(II) salts were the superior choices. Another homogeneous catalyzed hydrogenation of carbon dioxide to DMF was achieved by using an *in situ* generated ruthenium catalyst from $RuCl_3 \cdot H_2O$ and the phosphine ligand 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBI).⁶⁵ An aqueous biphasic solvent system was utilized, where the catalyst could be recycled by immobilization in a nonpolar alcoholic solvent and the product could be extracted *in situ* into



Scheme 9 Ruthenium-catalyzed DMF synthesis from CO_2 .

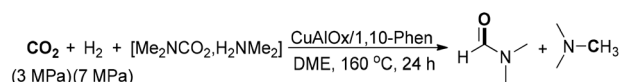


Scheme 10 Ni(II)-catalyzed DMF synthesis from CO_2 .

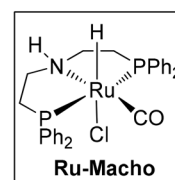
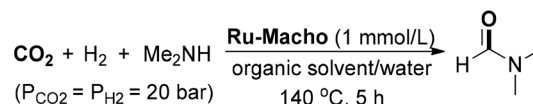
the aqueous phase. Then, the developed reaction system of DMF production was successfully transferred from lab-scale to a continuously operated miniplant with a low concentration of carbon monoxide as the only byproduct.⁶⁶ The positive results highlighted long-term (over 95 h) stability and selectivity of the catalytic system. The continuous addition of the ternary amine could result in the increase of the yield by tuning the basicity of the reaction system. The obtained product could be easily isolated through distillation without decomposition, exhibiting good prospects for scaled-up production.

Recently, Shi and co-workers developed a method for the integration of nano- and molecular catalysis through the synthesis of N-doped carbon layers on AlO_x -supported nano-Cu, which could be employed for the preparation of DMF in a controllable manner from dimethylamine and CO_2/H_2 (Scheme 11).⁶⁷ The catalytic material was *in situ* formed by the reaction of $CuAlO_x$ and 1,10-phen under a H_2 atmosphere. The active catalyst could be easily recycled in three runs for the production of DMF with high yield and selectivity. In addition, the $CuAlO_x$ catalyst also exhibited good performance for the catalytic hydrogenation of DMF to $N(CH_3)_3$. Later, the same authors demonstrated a heterogeneous Pd supported on natural palygorskite catalyst for amine formylation with CO_2 and H_2 .⁶⁸ In the transformation, DMF could be produced in 86% yield by using dimethylamine aqueous solution as the starting reagent. Another heterogeneous Pd-catalyzed CO_2 fixation of amine to prepare DMF was described by Islam and co-workers, which utilized Merrifield resin supported palladium nanomaterial (Pd-PS-amp catalyst) as a catalyst and poly(methylhydrosiloxane) (PMHS) as a hydride transferring agent.⁶⁹

Vorholt and co-workers demonstrated a ruthenium-catalyzed synthesis of DMF from CO_2 in a biphasic solvent system (Scheme 12).⁷⁰ The PNP-pincer complex Ru-Macho was used as an active catalyst, which was identical to the catalyst in Ding and co-workers work.⁵⁵ Several key factors of the reaction were



Scheme 11 $CuAlO_x$ -catalyzed DMF synthesis from CO_2 .



Scheme 12 Ru-Macho-catalyzed DMF synthesis from CO_2 .

investigated, including organic solvent, reaction pathways, the formate route and the concentration of CO₂/amine. Adding carbon dioxide *via* reactive absorption to aqueous dimethylaminoethanol could enable DMF production in up to 81% yield, presumably due to the higher activities resulting from high basicity. Recently, this homogeneous biphasic protocol has been implemented on a miniplant scale by the same authors.⁷¹ The catalyst Ru-Macho complex could be recycled through immobilization in an alcohol phase and maintained high stability over 230 h, providing DMF in an average yield of 48%. A two-step process was designed to be applied for the synthesis of other formamides.

Very recently, an efficient heterogeneous catalytic system for DMF synthesis by hydrogenation of CO₂ was established by Yoon and co-workers,⁷² which employed ruthenium-grafted bisphosphine-based porous organic polymer (Ru@PP-POP) as a recyclable catalyst. In a batch process, a TON of up to 160 000 was obtained and excellent productivity and durability were observed in a continuous-flow process, thus offering great potential for industrial application of CO₂ hydrogenation for DMF production.

A bifunctional heterogeneous Ru catalyst was developed by Ding, Yan and co-workers for the N-formylation of amine and CO₂.⁷³ The Ru-PPh₃-SO₃Na@POP catalyst, generated from the copolymerization of 3v-PPh₃ and sodium *p*-styrenesulfonate, could immobilize metals and alkali on porous organic polymers, enabling the formation of DMF from dimethylamine in 62% yield with 3 MPa of CO₂ and H₂.

3 Synthesis of MeOH from CO₂

As the simplest aliphatic alcohol and a kind of important industrial raw material, the annual production of methanol exceeds 100 million tons and still increases year by year.⁷⁴ Methanol is currently produced from coal, biomass, especially natural gas and syngas,^{75–77} which is usually utilized as the precursor of many important industrial products, alternative fuels and hydrogen storage materials (12.5 wt% H₂).^{78,79}

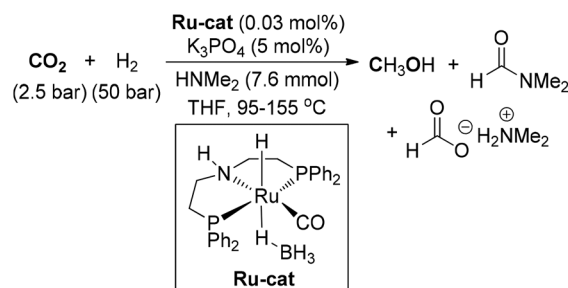
The industrial-scale synthesis of methanol lies in the catalytic reactions of syngas in the presence of Cu/ZnO/Al₂O₃-type heterogeneous catalysts under high pressure and elevated temperature.^{80,81} The production of MeOH solely from the hydrogenation of CO₂ with heterogeneous catalysts has been intensively investigated and several excellent relevant reviews have been published.^{4,82–87} Very recently, Zhang and co-workers have summarized the significant advances in heterogeneous catalysis of CO₂ hydrogenation to methanol in detail.⁸⁸ In addition, the catalytic reduction of CO₂ to methanol could be realized in the presence of stoichiometric amounts of reducing agents, such as boranes or silanes.^{89–95} In this section, we will selectively introduce some seminal work regarding MeOH synthesis from the hydrogenation of CO₂ with homogeneous catalysts.

In 2011, Milstein and co-workers reported the first homogeneous catalytic synthesis of MeOH from the hydrogenation

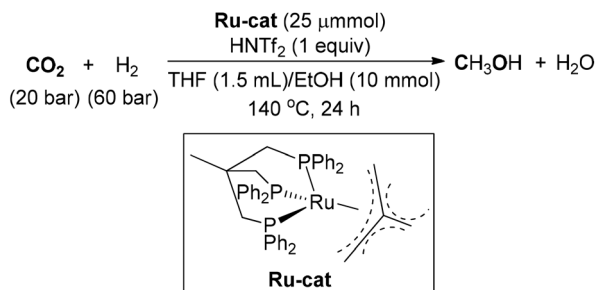
of carbonic acid derivatives and formates using pincer-type Ru^{II} catalysts, which constituted indirect routes from CO₂ to methanol.^{96,97} Although the hydrogenation of dimethyl carbonate could generate methanol, the dimethyl carbonate was more expensive than methanol, which made it not an economical choice. After one year, Ding and co-workers described the catalytic hydrogenation of cyclic carbonates from CO₂ and epoxides for the preparation of methanol and diols with readily available (PNP) Ru^{II} pincer complexes as catalysts.⁹⁸ Starting from ethylene carbonate, two important bulk chemicals, methanol and ethylene glycol (EG), were readily produced with high TON values under relatively mild conditions. It should be noted that ethylene carbonate could be industrially obtained by reacting ethylene oxide with CO₂. Poly(propylene carbonate) could also be hydrogenated to deliver 1,2-propylene diol and methanol. Another indirect methanol production from CO₂ through a formic acid disproportionation strategy with a homogeneous iridium catalyst was reported by Laurency and co-workers.⁹⁹

Sanford and Huff developed a cascade reaction with three different homogeneous catalysts to complete the hydrogenation of CO₂ to methanol *via* formic acid and methyl formate intermediates with a maximum TON of 21.¹⁰⁰ Then, they achieved the homogeneous Ru-pincer complex catalyzed reduction of CO₂ to methanol in the presence of NHMe₂ (Scheme 13).¹⁰¹ Under basic reaction conditions, MeOH could be produced with a TON of up to 550. The additional amine reacted with CO₂ to generate dimethylammonium dimethylcarbamate, which coupled with formic acid to deliver DMF. In the same year, Ding and co-workers also accomplished a one-pot sequential N-formylation and hydrogenation process for the conversion of CO₂ to MeOH *via* a formamide intermediate by using Ru-pincer complex as catalyst.⁵⁵

In 2012, a homogeneous catalytic hydrogenation of CO₂ to methanol with a single ruthenium phosphine complex was investigated by Leitner, Klankermayer and co-workers (Scheme 14).¹⁰² By adopting (Triphos)Ru-(TMM) (TMM = trimethylenemethane) as catalyst and bis(trifluoromethane)sulfonimide (HNTf₂) as acidic additive, a TON of up to 221 for MeOH synthesis was attained under 20/60 bar of CO₂/H₂. The counterion introduced from the acid exerted a great impact upon the catalyst's performance. The reaction was further explored through a detailed mechanistic study, which demon-



Scheme 13 Ru-catalyzed hydrogenation of CO₂ to MeOH.

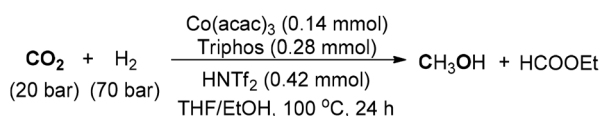
Scheme 14 Ru-catalyzed synthesis of MeOH from CO₂.

strated that the hydrogenation of CO₂ to methanol could occur under a single cationic Triphos–Ru catalytic system without the need for an alcohol additive.¹⁰³ Furthermore, an aqueous biphasic system of 2-MTHF–water was developed for MeOH synthesis and catalyst recycling.

Milstein and co-workers described a CO₂ hydrogenation reaction by using PNN pincer Ru catalysts, in which CO₂ was captured by aminoethanols combined with hydrogenation of the captured oxazolidinone product for the formation of MeOH.¹⁰⁴ The above two procedures could be performed in the same reaction mixture without additional isolation or purification steps. Valinol was also used to capture CO₂ at 1 bar in the presence of catalytic Cs₂CO₃. The approach features a low pressure of CO₂ and high energy utilization rate, promoting the development of CO₂ conversion into other value-added chemicals.

The Ru-pincer complex was applied for the synthesis of MeOH from CO₂ with pentaethylenehexamine (PEHA) in an ethereal solvent, which was presented by Olah, Prakash and co-workers.¹⁰⁵ It was the first example of reductive conversion of CO₂ from air to MeOH with a homogeneous catalyst, despite the low CO₂ concentration (400 ppm). Then, the group of Prakash developed a tandem system for CO₂ capture in aqueous amine solution and hydrogenation to methanol in a biphasic 2-MTHF/water system.¹⁰⁶ The catalytic combination of Ru-MACHO-BH complex with high-boiling polyamine PEHA exhibited the best activity for MeOH synthesis. Further investigation towards mechanistic insights into Ru pincer/amine mediated hydrogenation of CO₂ to MeOH was performed by the same authors.¹⁰⁷ The observation revealed that Ru-Macho showed the highest catalytic activity in both amine formylation and formamide hydrogenation. In addition, (di/poly)amines were also effective for MeOH formation.

In 2017, Beller and co-workers disclosed the first homogeneous non-noble-metal catalyst for the synthesis of MeOH from hydrogenation of CO₂ (Scheme 15).¹⁰⁸ The reaction could

Scheme 15 Co-catalyzed synthesis of MeOH from CO₂.

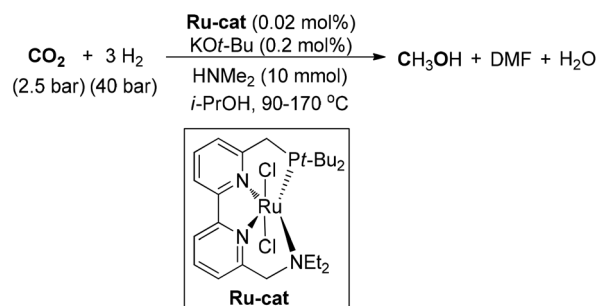
be operated at 100 °C with high reactivity in the presence of *in situ* generated catalyst from [Co(acac)₃], Triphos, and HNTf₂. Mechanistic studies revealed that a cationic cobalt/Triphos complex was regarded as an active catalyst, which was produced after slow removal of the acetylacetonate ligands. The study will stimulate the development of other non-noble-metal-catalyzed homogeneous hydrogenation of CO₂ to methanol. Other studies involving Earth-abundant metal-based complexes as catalysts for hydrogenation of CO₂ to methanol were consecutively reported in the same year.^{109,110}

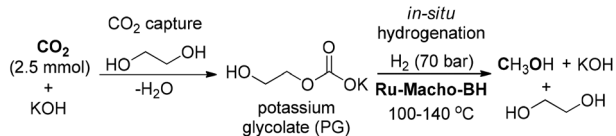
Zhou and co-workers designed a ruthenium complex with a tetradentate bipyridine ligand and applied it for the conversion of CO₂ to achieve MeOH synthesis (Scheme 16).¹¹¹ Under 2.5 atm of CO₂ and 40 atm of H₂, catalytic hydrogenation of CO₂ could enable the production of MeOH with a TON of 2100 in the presence of HNMe₂. The tetradentate bipyridine ligand proved to be the key factor for the stability of the ruthenium catalyst. In addition, hydrogenation of CO₂ to formamides and hydrogenation of formamides to methanol and amines was accomplished with a high TON value under the catalytic system.

In comparison with the three-catalyst cascade strategy established by Sanford and co-workers,¹⁰⁰ an improved homogeneous catalytic cascade system for CO₂ hydrogenation to MeOH was demonstrated by Goldberg and co-workers.¹¹² The combination of Ru(H)₂[P(CH₂CH₂PPh₂)₃]/Sc(OTf)₃/Ir(^tBuPCP) (CO) was identified as an active catalyst for the synthesis of MeOH with a TON of 428 *via* formic acid and formate ester intermediates. Sc(OTf)₃ in the transformation served as both a Lewis and Brønsted acid donor.

Very recently, Leitner, Werlé and co-workers established a cobalt-based catalytic system that could achieve selective transformation of CO₂ individually to the formic acid, the formaldehyde, or the methanol level.¹¹³ The catalyst was prepared based on the 3d transition-metal cobalt with a PNP pincer-type triazine ligand. For methanol synthesis, the catalytic hydrosilylation of CO₂ was conducted in [D₆]-DMSO at 80 °C under a constant flow of CO₂ at 1 bar for 4 h with phenylsilane, producing the methoxysilane species with 99% selectivity.

Prakash and co-workers reported a Ru-catalyzed system for CO₂ capture and conversion to MeOH by using alkali-metal hydroxide as a CO₂ capturing agent and ethylene glycol as a formate ester promoter (Scheme 17).¹¹⁴ In the one-pot trans-

Scheme 16 Ru-catalyzed synthesis of MeOH from CO₂.



Scheme 17 Ru-catalyzed hydrogenation of CO₂ captured in ethylene glycol for MeOH synthesis.

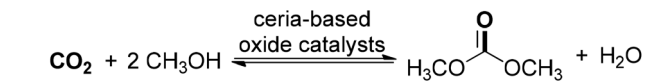
formation, CO₂ could be readily captured by ethylene glycol in the presence of KOH to form potassium glycolate (PG), which underwent *in situ* hydrogenation using Ru-PNP catalyst under 70 bar of H₂ at 100–140 °C to realize MeOH production with high activity. The high CO₂ capture efficiency of this protocol and regeneration of the hydroxide base rendered it superior to the previously established amine-based methods for the conversion of CO₂ from ambient air to methanol in a scalable process. The novel protocol is of great significance for the development of CO₂ capture and conversion in a highly efficient manner.

4 Synthesis of DMC from CO₂

Dimethyl carbonate (DMC) is regarded as an environmentally benign solvent and versatile reagent for organic synthesis owing to its low toxicity, low viscosity and high biodegradability.^{115–119} DMC also act as an alternative for several toxic organic compounds and as non-aqueous electrolyte for lithium batteries.^{120,121} Conventional approaches for the synthesis of DMC lie in phosgenation and carbonylation of methanol, and transesterification of ethylene carbonate (EC) and methanol, which suffer from considerable issues regarding operational safety and environmental protection. Thus, direct DMC synthesis from abundant CO₂ and methanol has emerged as an attractive and powerful pathway from the viewpoint of sustainable development and green chemistry.

Although the direct synthesis of DMC from carbon dioxide and methanol constitutes a state-of-the-art process, some drawbacks still exist, which include the low yield and slow reaction rate, resulting from highly stable CO₂ and thermodynamic limitations of the reaction. Key solutions to overcome these difficulties focus on the development of novel catalysts and diverse dehydrating agents. In this regard, tremendous effort has been devoted to this aspect and several excellent reviews summarizing relevant achievements have been thereby presented.^{122–124} Therefore, in this section we will emphatically describe the latest developments on DMC synthesis from CO₂ in the last five years.

Due to their excellent catalytic activity, selectivity, oxidation–reduction properties and larger specific surface area, ceria-based oxide catalysts have attracted considerable attention for the direct synthesis of DMC from CO₂ (Scheme 18).^{125–129} Ceria could provide selective catalytic sites to activate CO₂ for the enhancement of the reaction rate of CO₂ and alcohols to organic carbonates.¹³⁰ Considering the



Scheme 18 Ceria-based oxide catalyzed synthesis of DMC from CO₂.

unfavourable nature of bare CeO₂, including small surface areas, poor durability and quick deactivation, doping CeO₂ with transition metals (M) to form M_xCe_{1-x}O₂ composites is usually employed in the catalytic reaction.

Wang and co-workers investigated the direct synthesis of DMC from CO₂ by using a series of CeO₂ nanocrystals of various structures (spindle, cube, and octahedron).¹³¹ With the addition of 2,2-dimethoxypropane (DMP) as an effective dehydrating agent, spindle-CeO₂ exhibited a more favourable catalytic activity than other CeO₂ catalysts. The hydrolysis of DMP could *in situ* remove water from the reaction system, thereby overcoming the thermodynamic limitation of the reaction and increasing the DMC yield. In 2017, Kumar and co-workers prepared several calcium–cerium mixed-metal oxide catalysts (CeO₂–CaO) with various Ce/Ca molar ratios and applied them with 3 Å molecular sieves to the direct conversion of CO₂ to DMC.¹³² The acidity and basicity of catalysts exerted a fundamental effect upon the DMC yield and the ceria–calcium oxide catalyst could be reused in five runs.

Owing to the surface properties and acid/base sites related to catalytic performance, the ceria/zirconia (Ce_xZr_{1-x}O₂) solid solutions have attracted considerable attention in the field of the catalytic synthesis of DMC from CO₂.^{133–135} Recently, Kim and co-workers synthesized a series of Ce_xZr_{1-x}O₂ solid solutions ($x = 0.25, 0.5, 0.75$) with distinct morphology, acid/base sites and high surface area.¹³⁶ The prepared Ce_xZr_{1-x}O₂ solid solutions with modified physicochemical properties possessed excellent catalytic activity and stability in DMC synthesis from CO₂ under mild conditions.

Diverse Zr-doped CeO₂ nanorods with different ratios of Zr/Ce were prepared and used for the catalytic synthesis of DMC from CO₂ and methanol at 6.8 MPa and 140 °C.¹³⁷ Doping of Zr atoms into the ceria lattice resulted in the formation of oxygen vacancy sites, which could promote the adsorption and activation of CO₂ and stabilize the final products by filling one oxygen atom of the CO₂ molecule.¹³⁸ It had been reported that CeO₂ nanorods with high density of defect sites and acid–base sites showed higher activity than nanocubes and nano-octahedra.¹³⁹ Among the developed Zr-doped CeO₂ nanorods, Zr_{0.1}Ce nanorods with the highest amount of oxygen vacancies showed the highest activity for DMC synthesis, implying a linear relationship between the concentration of surface oxygen vacancies and catalytic activity.

TiO₂-doped CeO₂ catalysts have also attracted considerable interest in the application of DMC synthesis because of the enhancement of the oxygen deficiency and acidity of the surface by doping TiO₂ into CeO₂.¹⁴⁰ Meng and co-workers synthesized a number of TiO₂-doped CeO₂ nanorods and applied them to the direct synthesis of DMC from CO₂ and CH₃OH in

a fixed-bed reactor.¹⁴¹ Better catalytic activities of ceria nanorods were observed with the introduction of TiO₂ and the highest catalytic performance was achieved on Ti_{0.04}Ce_{0.96}O₂ nanorod catalyst with a DMC selectivity of 83.1%. Kinetic and mechanistic studies revealed CO₂ adsorption and activation were rate-determining steps.

Ionic liquids have many excellent properties, such as thermal stability, negligible vapor pressure, reusability, high solubility in various solvents, and high CO₂ adsorption capacity under mild conditions.¹⁴² The combination of porous metal oxide with ionic liquids (ILs) could be used as an effective method to overcome the limitations of the direct conversion of CO₂ to DMC. Very recently, Kim and co-workers prepared a series of ionic liquids with electrospun MgO–CeO₂ metal oxide nanofiber sponge-500 (EMCMONS-500).¹⁴³ The synergism between the ILs and EMCMONS-500 enabled a high catalytic performance towards DMC synthesis, as demonstrated that around 73.1 mmol g⁻¹ cat DMC yield and 98.9% selectivity were obtained under 3 MPa CO₂ pressure. The ILs-EMCMONS-500 catalyst exhibited superior catalytic activity for DMC production to that of other ceria or ILs-based catalysts.^{132,144–147}

Except for ceria-based oxide catalysts, a variety of other catalysts, namely, zirconia,^{148,149} heteropoly compounds,^{150,151} ionic liquids,^{152,153} potassium methoxide,¹⁵⁴ tin(IV) oxide,^{155–157} H₃PO₄–V₂O₅,¹⁵⁸ and Cu–Ni or Cu–Fe bimetallic species supported on different carriers,^{159–162} have been extensively studied for DMC preparation through the conversion of CO₂ with methanol.

In 2017, Wu, Hu and co-workers employed an imidazolium hydrogen carbonate ionic liquid ([C_nC_mIm][HCO₃]) for the direct synthesis of DMC from CO₂ and methanol at room temperature.¹⁶³ Bifunctional [C₁C₄Im][HCO₃] was used as an effective and recyclable catalyst and dehydrant, producing DMC with 74% CH₃OH conversion (Scheme 19). The two roles of the imidazolium hydrogen carbonate ionic liquid system have many advantages and remarkably simplify the whole chemical process, offering the possibility of the further scaled application of this method.

The utilization of zirconium oxide (ZrO₂) as catalyst for the synthesis of DMC from CO₂ was previously reported by Tomishige and co-workers.^{133,134,148,164} Bell and Jung performed a relevant mechanistic investigation in detail using *in situ* infrared (IR) spectroscopy.^{165,166} Inumaru and co-workers prepared diverse ZrO₂ nanocrystals by hydrothermal

synthesis at different temperatures and tested the catalytic activity in DMC formation.¹⁶⁷ Due to their high surface area and high reaction rate per unit surface area, a high catalytic activity of ZrO₂ nanocrystals was observed and the surface sites had a positive impact on the rate-determining step of the reaction.

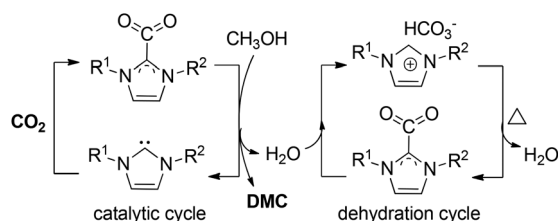
Meng, Xiao and co-workers designed and prepared a series of alkali-adopted Cu–Ni/diatomite catalysts for application in DMC synthesis from CO₂ and methanol.¹⁶⁸ The results revealed that alkali adoption could promote polarization of the Cu–Ni lattice and increase electron transformation from Cu–Ni to CO₂, thereby greatly promoting the catalytic activity of Cu–Ni bimetallic catalysts. DMC could be obtained with 85.9% selectivity and 9.22% CH₃OH conversion under the reaction conditions. The incorporation of an alkali into the Cu–Ni bimetallic catalyst could decrease the decomposition and reduction temperatures, which contributed to the formation of a nano-scale dispersion of bimetallic particles. The authors further investigated the highly active K₂O-promoted Cu–Ni catalyzed direct DMC synthesis with 3 Å molecular sieves (MS) as a dehydrating agent.¹⁶⁹ The developed *in situ* dehydrating system enabled higher methanol conversion and selectivity by shifting the reaction equilibrium to a high DMC yield. Recently, a novel Cu_xNi_y@POP-PPH₃ catalyst was synthesized and used in direct DMC synthesis by Chen, Ye and co-workers.¹⁷⁰ The CuNi alloy nanoparticles were encapsulated in thermally stable triphenylphosphine porous organic polymers, which exhibited high catalytic performance to achieve DMC production with 10.5% CH₃OH conversion and 80% selectivity.

Wang and co-workers prepared a series of Y₂O₃–T catalysts through a one-pot calcination method from Y(NO₃)₃·6H₂O and applied them to study the thermodynamics of the direct synthesis of DMC from CO₂.¹⁷¹ The efficiency of DMC formation was closely related to the moderate acidity–basicity amounts of the catalysts. Y₂O₃–750 showed the best catalytic performance to give the highest yield of DMC at 90 °C under 8 MPa of CO₂. It is the first example of utilizing yttrium oxide as a single metal oxide catalyst to catalyze DMC synthesis from CO₂ and methanol.

5 Synthesis of DME/DMM from CO₂

Dimethyl ether (DME) and dimethoxymethane (DMM) are known to be excellent fuel additives and green solvents, which have attracted considerable interest in recent years.^{172–174} DME can be synthesized by acid-catalyzed dehydration of methanol or from syngas with bifunctional catalysts.¹⁷⁵ DMM is industrially produced through direct oxidation of methanol and a condensation sequence in the presence of suitable catalysts.^{176–178} On the basis of extensive studies on CO₂ hydrogenation transformation, the direct conversion of CO₂ has emerged as an appealing alternative route to the generation of DME/DMM.

DME is prepared through CO₂ hydrogenation in a one-pot reaction comprising a methanol synthesis and methanol de-

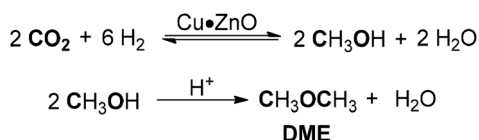


Scheme 19 The catalytic and dehydration cycle of [C_nC_mIm][HCO₃].

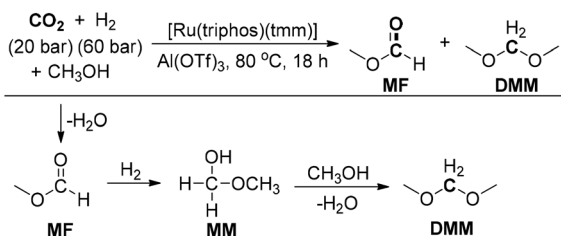
hydration sequence. The latter process can facilitate CO₂ hydrogenation to methanol by shifting the thermodynamic equilibrium,¹⁷⁹ and an effective catalyst for promoting methanol production is also significant. The Cu–Zn bimetallic system has been considered as an excellent catalyst for methanol synthesis from CO₂ hydrogenation.¹⁸⁰ In 2015, Zha and co-workers developed HZSM-5 packed CuO–ZnO–Al₂O₃ nanoparticles for the catalysis of CO₂ hydrogenation with methanol to produce DME. Under the conditions of 3 MPa of CO₂/H₂ at 270 °C, 23.4% yield of DME was obtained with 48.5% selectivity.¹⁸¹ The combination of sulfated zirconia catalysts with a Cu/ZnO/ZrO₂ catalyst for the synthesis of DME was developed by Chareonpanich and co-workers, in which the prepared hybrid catalyst with 20 wt% sulfur loading could lead to a superior DME production yield.¹⁸²

Later, Mota and co-workers prepared several Cu–ZnO catalysts supported on Al₂O₃/Nb₂O₅ and employed them to study the conversion of CO₂ to methanol and dimethyl ether (Scheme 20).¹⁸³ The preparation procedure of the catalyst had a crucial influence on DME production, as demonstrated that the impregnated Cu–ZnO/Al₂O₃ catalyst with better reducibility exhibited the highest activity and selectivity for the formation of DME. The acid function was not the key factor in the process of DME synthesis. Pd/HZSM-5 bifunctional catalysts modified with CeO₂ and CaO promoters were applied for the synthesis of DME through sulfur-containing CO₂ hydrogenation.¹⁸⁴ The addition of CaO reduced the acidity and weakened the CO₂ adsorption of the catalyst, whereas the promoter CeO₂ could increase the acidity and the quantity of adsorbed CO₂, thereby greatly improving the catalytic activity. Optimal amounts of the promoters were 3 wt% CeO₂ and 1 wt% CaO.

Klankermayer and co-workers reported a ruthenium-catalyzed multistep reaction for the synthesis of dimethoxy-methane (DMM) from CO₂/H₂ and methanol (Scheme 21).¹⁸⁵ Ru(Triphos)(tmm) was chosen as a catalyst and the Lewis acid



Scheme 20 Cu–ZnO-catalyzed synthesis of DME from CO₂ hydrogenation.



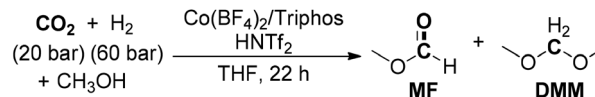
Scheme 21 Ruthenium-catalyzed synthesis of DMM from CO₂/H₂.

Al(OTf)₃ was employed as an effective additive. Mechanistic studies indicated that methyl formate (MF) and methoxy-methanol (MM) were formed as possible intermediates during the reaction. The reaction presumably involved the hydrogenation of CO₂ to form the formic acid and subsequent esterification for producing MF. Then, MF was hydrogenated to MM in the presence of the Ru–Triphos–H₂ catalyst system. Finally, transacetalization of MM with the solvent methanol could give the DMM product. Furthermore, the versatility of this reaction was further investigated by using several other alcohols to successfully produce various dialkoxymethanes with slightly lower TONs. The present catalytic reaction constitutes the first example of the selective conversion of CO₂ and H₂ to formaldehyde.

After one year, the group of Klankermayer achieved the selective transformation of CO₂ to dialkoxymethane ethers using a non-precious transition-metal catalyst system.¹⁸⁶ A tailored Co(BF₄)₂/Triphos/HNTf₂ catalytic system was utilized for the production of DMM with a TON of up to 92 at 100 °C (Scheme 22). The developed protocol was also amenable for the formation of dialkoxymethane ethers (DAM) from other selected alcohol substrates. When isopropanol and more acidic hexafluoroisopropanol were used as substrates, methanol was selectively generated as the major product, implying switching of the catalyst system for methanol formation by variation of the alcohol additive or solvent. Moreover, the alteration of substituents on the phenyl groups of the Triphos ligand also affected the catalytic activity, as verified that sterically more demanding and electron-rich Triphos^{Xyl} and Triphos^{ToI} could enable the production of DMM with higher TONs of 120 and 157, respectively.

The conversion of methanol and CO₂ to produce DMM at 3 MPa and 150 °C in the basic functionalized ionic liquid BmimOH was developed by Cai and co-workers.¹⁸⁷ It was the first example of employing an ionic liquid as catalyst for the synthesis of DMM from CO₂ and methanol.

On the basis of Klankermayer's work on the ruthenium–Triphos–aluminum triflate catalytic system, Trapp and co-workers modified the structure of Triphos ligands and ruthenium catalysts to tune the steric and electronic properties, as well as the coordinating units, thereby increasing the catalytic activity for the production of DMM with higher TONs.¹⁸⁸ Under 90 bar of H₂ and 20 bar CO₂ in the presence of methanol, DMM and MF were produced using a ruthenium catalyst with an N–Triphos^{Ph} ligand with maximum turnover numbers of 786 and 1290, in which MF was transformed into DMM with high selectivity. Formaldehyde and methanol could be readily obtained by distillation from the hydrolysis of DMM. Later, the same authors further investigated steric and elec-



Scheme 22 Cobalt-catalyzed synthesis of DMM from CO₂/H₂.

tronic modifications of the Triphos ligand structure and varied the substitution of the apical atom in the backbone with silicon and phosphorus to explore the catalytic activity.¹⁸⁹ Under the optimized conditions, DMM and MF could be formed with maximum turnover numbers of 685 and 1370, which were comparable with the reactivity of their previous work.¹⁸⁸ For ruthenium-catalyzed DMM synthesis, the employment of ^{Ph}Si-Triphos^{Ph} and ^{Me}Si-Triphos^{Ph} as ligands was also a good choice to attain high reactivity.

6 Conclusions

Considering the increased global emission of CO₂ and from the viewpoint of sustainability, the development of efficient transformations of CO₂ into useful organic solvents constitutes an attractive and long-term goal for the chemical community. A wide range of strategies of CO₂ conversion have been exploited to produce diverse solvents in the past few decades. Apart from transformations involving precious transition-metal catalysts, reactions using inexpensive Earth-abundant metals have also developed rapidly. However, the wide industrialization of the developed protocol for the transformation of CO₂ to organic solvents is far from realized. Obvious limitations of the developed methodologies still remain, such as the necessity for precious-metal catalysts, harsh reaction conditions, low conversion rate and relatively poor chemo- and regioselectivity. Tremendous efforts should be devoted to solving these troublesome problems in the future. It will be of great significance for developing the efficient industrial-scale production of organic solvents from CO₂ due to the huge demand for solvents in academic research and the chemical industry. It is a very promising and fascinating, but also challenging, field for chemists working on organic synthesis or industrial catalysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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