CO_2 Utilization

COVER PICTURE

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Selective Catalytic Synthesis Using the Combination of Carbon Dioxide and Hydrogen: Catalytic Chess at the Interface of Energy and Chemistry

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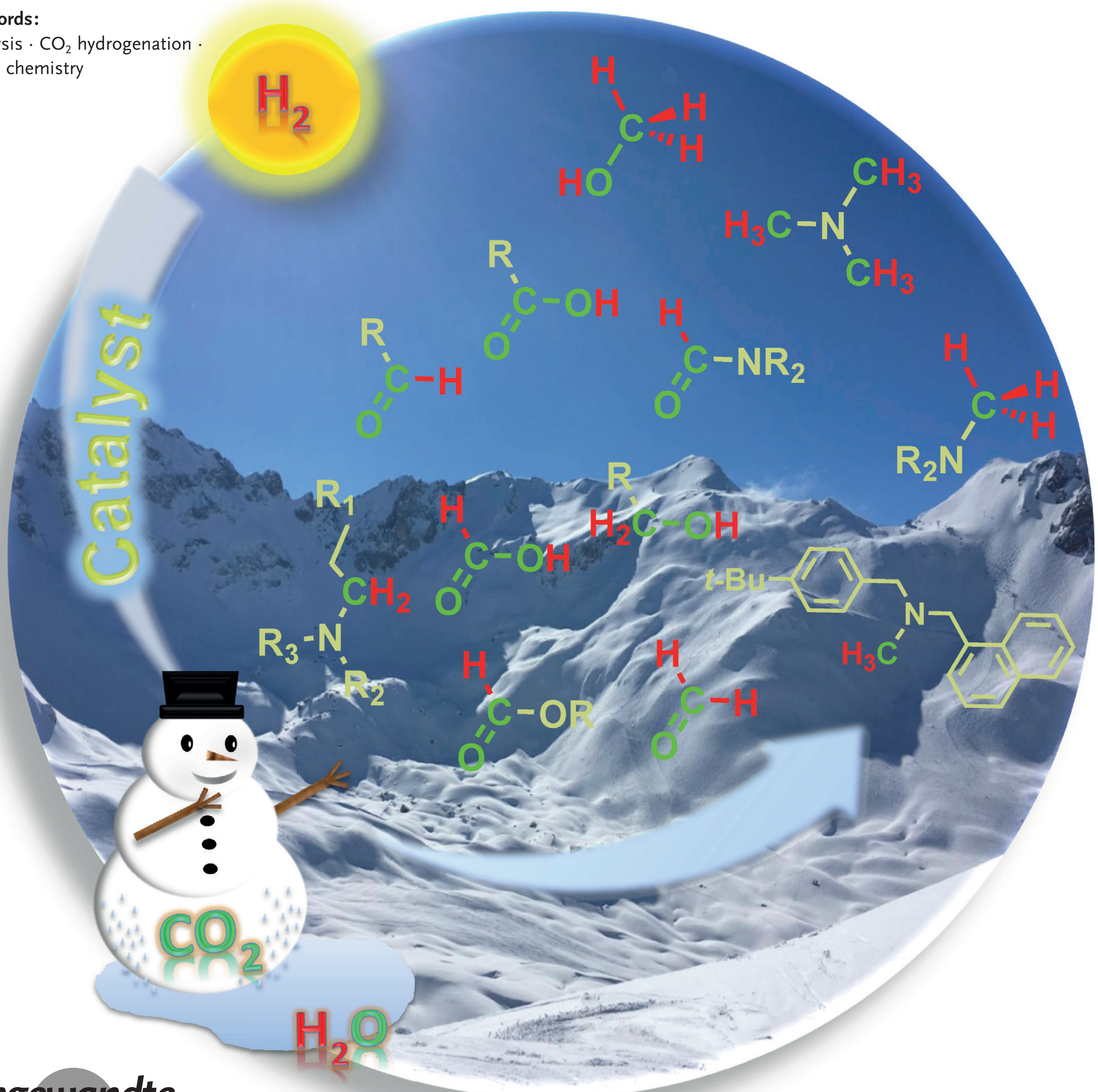

The present Review highlights the challenges and opportunities when using the combination CO_2/H_2 as a C_1 synthon in catalytic reactions and processes. The transformations are classified according to the reduction level and the bond-forming processes, covering the value chain from high volume basic chemicals to complex molecules, including biologically active substances. Whereas some of these concepts can facilitate the transition of the energy system by harvesting renewable energy into chemical products, others provide options to reduce the environmental impact of chemical production already in today's petrochemical-based industry. Interdisciplinary fundamental research from chemists and chemical engineers can make important contributions to sustainable development at the interface of the energetic and chemical value chain. The present Review invites the reader to enjoy this exciting area of "catalytic chess" and maybe even to start playing some games in her or his laboratory.

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1. Introduction

The utilization of carbon dioxide (CO_2) as a raw material for chemical synthesis has intrigued chemists ever since it was recognized that nature capitalizes on this molecule to harness the energy of the sun for production of organic matter through photosynthesis. In contrast, the anthropogenic value chains of today's global economy rely on fossil feedstocks that provide resources, but not sources, for the supply of both energy and materials. The exploitation of these finite reservoirs of reduced forms of carbon inevitably releases CO_2 into the atmosphere. In his wonderful book "Il Sistema Periodico", published in 1975, the chemist and writer Primo Levi contemplated on the journey of carbon through the natural and man-made cycles: "*Knowingly or not, man has not tried until now to compete with nature on this terrain, that is, he has not striven to draw from the carbon dioxide in the air the carbon that is necessary to nourish him, clothe him, warm him, and for the hundred other more sophisticated needs of modern life. He has not done it because he has not needed to: he has found, and is still finding (but for how many more decades?) gigantic reserves of carbon already organicized or at least reduced.*"[1]

Whereas nature has found an ingenious mechanism to capitalize on CO_2 from the air at concentrations around 400 ppm, the chemical conversion of a gaseous feedstock at a partial pressure of about 0.04 bar would be technologically very challenging.[2] There are, however, a number of localized sources of concentrated and sometimes even pressurized gas streams that provide access to CO_2 in quantities that are more than sufficient for even large-scale synthetic purposes.[3] The CO_2 emissions from state-of-the-art coal-fired power stations frequently amount to tens of millions of tons of CO_2 per plant per year. Gas and oil refining, petrochemical processes, including hydrogen production, and a number of chemical processes such as the production of ethylene oxide make CO_2 readily available on a significant scale at many industrial complexes. Other industrial sectors such as the iron, steel, and cement industries, are major sources of CO_2, with emissions in the range of tens to hundreds of million tons per year in total, with large volumes of quite concentrated streams generated at individual sites. Less centralized point sources of high concentration include fermentation processes or biogas units. There are also large natural wells of CO_2, which are still tapped upon for industrial use today.

Technical solutions for the separation of CO_2 in sufficient purity from such streams are an important factor for the availability of CO_2 as a carbon source. A widely applied strategy for removing CO_2 from natural gas, syngas, and flue gas is absorption with the help of a solvent. Reactive solvents, such as aqueous solutions containing triethanolamine (TEA), diethanolamine (DEA), monoethanolamine (MEA), diisopropanolamine (DIPA), or methyldiethanolamine (MDEA), are commonly used for lower CO_2 partial pressures and for meeting tighter CO_2 specifications. These technologies are well-established on an industrial scale and several examples from recent research and demonstration units have shown that the purity of captured CO_2 can be compatible with direct catalytic conversion.[4] However, the development of optimized CO_2 absorbents through applied and fundamental research remains an area where important improvements are possible in the energetic and economic balance for the use of CO_2 as a resource. A more detailed overview of CO_2 separation technologies can be found elsewhere.[3b,c,5]

Although CO_2 reacts readily with medium to strong nucleophiles such as water, amines, or carbanions, it is perceived generally as an "inert" molecule. This reflects the high kinetic barrier for synthetically useful transformations

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such as C–H and C–C bond formations as well as the thermodynamic constraints resulting from the extremely low energy level of the CO_2 molecule. Fundamental research, in particular in the last quarter of the 20th century, has resulted in impressive progress in the development of catalyst systems that address the kinetic challenge of "CO_2 activation".[6] It is important to note that the co-reagent is in fact often "activated" at the catalytic center, with formation of a very reactive intermediate that is intercepted by reaction with CO_2.[6h] At the same time, the use of reagents that have a high intrinsic energy content provides a driving force to render the transformations thermodynamically feasible.

Rooted in these groundbreaking studies, the area concerning the catalytic conversion of CO_2 has undergone a remarkably dynamic development during the last decade.[3b,c,7] The research activities that have emerged from this evolution can be grouped into three major areas according to the nature of the chemical transformation (Figure 1). They can be distinguished on the basis of the reduction level of the CO_2 molecule and the replacement of C–O by C–H or other carbon–element bonds. In the two extreme cases, carbon dioxide is either incorporated into products without formal reduction of the oxidation state at the carbon atom (Figure 1, left) or fully reduced to saturated hydrocarbons under removal of both oxygen atoms (Figure 1, right). These two scenarios are currently evaluated in a number of large-scale demonstration projects or are already in the process of being implemented on an industrial scale.

The reaction of epoxides with carbon dioxide is a prominent example of the nonreductive incorporation of the entire CO_2 molecule into organic products.[3c,4a,c,d,8] The strained three-membered-ring substrates provide the thermodynamic driving force to render those transformations feasible, with the choice of catalyst controlling the kinetics of the pathways to the individual targets. The cyclic carbonates ethylene and propylene carbonate have been produced on a scale of several tens of thousands of tons per year for decades by using this transformation. The fully alternating copolymerization of epoxides and CO_2 has been, and still is, an intensively investigated pathway to high-molecular-weight polycarbonates as novel polymeric materials. A process to synthesize oligomeric polyether-polycarbonate-polyols from propylene oxide and CO_2 as building blocks for the production of polyurethane foams is currently being implemented on a kiloton scale in Dormagen, Germany, by the company Covestro (previously Bayer MaterialScience).[9] Fundamental research on the relationships between the catalytic procedure, reaction engineering, and product properties provided crucial information for the commercialization of this technology.[10] A detailed life-cycle assessment confirms that the carbon footprint and depletion of the fossil raw material are reduced by 10–20% with the CO_2-based process compared to conventional production.[11] The improvements in sustainability parameters result mainly from the fact that the incorporated CO_2 reduces the amount of petrochemical-based epoxide required as a feedstock.

The conversion of CO_2 into saturated hydrocarbons is currently discussed intensively as part of concepts to balance potential overcapacities resulting from the fluctuations in power generation from renewable primary sources, such as wind energy and photovoltaics.[3c,5b,12] Non-fossil-based electricity that cannot be distributed or stored in the grid is proposed to be used for water electrolysis to generate H_2. Several electrochemical, photochemical, and thermochemical water-splitting methods have been developed. However, electrolysis is the only method which is operating on an

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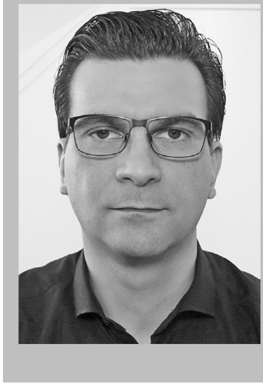
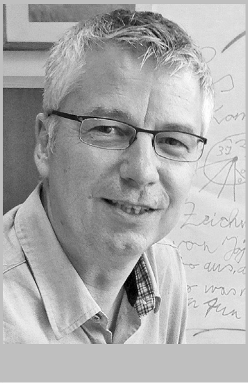


Jürgen Klankermayer obtained his diploma (1999) and PhD (2002) in organometallic chemistry from the University of Regensburg (Germany) under the supervision of Henri Brunner. He then pursued postdoctoral studies with Duncan Carmichael and François Mathey at the École Polytechnique (Palaiseau, France), and John M. Brown at the University of Oxford (UK). In 2005, he joined RWTH Aachen University (Germany), where since 2009 he has been Junior-Professor for "Mechanisms in Catalysis" within the cluster of Excellence "Tailor-made fuels from biomass".



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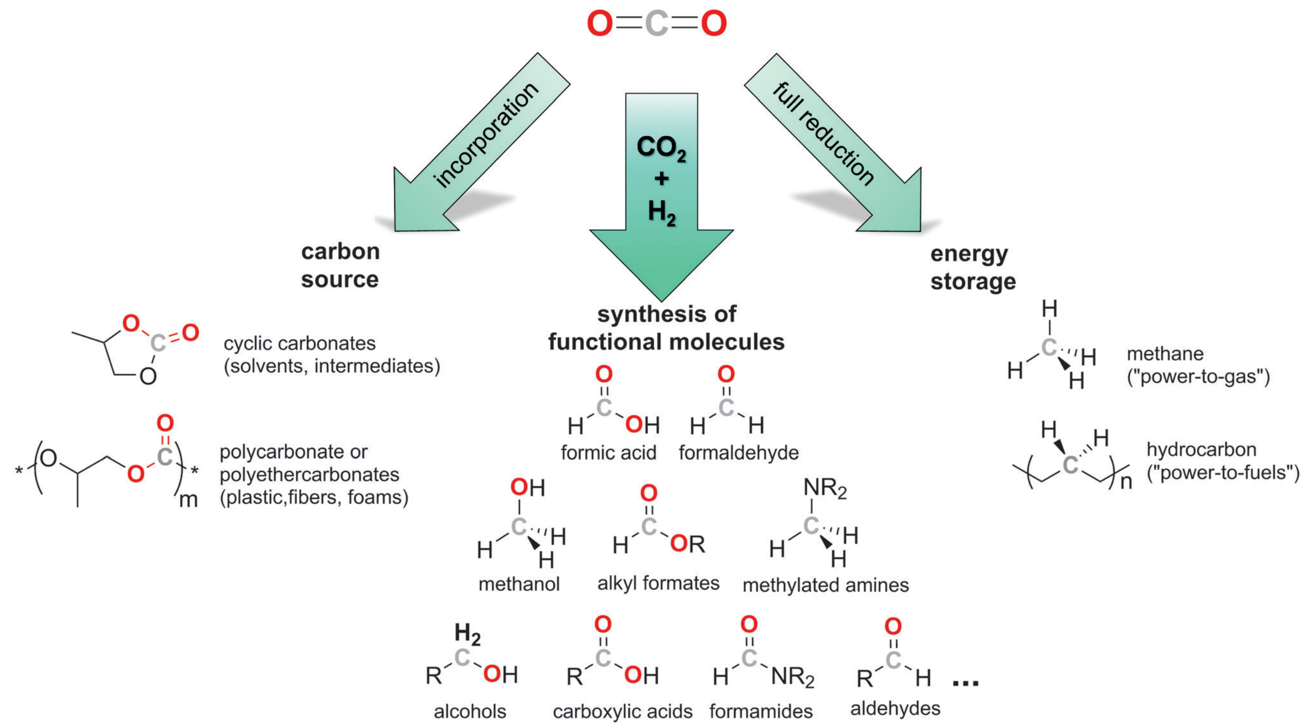


Figure 1. Illustrative examples of how the research lines for the utilization of carbon dioxide as a carbon source at the interface of the chemical and energetic value chains can be classified according to the molecular transformation: incorporation of the CO_2 molecule without formal reduction (left), complete reduction of CO_2 to methane and saturated hydrocarbons (right), or combined reduction and bond formation to result in a large synthetic diversity (middle).

industrial scale at the moment. Existing technologies for coupling photovoltaic cells with electrolysis have solar-to-hydrogen conversion efficiencies in the range of 5 to 20%. Selected overviews on the generation of hydrogen from water splitting can be found in the literature.[13] The complete hydrogenation of CO_2 to methane is known as the Sabatier reaction and, as such, is one of the corner stones in the historical development of heterogeneous metal catalysis. Currently, the process is discussed as part of so-called "power-to-gas" concepts that convert electric energy from non-fossil-based power sources into chemical energy storage materials. The catalytic conversion of H_2 and CO_2 into methane provides access to the existing infrastructure for the storage, transport, and utilization of natural gas. Similarly, hydrogen and CO_2 can be converted into liquid hydrocarbons through a combination of the reverse water-gas-shift (rWGS) reaction and Fischer–Tropsch synthesis. Although methane and saturated hydrocarbons can both be used for the regeneration of electricity, heating, or as fuels in the mobility sector, it is usually only the Fischer–Tropsch-type route that is referred to as "power-to-fuels" (sometimes "power-to-liquids"). A number of pilot and demonstrator-scale projects are currently operating to evaluate the current state-of-the-art technologies for these concepts.[14] This has led to a growing understanding of issues of scale-up and instationary operation of water electrolysis, thereby stimulating numerous activities on further improvements or towards disruptive novel techniques in this field.

Although the main goal of the full hydrogenation of carbon dioxide is the intermediate storage of non-fossil-based electricity in hydrocarbons as energy carriers, the combination of H_2 and CO_2 also opens the opportunity for the synthesis of functional molecules as an entry into the chemical value chain (Figure 1, middle). As will be shown in this Review, this can open efficient synthetic pathways in line with the principles of "green chemistry"[15] that avoid, for example, toxic or wastefull conventional reagents. In such cases, the combination of H_2 and CO_2 presents an attractive synthetic C_1 synthon independent of the H_2 source.[16] If the hydrogen stems from "decarbonized" energy sources, the combination has the additional potential to reduce significantly the carbon footprint of a given chemical product relative to the conventional petrochemical pathway.[11a,17] Even though the CO_2 will most likely stem from concentrated sources rather than be "drawn from the air", such processes come close to Primo Levi's vision of an anthropogenic technology to harness the energy of the sun into the material value chain, thus following, but not mimicking, nature's role model.

Possible target molecules include the partially reduced C_1 compounds formic acid, formaldehyde, and methanol, but most-recent progress, in particular, has demonstrated that the concept can be widely extended to more complex molecular structures. Multiple bond cleavage and bond-forming events are involved in the coupling of the sequentially reduced CO_2 building blocks with other substrates. Cantat and co-workers have referred to such kinds of transformations as a "diagonal" approach for the utilization of CO_2.[18] To cover the whole range of conceivable synthetic pathways that utilize the combination of CO_2 and H_2, the catalytic transformations must be controlled in a similar way as strategic moves on

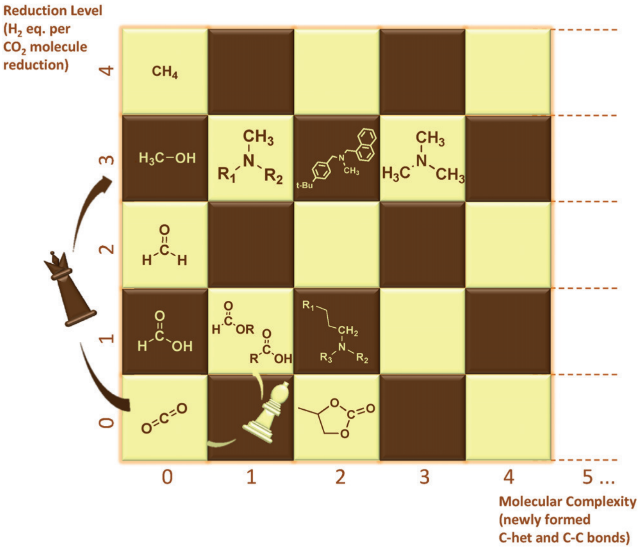


Figure 2. "Catalytic chess" to map out the molecular space of synthetic transformations involving CO_2 and H_2. Potential products are classified according to the "reduction level" expressed as H_2 equivalents needed for CO_2 reduction (y-axis) and "molecular complexity" related to the number of newly formed carbon–heteroatom or C–C bonds (x-axis).

a chessboard. In Figure 2, the stages of CO_2 reduction are displayed through the required H_2 equivalents on the y-axis. The x-axis represents the increasing molecular complexity expressed as the total number of newly formed C–C and carbon–heteroatom bonds during the synthesis, including, but not restricted to, the bonds formed at the CO_2 carbon atom.

The present Review invites the reader to enjoy this exciting area of "catalytic chess" and maybe even to start playing some games in her or his laboratory: It will highlight challenges and opportunities for catalytic research resulting from multistep reaction sequences based on CO_2 and hydrogen as starting materials. Reactions involving "H_2-like" reducing agents such as boranes and silanes will be selectively included for mechanistic analogies or in cases where reactions with H_2 are still in their infancy. The discussion will focus on organometallic catalysts as the pawns, knights, bishops, rooks, or even queens to reach synthetic targets on the molecular chessboard, but examples from heterogeneous and metal-free catalysis will be included frequently to illustrate similarities and differences where appropriate.

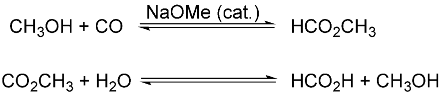
2. Formic Acid/CO Level

2.1. Formic Acid and Formate Salts

The addition of one equivalent of H_2 to CO_2 gives HCO_2H (formic acid) in a 100 % atom-efficient reaction. In the chess analogy, only one step forward in the vertical direction has to be achieved, a move which can be done easily using a pawn—however, it faces significant kinetic and in particular thermodynamic challenges.

2.1.1. Properties, Current Production, and Uses of Formic Acid and Formate Salts

Formic acid was discovered in 1670 in the poison of *Formica rufa*, the red ant.[19] It is a colorless, very corrosive ($pK_a = 3.739$) liquid at room temperature (m.p. = 8.3 °C) with a boiling point of 100.8 °C. The production volume of formic acid increased from about 260 000 $t\,a^{-1}$ in 1987 to 390 000 $t\,a^{-1}$ in 1995,[20] and to over 600 000 $t\,a^{-1}$ today.[3c] BASF is the world market leader, with a capacity of around 230 000 $t\,a^{-1}$,[21] followed by BP and Eastman (former Taminco/Kemira).[20] The most prominent production process of formic acid today is an indirect carbonylation of water (Scheme 1) via methyl formate as an intermediate.[19] In the first step, methanol is carbonylated with CO in the presence of $NaOCH_3$ as the catalyst to form methyl formate. In the second step, methyl formate is hydrolyzed in the presence of an excess of water to methanol and formic acid. Downstream processing is tedious, as formic acid forms a high-boiling azeotrope with water (b.p. 107.6 °C, 22.4 wt % water). Other less-important production processes are the carbonylation of hydroxides followed by acidification of the formed formate salt and the hydrolysis of formamide or formation as a side product during the production of acetic acid by oxidation of hydrocarbons. Recently, processes for the production of formic acid from biomass were proposed by the groups of Fu and Wasserscheid[22] using Keggin-type polyoxometalates and by Marsh and co-workers[23] employing $NaVO_3/H_2SO_4$ as the catalyst.



$$CH_3OH + CO \xrightleftharpoons{\text{NaOMe (cat.)}} HCO_2CH_3$$

$$HCO_2CH_3 + H_2O \rightleftharpoons HCO_2H + CH_3OH$$

Scheme 1. The current most important process for the production of formic acid from CO and water via methyl formate.

Formic acid has various applications based on its acidity and reducing properties. The largest volume application of formic acid is as a silage aid: formic acid promotes the fermentation of lactic acid and suppresses the formation of butyric acid.[19] Today, this is mainly carried out in Europe, however, this is also a growing market in other regions.[3c] A large potential market has been anticipated in steel pickling and wood pulping on the basis of its acidity.[19,24] Other important applications include its use in the leather and textile industries, where formic acid is used as a strong acid that leaves no residues upon evaporation, and use in the rubber industry, where it is used as a coagulant. Some 10 % of the produced formic acid is used for the synthesis of organic chemicals, such as pharmaceuticals, crop protection products, and aspartame. Various reactions of formic acid are known in organic synthesis, such as the reduction of Schiff bases, the esterification of alcohols, the formylation of amines to formamides, and the Koch carboxylic acid synthesis (formic acid as a CO source), just to name a few. The salts of formic acid also have several applications: aluminum and sodium salts of formic acid are used as auxiliary agents in the leather and textile industries,[20] sodium and potassium salts of formic acid are used for deicing at airports,[3c] and sodium formate is a starting material for the industrial production of sodium dithionite. Sodium formate is also used in electroplating baths and photographic fixing baths. Calcium formate can be used in construction as an additive to concrete. Ammonium formate is used as a silage aid, for the preparation of primary amines in the Leuckart reaction, and for the transfer hydrogenation of functional groups.[25]

Formic acid has also been discussed as an energy carrier. The development of direct formic acid fuel cells (DFAFCs) has been suggested for applications in small, portable electronics.[26] Another concept that was already discussed by Williams et al. in 1978[27] and that found significant interest recently is the use of formic acid as a hydrogen carrier.[28] As a consequence of the principle of microscopic reversibility, many organometallic catalysts that enable the hydrogenation of CO_2 to formic acid/formate are also active for the back reaction, that is, the selective dehydrogenation/decarboxylation of formic acid/formate to CO_2 and H_2 (Figure 3). No formation of CO was observed during the decomposition of formic acid/formate in the cited publications, which is an important prerequisite for the prospective use of the generated H_2 in fuel cells[28f] or other CO-sensitive applications.

Although the gravimetric H_2 storage capacity of formic acid is, at 4.4 wt %, relatively low compared to other technologies,[28c] formic acid has the advantage of being a liquid at room temperature, thereby facilitating transportation, storage, and refueling. However, one has to consider its highly corrosive nature, which requires the use of special equipment [for example, steel with high Cr, Ni, and Mo content, special nickel-rich alloys, polytetrafluorethylene (PTFE), poly(vinylidene fluoride) (PVDF)].[19] The melting point of 8.3 °C also has to be considered in transportation and storage. Formic acid is completely biodegradable and has relatively low acute toxicity.[19] Its hazardousness mainly results from its corrosive effect upon skin and mucous membranes, and requires protective measures to avoid any contact when handling pure formic acid.

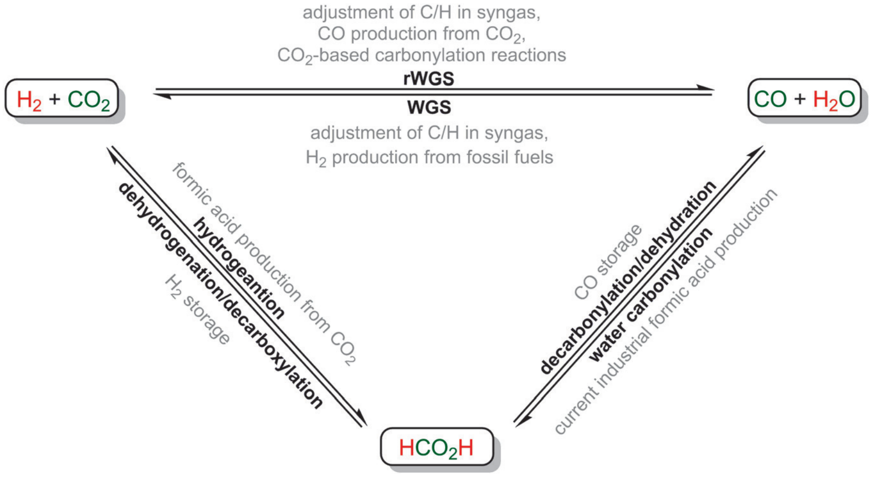


Figure 3. The "formic acid triangle" illustrates the connection between carbon dioxide, carbon monoxide, and formic acid under hydrogenating conditions and its applications.

Highly concentrated formic acid slowly decomposes to carbon monoxide and water (Figure 3, formic acid decarbonylation/dehydration). The decomposition rate is strongly dependent on the concentration of the formic acid and the temperature.[19] Therefore, storage or transportation tanks containing highly concentrated formic acid have to be protected from heat and have to be ventilated. On the other hand, the selective decomposition of formic acid to CO and water also offers the possibility to view HCOOH as a liquid-storage and carrier form of CO.[29]

In contrast to the use of formic acid as a hydrogen storage system, the use of formic acid as a CO storage system has received much less attention. The gravimetric CO storage capacity of formic acid is 60.8 wt %, and the toxicity of formic acid is much less than that of the highly toxic CO.[29] The decarbonylation/dehydration of formic acid to give CO is catalyzed by, for example, mineral acids, silicon dioxide, aluminum oxide, charcoal, and zeolites.[19,29,30] The combination of CO_2 hydrogenation to formic acid with the decarbonylation of formic acid represents an indirect, reversed water gas shift reaction (indirect rWGS). In such a scenario, formic acid could be produced from CO_2 and H_2 and later decomposed to release CO on demand. Thus, carbon monoxide could be stored and transported in the much safer form of formic acid.

The interchangeability of CO_2/H_2, HCO_2H, and CO/H_2O can be displayed by the "formic acid triangle", as summarized in Figure 3.

2.1.2. *Catalytic Synthesis of Formic Acid and Formate Salts by the Hydrogenation of CO_2*

2.1.2.1. *Thermodynamics and Kinetics of the Hydrogenation of CO_2 to Formic Acid and Formate Salts*

The thermodynamics of the direct hydrogenation of CO_2 to formic acid are challenging for the development of catalytic processes based on this transformation.[6f,7a] The gas-phase reaction of CO_2 and H_2 to formic acid is exothermic, but strongly endergonic because of the large and unfavorable entropic contribution [Scheme 2, Eq. (1)]. To achieve appreciable concentrations of formic acid, conditions have to be exploited which reduce the entropy difference between the reactants and the product, or which overcompensate the entropic factor with a highly negative enthalpy contribution (44–50 kJ per mole formic acid).[21] Crucial parameters by which this can be achieved are basic additives and the reaction solvent.[6f,7a] If the CO_2 hydrogenation is performed in the presence of a base such as ammonia, the exothermic protonation of ammonia by formic acid makes the reaction exergonic [Scheme 2, Eq. (2)]. If the reaction is carried out in water, solvation effects lead to a similarly exergonic reaction [Scheme 2, Eq. (3)].[31]

$$CO_2\,(g) + H_2\,(g) \longrightarrow HCO_2H\,(l)$$
$$\Delta G^0 = 32.8\ \mathrm{kJ\,mol^{-1}},\ \Delta H^0 = -31.5\ \mathrm{kJ\,mol^{-1}},\ \Delta S^0 = -215\ \mathrm{J\,K^{-1}\,mol^{-1}} \tag{1}$$

$$CO_2\,(g) + H_2\,(g) + NH_3\,(aq) \longrightarrow HCO_2^-\,(aq) + NH_4^+\,(aq)$$
$$\Delta G^0 = -9.5\ \mathrm{kJ\,mol^{-1}},\ \Delta H^0 = -84.3\ \mathrm{kJ\,mol^{-1}},\ \Delta S^0 = -250\ \mathrm{J\,K^{-1}\,mol^{-1}} \tag{2}$$

$$CO_2\,(aq) + H_2\,(aq) \longrightarrow HCO_2H\,(aq)$$
$$\Delta G^0 = -9.5\ \mathrm{kJ\,mol^{-1}} \tag{3}$$

Scheme 2. Influence of reaction media on the thermodynamics of the hydrogenation of CO_2 to formic acid.

As a consequence of these thermodynamic boundary conditions, most hydrogenations of CO_2 to formic acid are performed in the presence of a base.[6f,7a,e,32] The use of tertiary amines such as triethylamine (NEt_3) leads to formic acid/amine adducts that often form nonstoichiometric azeotropes. Formic acid salts are formed with primary amines or inorganic bases such as KOH or Na_2CO_3. The development of efficient downstream processing to recycle the organometallic catalyst while avoiding the back reaction and to separate the pure formic acid from the resulting salts or adducts is a major challenge for the industrial application of this transformation.[21]

A large number of catalysts with remarkable activities even under mild reaction conditions have been developed in the last decades to overcome the kinetic barrier of the seemingly simple hydrogenation of CO_2. These catalysts and the respective mechanistic details have been reviewed extensively.[6f,g,7a,e,17b,32,33] Therefore, this section will focus mainly on certain milestones in catalyst development (high turnover number: TON and/or high turnover frequency: TOF), reaction media, near ambient conditions, nonprecious metal catalysts, reversible systems for hydrogen storage), and in particular also on developments of downstream processing strategies (reactions in the absence of base, immobilized catalysts, new process schemes).

2.1.2.2. *Milestones in Catalyst Development for the Hydrogenation of CO_2 to Formic Acid and Formate Salts*

Catalysts with High TONs and TOFs in the Presence of Base

Remarkably, Farlow and Adkins discovered the formation of formic acid from H_2 and CO_2 in 1935 by using a heterogeneous Raney nickel catalyst.[34] Since then, only a few studies on heterogeneous catalysts for these reactions have been reported. Ruthenium on Al_2O_3 (2.0 wt%) was shown to be active at 80 °C, but only with a TON of up to 120.[35] Recently, Preti et al. demonstrated the solvent-free hydrogenation of CO_2 in neat NEt_3 in the presence of a titania-supported gold catalyst.[36] The catalyst was found to be stable towards CO and maintained its activity for 37 days, with a total TON of 18040. A process using this gold catalyst is described in a recent patent by BASF.[37] In general, the activities of heterogeneous catalysts remain limited and much better performances have been achieved using organometallic catalysts. One strategy to combine the advantages of organometallic and heterogeneous catalysts is the immobilization of organometallic catalysts. These immobilized organometallic catalysts will be described in the Section 2.1.2.3.

The hydrogenation of CO_2 to formic acid with homogeneous catalysis was reported for the first time by Inoue et al. in 1976.[38] Complexes of Pd, Ni, Rh, Ru, and Ir modified with mono- and bisphosphine ligands were tested and the researchers stated that "complexes of most group VIII transition metals can be used as the catalyst component." The highest TON of 87 was achieved using $[Ru(H)_2(PPh_3)_4]$ in the presence of NEt_3 as the base under mild conditions (ca. 25 °C, 25 bar CO_2, 25 bar H_2).[38] Following this groundbreaking work, metal catalysts of the platinum group achieved remarkably high productivities of up to several million moles of formic acid being formed per metal at turnovers of tens of thousands per hour. Systems operating in the presence of a base will be highlighted in this section (Table 1), followed by nonprecious metal catalysts operating in the presence of a base in the next section. The systems operating in the absence of a base are discussed later in the Section 2.1.2.3.

In the early 1990s, research from the group of Leitner resulted in greatly improved catalyst efficiency and shed some light on design principles for efficient catalytic systems.[6f] A major step forward was achieved in 1992 by using an in situ catalyst consisting of $[\{Rh(cod)Cl\}_2]$ (cod = cyclooctadiene) and the bidentate ligand dppb (1,4-bis(diphenylphosphino)-butane) to reach a TON of 1150 in DMSO in the presence of NEt_3 under mild reaction conditions (ca. 25 °C, 20 bar CO_2, 20 bar H_2).[39] The concentration of the base was the limiting factor for the yield of formic acid, with the maximum equilibrium concentration corresponding to the 5:2 azeotropic adduct. Formation of formic acid was also observed in the absence of base, but the TON of the catalyst was two orders of magnitude lower under these conditions. A TON of 2198 and a TOF of 375 h^{-1} could be achieved in DMSO/NEt_3 with the in situ system $[\{Rh(cod)(\mu\text{-}H)\}_4]$/dppb,[28b] and the TOF could be improved up to 1335 h^{-1} with the isolated complex [Rh(hfacac)(dcpb)] (hfacac = hexafluoroacetylacetonate, dcpb = $Cy_2P(CH_2)_4PCy_2$) as the catalyst in this medium.[40]

In 1993, the same group reported the first example of the efficient hydrogenation of CO_2 in aqueous media.[41] A TON of 3439 was achieved with $[RhCl(TPPTS)_3]$ (TPPTS = tris(*m*-sulfonatophenyl)phosphine) in the presence of the water-soluble amine $HNMe_2$ under mild reaction conditions (ca. 25 °C, 20 bar CO_2, 20 bar H_2). No formation of *N*,*N*-dimethylformamide was observed under these mild reaction conditions. Later, it was shown that a TOF of 1364 h^{-1} could be achieved at room temperature and of 7260 h^{-1} at 81 °C.[42] Higher temperatures are possible in this medium without compromising the equilibrium concentration too much because of the higher stability of the ammonium salt in water. More interestingly, aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) could also be used as basic reaction media, and gave TOFs of 98 h^{-1}, 48 h^{-1}, and 22 h^{-1}, respectively.[42] These media are of special interest, as aqueous solutions of these amines are used for scrubbing CO_2 from flue gases. Indeed, formic acid could be generated with a TOF of 35 h^{-1} from

Table 1: Selected precious metal catalysts for the hydrogenation of CO_2 to formic acid in the presence of base.

Entry	Catalyst	Additives	*T* [°C]	p_{H_2}/p_{CO_2} [bar/bar]	*t* [h]	TOF [h^{-1}]	TON	Ref.
1	$[RuH_2(PPh_3)_4]$	NEt_3	RT	25/25	20	4	87	[38]
2	$[\{Rh(cod)Cl\}_2]$ + dppb	NEt_3	RT	20/20	22	52	1150	[39]
3	$[RhCl(TPPTS)_3]$	$HNMe_2$	RT	20/20	12	287	3439	[41]
4	$[\{Rh(cod)(\mu\text{-}H)\}_4]$ + dppb	NEt_3	RT	20/20	18	122	2198	[28b]
5	[Rh(hfacac)(dcpb)]	NEt_3	RT	20/20	–	1335	–	[40]
6	$[RuH_2(PMe_3)_4]$	NEt_3	50	85/120	1	1400	1400	[42]
7	$[RuCl_2(PMe_3)_4]$	NEt_3	50	85/120	47	153	7200	[42]
8	$[RuH_2(PMe_3)_4]$	NEt_3, MeOH	50	85/125	0.5	> 4000	> 2000	[43]
9	$[RuCl(O_2CCH_3)(PMe_3)_4]$	NEt_3, C_6F_5OH	50	70/120	0.3	95000	32000	[44]
10	$[RhCl(TPPTS)_3]$	$HNMe_2$	81	20/20	0.5	7260	3630	[42]
11	$[RuCl_2(PTA)_4]$	$NaHCO_3$	80	60/na	–	807	–	[54]
12	$[\{RuCl_2(TPPSM)_2\}_2]$	$NaHCO_3$	80	60/35	–	9600	–	[46]
13	[IrCp*Cl(dhpt)]Cl	KOH	120	30/30	–	42000	–	[48]
14	[IrCp*Cl(dhpt)]Cl	KOH	60	0.5/0.5	–	33	–	[48]
15	$[IrH_3(PNP)]$	KOH	120	30/30	48	73000	3500000	[49]
16	$[IrH_3(PNP)]$	KOH	200	25/25	2	150000	300000	[49]
17	$[IrI_2(AcO)(bis\text{-}NHC)]$	KOH	200	30/30	75	2533	190000	[50]
18	$[IrH_2(CO_2H)(PNP)]$	KOH	185	28/28	24	14500	348000	[51]
19	$[\{IrCp^*(H_2O)\}_2(thbpym)]$	KOH	25	0.5/0.5	1	64	–	[28j]
20	[RuCl(H)(CO)(PNP)]	DBU	120	30/10	–	1500000	–	[28m]
21	[RuCl(H)(CO)(PNP)]	DBU	65	2.5/2.5	–	7900	–	[28m]

a H_2O/MEA solution saturated with CO_2 at ambient pressure by applying only 20 bar of H_2 at room temperature without an additional supply of CO_2. The direct use of CO_2-saturated scrubbing solutions as feedstock is certainly worth investigating further in the future.

In 1994, Jessop, Ikariya, and Noyori introduced supercritical CO_2 ($scCO_2$) as a reaction medium for the hydrogenation of CO_2 to formic acid.[42] TOFs up to 1400 h^{-1} and TONs up to 7200 were achieved at 205 bar and 50 °C by using the $scCO_2$-soluble catalysts $[RuH_2(PMe_3)_4]$ and $[RuCl_2(PMe_3)_4]$ in the presence of NEt_3. These, at the time, outstanding activities were attributed to the high miscibility of $scCO_2$ with H_2 and reduced mass-transfer limitations in this medium. The TONs and TOFs could be enhanced further by using additives such as water, methanol, and DMSO.[43] TOFs in the range of 4000 h^{-1} could be achieved in the presence of methanol or DMSO under conditions where a single homogeneous phase was present at the beginning of the reaction, and a second phase was formed during the reaction by the produced formic acid/amine adduct. The additives were discussed to work as cosolvents to increase the catalyst solubility in the supercritical phase and/or to take part in the mechanism by hydrogen bonding during the CO_2 insertion. In 2002, the Jessop group published an extensive study on the use of additives in the hydrogenation of $scCO_2$ with $[RuCl(O_2CCH_3)(PMe_3)_4]$.[44] A TOF of 95000 h^{-1} was observed in the presence of NEt_3 as a base and pentafluorophenol as an acidic alcohol additive. The authors could show by in situ NMR spectroscopy that the alcohol additive induces the catalyst precursor to transform into a cationic species and the results supported the role of the alcohol as a hydrogen-bond and/or a proton donor. Clearly, the dual use of $scCO_2$ as a feedstock and reaction medium is a promising approach, although the conditions used are much more drastic compared to the mild reaction conditions used for Rh-catalyzed reactions in conventional organic solvents or water.

In 2000, Joó, Laurenczy et al. reported the hydrogenation of CO_2 in aqueous solutions of alkali hydrogen carbonates.[45] By using the water-soluble catalyst $[RuCl_2(PTA)_4]$ (PTA = 1,3,5-triaza-7-phosphaadamantane), a maximum TOF of 807 h^{-1} could be obtained using the optimum ratio of 10% HCO_3^-/90% CO_2 (pH 5.86). The authors concluded on the basis of kinetic measurements that HCO_3^- is the actual substrate that is hydrogenated under these conditions. TOFs as high as 9600 h^{-1} could be achieved by the same team using $[\{RuCl_2(TPPMS)_2\}_2]$ (TPPMS = monosulfonated triphenylphosphane) as the catalyst in 0.3 M $NaHCO_3$ solution at 80 °C and 95 bar total pressure.[46]

In 2004, Himeda et al. presented iridium half-sandwich complexes bearing Cp* (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) and *N*-donor ligands for the hydrogenation of CO_2 in aqueous solutions of KOH.[47] A TOF of 23000 h^{-1} was achieved at 120 °C and 60 bar in the hydrogenation of CO_2 with [IrCp*Cl(dhpt)]Cl (dhpt = 4,7-dihydroxy-1,10-phenanthroline) and molecular hydrogen. The high activity was attributed to the formation of a strong electron-donating oxyanion by deprotonation of the two hydroxy substituents in the dhpt ligand. The deprotonation of the ligand also increased the water solubility of the catalyst. A huge drop in activity as well as precipitation of the catalyst was observed upon protonation of the ligand. Interestingly, this catalyst also worked under ambient pressure (1 atm) at 80 °C, with a TON of 800 and a TOF of 35 h^{-1}. In 2007, they reported an improved TON of 190000 and TOF of 42000 h^{-1} with the same catalyst.[48] A TON of 222000 and a TOF of 33000 h^{-1} was achieved by using the slightly modified complex [IrCp*Cl(4dhbp)]Cl (4dhbp = 4,4′-dihydroxy-2,2′-bipyridine). In 2012, the same team developed the dinuclear Ir complex

$[\{IrCp^*(H_2O)\}_2(thbpym)]$ bearing 4,4′,6,6′-tetrahydroxy-2,2′-bipyrimidine (thbpym) as a bridging ligand.[28j] This catalyst showed a higher TOF of 53 800 h^{-1} and a TON of 153 000 under milder reaction conditions (40–50 bar, 50–80 °C) compared to their previous systems. A TOF of 64 h^{-1} and a TON of 7200 was even achieved at ambient pressure and temperature (1 atm, 25 °C).

In 2009, the research group of Nozaki set a remarkable milestone in terms of TON and TOF by using Ir^{III}-PNP pincer complexes for the hydrogenation of CO_2 in aqueous KOH solution.[49] With $[IrH_3(PNP)]$ (PNP = 2,6-$(CH_2PiPr_2)_2C_5H_3N$), a maximum TOF of 150 000 h^{-1} was obtained at 200 °C, and a maximum TON of 3 500 000 was obtained after 48 h at 120 °C, which corresponds to a formate concentration of about 0.7 mol L^{-1}. Azua et al. showed in 2011 that complexes of the type $[IrI_2(AcO)(bis\text{-}NHC)]$ with NHC ligands bearing sulfonate substituents give high TONs of up to 190 000, which corresponds to a formate concentration of 0.4 mol L^{-1}, under very similar conditions.[50] The transfer hydrogenation of CO_2 with *i*PrOH in the presence of this complex was also possible with a high TON of 2700. In the same year, Crabtree, Hazari, and co-workers reported the air-stable and water-soluble formate complex $[IrH_2(CO_2H)(PNP)]$ (PNP = HN($iPr_2PC_2H_4)_2$) to be a highly active catalyst for the hydrogenation of CO_2 in aqueous KOH.[51] TONs of up to 348 000 (corresponding to a formate concentration of 0.7 mol L^{-1}) and TOFs up to 18 780 h^{-1} were achieved, although at even higher temperatures of 185 °C. The hydrogen bond donor interaction of the PNP ligand with the formate was shown to facilitate CO_2 insertion into the Ir^{III} hydride. Iridium complexes with *N*-donor ligands are also highly active catalysts for the hydrosilylation of CO_2.[52]

Recently, Pidko and co-workers reported the highest TONs and TOFs achieved to date.[28m,53] They used a Ru-PNP complex $[RuCl(H)(CO)(PNP)]$ (PNP = 2,6-$(CH_2PtBu_2)_2C_5H_3N$) similar to the Ir-PNP complex used by Nozaki and co-workers for the CO_2 hydrogenation, but in an organic medium consisting of dimethylformamide as the solvent and DBU as the amine base. An outstanding TOF of 1 100 000 h^{-1} was achieved at 40 bar and 120 °C, which leads to a formate concentration of about 1.2 mol L^{-1}. A TOF of 60 000 h^{-1} was still achieved at a total pressure of only 5 bar and a reaction temperature of 90 °C, which was lowered significantly to 7900 h^{-1} at a reaction temperature of 65 °C.

Nonprecious Metal Catalysts

The productivities that can be achieved today with platinum group metal catalysts for the synthesis of formic acid from CO_2 and H_2 are well in the range of those using similar metal catalysts in large-scale industrial processes such acetic acid production or hydroformylation. Efficient separation and recycling of these transition-metal catalysts to achieve a continuous or quasicontinuous operation is essential for possible industrial applications, as discussed later. Another direction is the development of catalysts based on cheap and abundant nonprecious metal catalysts, especially for applications where dissipation of the catalyst is more difficult to prevent, such as H_2 storage systems for mobility. Table 2 provides an overview on the performance of representative catalysts based on first-row transition metals.

In fact, Inoue et al. already used $[Ni(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) in their groundbreaking studies of 1976.[38] A TON of 7 was obtained after 20 h in the presence of NEt_3 as the amine base. This does not sound much, but this TON was obtained under mild reaction conditions (ca. 25 °C, 25 bar H_2, 25 bar CO_2). In 2003, Jessop and co-workers used a high-pressure combinatorial screening method to identify catalytically active combinations of metal precursors and ligands under a standard set of conditions.[55] A series of non-platinum group metal salts were found to be active, among these were salts of Co, Cr, Fe, In, Mo, Nb, Ni, and W. The most active combinations in the presence of DBU at 100 bar total pressure and 50 °C were $NiCl_2$/dcpe (dcpe = $Cy_2PCH_2CH_2PCy_2$; TON = 117, TOF = 16 h^{-1}), $FeCl_3$/dcpe (TON = 113, TOF = 15 h^{-1}), and $MoCl_3$/dcpe (TON = 63, TOF = 8 h^{-1}). The use of a higher total pressure of 200 bar resulted in a TON of 4400 being achieved with $[NiCl_2(dcpe)]$.

In 2010, Beller, Laurenczy, Dyson, and co-workers showed in a collaborative effort that the in situ iron-based catalyst $Fe(BF_4)_2/PP_3$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) is active in the hydrogenation of sodium bicarbonate to sodium formate with a TON of 660, which corresponds to a conversion of 88 % in the absence of CO_2 (80 °C, 60 bar H_2).[56] The catalyst was also active in the hydrogenation of CO_2 to alkyl formates and

Table 2: Selected nonprecious-metal catalysts for the hydrogenation of CO_2 to formic acid in the presence of base.

Entry	Catalyst	Additives	*T* [°C]	p_{H_2}/p_{CO_2} [bar/bar]	*t* [h]	TOF [h^{-1}]	TON	Ref.
1	$[Ni(dppe)_2]$	NEt_3	RT	25/25	20	0.35	7	[38]
2	$NiCl_2$/dcpe	DBU	50	40/160	216	20	4400	[55]
3	$FeCl_3$/dcpe	DBU	50	40/60	7.5	15	113	[55]
4	$MoCl_3$/dcpe	DBU	50	40/60	7.5	8	63	[55]
5	$[Fe(H)_2(CO)(tBu\text{-}PNP)]$	NaOH	80	6.66/3.33	5	156	788	[58]
6	$[FeF(L)]BF_4$	NEt_3, H_2O	100	30/30	20	95	1897	[57]
7	$[CoCp^*(L)(4dhbp)]^{n+}$	$NaHCO_3$	100	20/20	1	39	39	[61]
8	$[Co(dmpe)_2H]$	Verkade's base	RT	10/10	–	74 000	–	[62]
9	$[Co(dmpe)_2H]$	DBU	RT	20/20	–	220	–	[63]
10	$FeCl_2$/ddpe	N(Hex)$_3$	70	80/28	1	88	88	[59]

formamides (see below). Yields for the hydrogenation of CO_2 to formic acid/amine adducts or formate salts were not reported. Interestingly, $Fe(BF_4)_2$ was found to be only active in combination with the tetradentate ligand PP_3; no active complex was formed with all the other tested ligands.

The performance of the iron catalyst could be further improved by using a modified tetradentate ligand P_4 = tris[(2-diphenylphosphino)phenyl]phosphine.[57] A very high TON of 7546 (yield = 77 %) and TOF of 377 h^{-1} could be achieved in the hydrogenation of bicarbonate in methanol solution by using the air-stable preformed catalyst $[FeF(P_4)][BF_4]$ in the absence of CO_2 pressure (100 °C, 60 bar H_2 at RT). The catalyst was shown to also catalyze the hydrogenation of CO_2 in methanol solution to formic acid, methyl formate, and formamides (see below). Formic acid could be formed with a high TON of 1897 after 20 h (100 °C, 60 bar total pressure at RT) in the presence of water and NEt_3 in methanol.

Polydentate ligands appear to be essential for the activity of the iron catalysts. In 2011, the Milstein group reported an iron pincer complex for the hydrogenation of CO_2 to sodium formate.[58] A TOF of 156 h^{-1} and a TON of 788 were achieved under relatively mild reaction conditions (80 °C, 10 bar total pressure at RT) by using the iron(II) pincer complex $[FeH_2(CO)($*t*Bu-PNP$)]$ (analogous to Nozaki's highly active Ir-PNP complex). Furthermore, the hydrogenation of sodium bicarbonate to sodium formate using the same catalyst under similar conditions but in the absence of CO_2 occurred with a TON of 320 (yield = 32 %). In a patent published in 2013, BASF described the use of $FeCl_2$/1,2-bis(didodecylphosphino)ethane ($FeCl_2$/ddpe) as a catalyst for the hydrogenation of CO_2 in methanol as solvent and in the presence of $N(Hex)_3$ as the amine. A TOF of 88 h^{-1} was obtained at 70 °C and 125 bar.[59]

In 2012, the group of Beller reported that the cobalt catalyst $Co(BF_4)_2/PP_3$ (PP_3 = tris[2-(diphenylphosphino)ethyl]phosphine or tetraphos) showed similar activity to the previously reported iron system under comparable conditions.[60] The cobalt salts $[Co(acac)_2]$ (acac = acetylacetonate), $[Co(acac)_3]$, and $CoCl_2$ gave similar results in combination with PP_3. Decreasing the catalyst concentration and increasing the temperature to 120 °C led to TONs up to 3877 (yield = 71 %) and TOFs up to 194 h^{-1} being achieved. The catalyst could be used in the hydrogenation of CO_2 to alkyl formates and formamides (see below), but no yields for the hydrogenation of CO_2 to formic acid/amine adducts or formate salts were reported. Again, the activity was uniquely dependent on the PP_3 ligand.

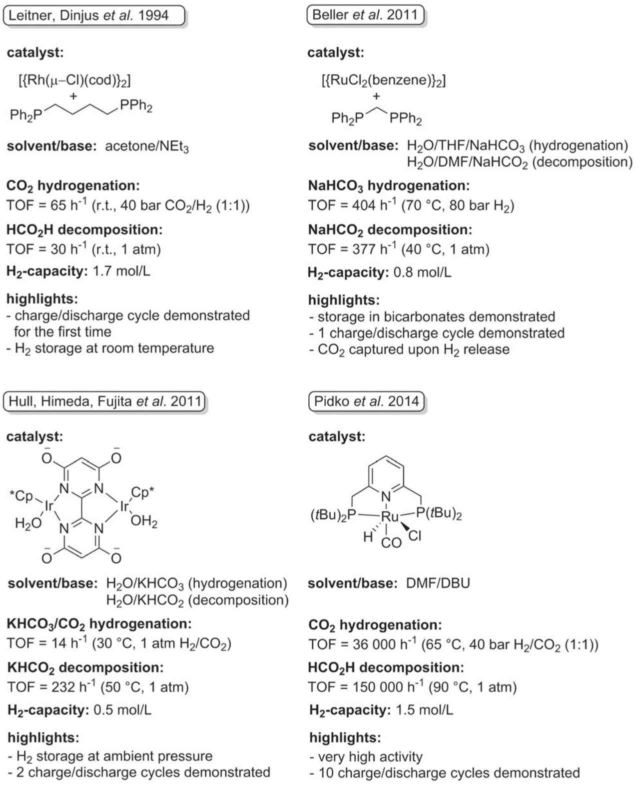
Shortly thereafter, Muckerman, Himeda, Fujita, and coworkers reported the cobalt analogue of their previously reported Cp^*Ir^{III} catalysts, $[CoCp^*(H_2O)(4dhbp)]^{2+}$ (4dhbp = 4,4′-dihydroxy-2,2′-bipyridine).[61] CO_2 could be hydrogenated in an aqueous bicarbonate solution with a TOF of 39 h^{-1} at 100 °C and 80 bar total pressure. In the same year, Jeletic et al. developed a highly active cobalt-based catalytic system for the hydrogenation of CO_2 to formic acid in THF solution in the presence of amines.[62] An outstanding TOF of 74000 h^{-1} was achieved under mild reaction conditions (RT, 20 bar total pressure) by using $[Co(dmpe)_2H]$ (dmpe = 1,2-bis(dimethylphosphino)ethane). However, this activity was only achieved using the very strong and very expensive Verkade base. With this system, a TOF of 3400 h^{-1} and a TON of 2000 was obtained even at ambient pressure and temperature. A TOF of 220 h^{-1} was still achieved at room temperature and 40 bar total pressure on using DBU as the base.[63] No reaction was observed in the presence of the weaker base NEt_3. The authors suggested that high basicity was needed to regenerate the $[Co(dmpe)_2H]$ complex by deprotonation of the intermediate $[Co(dmpe)_2(H)_2]^+$.

In summary, the use of first-row transition metals is now possible even though TON and TOF values are typically one or two orders of magnitude below the best platinum group systems (cf. Tables 1 and 2). Modification of the ligand structure is expected to improve the catalyst performance, and the specific coordination features of these metals must be considered. Thus, the ligand prices need to be considered in combination with the metal catalysts when comparing systems based on different metals. The ligand price might contribute significantly to the overall price of the organometallic catalyst, depending on the complexity and the effort involved in its synthesis. One should also keep in mind that third-row metals can also have a significant environmental impact (for example, high acute and high chronic aquatic toxicity according to GHS material safety data sheets for $CoCl_2$ and $CoCO_3$). Thus, it is also mandatory to develop processing schemes for these catalysts that avoid release of the metal into the environment.

Catalyst Systems for Reversible Hydrogen Storage

Whereas the possible implementation of CO_2 and H_2 for the production of formic acid and its derivatives as chemical products can be evaluated at least in principle on the basis of the feedstock costs and process schemes, the analysis of its use as a hydrogen carrier is more complex and depends strongly on factors such as the application area, infrastructure, etc. A general prerequisite is, however, the design of a system or device that can be reversibly charged and discharged through a catalytic process. Although many studies motivated by the aim of hydrogen storage showed highly efficient catalysts for the hydrogenation of CO_2 to formic acid/formates, and other studies showed highly efficient catalysts for the decomposition of formic acid/formates to generate H_2, the two reactions were studied separately in most of these studies. In this section, only the most efficient systems are highlighted, and a special focus is on examples where CO_2 hydrogenation and formic acid decomposition are catalyzed by the same catalyst and in the same reaction medium. Selected milestones in the development of such fully reversible systems are summarized in Figure 4.

The use of formic acid for hydrogen storage was already discussed by Williams et al. in 1978.[27] In 1992, Tsai and Nicholas reported that $[RhH_2(PMe_2Ph)_3(S)]BF_4$ (S = H_2O, THF) catalyzed the hydrogenation of CO_2 to formic acid as well as the decomposition of formic acid to CO_2 and H_2.[28a] No cycle was demonstrated, however, in this study. In 1994, Leitner, Dinjus, and Gassner demonstrated the first fully reversible cycles of CO_2 hydrogenation/formic acid decomposition.[28b] By using the in situ catalyst $[\{Rh(cod)(Cl)\}_2]$/



Leitner, Dinjus *et al.* 1994

catalyst:
$[\{Rh(\mu{-}Cl)(cod)\}_2]$

solvent/base: acetone/NEt_3

CO_2 hydrogenation:
TOF = 65 h^{-1} (r.t., 40 bar CO_2/H_2 (1:1))

HCO_2H decomposition:
TOF = 30 h^{-1} (r.t., 1 atm)

H_2-capacity: 1.7 mol/L

highlights:
- charge/discharge cycle demonstrated for the first time
- H_2 storage at room temperature

Beller *et al.* 2011

catalyst:
$[\{RuCl_2(benzene)\}_2]$

solvent/base: $H_2O/THF/NaHCO_3$ (hydrogenation)
$H_2O/DMF/NaHCO_2$ (decomposition)

$NaHCO_3$ hydrogenation:
TOF = 404 h^{-1} (70 °C, 80 bar H_2)

$NaHCO_2$ decomposition:
TOF = 377 h^{-1} (40 °C, 1 atm)

H_2-capacity: 0.8 mol/L

highlights:
- storage in bicarbonates demonstrated
- 1 charge/discharge cycle demonstrated
- CO_2 captured upon H_2 release

Hull, Himeda, Fujita *et al.* 2011

catalyst:

solvent/base: $H_2O/KHCO_3$ (hydrogenation)
$H_2O/KHCO_2$ (decomposition)

$KHCO_3/CO_2$ hydrogenation:
TOF = 14 h^{-1} (30 °C, 1 atm H_2/CO_2)

$KHCO_2$ decomposition:
TOF = 232 h^{-1} (50 °C, 1 atm)

H_2-capacity: 0.5 mol/L

highlights:
- H_2 storage at ambient pressure
- 2 charge/discharge cycles demonstrated

Pidko *et al.* 2014

catalyst:

solvent/base: DMF/DBU

CO_2 hydrogenation:
TOF = 36 000 h^{-1} (65 °C, 40 bar H_2/CO_2 (1:1))

HCO_2H decomposition:
TOF = 150 000 h^{-1} (90 °C, 1 atm)

H_2-capacity: 1.5 mol/L

highlights:
- very high activity
- 10 charge/discharge cycles demonstrated

Figure 4. Selected milestones in the development of fully reversible catalyst systems for the reversible adjustment of the CO_2-H_2/HCOOH equilibrium.

dppb (dppb = 1,4-bis(diphenylphosphino)butane) in acetone/NEt_3, formic acid was formed with a TOF of 54 h^{-1} up to a concentration of 1.7 molL^{-1} under 40 bar CO_2/H_2 at room temperature, which corresponds to a H_2 storage capacity of 1.7 mol H_2 per liter storage medium. After the pressure was reduced to 1 atm, the docomposition of formic acid started with a nearly constant TOF of 30 h^{-1} down to a concentration of 0.07 molL^{-1}. Upon pressurizing with 40 bar CO_2/H_2, the system could again be recharged with a TOF of 65 h^{-1}.

Since 2008, a number of research groups have started to investigate the organometallic catalytic interconversion of the CO_2-H_2/HCOOH couple for hydrogen storage.[28c–f] In 2012, the group of Beller reported a Ru catalyst which also enabled the reversible storage of H_2 in an organic solvent/amine mixture.[28i] The DMF/NEt_3 solution was charged for 16 h at room temperature (30 bar H_2, 30 bar CO_2) in the presence of $[RuH_2(dppm)_2]$ (dppm = bis(diphenylphosphino)methane). Afterwards, the decomposition of the formic acid/amine adduct was initiated by reducing the pressure to 1 atm. Gas volumes between 2170 mL and 1620 mL were obtained in eight subsequent cycles. In this study, another problem of amine-based H_2 storage systems became apparent: During decomposition, around 5% of the volatile base NEt_3 was lost with the gas flow, which had to be replaced in each cycle. The H_2 storage capacity of the system was about 2 molL^{-1}, which is still too low for efficient H_2 storage. However, the authors suggested using this system for reducing the overall pressure in H_2 storage tanks.

In 2014, Hsu et al. demonstrated a similar hydrogen charging/discharging device based on DBU/toluene (11.4 mL/9.8 mL).[28l] The authors stated that toluene was needed to reduce undesired crystallization of the DBU/formic acid salt, thereby avoiding low miscibility and problematic reactivation of the charged battery after longer storage times. By using a $[RuCl(MeCN)(PNNP)]PF_6$ complex under quite harsh conditions (100 °C, 140 bar total pressure at reaction temperature), CO_2 could be hydrogenated with a TOF of up to 1587 h^{-1}. Decomposition was induced by reducing the pressure to 1 atm and heating to 100 °C, and proceeded with a TOF of around 1140 h^{-1}. Five charging/discharging cycles were carried out without a pronounced loss of efficiency. Interestingly, the charged "battery" could be stored for five days without loss of efficiency. The storage capacity of this system was 3.8 molL^{-1}.

The extremely active CO_2 hydrogenation catalyst [RuCl(H)CO(PNP)] developed by Pidko and co-workers (see above) was also shown to be active in the decomposition of formic acid/amine to CO_2/H_2, with activities up to 257 000 h^{-1}.[28m] Both reactions could be coupled to a closed cycle by using DMF/DBU (30 mL/5 mL) as a reaction medium. CO_2 hydrogenation (charging) could be achieved within 3 h at 65 °C and 5 bar total pressure to yield an acid/amine ratio of close to one, which corresponds to a H_2 storage capacity of 1.5 molL^{-1}. The decomposition of formic acid (discharging) was finished within 1 h at ambient pressure and 90 °C, which corresponds to a TOF of 150 000 h^{-1}. Several cycles could be performed. This is by far the fastest charge/discharge system known today.

Although the catalytic efficiencies for the charge and discharge processes have been greatly improved, the systems generally suffer from a low storage capacity in organic solution because large volumes of the reaction media need to be used and because of the fact that CO_2 also leaves the device together with H_2. Aqueous solutions of inorganic bases might partly reduce these drawbacks and have thus also found interest as storage media.

In 2009[28g] and 2011,[64] Himeda et al. showed that catalysts of the type $[MCp^*(L)(4dhbp)]^{n+}$ (M = Ir, Rh, Ru; 4dhbp = 4,4′-dihydroxy-2,2′-bipyridine) were active in aqueous KOH solution for the hydrogenation of CO_2 to formate as well as for the decomposition of formate to H_2 and CO_2. However, they performed the reactions independently and did not show the combination of the two reactions in a closed cycle. One of the challenges is that, for many catalytic systems, the hydrogenation of CO_2 occurs under basic conditions, whereas the decomposition requires acidic media, as exemplified by the system that Maenaka et al. reported in 2012.[17b,28k,65] A TOF of 6.8 h^{-1} was obtained at atmospheric pressure and 30 °C during the hydrogenation of CO_2 in 0.1 M K_2CO_3 in the presence of a cationic Cp*-iridium complex. Under acidic conditions, the same catalyst could be used for the decomposition of formate with a TOF of 1880 h^{-1} at 25 °C. Interestingly, in 2004 Hayashi et al. reported a base-free aqueous system for the formation and decomposition of formic acid.[66] By using $[Ru(\eta^6\text{-}C_6Me_6)(4,4'\text{-OMe-bpy})$-

$(H_2O)](SO_4)$ (4,4′-OMe-bpy = 4,4′-dimethoxy-2,2′-bipyridine), a formic acid concentration of $0.06\,mol\,L^{-1}$ was obtained after 70 h (55 bar H_2, 25 bar CO_2, 40 °C). Decomposition of formic acid was also possible at 40 °C and atmospheric pressure (TON = 9 after 1 h); however, no closed cycle was demonstrated.

In 2012, Hull, Himeda, Fujita et al. used their dinuclear Cp*Ir catalyst with 4,4′,6,6′-tetrahydroxy-2,2′-bipyrimidine (thbpym) as a bridging ligand for reversible hydrogen storage in aqueous media under mild conditions.[28j] They exposed a 2 M $KHCO_3$ solution containing the catalyst to a stream of CO_2/H_2 at 1 atm and 30 °C for 136 h, which yielded a 0.48 M formate solution. After acidifying the solution to pH 1.7 with sulfuric acid and warming to 50 °C, decomposition of the formate started. Decomposition ended when a pressure of 23 bar H_2/CO_2 (1:1) was built up. This system is remarkable, as the forward reaction occurred at ambient pressure and both directions required only very mild temperatures. However, recharging the system required adjustment of the pH value with $KHCO_3$, thereby resulting in a build-up of potassium sulfate in each cycle.

Beller and co-workers demonstrated in 2011 that sodium bicarbonate/sodium formate solutions allow the CO_2 to be retained in the system.[67] The hydrogenation of bicarbonate to formate with $[\{RuCl_2(benzene)\}_2]$/dppm in H_2O/THF as well as the decompostion of formate in H_2O/DMF was demonstrated. When the decomposition of formate was performed sufficiently slowly with a TOF of $377\,h^{-1}$ at 40 °C, bicarbonate was reformed and less than 1 % of the CO_2 was released into the gas phase. This was a major step forward to obtaining a completely reversible storage system in which CO_2 is used as the hydrogen carrier, as the CO_2 released during the decomposition of formic acid could be largely fixed inside the storage device. However, coupling of the bicarbonate hydrogenation (charging) and formate decomposition (discharging) steps to a closed cycle remained a challenge with this catalytic system, as the solvent had to be removed and changed from H_2O/THF (charging) to H_2O/DMF (discharging). The storage capacity of this system was $0.79\,mol\,L^{-1}$.

In the same year, Joó, Laurenczy, and co-workers demonstrated the reversible hydrogenation of sodium bicarbonate to sodium formate by using $[\{RuCl_2(TPPMS)_2\}_2]$ in aqueous solution in a closed reactor.[68] Sodium bicarbonate could be hydrogenated with a yield of 90 % within 200 min at 83 °C and 100 bar H_2. Decomposition was started without any change of the reaction medium by decreasing the pressure to 1 bar, and H_2 was produced with conversions of up to 40–50 %. Overall, three consecutive cycles were carried out. The maximum storage capacity of this system was $0.26\,mol\,L^{-1}$.

The main issues which remain unsolved with the presented catalytic systems if considered as hydrogen storage devices are the following: 1) In the systems with organic solvents and amines, the volatile components are partially lost with the generated CO_2/H_2 stream. 2) Except for the system using bicarbonate as a storage medium, CO_2 is liberated into the gas phase during the discharging process together with H_2. This greatly dilutes the energy content of the gas phase and raises issues of compatibility with applications requiring pure H_2, such as fuel cells. 3) The pH requirements for the formation/decomposition reactions have to be matched with the shifts in pH values because of changes in the formic acid concentration. 4) The gravimetric H_2 storage capacities of all the systems are much lower (typically < 1 wt %) than the maximum capacity of pure formic acid (4.4 wt %), because amine adducts or salts are formed and large amounts of solvent are necessary. For example, a 1M aqueous sodium formate solution can be considered a typical achievable concentration in terms of practical aspects such as charging rates and solubilities of the involved components; this corresponds to a gravimetric H_2 storage capacity of around 0.2 wt %.

2.1.2.3. Downstream Processing

Although it can be interesting to produce formic acid adducts or salts as products in certain applications, the isolation of pure formic acid offers the most direct entry into the existing market of this product and is also crucial for possible future applications such as H_2 storage. Although the thermodynamic boundaries of the $CO_2/H_2/HCOOH$ equilibrium are the basis for the reversible storage systems, they present a challenge for process schemes including the downstream processing to isolate formic acid. This is due to several facts: 1) High yields of formic acid have only been achieved in the presence of additives such as bases, which lead to the formation of formic acid derivatives rather than the formation of pure formic acid. 2) Cleavage of the formic acid derivatives to obtain pure formic acid is often not economic, as by-products are produced and/or the components form an azeotrope. 3) Thorough separation and recycling of the catalyst is needed before downstream processing, as most active catalysts are expensive precious metal catalysts, and metal traces can catalyze the decomposition of formic acid (see above), which causes decreased yields. Several proficient strategies have been developed to minimize the energetic requirements for the overall processing sequence and to operate as closely as possible at the thermodynamic limits.

Production of Formic Acid in the Absence of Base

The direct production of pure formic acid in the absence of base is desirable to reduce the number of components in the reaction mixture before downstream processing (Table 3). As mentioned above, appreciable concentrations of formic acid can only be achieved if effects are exploited which reduce the entropy difference between the reactants and the product, or which contribute with a negative enthalpy. If the base additive is avoided, the only parameters left that influence the thermodynamics are temperature, pressure, and the reaction solvent.

In 1989, Khan et al. reported the formation of formic acid and formaldehyde as the initial products in the reversed water-gas-shift reaction on using the complex K[RuCl(EDTA-H)] (EDTA-H = ethylenediamine tetraacetate, singly protonated) in water.[69] In the absence of a base additive, the initial rate of formation of formic acid was $0.02\,M\,min^{-1}$, which corresponds to a TOF of $1200\,h^{-1}$ under

Table 3: Selected catalysts for the hydrogenation of CO_2 to formic acid in the absence of base.

Entry	Catalyst	Solvent	T [°C]	p_{H_2}/p_{CO_2} [bar/bar]	t [h]	TOF [h^{-1}]	TON	HCOOH conc. [$mol\,L^{-1}$]	Ref.
1	K[RuCl(EDTA-H)]	H_2O	40	3/17	0.5	1200	–	–	[69]
2	$[Ru(\eta^6\text{-}C_6Me_6)(4,4'\text{-OMe-bpy})(H_2O)]SO_4$	H_2O	40	55/25	70	0.8	55	0.06	[66]
3	$[RhCl(TPPMS)_3]$	$H_2O/NaHCO_2$	50	50/50	20	–	–	0.11	[70]
4	$[RuCl_2(PTA)_4]$	H_2O	60	150/50	48–84	–	159	0.20	[71]
5	$[Rh(nbd)(PMe_2Ph)_3]BF_4$	THF	40	48/48	72	0.5	34	0.05	[28a]
6	$[Rh(nbd)(PMe_2Ph)_3]BF_4$	aqueous THF	40	48/48	72	1.1	78	0.11	[28a]
7	$[Ru(C_5H_4(CH_2)_3NMe_2)(dppm)]BF_4$	THF	80	40/40	16	0.5	8	0.01	[72]
8	$[\{Rh(cod)(\mu\text{-}H)_4\}]$/dppb	DMSO	RT	20/20	6.5	0.9	5.7	0.03	[28b]
9	$[RuCl_2(PTA)_4]$	DMSO	50	50/50	120	5.8	700	1.93	[71]
10	$[Ru(cod)(methylallyl)_2]/TPPMS/Cl^-$	$[PMMIM][HCO_2]$	50	50/50	1	295	295	0.59	[73]
11	$[Ru(cod)(methylallyl)_2]/TPPMS/Cl^-$	$[PMMIM][HCO_2]$	50	50/50	20	98	1968	3.94	[73]

relatively mild reaction conditions (3 bar H_2, 17 bar CO_2, 40 °C). However, the initially formed formic acid and formaldehyde subsequently decomposed to CO and H_2O. Therefore, no selective formation of formic acid was possible with this system.

The second report of base-free hydrogenation of CO_2 in water was published in 2004. Hayashi et al. reported that, in the presence of the water-soluble aqua complex $[Ru(\eta^6\text{-}C_6Me_6)(4,4'\text{-OMe-bpy})(H_2O)]SO_4$ (4,4′-OMe-bpy = 4,4′-dimethoxy-2,2′-bipyridine), formic acid was formed with TONs up to 55 after 70 h, which corresponds to a formic acid concentration of 0.06 $mol\,L^{-1}$ (55 bar H_2, 25 bar CO_2, 40 °C).[66] The pH value of the solution was 2.5–5 under these conditions. In a follow-up study by the same group in 2006, the Ir complex $[Ir(\eta^5\text{-}C_5Me_5)(4,4'\text{-OMe-bpy})(H_2O)](SO_4)$ was tested for its activity in acidic aqueous solution.[74] A TOF of 27 h^{-1} was obtained for a reaction in the presence of citrate buffer at pH 3.0 (55 bar H_2, 25 bar CO_2, 40 °C). The exact activity in pure water remains unclear, but from the time/TON plot in the supporting information one can conclude that the reaction rate is in the same range or a little bit faster in pure water.

In 2011 Zhao and Joó reported the formation of excess formic acid in aqueous solution in the presence of small concentrations of sodium formate.[70] An excess concentration of formic acid of 0.11 $mol\,L^{-1}$ was obtained after 20 h in a 0.05 M HCO_2Na solution (50 bar H_2, 50 bar CO_2, 50 °C) in the presence of the complex $[RhCl(TPPMS)_3]$. Only negligible formation of formic acid was observed in the absence of the sodium formate additive. This finding indicates that HCO_2Na most likely also plays a role in the generation of the active catalyst.

In 2014, Moret, Dyson, and Laurenczy studied different catalysts and solvents for the base-free hydrogenation of CO_2 to formic acid.[71] The best results were obtained using $[RuCl_2(PTA)_4]$ (PTA = 1,3,5-triaza-7-phosphaadamantane). In pure water, a formic acid concentration of up to 0.204 $mol\,L^{-1}$ was achieved under relatively high pressures (150 bar H_2, 50 bar CO_2, 60 °C, RT). The highest TON observed was 159 and thus higher than that observed by Hayashi et al.[66] in 2004 (TON = 55). Interestingly, the catalyst could be reused four times without loss of activity by removing the formed formic acid and solvent (water) under reduced pressure, and re-dissolving the remaining solid catalyst in water. Partial decomposition of formic acid to CO_2 and H_2 is expected to occur during this distillation process, as the catalyst was also shown to be active for the decomposition reaction.

The formation of formic acid in the absence of base is also possible in organic solvents, which shift the equilibrium through solvation effects. Tsai and Nicholas reported in 1992 the base-free hydrogenation of CO_2 to formic acid in THF.[28a] By using $[Rh(nbd)(PMe_2Ph)_3]BF_4$ (nbd = norbornadiene) in dry THF, a TON of 34 was obtained after three days (40 °C, 48 bar H_2, 48 bar CO_2), which corresponds to a formic acid concentration of 0.05 $mol\,L^{-1}$. Under the same conditions but using wet THF (0.4 vol % H_2O), a TON of 78 was obtained, which corresponds to a concentration of 0.11 $mol\,L^{-1}$. Chu et al. used a catalyst with an amine function incorporated into the ligand.[72] The use of $[Ru(\eta^6\text{-}C_5H_4(CH_2)_3NMe_2)(dppm)][BF_4]$ in THF in the absence of a base additive led to a TON of 8, which corresponds to a formic acid concentration of 0.01 $mol\,L^{-1}$ after 16 h at 80 °C under 40 bar H_2 and 40 bar CO_2.

In their early studies, Leitner, Dinjus, and co-workers introduced DMSO as a very favorable solvent for the hydrogenation of CO_2 to formic acid.[28b,39] They suggested that the dipolar aprotic solvent results in cleavage of the hydrogen bonds between the formic acid molecules, thereby increasing the entropy of the product. Indeed, the use of $[\{Rh(cod)(\mu\text{-}H)\}_4]$/dppb in DMSO in the absence of base yielded a formic acid concentration of 0.034 $mol\,L^{-1}$ after 6.5 h under mild conditions (RT, 20 bar CO_2, 20 bar H_2). This corresponds to a TON of 5.7 and a TOF of 0.9 h^{-1}. These values were, however, greatly increased in the presence of NEt_3.

In their studies published in 2014, Moret, Dyson, and Laurenczy assessed in detail the maximum concentrations of formic acid that could be obtained in organic solvents in the absence of base with $[RuCl_2(PTA)_4]$ as catalyst.[71] A formic acid concentration of 0.20 $mol\,L^{-1}$ (TON = 72) was obtained in ethanol, methanol, acetonitrile, and propylene carbonate after 120 h at 50 °C and 100 bar (CO_2/H_2 = 1:1). The best result was obtained using DMSO under the same conditions, which yielded a formic acid concentration as high as 1.93 $mol\,L^{-1}$ and a TON of 700 after 120 h (average TOF =

5.8 h^{-1}). At a reduced pressure of 50 bar, and at 50 °C a formic acid concentration of 0.39 $mol\,L^{-1}$ was still obtained after 120 h (TON = 141, average TOF = 1.2 h^{-1}). $[RuCl_2(PTA)_4]$ was the most productive of the tested catalyst precursors. It is currently not fully clear whether the amine function of the PTA ligand plays an important role for the formation of formic acid in this case. The authors demonstrated recycling of the catalyst, which was obtained as a dry powder upon removing DMSO together with formic acid under vacuum. Although the composition of the distillate was not reported, separation of the catalyst from formic acid and DMSO by distillation most probably leads to decreased yields of formic acid, as the catalyst was shown to also catalyze the decomposition of formic acid, which is favored under reduced pressure.

In a study on the decomposition of formic acid, Yasaka et al. reported in 2010 that the equilibrium can be shifted far to the formic acid side if the reaction is performed in the ionic liquid (IL) 1,3-dipropyl-2-methylimidazolium formate without additional base.[75] The authors attributed this behavior to the strong solvation of formic acid by formate anions through Coulombic and/or hydrogen-bonding interactions. In 2012, Leitner and co-workers showed that high TONs (1968), corresponding to a formic acid concentration of 3.94 $mol\,L^{-1}$, and TOFs (295 h^{-1}) can indeed also be obtained for the forward reaction if the CO_2 hydrogenation reaction is performed in the IL 1-propyl-2,3-dimethylimidazolium formate ($[PMMIM][HCO_2]$), which comprises a formate anion.[73]

Clearly, the hydrogenation of CO_2 under base-free conditions is worth investigating in more detail. Research should focus on understanding the role of the base for the activation of the catalysts, as this might be key to identifying catalysts with improved performance in the absence of base (see, for example, Ref. [76] and references therein). Furthermore, the downstream processing is not only affected by the number of components present in solution, but the overall complexity and energy requirements have to be considered. As the base-free systems exploit other strong interactions of HCOOH with the reaction medium for the compensation of the unfavorable entropic contribution, this is not easily assessed a priori. In particular, there is a need for alternative strategies for separation of the product and recycling of the catalyst, as the product mixtures cannot be distilled in the presence of the catalyst because of the decomposition reaction.

Immobilized Catalysts

The separation of the catalyst before downstream processing—to avoid formic acid decomposition—requires the introduction of a phase boundary between the active component and the product. This can be achieved by immobilizing the organometallic catalysts on solid supports or with multiphase reaction systems.

In 2004, Zhang et al. reported Ru-phosphine catalysts that were immobilized on amino-functionalized silica.[77] The most active system was “Si”-$(CH_2)_3$-$NH(CH_2)_3CH_3$-$RuCl_3$ in the presence of PPh_3 as a ligand. High TOFs of up to 1384 h^{-1} were obtained in $EtOH/NEt_3/scCO_2$ (80 °C, 40 bar H_2, 120 bar CO_2) with this system. The catalyst could be reused two times with only slight losses in activity. A hot filtration test showed the homogeneous phase had no catalytic activity, thereby supporting the assumption that catalysis occurred only at the solid material. Similar catalysts were used and similar results were obtained by Ying-Min et al. in 2005.[78] In 2006 they showed that amine-functionalized polystyrene can also be used as a support material to give catalysts of the type polystyrene-$CH_2NH(CSCH_3)$-$RuCl_3/PPh_3$.[79]

In 2013, the group of Hicks investigated iridium catalysts tethered to the mesoporous silica support SBA-15.[80] The best results were obtained by covalently binding an iminophosphine ligand to the silica support and immobilizing $IrCl_3$ by coordination to the immobilized ligand. TOFs up to 1200 h^{-1} were obtained in H_2O/NEt_3 (120 °C, 40 bar total pressure at RT). A TOF of 880 h^{-1} was still observed at 60 °C. The catalyst could be recovered by filtration and reused in 10 cycles with only slight deactivation. A filtration test showed the homogeneous filtrate had no activity, thus suggesting minimal leaching of the catalyst. Subsequently, the same iminophosphine ligand was tethered to a polyethyleneimine (PEI) backbone for coordination with $IrCl_3$.[81] The resulting material was suggested to be capable of both capturing CO_2 and converting CO_2 into formic acid. The CO_2 capture was demonstrated for the neat material by thermogravimetric analysis, whereas the catalytic activity was tested using a small amount of the catalyst material in water/NEt_3 at 120 °C, 20 bar CO_2, and 20 bar H_2 (maximum TOF = 248 h^{-1}). A TON of 6 was obtained in the absence of NEt_3. The actual combination of CO_2 capture with subsequent conversion of only the adsorbed CO_2 was not reported.

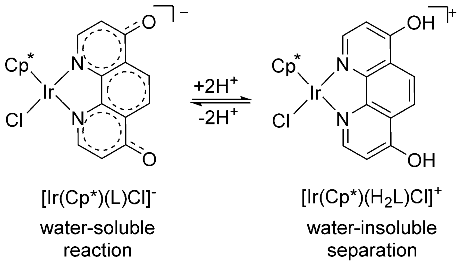
In all of these reports the solutions of the formic acid/amine adducts could be readily separated from the catalyst by filtration, but the further work-up of these solutions was not included. This is the most energy-intensive step, however, where most of the “thermodynamic penalty” is paid. Hence, the development of intensified processing schemes that integrate the reaction and separation step is of crucial importance for the potential industrial application of this transformation.

Process Schemes

Already in the 1980s, BP filed a series of patents on process schemes for the hydrogenation of CO_2 to formic acid in the presence of trialkylamines. In a patent from 1983, the resulting formic acid/NEt_3 was cleaved by hydrolyzing it with hydrochloric acid to yield formic acid and $HNEt_3Cl$ waste.[82] In later patents published in 1984 and 1986, formic acid was liberated from formic acid/NEt_3 by a base exchange with a high-boiling base such as 1-butylimidazole and subsequent thermal cleavage of the adduct.[83] In this case, the amines could be recycled, but the additional process step further complicates the sequence.

In 1992, the group of Leitner cleaved the formic acid/NEt_3 adduct in organic solvents by the addition of NaOH.[39] This led to a precipitate containing both the catalyst and sodium formate, which could be separated by extracting the formate salt with water. The remaining catalyst could be recycled and sodium formate was obtained from the aqueous phase in pure form.

Himeda et al. proposed a process scheme for the production of potassium formate based on the separation of the catalyst by self-precipitation (Scheme 3).[84] They used complex [Ir(Cp*)(H_2L)Cl]Cl (H_2L = 4,7-dihydroxy-1,10-phenanthroline) for the hydrogenation of CO_2 in aqueous KOH solution. Under the basic conditions of the 0.1 M KOH solution, the hydroxy groups of the ligand were deprotonated to afford a water-soluble catalyst with oxyanions [Ir(Cp*)(L)Cl]$^-$. After 20 h reaction a formate concentration of 0.1 mol L^{-1} was obtained, which neutralized the KOH (30 bar total pressure at RT, 60 °C). Under these conditions, the ligand was protonated to the water-insoluble form [Ir(Cp*)(H_2L)Cl]$^+$, which caused precipitation of the catalyst. The catalyst could be removed by filtration and reused three times. The leaching of the catalyst increased from 0.11 ppm in the first cycle to 0.61 ppm in the last cycle. Potassium formate could be obtained from the filtrate by evaporating the water.



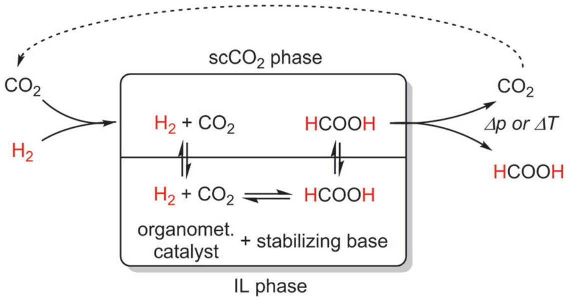
Scheme 3. Catalyst separation by precipitation caused by a change in the pH value, as presented by Himeda et al.[84]

Although the catalyst is separated effectively in these two examples, additional separation steps would be needed to obtain pure formic acid from the alkali salts, thereby making such sequences energy intensive and wasteful unless the salts constituted the products.

In 2003, Behr et al. demonstrated the feasibility of performing the hydrogenation of CO_2 to formic acid in a biphasic system.[85] Formic acid could be extracted from an aqueous reaction phase containing the water-soluble organometallic catalyst $RuCl_3$/TPPTS by using *N*,*N*-dibutylformamide as solvent. The loss of catalyst after the first extraction was 6–9 wt %, thus making a subsequent second extraction of the organic product phase with water necessary. Nevertheless, in situ extraction seems to be an attractive concept if the partition coefficients of the catalyst and HCOOH product can be differentiated sufficiently.

In 2008, the group of Han combined a silica-immobilized Ru-phosphine complex “Si”-$(CH_2)_3NH(CSCH_3)$-$RuCl_3/PPh_3$ with an immobilized base (Figure 5).[86] The authors incorporated the tertiary dimethylamine group into the ionic liquid 1-(*N*,*N*-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate to immobilize the base. By using this system, TOFs of up to 103 h^{-1} were obtained in water as solvent (70 °C, 180 bar total pressure). The catalyst was separated by filtration, the water was evaporated at 110 °C, and pure formic acid was isolated from the ionic liquid by passing a N_2 stream through the solution at 130 °C. The catalyst and base could be reused in four consecutive reactions. The productivity of this process could be increased by using an ionic liquid containing two tertiary amino groups instead of one.[87] This interesting concept requires three unit operations for the downstream processing, but demonstrates the potential use of advanced fluids, such as ionic liquids, in the separation steps.

In 2012, the group of Leitner used basic ionic liquids as nonvolatile bases in the continuous-flow hydrogenation of carbon dioxide to formic acid in an integrated process (Scheme 4).[73] The concept is based on a biphasic system consisting of a stationary ionic liquid phase and a supercritical CO_2 ($scCO_2$) mobile phase. The $scCO_2$ mobile phase, which is also the substrate of this reaction, carries H_2 efficiently into the ionic liquid solution containing the catalyst as well as the base. In the ionic liquid phase, CO_2 is hydrogenated effectively to formic acid, which is partly stripped away with the $scCO_2$ mobile phase and leaves the reactor. The thermodynamic driving force for the integrated formation and separation of formic acid is the solvation of the formic acid in the $scCO_2$ phase. However, the presence of a nonvolatile base in the stationary catalyst phase was necessary to achieve significant formation of formic acid. As formic acid is



Scheme 4. Process scheme of a fully integrated process for the continuous-flow hydrogenation of CO_2 to pure formic acid by using a stationary IL phase and supercritical CO_2 as the mobile phase.[73]

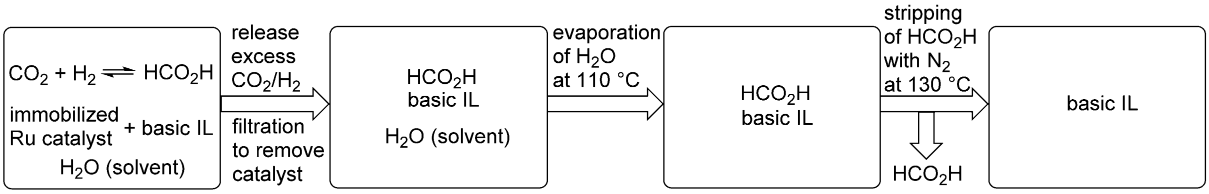


Figure 5. Batch process for the hydrogenation of CO_2 to formic acid using a basic ionic liquid, as demonstrated by Han and co-workers.[86]

continuously removed from the reaction system, the equilibrium in the reactive phase can readjust. Pure formic acid was recovered by decompression of the CO_2 flow in the laboratory experiments, but other methods such as countercurrent extraction would also be feasible. Thus, the reaction and separation are fully integrated in a single processing unit and a stable performance has been achieved under continuous-flow conditions over 200 h (Figure 6).

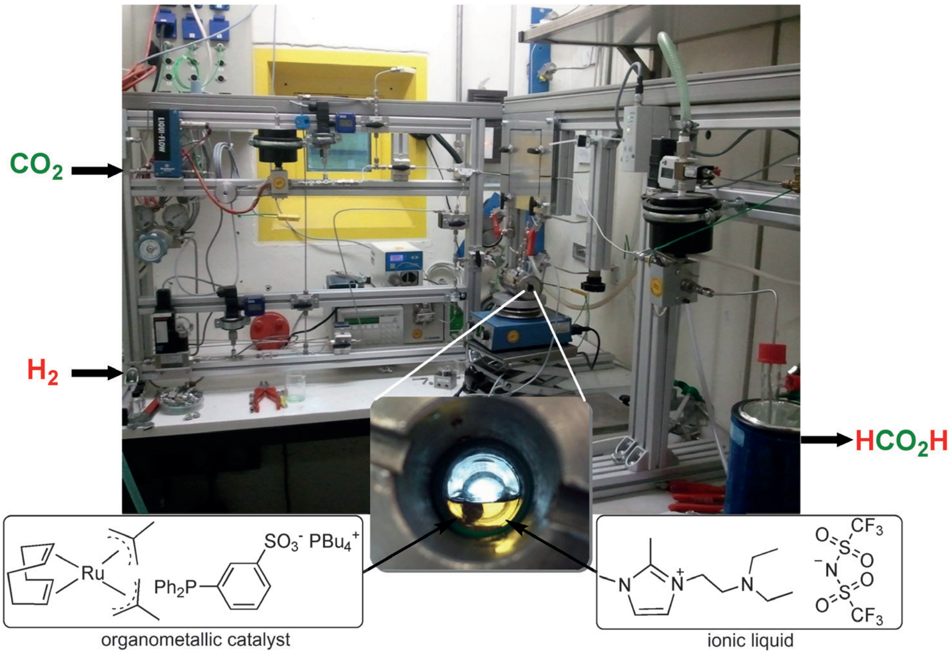
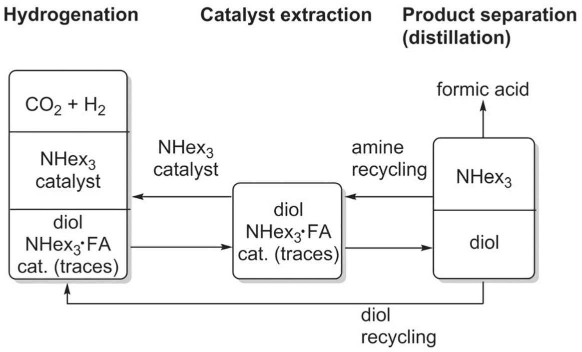


Figure 6. Set-up for the fully integrated continuous-flow hydrogenation of CO_2 to pure formic acid.[73]

An integrated process that was intensively investigated in an industrial environment was patented by Schaub and Paciello from BASF in 2010 and presented in a journal article in 2011 (Scheme 5).[21,88] The main aspects of this process are the judicious choice of amine base and solvent, which lead to the following key features: 1) The hydrogenation of CO_2 in the presence of diols and the amine $NHex_3$ leads to the formation of the formic acid adduct with $NHex_3$ ($NHex_3{\cdot}FA$). 2) $NHex_3{\cdot}FA$ dissolved in the diol forms a biphasic system with the free amine $NHex_3$. 3) $NHex_3{\cdot}FA$ can be cleaved thermally into formic acid and $NHex_3$. Thus, the hydrogenation of CO_2 can be performed in a biphasic system consisting of $NHex_3{\cdot}FA$/diol as the polar phase and $NHex_3$ as the nonpolar phase, which contains the unpolar catalyst $[RuH_2(PnBu_3)_4]$. After the reaction, the immiscible phases are separated. The product phase still contains trace amounts of the catalyst, which are extracted with $NHex_3$ and recycled back to the nonpolar phase for the hydrogenation step. The now catalyst-free product phase is distilled to separate diol, amine, and free formic acid. This process scheme involves closed loops for the catalyst, the amine, and the solvent, and was tested on a pilot-plant scale.[89] In 2013, a patent by BASF reported further improvements of the initial process:[90] The use of low-boiling polar solvents such as methanol, ethanol, and/or water instead of the previously used high-boiling diols gave higher yields of the formic acid/amine adduct. Decomposition of formic acid to CO_2 and H_2 occurred if trace amounts of catalyst were still present during distillation. It was shown that this could be avoided by adding CO to the mixture prior to distillation. The complex was deactivated by CO, but could be reactivated under reaction conditions after recycling the catalyst back to the hydrogenation reactor.



Scheme 5. Process concept for the production of formic acid from CO_2 and H_2, as presented by BASF.[21,88,90]

2.2. Alkyl Formates

The formation of alkyl formates is a combination of the reduction of CO_2 with one equivalent of H_2 and the formation of a new C−O bond in a subsequent esterification reaction. In analogy to chess, the first step on the chessboard could be accomplished by a pawn, and the second step by a rook. Alternatively, a catalyst acting as a bishop is needed to move directly from CO_2 to alkyl formates.

2.2.1. Properties, Current Production, and Uses of Alkyl Formates

The current industrial production of alkyl formates is based mainly on two technologies: the carbonylation of alcohols and the esterification of formic acid with the appropriate alcohol (Scheme 6).[19,20] For example, methyl formate, a volatile liquid at room temperature (m.p. = −99 °C, b.p. = 31.7 °C), is produced by the carbonylation of methanol,

$$\mathrm{ROH + CO \longrightarrow HCO_2R} \quad \text{(a)}$$
$$\mathrm{ROH + HCO_2H \longrightarrow HCO_2R + H_2O} \quad \text{(b)}$$

Scheme 6. Industrially used reactions for the production of alkyl formates.

$$\mathrm{CO_2 + H_2 \rightleftharpoons HCO_2H \xrightleftharpoons{+\,ROH} HCO_2R}$$

Scheme 7. Reaction pathway of the hydrogenation of CO_2 to alkyl formates.

which is also the first step in the current industrial production of formic acid (see above).

Most of the methyl formate produced today is used as an intermediate for the production of formic acid and formamide. Smaller amounts of methyl formate are used as solvent, as insecticide, and for curing phenol-formaldehyde resin. It is anticipated that the importance of methyl formate as a versatile C_1 building block will increase in the future:[19] methyl formate can be used as a building block in the production of methyl glucolate, ethylene glycol, methyl propionate, acetaldehyde, acetic acid, and dimethyl carbonate. Furthermore, methyl formate can be used for the production of high-purity CO.[91] In this way, methyl formate could play an important role as a CO storage medium. Other alkyl formates, such as ethyl, isobutyl, benzyl, and isopentyl formate are used as solvents, perfumes, and flavorings.

2.2.2. *Catalytic Synthesis of Alkyl Formates by the Hydrogenation of CO_2*

The synthesis of formate esters by the hydrogenation of CO_2 can be achieved using either alkyl halides or alcohols as the alkylating reagent. In general, TONs are low when alkyl halides are used. Much higher TONs were found in studies using alcohols such as methanol and ethanol. The reaction pathway is believed to be a sequential process of CO_2 hydrogenation to formic acid followed by esterification with the alcohol present (Scheme 7).[92] Consequently, high TONs and TOFs have mostly been achieved in the presence of a base (most commonly NEt_3), which stabilizes the intermediate formic acid. However, the presence of base can compromise the selectivity, as the stable formic acid/base adduct is often not completely converted into the formate ester. Catalysts and mechanistic insights for the hydrogenation of CO_2 to alkyl formates have been reviewed previously.[7a,33c] We therefore focus again on milestones in catalyst development and on the integration of the reaction and separation. Representative examples are summarized in Table 4.

2.2.2.1. *Platinum Group Metal Catalysts with High TONs and TOFs*

Organometallic catalysts were already shown to catalyze the hydrogenation of CO_2 to methyl formate by Kolomnikov et al. in 1972,[93] who obtained a TON of 17 under base free conditions with the catalyst system $[RuHCl(PPh_3)_3]/BF_3$. It was not until 1995 that Jessop, Noyori et al. achieved greatly improved TONs and TOFs in the production of methyl formate by the hydrogenation of CO_2 in the presence of methanol and supercritical CO_2.[92] A TON of 3500 (corresponding to a TOF of 55 h^{-1}) was obtained by using $[RuCl_2(PMe_3)_4]$ as the catalyst at 80 °C, 80 bar H_2, and 125 bar CO_2. The addition of NEt_3 to stabilize the intermediate formic acid was a prerequisite for high TONs. However, the selectivity was only 34 % under these conditions, as the stable formic acid/NEt_3 adduct was not completely converted into the ester. The production of ethyl formate was also possible, although with a lower TON of 190. In 1997, the group of Baiker used $[RuCl_2(dppe)_2]$ under similar conditions and obtained a remarkable TOF of up to 850 h^{-1} and a TON of up to 12 900.[94]

A system for the combined capture of CO_2 and subsequent hydrogenation to methyl formate in the same reaction medium was presented by Yadav et al. in 2014.[101] CO_2 could be efficiently captured by a mixture of DBU (1,8-

Table 4: Selected catalysts for the production of alkyl formates for CO_2.[a]

Entry	Catalyst	Product	Additives	T [°C]	p_{H_2}/p_{CO_2} [bar/bar]	t [h]	TOF [h^{-1}]	TON	Ref.
1	$[RuHCl(PPh_3)_3]/BF_3$	MF	–	100	30/30	n.a.	n.a.	17	[93]
2	$[RuCl_2(PMe_3)_4]$	MF	NEt_3	80	80/125	64	55	3500	[92]
3	$[RuCl_2(dppe)_2]$	MF	NEt_3	100	85/130	16	830	12 900	[94]
4	$[Fe_3H(CO)_{11}]^-$	MF	–	175	20/20	96	0.06	6	[95]
5	$Fe(BF_4)_2{\cdot}6\,H_2O/PP_3$	MF	NEt_3	100	60/30	20	29	585	[56]
6	$Co(BF_4)_2{\cdot}6\,H_2O/PP_3$	MF	NEt_3	100	60/30	20	33	659	[60]
7	$Fe(BF_4)_2{\cdot}6\,H_2O/L$	MF	NEt_3	100	30/30	20	40	795	[57]
8	$[Ru_4H_3(CO)_{12}]^-$	MF	–	125	17/17	24	0.3	7	[96]
9	$[W(HCO_2)(CO)_5]^-$	MF	–	125	17/17	24	0.7	16	[97]
10	$[Cr(HCO_2)(CO)_5]^-$	MF	–	125	17/17	24	0.6	15	[97]
11	$[Ru(Cl_2bpy)_2(H_2O)_2][CF_3SO_3]_2$	EF	–	100	30/30	8	20	160	[98]
12	$[RuCl(OAc)(PMe_3)_4]$	MF	–	135	30/10	16	0.2	3	[99]
13	$[RuCl(OAc)(PMe_3)_4]$	MF	NEt_3	135	30/10	16	1	18	[99]
14	$[RuCl(OAc)(PMe_3)_4]$	MF	$Sc(OTf)_3$	135	30/10	16	3	40	[99]
15	“Si”-$RuCl_2\{PMe_2(CH_2)_2Si(OEt)_3\}_3$	MF	NEt_3	100	85/130	64	50	3180	[100]

[a] $PP_3 = P(CH_2CH_2PPh_2)_3$; L = tris[(2-diphenylphosphino)phenyl]phosphine; MF = methyl formate; EF = ethyl formate. n.a. = not available.

diazabicyclo[5.4.0]undec-7-ene) and methanol at 1 atm pressure and room temperature to form the ionic liquid $[DBUH]^+$ methyl carbonate, a so-called "switchable ionic liquid".[102] In a second step, this $[DBUH]^+$ methyl carbonate could be hydrogenated in the absence of additional CO_2 to $[DBUH]^+$ formate and free methanol by using Ru and Fe catalysts. In a consecutive reaction, $[DBUH]^+$ formate reacts with the free methanol to afford methyl formate, water, and DBU. A 45% conversion of $[DBUH]^+$ methyl carbonate was obtained after 40 h using $[RuCl_2(PPh_3)_3]$ at 140 °C and 20 bar H_2. However, under the applied reaction conditions DBU was hydrolyzed into a cyclic lactam and thereby destroyed, thus preventing recycling of the expensive DBU.

2.2.2.2. Nonprecious Metal Catalysts

In 1978 Evans and Newell already showed that the anionic iron carbonyl complex $[Fe_3H(CO)_{11}]^-$ catalyzes the hydrogenation of CO_2 to methyl formate and ethyl formate in the presence of the corresponding alcohol.[95] A TON of 6 was obtained after 96 h in the absence of base (20 bar CO_2, 20 bar H_2, 175 °C). However, it was not until 2010 that Beller, Laurenczy, Dyson, and co-workers showed that the in situ catalyst $Fe(BF_4)_2{\cdot}6\,H_2O/PP_3$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] as well as the preformed catalyst $[FeH(H_2)PP_3][BF_4]$ catalyze the effective hydrogenation of CO_2 to methyl formate (TON = 585), ethyl formate (TON = 167), and propyl formate (TON = 94) in the presence of the corresponding alcohols (100 °C, 60 bar H_2, 30 bar CO_2, pressures at RT).[56] Again, the addition of NEt_3 as a base was necessary, and the highest yield based on NEt_3 was 56%. In 2012, the Beller group showed that the analogous Co catalysts are also active.[60] With the in situ system $Co(BF_4)_2{\cdot}6\,H_2O/PP_3$ or the preformed catalyst $[Co(H_2)PP_3][BPh_4]$ under the same reaction conditions, methyl formate was obtained with a TON of up to 659, which corresponds to a yield of 83% based on NEt_3. Ethyl formate could be produced with a lower TON of 103. In the same year, they reported that using $Fe(BF_4)_2{\cdot}6\,H_2O$ together with the tetradentate ligand tris[(2-diphenylphosphino)phenyl]phosphine gave methyl formate with a TON of 795 in the presence of methanol and NEt_3 (100 °C, 30 bar H_2, 30 bar CO_2, pressures at RT).[57] The selectivity was 47%, and the other product formed was again the NEt_3/formic acid adduct.

2.2.2.3. Hydrogenation of CO_2 to Alkyl Formate in the Absence of Base

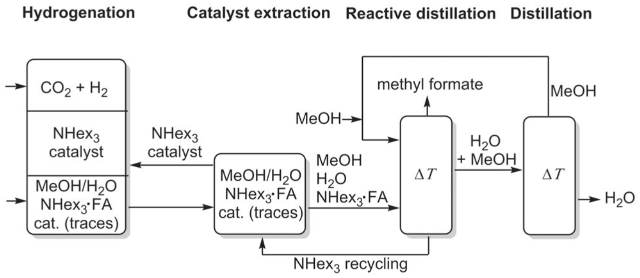
As the addition of base generally results in mixtures of formate adducts and esters, it is desirable to carry out the reaction in the absence of base to simplify downstream processing. Interestingly, pioneering studies in the 1970s already made use of Lewis acids[93] or no additives at all.[95] Darensbourg et al. used $[Ru_4H_3(CO)_{12}]^-$ without additives to obtain methyl formate with a TON of 7 in 1983.[96] One year later, the same group showed that $[W(HCO_2)(CO)_5]^-$ and $[Cr(HCO_2)(CO)_5]^-$ give methyl formate with TONs of up to 16 and 15, respectively.[97] The highest TON (160) and TOF (20 h^{-1}) in the absence of base was obtained by Lau and Chen in 1995, who used $[Ru(Cl_2bpy)_2(H_2O)_2][CF_3SO_3]_2$ in ethanol for the hydrogenation of CO_2 to ethyl formate.[98] In 2011, Huff and Sanford studied the formation of methyl formate as an intermediate in the catalytic cascade from CO_2 and H_2 to methanol.[99] They investigated the catalyst $[RuCl(OAc)(PMe_3)_4]$ without additive, in the presence of NEt_3 and with $Sc(OTf)_3$ as a Lewis-acidic co-catalyst under identical conditions (135 °C, 10 bar CO_2, 30 bar H_2). The best results were obtained with $Sc(OTf)_3$, which resulted in a TON of 40 after 16 h and a TOF of 32 h^{-1} in the first hour. It would be worth investigating Lewis-acidic co-catalysts more systematically to also enhance the esterification step in combination with other catalysts, especially to also enhance the very slow esterification with bulkier alcohols.

2.2.2.4. Integration of Reaction and Separation

There have been very few reports on heterogeneous catalysts catalyzing the hydrogenation of CO_2 to alkyl formates. In 2007, Yu et al. demonstrated the production of methyl formate from the hydrogenation of CO_2 in the presence of methanol by using a Pd/Cu/ZnO catalyst in a batch process.[103] High selectivity (> 96%) to methyl formate was achieved. A TOF of 38 h^{-1} was obtained at 150 °C, 10 bar CO_2, and 50 bar H_2. Notably, no addition of a base was needed. Small amounts of CO were detected as byproduct, possibly from the rWGS reaction. In a patent published in 2013, supported gold catalysts were shown to be active in the formation of alkyl formates from CO_2, H_2, and alcohol and applied in a semibatch mode.[104] A product mixture containing 5.2% methyl formate was obtained after 10 h by using Au/TiO_2 in methanol at 200 bar total pressure and 125 °C. Under the same conditions, but in ethanol instead of methanol, a product mixture containing 2.5% ethyl formate was obtained. No gold was found in the resulting product mixtures, within the detection limits (< 1 ppm), after filtration. The resulting product mixture was fed into a distillation unit, in which alkyl formate, water, and unreacted alcohol were separated.

In 1998, the group of Baiker synthesized a heterogeneous molecular catalyst by incorporation of the transition-metal complex $[RuCl_2\{PMe_2(CH_2)_2Si(OEt)_3\}_3]$ into a silica matrix and tested it in the hydrogenation of CO_2 to methyl formate in the presence of NEt_3 and methanol under batch conditions.[100] After 15 h under supercritical conditions (100 °C, 85 bar H_2, 130 bar CO_2), a TOF of 115 h^{-1} and after 64 h a TON of 3180 was obtained. The addition of NEt_3 was crucial to obtain high yields. The addition of alumina as an acidic catalyst for the esterification step in the absence of base led only to low yields of methyl formate.

As a result of the higher activities of homogeneous catalysts in CO_2 hydrogenation reactions, BASF developed a process for the production of methyl formate based on liquid/liquid extraction.[105] In principle, this process is a combination of the hydrogenation of CO_2 to formic acid/amine adducts, as described in the section on formic acid (see above), with a subsequent reactive distillation, in which the formic acid/amine adduct is esterified with methanol. The process scheme is shown in Scheme 8. The $NHex_3{\cdot}FA$ adduct is produced in the hydrogenation step with a TOF of 551 h^{-1}.



Scheme 8. Process for the production of methyl formate, as presented by BASF.[105]

After back-extraction of trace contaminations of the catalyst, the raffinate containing the $NHex_3$·FA adduct, methanol, and water is introduced into the reactive distillation column to give methyl formate and free $NHex_3$. Methyl formate is obtained as the overhead product, and $NHex_3$ is obtained as the bottom product and recycled into the catalyst extraction unit. To reach conversions of the formate adduct up to 43 %, water must be removed from the raffinate stream by an additional distillation step before entering the reactive unit (not shown). The water/methanol mixture obtained is separated in another distillation step downstream, and the methanol is recycled to the reactive distillation column. The recirculation of catalyst, amine, and unreacted methanol is possible with this process, but the large number of energy-demanding operations is clearly a challenge.

2.3. Formamides

The formation of formamides is a combination of the reduction of CO_2 with one equivalent of H_2 and of the formation of a new C−N bond by a condensation reaction. Similar to the production of alkyl formate, a catalyst acting like a bishop is needed to make the strategic move from CO_2 to formamide directly.

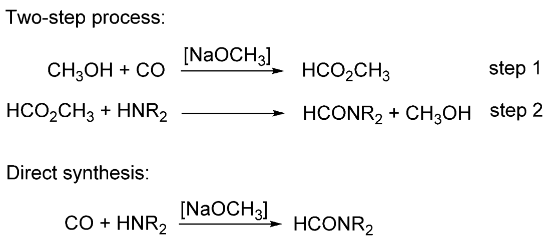
2.3.1. Properties, Current Production, and Uses of Formamides

The two formamides with the highest industrial relevance are formamide ($HCONH_2$) and *N*,*N*-dimethylformamide ($HCON(CH_3)_2$, DMF).[106] Formamide is a pH-neutral, odorless, hygroscopic liquid at room temperature (m.p. = 2.55 °C) with a boiling point of 210 °C.[106] Not long ago, formamide was mainly used for the production of formic acid by reaction with sulfuric acid. This production route was displaced by the methyl formate method (see above). Formamide is widely used as a solvent, as it has good solubility properties for many inorganic salts, polymers, and natural products. Formamide is also a valuable component in organic synthesis: examples are the *N*-formylation of amines and the production of formanilide, nitrogen-containing heterocycles (e.g. caffeine, imidazole, theophylline, pyrimidine), and methyl formates.[106] Formamide starts to decompose above 100 °C to mainly carbon monoxide and ammonia. The dehydration of formamide also commences and yields traces of hydrogen cyanide. In fact, the dehydration of formamide at 380–430 °C in the presence of Fe or Al phosphate catalysts with Mg, Ca, Zn, or Mn as promoters was still used for the industrial production of HCN in 1991.[20] If formamide could be synthesized efficiently by the hydrogenation of CO_2, "HCN" could be stored and transported in the form of formamide and decomposed to HCN on the production site where it is needed (storage capacity = 60 wt %). Similarly, if the selective decomposition of formamide to CO was possible, it could be used as a storage medium in an indirect rWGS production of CO from CO_2 (storage capacity = 62 wt %).

DMF is a highly polar, hygroscopic liquid at room temperature (m.p. = −61 °C) with a boiling point of 153 °C.[106] The production capacity of DMF is estimated to be around 250 000 t a^{-1}.[20] The main application for DMF is as a solvent for polyacrylonitrile during the manufacture of synthetic fibers and in the processing of polyurethanes. Another application is as a selective solvent (e.g. the separation of acetylene from ethylene; H_2S or SO_2 from CO_2-containing gases). Above the boiling temperature, decomposition into carbon monoxide and *N*,*N*-dimethylamine is observed, thus also making DMF an interesting compound for CO storage,[29] although with a lower storage capacity of 38 wt % compared to formamide (62 wt %) and formic acid (61 wt %).

There are three more *N*-substituted formamides which are of commercial significance:[20,106] *N*-methylformamide is used as an intermediate in the synthesis of insecticides and as a selective solvent for aromatic hydrocarbons in oil refineries. *N*-formylmorpholine is used as an anticorrosive agent in fuel oil and as a solvent for the extraction of aromatic compounds in refinery processes. Formanilide is used as an antioxidant in the rubber industry and as an intermediate in the pharmaceutical industry.

Formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide are manufactured in a two-step process or in a direct synthesis (Scheme 9).[20,106] In the two-step process, methyl formate is produced in the first process step as described in the section on alkyl formate (see above). In the second step, methyl formate of 96 % purity is reacted with ammonia, methylamine, or dimethylamine to give the corresponding products and methanol. The methanol is recycled into the methyl formate synthesis step. No catalyst is needed in the second process step. In the direct synthesis, formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide are synthesized directly from CO and NH_3, methylamine, or dimethylamine in the presence of an alcoholate as a catalyst.



Scheme 9. Current production processes for formamides.

2.3.2. *Production of Formamides by the Hydrogenation of CO_2*

Formamides can be prepared by the hydrogenation of CO_2 in the presence of amines with one or more N-H functionalities. The mechanism is believed to involve the hydrogenation of CO_2 to ammonium formate followed by uncatalyzed thermal condensation to formamide (Scheme 10a).[6g,7a] In contrast to the preparation of alkyl formates, the preparation of formamide and dimethylformamide is highly efficient, and nearly complete conversion and selectivity is obtained. The yield obtained for more bulky amines is usually lower. The formation of solid carbamate salts from CO_2 and amine (Scheme 10b) seems to be at least partly responsible for the reduced reactivity.[107] The interconnection of the species in Scheme 10ab is, however, quite complex and controlled by steric as well as electronic factors, both of which influence the basicity of amines.

$$CO_2 + H_2 + NHR_2 \rightleftharpoons [NH_2R_2][O_2CH] \longrightarrow HCONR_2 + H_2O \qquad (a)$$

$$CO_2 + 2\,NHR_2 \rightleftharpoons [NH_2R_2][O_2CNR_2] \qquad (b)$$

Scheme 10. a) Reaction pathway for the formation of formamides from CO_2; b) formation of carbamates from CO_2 and amine.

2.3.2.1. *Milestones in Catalyst Development*

The first report on the formation of formamides by the hydrogenation of CO_2 in the presence of the corresponding alkylamines was by Farlow and Adkins, who used heterogeneous nickel catalysts as early as 1935.[34] Surprisingly few efforts have been made with solid catalysts since then. The group of Han showed in 2010 that dimethylamine is converted into DMF in 96% yield in the presence of Cu/ZnO catalysts under solvent-free conditions (6 h, 140 °C, 120 bar total pressure).[108] In a patent by BASF, the use of a titania-supported gold catalyst[36] was claimed for the formation of formamide, DMF, and dibutylformamide.[104,109] In 2014, Bi et al. used partially reduced iridium oxide supported on TiO_2 for the synthesis of DMF from CO_2, H_2, and aqueous dimethylamine.[110] The activities of heterogeneous catalysts are so far limited and many more active organometallic catalysts have been developed for the production of formamides from CO_2, with representative examples being summarized in Table 5.

In 1970, Haynes et al. reported on the homogeneously catalyzed formation of formamides from CO_2 in the presence of a wide variety of phosphine complexes of metals as diverse as Co, Rh, Ir, Pt, Pd, Ru, and Cu.[111] The highest TONs obtained after 17 h at 125 °C and 55 bar (at RT) were 1000 for [CoH(dppe)], 1200 for $[IrCl(CO)(PPh_3)_2]$, and 900 for $[CuCl(PPh_3)_3]$. A major improvement in the TON and TOF was achieved by Jessop et al. in 1994 by performing the hydrogenation of CO_2 to DMF in supercritical CO_2.[112] The product DMF was produced with a maximum TON of 370000 after 19 h (100 °C, 80 bar H_2, 130 bar CO_2) with $[RuCl_2(PMe_3)_4]$. Conversions and yields up to 99% based on $HNMe_2$ were obtained. The high rate of reaction was attributed to rapid diffusion, weak catalyst solvation, and the high miscibility of H_2 in $scCO_2$.[112] In a follow-up study, formamide, diethylformamide, and *n*-propylformamide were produced under similar reaction conditions, with TONs of 500, 820, and 260, respectively.[43] However, no complete conversions were obtained in these cases because of the slow rates of dehydration.

The group of Baiker further increased the TOF up to 360000 h^{-1} for the production of DMF by using the complex $[RuCl_2(dppe)_2]$ together with $scCO_2$.[94] To obtain appreciable yields of formanilide (up to 85%), the addition of the strong base DBU in overstoichiometric amounts to the weakly basic aniline was necessary to promote the hydrogenation of CO_2 to the formate intermediate.[113] The production of *N*-formylmorpholine was also possible with a quantitative yield by using $[RuCl_2(dppe)_2]$ in the presence of $scCO_2$. For this substrate, the TOF could be increased by an order of magnitude to 68400 h^{-1} by the addition of small amounts of

Table 5: Selected catalytic systems for the production of formamides from CO_2.[a]

Entry	Catalyst	Product	Amine	T [°C]	p_{H_2}/p_{CO_2} [bar/bar]	t [h]	TOF [h^{-1}]	TON	Ref.
1	[CoH(dppe)]	DMF	$HNMe_2$	125	55 total	17	59	1000	[111]
2	$[IrCl(CO)(PPh_3)_2]$	DMF	$HNMe_2$	125	55 total	17	71	1200	[111]
3	$[CuCl(PPh_3)_3]$	DMF	$HNMe_2$	125	55 total	17	53	900	[111]
4	$[RuCl_2(PMe_3)_4]$	DMF	$HNMe_2$	100	80/130	19	19474	370000	[112]
5	$[RuCl_2(dppe)_2]$	DMF	$HNMe_2$	100	85/130	2	360000	740000	[94]
6	$[RuCl_2(PMe_3)_4]$	formanilide	aniline/DBU	100	80/120	10	140	1400	[113b]
7	$[RuCl_2(dppe)_2]$	*N*-formylmorpholine	morpholine	100	87/128	3	68400	210000	[107]
8	$Fe(BF_4)_2{\cdot}6\,H_2O/PP_3$	DMF	$HNMe_2$	100	60/30	20	36	727	[56]
9	$Co(BF_4)_2{\cdot}6\,H_2O/PP_3$	DMF	$HNMe_2$	100	60/30	20	65	1308	[60]
10	$Fe(BF_4)_2{\cdot}6\,H_2O/L$	DMF	$HNMe_2$	100	70/30	20	211	4229	[57]
11	“Si”-$[RuCl_2\{PMe_2(CH_2)_2]Si(OEt)_3\}_3$	DMF	$HNMe_2$	133	85/130	60	1847	110800	[115]
12	“Si”-$[RuCl_2\{RPhP(CH_2)_3PPhR\}_2]$	diethylformamide	$HNEt_2$	110	180 total	–	18400	–	[116]
13	PS-PEG-“Ru”	DMF	$HNMe_2$	100	86/130	15	108	1620	[117]
14	“Si”-$[RuCl_2(L)(NHC)]$	formylpyrrolidine	pyrrolidine	100	30/50	24	121	2900	[118]
15	[RuCl(H)CO(PNP)]	*N*-formylmorpholine	morpholine	120	35/35	96	20208	1940000	[114]

[a] $PP_3 = P(CH_2CH_2PPh_2)_3$; L = tris[(2-diphenylphosphino)phenyl]phosphine; $PNP = MeN(CH_2CH_2PPh_2)_2$.

water to the reaction mixture. The water additive enhanced the solubility of the solid carbamate formed from CO_2 and morpholine.[107,113a]

Very recently, the group of Ding reported the use of a highly efficient catalyst system based on ruthenium-pincer-type complexes for the *N*-formylation of various amines with CO_2 and H_2. The catalysts afforded the corresponding formamides with excellent productivity (turnover numbers of up to 1 940 000 in a single batch) and selectivity in THF as the solvent. By using a simple catalyst-recycling procedure, the catalyst was reused for twelve consecutive runs of *N*,*N*-dimethylformamide synthesis without significant loss of activity.[114]

The nonprecious metal catalysts based on iron and cobalt developed in the group of Beller since 2010 are also active for the formation of formamides.[56,57,60] DMF was obtained in 75 % yield (TON = 727)[56] and *N*-formylpiperidine was obtained in 41 % yield (TON = 373) with the in situ catalyst $Fe(BF_4)_2\cdot 6H_2O/PP_3$ [$PP_3 = P(CH_2CH_2PPh_2)_3$]. DMF was obtained in 73 % yield (TON = 1308) and *N*-formylpiperidine in 70 % yield (TON = 1254) with the analogous cobalt complex $Co(BF_4)_2\cdot 6H_2O/PP_3$ under similar reaction conditions.[60] Again, the TONs could be improved up to 4229 by using the iron catalyst containing the tetradentate ligand tris[(2-diphenylphosphino)phenyl]phosphine.[57] The production of diethylformamide was also possible, although with a lower yield (39 % versus 74 %).

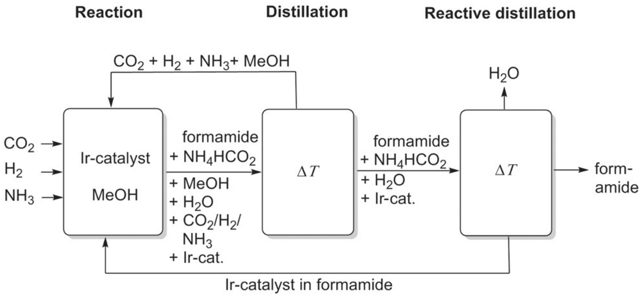
2.3.2.2. *Integrated Reaction and Separation*

Immobilized organometallic catalysts have shown particularly high efficiency in this reaction. In 1996, the group of Baiker showed that DMF was obtained in 82 % yield with high activity (TOF = 1860 h^{-1}, TON = 110 800) using the hybrid "Si"-$RuCl_2\{PMe_2(CH_2)_2Si(OEt)_3\}_3$ catalyst and $scCO_2$ as the solvent.[100,115,119] The catalyst could be recycled and used three times without pronounced deactivation. The same group synthesized a mesoporous hybrid aerogel based on the complex [$RuCl_2(dppp)_2$] (dppp = $Ph_2P(CH_2)_3PPh_2$).[116] A high TOF of 18 400 h^{-1} was obtained in the production of *N*,*N*-diethylformamide with "Si"-$RuCl_2\{RPhP(CH_2)_3PPhR\}_2$. In 2003, Ikariya and co-workers reported amphiphilic resin-supported ruthenium complexes and obtained DMF in 98 % yield (TON = 1620, TOF = 108 h^{-1}).[117] The support material was based on a cross-linked polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) which was modified with tertiary phosphines. Ru^{II} complexes such as [$RuCl_2\{P(C_6H_5)_3\}_3$] were immobilized on this material by exchange of the phosphine ligands by the tertiary phosphine groups on the solid material to give the material PS-PEG-"Ru". The catalyst could be recycled by filtration, although a slight decrease in productivity was observed from cycle to cycle. Baffert et al. synthesized ruthenium-NHC (NHC = N-heterocyclic carbene) hybrid catalyst materials by coordinating [{$RuCl_2$(*p*-cymene)}$_2$] to a 1-mesitylimidazolium-functionalized silica support.[118] 1-Formylpyrrolidine was produced with TONs up to 2900 by using this "Si"-[$RuCl_2$(L)(NHC)] (L = *p*-cymene, THF, PMe_3) material. However, pronounced leaching (50 % based on Ru) of the catalyst was observed.

Although these immobilized catalysts have so far only been used in repetitive batch mode, they clearly offer the possibility for continuous-flow operation. The fundamental operation would be similar to a process described in a BASF patent involving their previously described heterogeneous Au/TiO_2 catalyst:[104,109] CO_2, H_2, and amine are reacted in a polar solvent over the solid catalyst and the resulting product mixture is separated by rectification. The water of the reaction is removed and the polar solvent, as well as the unreacted amine, is recycled to the reactor. About 11 g of DMF were produced per 1 g catalyst (1 % Au on TiO_2) within 10 h in a semibatch experiment (140 bar, 125 °C). Given their much higher activities, significantly higher productivities would be expected using such a process scheme with some of the immobilized organometallic catalysts.

In 2004 Behr et al. suggested a biphasic reaction system consisting of an organic catalyst phase (toluene) and an aqueous extraction phase for the production of DMF.[85b] By using [$RuCl_2(dppb)_2$] in this biphasic system, the catalyst phase could be recycled five times. The catalyst leaching was around 4 wt % per cycle, thus making further catalyst extraction steps with toluene necessary for a proposed continuous process. Thus, the envisaged overall process is very similar to the flow scheme for alkyl formates shown in Scheme 8. Tumas, Baiker, and co-workers reported an alternative biphasic system consisting of an ionic liquid as the catalyst phase and $scCO_2$ as the extraction phase.[120] By using [$RuCl_2(dppe)_2$], *N*,*N*-di-*n*-propylformamide was obtained in nearly 100 % yield with a TON of 110 and a TOF of 22 h^{-1}. The product could be separated from the catalyst by extraction with $scCO_2$, whereas the catalyst remained active for reuse in the ionic liquid phase. Although no continuous operation was shown, this should be possible by using a similar set-up as the one depicted in Scheme 4.

A liquid/liquid phase process has also been developed for formamide itself by using a homogeneous Ir/phosphine catalyst (Scheme 11):[121] In the reactor, CO_2, H_2, and NH_3 are reacted in methanol in the presence of the Ir/phosphine complex. The resulting formamide, ammonium formate, water, and the Ir catalyst are separated by distillation from the reaction gases (CO_2, H_2, NH_3) and the solvent methanol. Formamide, ammonium formate, water, and the Ir catalyst are introduced into a reactive distillation unit, in which the remaining ammonium formate is converted into formamide. The water formed in the reaction is distilled off and disposed



Scheme 11. Production of formamides from CO_2 by using a homogeneous Ir catalyst, as presented by BASF.[121]

of, followed by distillation of the formamide product. Enough formamide to keep the Ir catalyst dissolved in its active form is retained and recycled to the reactor stage.

2.4. Formation of CO and Integrated Carbonylation Reactions

As an alternative to the formation of formic acid, the reaction of CO_2 with one equivalent of H_2 can lead to the formation of CO and H_2O, depending on the applied catalyst and reaction conditions. In the chess picture, this would again be only one step in the vertical direction. However, this also opens the possibility to utilize in situ formed CO as a C_1 building block directly, thereby needing catalysts that are capable of more complex strategic moves. After a short introduction on the conversion of CO_2 into CO, this section will focus on such transformations involving multiple bond-breaking and bond-forming events.

2.4.1. Equilibrating CO_2 and CO: The Water-Gas Shift (WGS) and Reversed Water-Gas Shift (rWGS) Reaction

The water-gas shift (WGS) reaction and its back-reaction, the reversed WGS (rWGS; Scheme 12) are important industrial processes that are today mainly used for the adjustment of the C/H ratio in synthesis gas, for example, in the manufacture of hydrogen (for ammonia production), methanol, and hydrocarbons. As a consequence of the principle of microscopic reversibility, catalysts which enable the WGS very often also catalyze the rWGS.[33c,122] The industrially most relevant, and therefore extensively studied, catalysts for both transformations are heterogeneous catalysts based on copper, such as Cu-Ni or Cu-Zn/Al_2O_3.[33c] Typically, the rWGS using these catalysts is conducted at high temperatures of around 600 °C to achieve high conversions for the endothermic process.

$$CO + H_2O \underset{\text{rWGS}}{\overset{\text{WGS}}{\rightleftharpoons}} CO_2 + H_2 \qquad \Delta_R H_{(298K,50bar)} = -42\ \text{kJ/mol}$$

Scheme 12. Water-gas-shift reaction (WGS) and reverse water-gas-shift reaction (rWGS).

Fewer reports exist on molecular catalysts for the WGS and rWGS. In 1932 Hieber and Leutert described the oxidation of CO (coordinated to an iron complex) to CO_2 trapped in the form of carbonates by the addition of basic additives (Scheme 13a).[123] This reaction is known as the "Hieber'sche base reaction" in organometallic chemistry. In 1953, Reppe extended the scope to nickel- and cobalt-carbonyl complexes (Scheme 13b).[124]

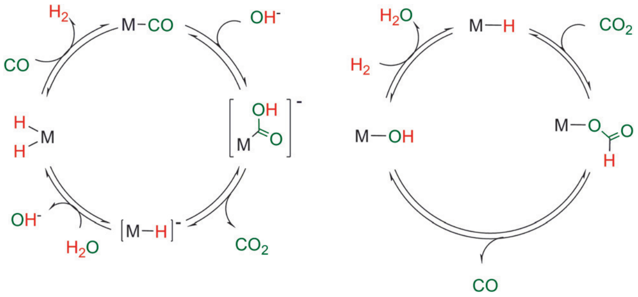
Only much later were metal complexes based on Ru, Rh, Fe, Ni, and Os studied as catalysts for the homogeneously catalyzed WGS.[125] In 1977, Ford and co-workers described the use of triruthenium dodecacarbonyl $[Ru_3(CO)_{12}]$ as a catalyst for the WGS reaction under homogeneous mild conditions (1 bar CO, 100 °C). It was concluded that $[Ru_3(CO)_{12}]$ was most likely acting as a precatalyst, converting in situ to not fully characterized ruthenium carbonyl complexes as the actual active species. In the same period, Eisenberg and co-workers reported the homogeneous system $[RhI_2(CO)_2]^-/H^+/I^-$ based on a mononuclear rhodium complex which was active at even lower temperatures (< 95 °C).[125b,126] Activities in the range of 5–10 turnovers per day were achieved with this system. In 2009, the group of Wasserscheid reported a $RuCl_3$-based supported ionic liquid phase (SILP) catalyst that promoted the WGS reaction under ambient pressure and at low temperatures with a TOF of $3\ h^{-1}$.[127] The induction period of 20 h was later reduced significantly to a few minutes when $RuCl_3$ was replaced by $[Ru(CO)_3Cl_2]$, and the results could be further improved to a TOF of $21.8\ h^{-1}$ by replacing the γ-alumina support by Boehmite.[128] Interestingly, the activity of this system exceeded the catalytic activity of the commercial WGS copper-based catalyst of Sued-Chemie AG (now Clariant SE) when applied under the same mild conditions.

$$[Fe(CO)_5] + 2\,NaOH \longrightarrow [Fe(CO)_4H_2] + Na_2CO_3 \qquad (a)$$

$$3\,[Co(CO)_4] + 2\,NaOH \longrightarrow 2\,[Co(CO)_4H] + [Co(CO)_3] + Na_2CO_3 \qquad (b)$$

Scheme 13. Conversion of CO coordinated to metal complexes into CO_2 trapped as carbonate salts

The interconversion of CO_2/H_2 and CO/H_2O in the presence of metal complexes can occur through different pathways. Scheme 14 shows a schematic representation of two generic possibilities. A generally accepted mechanism for the WGS catalyzed by metal complexes is shown in Scheme 14, left. To achieve the rWGS, by reversing this pathway, requires very electron-rich metal centers to attack the weakly electrophilic carbon center of CO_2 under formation of a metal carboxylate intermediate.[129] Alternatively, the homogeneously catalyzed rWGS can be achieved by insertion of CO_2 into a metal hydride bond to give a formato complexe followed by CO elimination and subsequent hydrogenolysis of the metal hydroxy unit (Scheme 14, right).[6g,130]



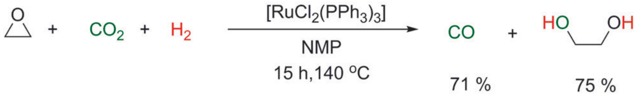
Scheme 14. Principle pathways for general reaction mechanisms of homogeneously catalyzed WGS and rWGS reactions.

The deoxygenation of metallacarboxylates or coordinated CO_2 to give CO is a well-known reaction for metal complexes.[6g] The driving force is typically the formation of M=O units or transfer of the oxygen to a oxophilic ligand (e.g. phosphine), thereby rendering these reactions mostly stoichiometric unless very strong co-reductants are provided.

Very recently, it was shown that carboxylato intermediates can also be formed in metal-free systems by using electron-rich Lewis bases in so-called “frustrated Lewis pairs” (FLPs).[131] Stephan, Erker, and co-workers showed that systems derived from sterically demanding phosphines as Lewis bases and boranes as Lewis acids are capable of binding CO_2 in a reversible manner.[132] Subsequently, they showed that FLPs derived from very oxophyilic components react with CO_2 to give stoichiometric amounts of CO.[131a,133] In contrast to these stoichiometric reagents, hydrogen takes the role of “sacrificial oxygen sink” in the catalytic rWGS reaction.

The most thoroughly investigated catalytic systems for the rWGS reaction is the triruthenium dodecacarbonyl $[Ru_3(CO)_{12}]$ precursor introduced by Ford and co-workers for the WGS reaction[125a] and studied in detail by the group of Sasaki and Tominaga for the reverse reaction.[134] In 1993, they reported the use of $[Ru_3(CO)_{12}]$ in the presence of an iodide salt as a catalyst for the hydrogenation of carbon dioxide to methane via carbon monoxide and methanol.[134a] The conversion/time profiles of the hydrogenation of carbon dioxide showed that the amount of carbon monoxide reaches a maximum in the early stages of the reaction before subsequent conversion into methanol and methane. The presence of metal iodides was found to drastically suppress the deposition of metallic ruthenium, thus leading to a better control of the hydrocarbon formation. In addition, the countercation of the iodide source had a significant effect. Alkaline-metal cations improved the yields of methanol and methane, while carbon monoxide was preferentially formed with ZnI_2[134a] and [PPN]Cl (bis(triphenylphosphine)iminium chloride)[134b] with TONs per mole of $[Ru_3(CO)_{12}]$ of 73 and 80, respectively. Detailed analysis of the reaction solutions by FTIR spectrosocopy indicated the presence of several anionic tetranuclear and trinuclear Ru-hydride clusters, among which $[H_2Ru_4(CO)_{12}]^{2-}$ is suggested to be the active species in a metal carboxylate pathway.

The conversion of CO_2 and hydrogen into CO and water is also possible with mononuclear coordination compounds. The first homogeneous systems for the reduction of CO_2 with hydrogen to give CO was described by Koinuma et al., who showed that $[RhCl(PPh_3)_3]$ is converted into $[RhCl(CO)(PPh_3)_2]$ in the presence of CO_2/H_2 pressure in a stoichiometric reaction.[135] Later, in 1989, Khan et al. described the use of K[Ru(EDTA-H)Cl] (EDTA = ethylenediamine tetraacetic acid disodium salt dehydrate) for the homogeneous catalytic reduction of carbon dioxide by hydrogen to give formic acid and formaldehyde as the initial reaction products, which later decompose to give CO and H_2O.[136] In 1995, Sasaki, Tominaga, and co-workers showed that the complex $[RuCl_2(PPh_3)_2]$ acts as the active catalyst for the formation of CO from CO_2 and H_2 in the presence of ethylene oxide.[137] In this reaction, ethylene oxide reacts with CO_2 to form ethylene carbonate, which is subsequently converted with hydrogen in the presence of the Ru catalyst to give CO and ethylene glycol, with NMP believed to act as the solvent and base (Scheme 15).



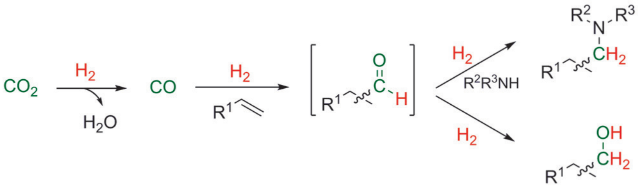
Scheme 15. Hydrogenation of CO_2 to form CO mediated by ethylene oxide by using $[RuCl_2(PPh_3)_2]$ as the catalyst.[137]

Recently, the group of Tominaga reported that the mononuclear ruthenium carbonyl complex exhibits higher catalytic activity per ruthenium atom than the previously described carbonyl cluster.[138] The use of $[PPN][RuCl_3(CO)_3]$ in the presence of [PPN]Cl afforded CO with TONs of 87 and 96 per ruthenium center at 160 °C and 180 °C, respectively. In contrast to the multinuclear ruthenium cluster, the mononuclear complex showed little dependence on the nature of the halogen salt and retained full activity and stability even in the absence of any salt. Again, a metal carboxylate pathway is assumed for the conversion at the mononuclear catalyst.

2.4.2. *Utilization of Carbon Dioxide as a C_1 Building Block in the rWGS Reaction*

In principle, the rWGS reaction and subsequent use of CO or synthesis gas can be coupled in two independent processing steps by using existing approaches. As a consequence of the endothermicity of the rWGS equilibrium, the process has to be operated at high temperatures, and coupling with an exothermic second process is highly desired. Alternatively, the formation of CO could be coupled directly with a subsequent conversion in a single operating unit. As a result of the strong binding of CO to metal centers, low equilibrium concentrations may even be sufficient for an effective overall reaction rate, even at relatively moderate temperatures. In fact, the low CO concentration may be advantageous, as many carbonylation reactions have an inverse reaction order in CO at higher partial pressures because of substrate inhibition. In addition, replacing toxic CO by CO_2 can be an additional driver for synthetic methods in the fine-chemical and pharmaceutical industry as well as in research laboratories.[139] Thus, the CO_2/H_2 mixture can be viewed as a reservoir for CO that is constantly regenerated “just in time” for the actual transformation by the rWGS reaction.

Hydroformylation comes to mind as a prototypical example of the various carbonylation reactions that can be envisaged. Hydroformylation, which was discovered during studies of the Fischer–Tropsch process in 1938 by Otto Roelen, who at the time called it an “oxo process”,[140] is the addition of CO and H_2 to olefins in the presence of a catalyst to afford the corresponding C_1-elongated aldehydes.[140] Today, “oxo products”, with a total capacity in the range of 10 million tons per annum, represents one of the largest homogeneously catalyzed reactions in industry. This reflects the importance of the aldehydes as intermediates in the synthesis of commodity and fine-chemicals such as alcohols, esters, and amines.[140] In addition, the generation of such functional groups by hydroformylation has a very large potential for the formation of complex organic molecules, including chiral structures. The following section summarizes the state of the art for the use of CO_2 as a C_1 building block for

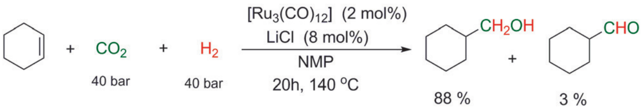


Scheme 16. Utilization of CO_2 for the hydroformylation reaction through the rWGS reaction and subsequent pathways.

this type of transformation (Scheme 16) as well as for related synthetically useful carbonylation reactions.[16a]

2.4.2.1. *Hydroxymethylation/Hydroformylation*

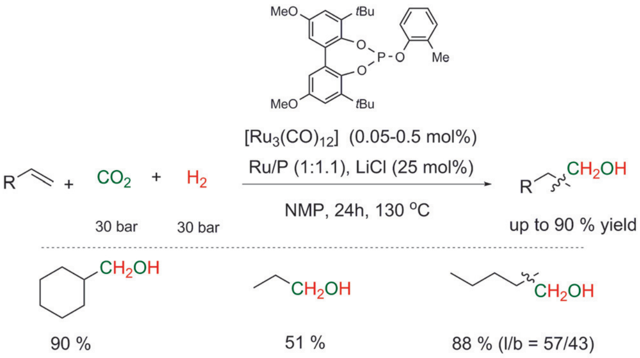
In 2000, Tominaga and Sasaki reported the ruthenium-catalyzed C_1 elongation of alkenes with carbon dioxide and hydrogen, whereby the corresponding alcohols were formed as the main products.[141] They found that hydroxymethylcyclohexane can be obtained in 88 % yield from cyclohexene, carbon dioxide, and molecular hydrogen by using $[H_4Ru_4(CO)_{12}]$ as a catalyst in the presence of LiCl (Scheme 17). In line with their previous studies on the rWGS reaction with the same catalyst, they proposed a cascade reaction of CO formation, hydroformylation, and subsequent hydrogenation of the aldehydes to the alcohols. The formation of the alcohols under hydroformylation conditions is desired in certain industrial processes of bulk chemicals (e.g. the Shell hydroformylation technology) and is referred to as hydroxymethylation in synthetic chemistry. Interestingly, the use of the CO_2/H_2 mixture as a C_1 source for the hydroxymethylation sequence showed better results than applying synthesis gas under otherwise identical conditions.



Scheme 17. Ruthenium-catalyzed hydroxymethylation of cyclohexene with CO_2 and molecular hydrogen.[141]

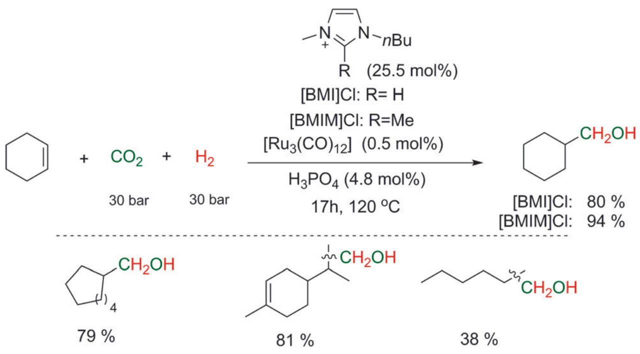
The rWGS/hydrofromylation pathway is strongly supported by the experimental detection of significant amounts of carbon monoxide in the gas phase of the reaction in the presence of anionic tetranuclear and trinuclear Ru-hydridocarbonyl complexes in solution. The direct influence of the halogenide anion of the salt additive ($Cl^- > Br^- > I^-$) also matches the previous findings on the rWGS catalysis with the Ru-carbonyl clusters.[142] The influence of the halide counterions and the catalytic activity was also studied in detail by Haukka and co-workers for the hydroformylation/hydrogenation sequence of 1-hexene with carbon dioxide and hydrogen. They concluded that the presence of halide was essential to achieve high activity. The best results were obtained upon using $[Ru(CO)_3Cl_2]_2/Li_2CO_3$ as the catalyst system, as it probably provided an optimum combination in terms of halide source and solubility in the reaction medium.[143]

The Ru-catalyzed hydroxymethylation with CO_2/H_2 provides good yields for the corresponding alcohols with a variety of olefins.[141,142] A limitation of the original procedure was the competing hydrogenation of the C=C bond for terminal alkenes and the use of *N*-methyl-2-pyrolidone (NMP) as solvent, which is difficult to remove due to its high boiling point and similar polarity to the products. The selectivity can be influenced by the partial pressures of the reactant gases, but the complex reaction network always results in a certain compromise in terms of the rate and yield.[144] Recently, the group of Beller described the use of a bulky phosphite ligand as a way to improve the catalytic system for a more efficient hydroxymethylation of terminal and internal olefins with CO_2/H_2 at lower temperature.[145] Compared to the ligand-free catalyst, the formation of hydrogenation by-products is retarded and the yield of the desired alcohols is improved (Scheme 18). The reaction was studied in the context of an industrial collaboration with the company Evonik.[146]



Scheme 18. Increased selectivity and substrate scope for the ruthenium-catalyzed hydroxymethylation of olefins with a bulky phosphite ligand.[145]

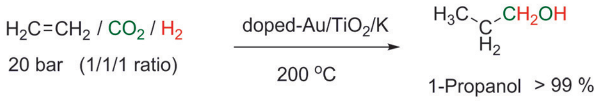
Replacing NMP by ionic liquids (ILs) as solvents positively affected the selectivity as well as the downstream processing.[147] A mixture of the ionic liquids [BMIM][Cl] and [BMIM][NTf_2] (BMIM: 1-butyl-3-methyllimidazolium) as a solvent for the hydroxymethylation of 1-hexene afforded an approximately 1:1 mixture of *n*-heptanol and isoheptanols in 82 % yield, with only 8 % hexane obtained as a side product. The alcohol mixture could be extracted with diethyl ether and the IL solution containing the ruthenium catalyst could be recycled to provide a 76 % yield of the alcohol after five runs. The group of Dupont reported that the $[Ru_3(CO)_{12}]$ catalyst already showed a significantly improved performance in the presence of catalytic amounts of the halogen-based IL.[148] This was related to the in situ formation of Ru-carbene complexes as efficient catalysts for the rWGS/hydroformylation/hydrogenation cascade reaction.[149] Compared to the original procedure, the use of the IL allowed the use of lower temperatures (120 °C) and shorter reaction times. The use of [BMIM][Cl] together with H_3PO_4 as additives improved the



Scheme 19. Ruthenium-catalyzed hydroxymethylation of neat cyclohexene in the presence of IL and H_3PO_4 as additives.[148]

chemoselectivity and resulted in the hydroxymethylation of cyclohexene in 94 % yield (Scheme 19).

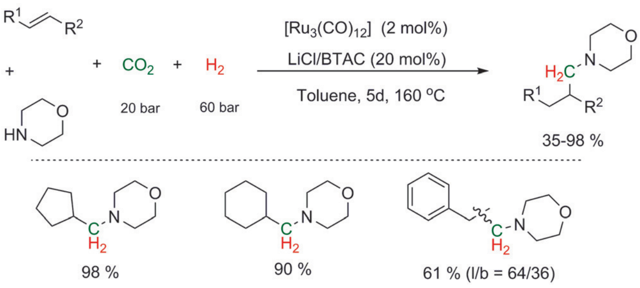
Recently, the first heterogeneously catalyzed gas-phase hydroxymethylation with CO_2/H_2 was introduced. Kondratenko and co-workers studied the use of Au nanoparticles (NPs) supported on TiO_2/K for the conversion of ethylene, CO_2, and H_2 into propanol. The activity and selectivity of the reaction depended strongly on the size of the NPs, which could be tuned by the method of Au deposition on TiO_2/K.[150] Under optimized conditions, propanol was reported to be formed with almost 100 % conversion/selectivity (Scheme 20).



Scheme 20. Formation of 1-propanol from CO_2, H_2, and ethylene with a Au/TiO_2/K catalyst.[150]

2.4.2.2. Hydroaminomethylation/Hydroformylation

Amines are large-scale industrial products or intermediates that are often produced by multistep processes.[20] Hydroaminomethylation is a one-pot cascade reaction for the formation of C_1-elongated amines from olefins.[151] The first step of this cascade is a hydroformylation of the olefin to an aldehyde, the second step is the reaction of the aldehyde with an amine to form an enamine/imine, and the last step is the hydrogenation of this enamine/imine to give the final amine. In 2009, Srivastava and Eilbracht demonstrated the use of CO_2/H_2 as a CO surrogate for this reaction.[152] Again, the use of the rWGS catalyst system $[Ru_3(CO)_{12}]$/LiCl/BTAC (BTAC = benzyltrimethylammonium chloride) proved to be an efficient system for the in situ formation of CO. The combination of salts as promotors revealed a synergetic effect on the yields and selectivities, most probably because of the enhanced solubility in the toluene solvent. Secondary and tertiary amines were formed effectively from a variety of olefins with yields in the range of 35–98 %. Isomeric mixtures were formed when *n* and *iso* products are possible (Scheme 21).

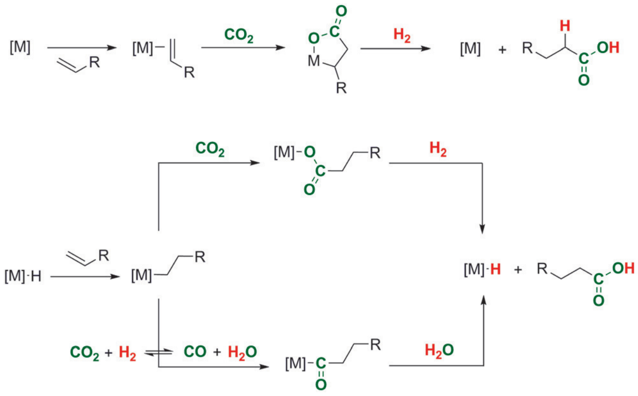


Scheme 21. Ruthenium-catalyzed hydroaminomethylation of alkenes with CO_2 and molecular hydrogen.[152]

2.4.2.3. Hydrocarboxylation/Hydroxycarbonylation

Carboxylic acids and their derivatives are important products and intermediates in the chemical industry, and are mostly produced by oxidation or carbonylation reactions.[20] The use of CO_2 as a C_1 building block in C−C bond-forming reactions would open new synthesis routes for the direct production of carboxylic acids. The direct insertion of CO_2 into C−H groups is currently limited to sp^1 units in alkynes or sp^2 units in (hetero-)aromatic substrates of sufficient reactivity (see Ref. [153] and references therein), whereas the carboxylation of sp^3 bonds remains a "dream reaction" because of thermodynamic and kinetic constraints.[13] An alternative pathway would be the reductive carboxylation of unsaturated substrates with CO_2 and reducing agents. The carboxylation of alkynes with strong reducing agents such as silanes has been studied and a number of synthetic procedures have recently emerged.[154] A particularly attractive approach towards saturated carboxylic acids could be provided by the reaction of olefins, CO_2, and H_2, a transformation that is exergonic, with $\Delta G^{\#}$ in the range of $-37\,\mathrm{kcal\,mol^{-1}}$.[155] The energy released from the saturation of the double bond provides the additional driving force, in contrast to the formation of formic acid described in Section 2.1.2.1. Formally, the reaction can be referred to as hydrocarboxylation, in analogy to the terminology of the hydroformylation reaction.[155] However, three mechanistically distinct pathways can be envisaged for the overall transformation at transition-metal centers as catalytically active species (Scheme 22).

In the first case, the olefin and CO_2 undergo oxidative coupling to form a five-membered metallalactone. This reaction is well-known and intensively studied as the initial step in the formation of acrylic acid from CO_2 and ethylene through subsequent β-H elimination.[156] Alternatively, hydrogenolysis of both the M−O and M−C bonds could lead to the saturated acid under regeneration of the low-valent metal center with loss of H_2. In the second scenario, a metal–alkyl unit is formed from a metal hydride and the olefin followed by CO_2 insertion to form a metal carboxylate. Hydrogenolysis again closes the catalytic cycle. There is ample precedence for all the individual steps from stoichiometric reactions or other catalytic cycles. For example, the long-known CO_2 insertion into Rh−C bonds was studied recently by computational methods for a wide variety of electronically and sterically very

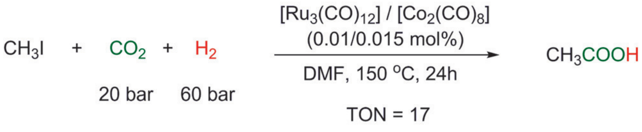


Scheme 22. Possible pathways for the metal-catalyzed synthesis of carboxylic acids from olefins and CO_2/H_2 as a C_1 synthon ("hydrocarboxylation").

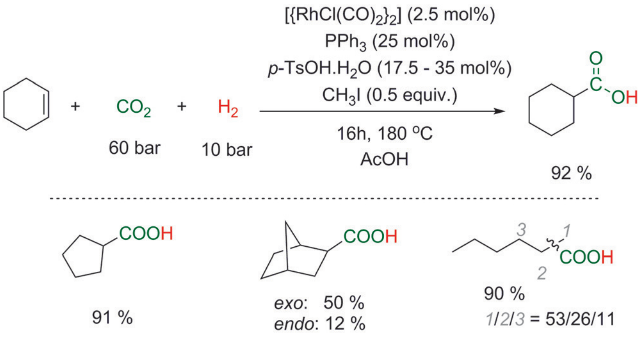
different ligand frameworks. It was found that this is a quite facile elementary step that is largely controlled by the nucleophilicity of the alkyl group, rather than by precoordination of CO_2.[157] A full catalytic cycle for the addition of H_2 and CO_2 to ethylene to afford propionic acid could be conceived, but the computational analysis also revealed the difficulties in controlling the productive cycle relative to possible side reactions, such as hydrogenation or olefin oligomerization.[155] The third possibility also involves the metal–alkyl intermediate, but in this case the carboxylic acid function is formed by CO insertion and hydrolysis. The latter process is well known as hydroxycarbonylation,[158] and the reagents CO and H_2O are again generated from a rWGS reaction in this pathway.

In 1995, Fukuoka, Komiya et al. reported the catalytic carboxylation of organic iodide by using CO_2/H_2 in the presence of homogeneous Ru/Co or Ni/Co bimetallic catalysts.[159] The significant feature of the reaction is the synergistic effect of the bimetallic catalysts used on the catalytic production of the carboxcylic acids. Starting from methyl iodide CH_3I, no acetic acid was formed with $[Ru_3(CO)_{12}]$ or $[Co_2(CO)_8]$ alone, but using a mixture of the two complexes resulted in the formation of acetic acid with a TON of up to 17 per Ru atom (Scheme 23). The side products detected were CH_4 (from CH_3I) and CO with maximum TONs of 50 and 58, respectively. Although the authors favored a mechanism involving direct insertion of CO_2 into a M−CH_3 bond, they did not rule out the possibility of carbonylation by in situ formed CO through the rWGS reaction.

In 2013, Klankermayer, Leitner, and co-workers reported an effective catalytic system for the direct formation of carboxylic acids from non-activated olefins, CO_2, and H_2 with high conversion and selectivity under optimized reaction conditions (Scheme 24).[158c]

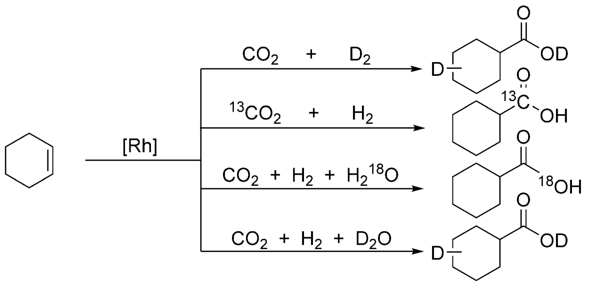


Scheme 23. Synthesis of acetic acid from methyl iodide by using CO_2 and H_2 as a source of the carboxylate group.[159]



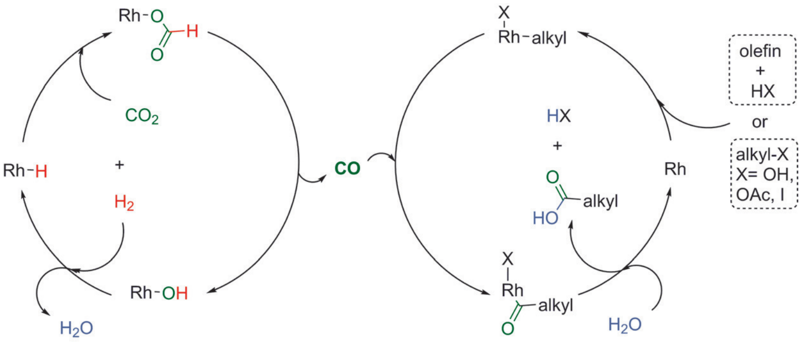
Scheme 24. Catalytic synthesis of carboxylic acids from olefins by using CO_2 and H_2 as the source of the carboxylate group.[158c]

From a range of metal precursors and complexes, a combination of $[\{RhCl(CO)_2\}_2]$ and PPh_3 proved to be the most efficient catalyst system for the conversion of cyclohexene into cyclohexanecarboxylic acid when CH_3I was added as a promoter in the presence of acidic additives. The choice of this catalyst system was inspired by the work of the group of Simonato, who showed that the carboxylation of olefins could be achieved with formic acid.[160] Given the acidic medium, the formation of free formic acid as an intermediate seems unlikely under the present conditions. Insight into the reaction mechanism was obtained from isotope-labeling studies (Scheme 25). The use of D_2 instead of hydrogen resulted in deuterium incorporation with a large degree of scrambling around the cyclohexyl ring. ^{13}C- labeled CO_2 showed that this was the only carbon source of the carboxylate group, as expected. However, experiments with addition of ^{18}O-labeled water resulted in significant incorporation of this isotope in the carboxyl group. This clearly indicates that the carboxylic acid group is not constructed by the incorporation of an intact CO_2 molecule, and one of the oxygen atoms stems from water as a reactive species. These findings together with the detection of CO in the gas phase of the reaction mixture are most consistent with a combination of two integrated rhodium-catalyzed cycles to facilitate the



Scheme 25. Isotopic labeling pattern observed by NMR spectroscopy and MS for the rhodium-catalyzed reaction of cyclohexene with CO_2 and H_2 (or D_2).[158c]

synthesis of carboxylic acids from olefins, CO_2, and H_2 in the present system (Scheme 26). In one cycle, the rhodium-catalyzed rWGS reaction sets up an equilibrium between CO_2/H_2 and CO/H_2O that effect the hydroxycarbonylation of a rhodium–alkyl intermediate. The reversible formation of the rhodium–alkyl complex explains the isomerization and deuterium scrambling. The exact details of the two cycles remain to be elucidated.



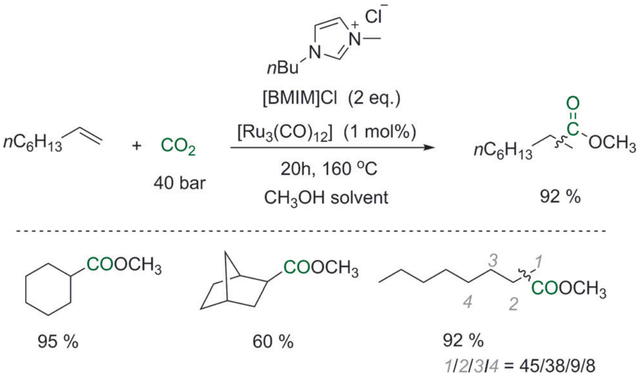
Scheme 26. Proposed mechanism for the formal hydrocarboxylation reaction shown in Scheme 24 through coupled rWGS and hydroxycarbonylation cycles.[158c]

Under the optimized reaction conditions, the hydrocarboxylation of cyclohexene and cyclopentene occurred selectively to give cyclohexanecarboxylic acid and cyclopentanecarboxylic acid in yields of 92% and 91%, respectively. A lower yield of 62% was obtained for the hydrocarboxylation of norbornene, with a high selectivity of the corresponding *exo* product. In the case of cyclohexenes with methyl substituents at different positions, isomeric mixtures of the carboxylation products were obtained in high yields, whereby the distribution of product isomers was largely independent of the original substitution pattern. Similar observations were made for the hydrocarboxylation of linear *n*-alkenes bearing the double bond at the 1-, 2-, or 3-position. The corresponding carboxylic acid products of such linear *n*-alkenes have distributions reminiscent of hydroformylation under isomerizing conditions (cf. Scheme 24), which further support the formation of the carboxylic acid involving a Rh-alkyl complex as a key intermediate. Other substrates which are able to form such a species under the given conditions might also be converted into carboxylic acids, at least in principle. Indeed, this was shown by successful conversion of different cyclic and linear alcohols, which resulted in the formation of the carboxylate products in yields of up to 74%. Moreover, the conversions and product distribution were almost identical to those observed with comparably substituted alkenes.

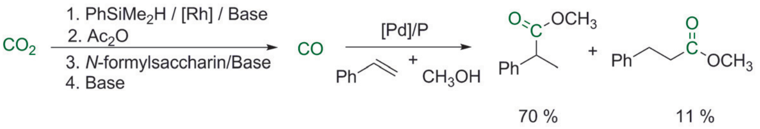
2.4.2.4. Alkoxycarbonylation

In 2014, the group of Beller described the use of the rWGS catalyst system $[Ru_3(CO)_{12}]/[BMIM]Cl$ for the direct conversion of olefins, CO_2, and alcohols into carboxylic acid esters (Scheme 27).[161] A variety of olefins and alcohols afforded the corresponding carboxylic acid esters with a yield range of 41–95%. No external hydrogen is used in this case, and the reduction of CO_2 is suggested to be affected by hydrogen transfer from the alcohol.[162] The CO formed this way can subsequently effect the alkoxycarbonylation reaction of the olefin and alcohol to yield the carboxylic acid ester product. Again, the pathway was supported by isotopic-labeling experiments.

Most recently, Fleischer et al. described the indirect utilization of CO_2 as a C_1 source under ambient reaction conditions by using *N*-formylsaccharin as a CO transfer reagent.[163] This method was applied to the alkoxycarbonylation of different olefins, and afforded the corresponding ester products in yields of up to 92%. The carbonylation catalyst is based on a Pd^0 precursor, a bidentate phosphine ligand, and a moderately strong acid, which enable a highly regioselective transformation of styrene derivatives to the corresponding branched ester in yields of up to 84% (Scheme 28).



Scheme 27. Alkoxycarbonylation of olefins with CO_2 and alcohols via formation of CO by hydrogen transfer.[161]



Scheme 28. Methoxycarbonylation of olefins with CO_2 via formation of CO through formylation/decomposition.[163]

3. Formaldehyde Level

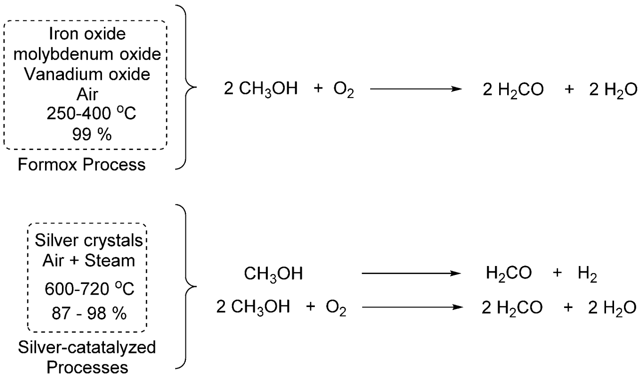
3.1. Formaldehyde

The reduction of CO_2 with two equivalents of H_2 gives formaldehyde and one equivalent of water as by-product. On the catalysis chessboard, two steps in the vertical direction have to be achieved, a move requiring precious chess pieces such as a rook or queen. The challenge is to stop them from moving on, because of the high affinity of the aldehyde function to undergo further reduction.

3.1.1. *Properties, Current Production, and Uses of Formaldehyde*

Formaldehyde or methanal (CH_2O) was first reported in 1859 by the Russian chemist Aleksandr Butlerov.[164] It is a colorless gas at room temperature (b.p. = −19 °C; m.p. = −92 °C) and it has a characteristic pungent, irritating odor. In nature, formaldehyde is emitted mainly by trees and other vegetation and to a lesser degree by animals (including humans). Formaldehyde is commercially available as the cyclic trimer 1,3,5-trioxane or in a polymeric form as paraformaldehyde, which is an important precursor to many other materials and chemical compounds. In aqueous solution, known as “formalin”, formaldehyde forms a hydrate, methanediol, with the formula $H_2C(OH)_2$.

Industrially, formaldehyde is produced by the catalytic oxidation of methanol using mainly two different types of catalyst (Scheme 29). The oxidation of methanol in the presence of excess air and a modified iron-molybdenum-vanadium oxide catalyst at 250–400 °C, which provides overall yields of 99 %, is the commonly used process (Formox). Silver catalysts are used either for the partial oxidation and dehydrogenation with air in the presence of steam and excess methanol at 680–720 °C (up to 98 %) or around 650 °C for direct dehydrogenation (87 %). Additionally, formaldehyde can be generated by the direct oxidation of methane, but this route is not industrially viable today, as formaldehyde is more easily oxidized than methane.[164]

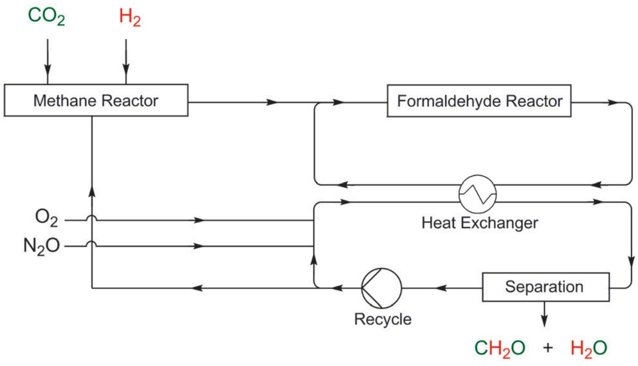


Scheme 29. Current industrial processes for the production of formaldehyde.

The worldwide production of formaldehyde is estimated to be more than 20 million tons per year,[164,165] and the demand is still growing. Formaldehyde and paraformaldehyde are important high-volume products, which are widely used in the chemical industry, in construction, wood processing, furniture manufacture, and the textiles industry.[164] Additionally, it is applied in medicine-related industries (forensic/hospital mortuaries and pathology laboratories) and a wide range of personal care and consumer products. Similar to formic acid, formaldehyde could potentially be used to store H_2 or CO, as selective decomposition reactions are established.[136,166]

3.1.2. *Catalytic Synthesis of Formaldehyde from CO_2*

In 1968, a NASA contractor, the General American Research Division of the General American Transportation Corp. (GATX), designed a breadboard prototype apparatus which accepted carbon dioxide, hydrogen, and oxygen as starting materials to produce formaldehyde and water, with all the intermediates and by-products recycled (Scheme 30).[167] This process was based on multiple steps:

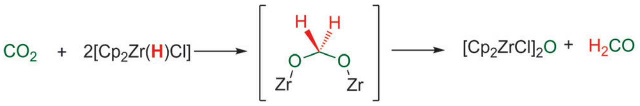


Scheme 30. Process scheme for the production of formaldehyde from CO_2 and H_2 by methanisation/oxidation.[167]

In the first step, methane is produced from CO_2 and H_2 through the Sabatier reaction. In the second step, methane is oxidized at 675° C in a reactor containing pellets coated with sodium tetraborate to afford a relatively low conversion into formaldehyde and some CO_2 as by-product. In a recycle loop, a fraction of the product stream is transferred to the methane reactor to convert remaining reaction gases and CO_2 by-product into methane. The laboratory system was shown to produce approximately 40 g day^{-1} of formaldehyde.

In 2001, Lee and co-workers reported the use of a Pt/Cu/SiO_2 catalyst for the hydrogenation of CO_2 to formaldehyde at 150 °C and 6 bar pressure.[168] The presence of a Pt/Cu-based catalyst was crucial for the formation of formaldehyde with an optimum atomic Pt/Cu ratio of 0.03:1. The authors proposed that hydrogen is adsorbed on the surface of the platinum and subsequently migrates onto the copper surface to promote the reduction of CO_2. The relative concentration of surface hydrogen strongly influenced the selectivity of the reaction, with methanol being the main by-product. As the H_2/CO_2 ratio increased, the relative rate of methanol formation decreased, and the formation of formaldehyde became more prevalent. At the optimum H_2/CO_2 ratio of 20:1, the formation of formaldehyde took place with a rate of 0.87×10^{-4} mol min^{-1} per gram catalyst and a selectivity of about 80 %.

Until recently, H_2CO was not isolated in any homogeneously catalyzed reductions of CO_2. However, early reports described the stoichiometric reduction of carbon dioxide to formaldehyde by using the Schwartz reagent[169] [$Cp_2Zr(H)(Cl)$] ($Cp = \eta^5$-C_5H_5 cyclopentadienyl).[170] The reaction involves two steps: the formation of formaldehyde and [$Cp_2Zr(Cl)]_2O$ (Scheme 31), and subsequently the reduction of formaldehyde to give [$Cp_2Zr(OCH_3)(Cl)$]. At the same time, the group of Cutler reported the reduction of heterobimetallic [$Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$] to its formaldehyde derivative [$Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$].[171]

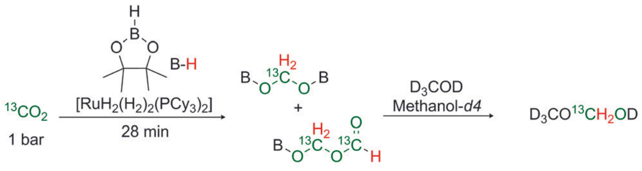


Scheme 31. Stoichiometric reduction of carbon dioxide to formaldehyde with Schwartz's reagent.[170]

Later, Khan et al. described the use of K[Ru(EDTAH)Cl]·2 H_2O for the catalytic hydrogenation of CO_2 to formic acid and formaldehyde, which subsequently decomposes to CO and H_2O.[136] At 40 °C and 34 bar CO_2/H_2 (1:1), formaldehyde was initially formed with a TOF of 2.8 h^{-1}. The rates of formation of formic acid and formaldehyde were found to have first-order dependence with respect to the catalyst, CO_2, and H_2 concentrations. Moreover, the subsequent decomposition of formic acid and formaldehyde to CO and H_2O at 40 °C and 34 bar CO_2/H_2 (1:1) also showed a similar behavior, with the formation of formaldehyde 12 times slower than the formation of formic acid. Additionally, the decomposition of formaldehyde was faster than its formation, thus imposing a huge hurdle for the practical application of this system to the production of formaldehyde.

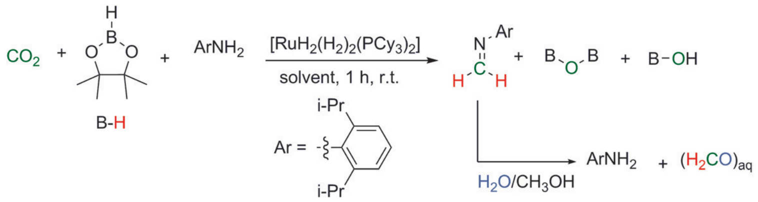
Although a system for the selective hydrogenation of CO_2 to formaldehyde with molecular H_2 still remains elusive, significant progress has been made with homogeneous catalysts and boranes as the reductants. In 2013, Sabo-Etienne and co-workers demonstrated the formation of formaldehyde from the ruthenium-catalyzed reduction of CO_2 in the presence of pinacolborane (B-H) as the reducing agent under mild conditions (1 bar CO_2, RT). The formation of several boryl compounds from CO_2 and pinacol borane could be observed as intermediates on the pathway to formic acid and methanol in the presence of the nonclassical hydride complex [$RuH_2(H_2)_2(PCy_3)_2$][172] (Cy = cyclohexyl). In particular, the group identified a boron complex of a C_2 compound as the product from the reaction of in situ formed formaldehyde. Finally, addition of d_4-methanol to the reaction solution enabled the formaldehyde to be "trapped" through the formation of CD_3OCH_2OD as the product (Scheme 32).

One year later, the same group reported the synthesis and isolation of formaldehyde from the reduction of CO_2 with borane catalyzed by the ruthenium complex [$RuH_2(H_2)_2(PCyp_3)_2$] (Cyp = cyclopentyl).[173] Guided by mechanistic studies, Sabo-Etienne and co-workers were able to trap formaldehyde as an imine by in situ condensation with a primary amine under very mild conditions (1 bar CO_2, RT; Scheme 33). Subsequent hydrolysis of the imine afforded the corresponding amine and formaldehyde in water, thereby demonstrating for the first time the use of CO_2 as a C_1 feedstock toward the isolation of formaldehyde.

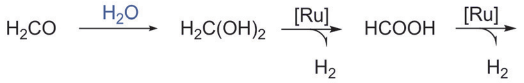


Scheme 32. Ruthenium-catalyzed reduction of CO_2 to formaldehyde derivatives.[172]

Although the hydrogenation of CO_2 to formaldehyde remains challenging, the back reaction has been demonstrated recently through the generation of CO_2 and H_2 from formaldehyde in aqueous solution. In 2014, Prechtl and co-workers investigated the use of aqueous formaldehyde and paraformaldehyde solutions as hydrogen storage media.[166] The group showed that the air-stable ruthenium catalyst [$(Ru(p\text{-cymene}))_2(\mu\text{-}Cl)_2Cl_2$] already catalyzed the formation of H_2 from these solutions at 95 °C. In contrast to the previously known decomposition of formic acid with the same catalyst,[174] the decomposition of formaldehyde and paraformaldehyde proceeded under base-free conditions. This catalytic process is tolerant to oxygen and gives a pure mixture of CO_2 and H_2. The best catalytic performance was observed at 95 °C, where hydrogen was obtained in 84 % yield within 60 min. Formaldehyde and paraformaldehyde react in aqueous solution to give $H_2C(OH)_2$, thereby resulting in a molecule with a higher hydrogen content/molecule (8.4 wt %) compared to formic acid (4.4 wt %). Since water is involved in the formation of the methanediol intermediate, this approach can be considered as a chemically indirect water-splitting system, where water acts as the proton source and formaldehyde as the hydride source to form H_2 (Scheme 34). Together with the studies by Sabo-Etienne, this result seems to indicate



Scheme 33. Ruthenium-catalyzed reduction of CO_2 to in situ trapped formaldehyde and subsequent hydrolysis.[173]



Scheme 34. Ruthenium-catalyzed hydrogen formation from formaldehyde and water.[240]

that heterolytic cleavage of H_2 will be a critical factor for future investigations towards the formation of formaldehyde from the hydrogenation of CO_2.

4. Methanol Level

4.1. Methanol

The reduction of CO_2 to methanol requires the activation of three equivalents of H_2 and the cleavage of a C=O bond. Thus, in terms of the vertical axis, sophisticated chess pieces such as a rook or queen are already necessary to reach this level. The moves get even more complex if further bond formation is desired along the horizontal axis.

4.1.1. Properties, Current Production, and Uses of Methanol

Methanol is a liquid at room temperature (m.p. = −97.6 °C) with a boiling point of 64.6 °C. In 2013, 65 million tons of methanol were consumed, thereby making it one of the most important commodities of the chemical industry.[5b,175] The largest methanol producer is Methanex.

Some important applications of methanol are shown in Figure 7.[5b,20,176] The main uses of methanol are the production of formaldehyde (36 %), methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME; together 13 %), as well as acetic acid (9 %). Other important chemicals produced from methanol are dimethyl ether (DME), olefins (MTO and MTP processes), methylamines, methyl methacrylate, and chloromethane. In his comprehensive book "Methanol—Chemie- und Energierohstoff" (translation: "Methanol—Raw Material for Chemistry and Energy") from 1986, Friedrich Asinger envisioned coupling the energetic and material value chains through methanol as the central molecule, a topic which today is more up-to-date than ever.[177] In 2005, George Olah proposed a "methanol economy" based on similar arguments.[178] A more recent book provides a detailed overview on current technologies and possible future perspectives.[5b]

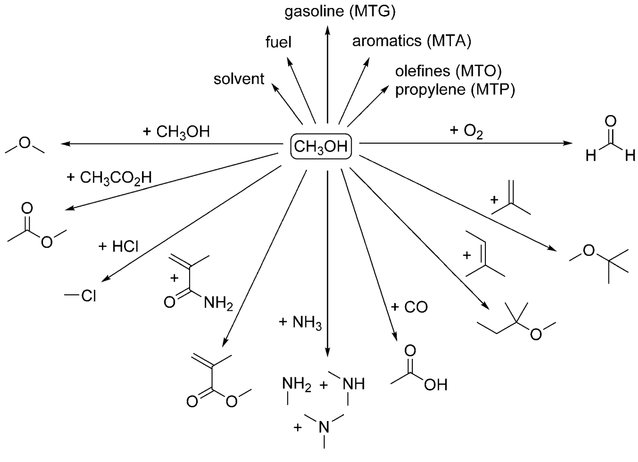


Figure 7. Methanol as a versatile platform chemical and energy carrier.[5b,20,176,180]

As the state of the art for methanol production is based on synthesis gas, it can be obtained from virtually any carbon feedstock following gasification. This is reflected in a regionally diverse utilization of feedstock. Whereas natural gas is the feedstock of choice in the mega methanol plants in the Middle East, coal-based production of methanol is becoming increasingly important in China: About 1 million tons of propylene were produced from methanol in 2013 by the MTP process.[5b] Another approach is the use of waste glycerol for the production of "biomethanol", as carried out by Evonik.[179] In addition to the use for chemical production, methanol can also serve as an energy vector. Its very high energy density of 22.7 MJ kg^{-1} makes it suitable for energy storage and for use as a fuel. This energy density is much higher than the energy density of Li-ion batteries (0.5–3.6 MJ kg^{-1}). The physicochemical properties of methanol allow it to be easily stored and transported using existing technologies. In contrast to oil, methanol is miscible with water and biodegradable. Methanol can be used as a fuel additive in conventional engines, or pure in modified engines and direct methanol fuel cells. Moreover, methanol can be converted into conventional fuels by the methanol-to-gasoline process (MTG), to dimethyl ether (DME) by etherification, or to oxymethylene ethers.[180] In 2011, 11 % of the produced methanol was already used in gasoline/fuel applications, and this sector is growing fast.[5b]

Another potential use of methanol is for the storage and transportation of hydrogen and CO. Methanol can be catalytically split or reformed to different CO, H_2, and CO_2 gas mixtures. Thus, methanol can serve as a liquid form of synthesis gas in the stoichiometric ratio required for many industrial applications. Large amounts of H_2 are generated from methanol reforming. This process is typically carried out with copper/zinc catalysts at 180–300 °C.[181] Recent developments have shown that aqueous methanol can be reformed to CO_2 and H_2 at much lower pressures and temperatures by using homogeneous organometallic catalysts.[182] Compared to formic acid, methanol has a higher gravimetric storage capacity for H_2 of 12.5 wt %. Interestingly, the equimolar methanol/water mixture produced by the hydrogenation of CO_2 to methanol has a similarly high H_2 storage capacity of 12 wt %. Therefore, the separation of methanol and water is not necessary for hydrogen storage applications.

Today, methanol is produced on a large scale by the conversion of synthesis gas derived from fossil feedstocks in the presence of heterogeneous catalysts (e.g. Cu/Zn/Al oxide) at elevated pressures (50–250 bar) and temperatures (200–350 °C; Scheme 35 a).[5b] CO_2 is added to hydrogen-rich synthesis gas mixtures as it consumes more H_2 than CO (Scheme 35 b). Both reactions are interconnected through the WGS reaction, which is also catalyzed by typical heterogeneous methanol catalysts under the reaction conditions

$$CO + 2\,H_2 \rightleftharpoons CH_3OH \qquad \Delta_RH_{(298K,50bar)} = -90.7\ \text{kJ/mol} \quad \text{(a)}$$

$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta_RH_{(298K,50bar)} = -40.9\ \text{kJ/mol} \quad \text{(b)}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta_RH_{(298K,50bar)} = -42\ \text{kJ/mol} \quad \text{(c)}$$

Scheme 35. Production of methanol from synthesis gas.[5b]

(Scheme 35 c). There is strong evidence that the formation of methanol from CO_2/CO/H_2 syngas mixtures over Cu/Zn catalysts proceeds through the direct hydrogenation of CO_2, however, in some cases the formation of CO from CO_2 and H_2 through the rWGS reaction and subsequent hydrogenation of CO is also believed to operate.[183] The direct synthesis of methanol from pure CO_2/H_2 mixtures remains a challenge, however.

4.1.2. *Production of Methanol from CO_2 and H_2*

Shifting from carbon monoxide to carbon dioxide as the principal raw material for the production of methanol provides the largest potential in terms of volume for chemical synthesis based on CO_2 and H_2. Whereas the higher stoichiometric requirement of hydrogen (Scheme 35 a versus 35 b) makes this route less sustainable than conventional fossil-based H_2, it turns into an attractive driver if hydrogen from renewable sources is utilized.[11a] The following section will discuss recent developments from a catalysis perspective.

4.1.2.1. *Milestones in Catalyst Development for the Hydrogenation of CO_2 to Methanol*

Heterogeneous Catalysis for the Hydrogenation of CO_2 to Methanol

The conversion of CO_2 and H_2 into methanol by heterogeneous catalysts is already occurring as part of the current methanol production processes in cases where CO_2 is added to the synthesis gas stream to adjust the C/H balance. It is estimated that about 2 million tons of CO_2 per year are converted into methanol this way,[5a] thus making this the second largest use of CO_2 today as a carbon source for the production of organic compounds after urea. Heterogeneous catalysts are known to catalyze the hydrogenation of CO and CO_2 to methanol, as well as the WGS reaction (Scheme 35 c).[5b] Catalysts based on Cu/Zn oxide, in particular, have been investigated in this respect.[183a,184] It was found that the addition of small amounts (up to 3 %) of CO_2 to the synthesis gas enhances the yield of methanol.[185] However, high amounts of CO_2 or pure CO_2 lead to the formation of water as a by-product, which reduces the rate of methanol formation.[183a,184b]

Lurgi already demonstrated the hydrogenation of CO_2 to methanol by using a Cu/Zn/Al catalyst from Sued-Chemie (now Clariant) in a pilot plant in 1994.[184a,186] At 60 bar pressure and about 260 °C, methanol was obtained with conversions of around 35–45 % per pass. A slight deactivation of the catalyst was observed. The selectivity was as high as 99.96 % (excluding water). An alternative approach is the CAMERE process of the Korean Institute of Science and Technology.[187] In this process, a rWGS reactor is coupled to a methanol formation reactor. In the rWGS reactor, CO_2/H_2 is partly converted into CO and H_2O. After removal of the water, the resulting CO/CO_2/H_2 stream is fed into the methanol reactor. The production capacity of the pilot plant is 100 kg methanol per day. In 1996, the NIRE and RITE institutes in Japan built a pilot plant (50 kg day^{-1}) based on a new Cu/ZnO/ZrO_2/Al_2O_3/SiO_2 catalyst, which underwent slow deactivation over time.[188] Another pilot plant that uses this catalyst has been operating since 2009 by Mitsui Chemicals with a capacity of 100 tons per year.[189] CRI operates a commercial plant in Iceland that produces methanol from CO_2 collected from industrial emissions and hydrogen produced by the electrolysis of water.[190] The process is powered by geothermal energy, thus rendering the process economic according to company statements. The "George Olah Renewable Methanol Plant" has been on stream since 2011 and has a production capacity of 5 million liters (ca. 4000 t) per year, which corresponds to the equivalent of about 2.5 % of the fuel demand in Iceland. In December 2014, CRI announced a collaboration with industrial partners, universities, and research institutions to implement its technology in Lünen, Germany, with the goal to recycle carbon dioxide emissions from a coal-fired power plant at this location.[191] The hydrogen used for this process is planned to be obtained from solar and wind energy through the electrolysis of water.

In 2012, Behrens, Schlögl et al. elucidated a detailed picture of the elementary steps and the role of the multicomponent catalyst material Cu/ZnO/Al_2O_3 in the hydrogenation of CO and CO_2 to methanol.[184c] A complex series of bond-cleavage and bond-forming processes on the catalyst surface involving the surface-bound species HCOO, HCO, HCOOH, H_2COOH, H_2CO, and CH_3O enable the seemingly simple overall transformation of CO or CO_2 and H_2 to methanol. A TOF of 75.6 h^{-1} (mol methanol/mol Cu sites) was calculated for a typical syngas mixture (59.5 % H_2, 8 % CO_2, 6 % CO, plus inert gases) at 60 bar and 210 °C–250 °C. Labeling experiments by the same group showed that the methanol formed from CO/CO_2/H_2 syngas mixtures mainly stems from CO_2.[183c]

In 2014, Nørskov and co-workers used computational methods to identify intermetallic Ni-Ga compounds on the basis of this detailed mechanistic insight into catalytically active materials for the hydrogenation of CO_2 to methanol.[192] The catalyst showed a similar activity as the Cu/ZnO/Al_2O_3 catalyst. In the same year, Graciani et al. demonstrated that the metal oxide interface in Cu/CeO_x/TiO_2 is highly active for the conversion of CO_2 into methanol.[193] At 300 °C, they estimated the TOF to be as high as 29 160 h^{-1}. However, one has to be careful when comparing this TOF value for Cu/CeO_x/TiO_2 with the one reported by Behrens et al. for Cu/ZnO/Al_2O_3, as they were calculated based on different models.[183b] Graciani et al. proposed a mechanism consisting of consecutive rWGS reactions and hydrogenation of CO to methanol for their system.[193]

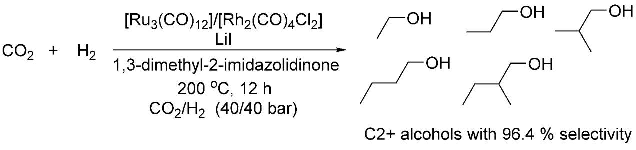
Homogeneous Catalysis for the Hydrogenation of CO_2 to Methanol

In contrast to heterogeneous catalysts, substantially fewer reports exist about homogeneous catalysts for the hydrogenation of CO_2 to methanol. This seems to be somewhat surprising, given that homogeneous organometallic catalysts have been known to accept CO_2 readily as a substrate in the generation of formic acid by hydrogenation since the discovery by Inoue et al. in 1976.[38] In 2007, Jessop concluded that the reduction of CO_2 beyond the formic acid level typically requires much higher temperatures, and that only a few organometallic catalysts could be envisaged to be both kinetically capable and stable at these reaction conditions.[7a] This reflects the general notion that the hydrogenation of carboxylic acids and their derivatives are challenging transformations for organometallic catalysts. Indeed, there is an interesting parallel in the most recent developments of homogeneous hydrogenation catalysts for both areas.

The first observations of the formation of methanol from CO_2 and H_2 in the presence of organometallic catalysts were reported from Sasaki, Tominaga, and co-workers during their investigation of the Ru-carbonyl catalyst system.[134a,d] In 1993, they reported a study on the hydrogenation of CO_2 to methane through the successive formation of CO and methanol as intermediates in the presence of a $[Ru_3(CO)_{12}]$/KI catalyst system under harsh reaction conditions (240 °C, 90–140 bar).[134a,d] Homogeneous complexes were found to be the active components in the rWGS reaction, whereby CO_2 and H_2 were converted into CO and H_2O, and in the successive hydrogenation of CO to methanol,[194] whereas methane formation was mainly catalyzed by deposited ruthenium metal. Consequently, the selectivity could be shifted towards methanol by the addition of KI, which prevented deposition of Ru metal. In a typical experiment in the presence of KI, methanol was obtained with a TON (based on the number of ruthenium atoms) of up to 32, together with CO with a TON of 11, methane with a TON of 8, and traces of ethanol.

Interestingly, they showed that the use of a bimetallic $[Ru_3(CO)_{12}]/[Co_2(CO)_8]$/ KI catalyst system significantly increased the amount of ethanol formed by homologation of methanol.[134c,195] At 200 °C, CO_2 was converted with this catalyst into CO (TON = 8), methanol (TON = 31), ethanol (TON = 12), methyl formate (TON = 1), and methane (TON = 13). The formation of methanol and ethanol using the trinuclear ruthenium carbonyl cluster was also claimed in a patent assigned to the Eastman company.[196] The formation of higher alcohols from CO_2 and hydrogen has been for many years the subject of studies with heterogeneous catalysts (for a pioneering and recent example, see Ref. [197]), but the overall selectivities for C_{2+} alcohols are generally low compared to the C_1 products (CH_3OH, and CH_4). In 2015, the group of Han reported that a homogeneous bimetallic system of $[Ru_3(CO)_{12}]$ and $[Rh_2(CO)_4Cl_2]$ in the presence of LiI as a promotor afforded C_{2+} alcohols with high selectivities up to 96.4 % in the hydrogenation of CO_2 using DMI (1,3-dimethyl-2-imidazolidinone) as the solvent (Scheme 36).[198]

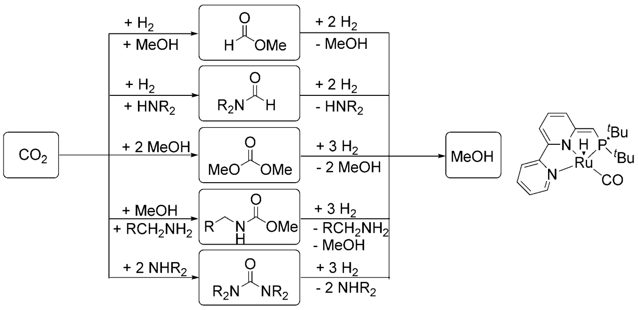
It took another 20 years after these first incidental observations before an organometallic catalyst was found for the selective homogeneous hydrogenation of CO_2 to methanol, however. The key to the selective formation of methanol under milder reaction conditions was finally the identification of catalysts that enable the hydrogenation of CO_2 to methanol via formate intermediates—as organic derivatives or in formate complexes—rather than taking the path via CO formed from the rWGS reaction.



Scheme 36. Synthesis of C_{2+} alcohols by CO_2 hydrogenation with a homogeneous bimetallic Ru/Rh system.[198]

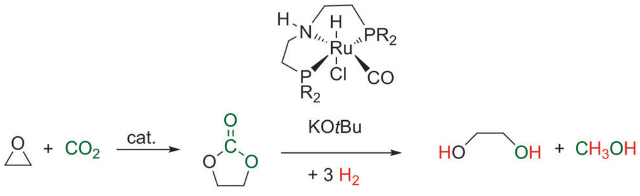
In 2010, the catalytic reduction of CO_2 to methanol with stoichiometric amounts of boranes as reducing agents was achieved using nickel pincer complexes.[199] Metal-free catalyst systems based on frustrated Lewis pairs (FLPs),[200] N-heterocyclic carbenes (NHCs),[201] or silyl cations[202] have also been shown to be active for the reduction of CO_2 to methanol. However, these systems are limited by the use of stoichiometric amounts of boranes and silanes as reduction agents, and require hydrolysis of the formed intermediates with H_2O and/or NaOH, which leads to large amounts of waste and to the destruction of the catalysts, at least in the FLP systems. Metal-free catalyst systems for the reduction of CO_2 are discussed in detail in two comprehensive reviews.[203]

A major breakthrough for systems using molecular hydrogen was achieved when multistep routes from CO_2 to methanol by the hydrogenation of CO_2-derived stable intermediates were proposed by Milstein's group in 2011 (Scheme 37). They demonstrated that their versatile Ru-PNN pincer complex enabled the efficient hydrogenation of methyl formate,[204] dimethyl carbonate,[204] methyl carbamates,[204] urea derivatives,[205] and formamides[206] to give methanol as the product or coproduct. As those substrates can be produced from CO_2, synthetic routes for the sequential production of methanol from CO_2 by organometallic catalysis could be envisioned. By using the Ru-PNN complex, dimethyl carbonate could be quantitatively hydrogenated to methanol with a TOF up to 2 500 h⁻¹ (60 bar H_2, 145 °C).[204] The CO_2-derived methyl formate could be hydrogenated using the same complex with a TOF of up to 531 h⁻¹ (50 bar H_2, 110 °C).[204] Various alkyl and aryl urea derivatives, such as 1,3-dihexylurea, could be hydrogenated at 110 °C and 13.6 bar H_2 to afford methanol in 46–94 % yield.[205] Hydrogenation of formylmorpholine at a H_2 pressure of 10 bar and a temperature of 110 °C resulted in the formation of methanol in 97 % yield.[206]



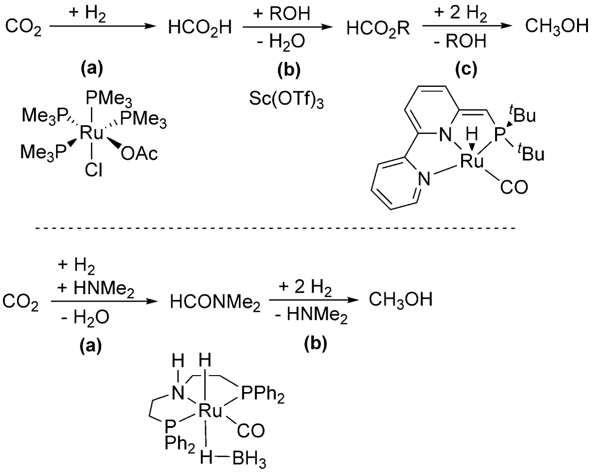
Scheme 37. Indirect routes for methanol synthesis from CO_2.[204–206]

Ding and co-workers proposed a method for the indirect production of methanol via ethylene carbonate (Scheme 38), thereby resulting formally in a hydrogenative variation of the Shell Omega process.[207] In the Omega process, ethylene



Scheme 38. Formation of methanol from CO_2 by the organometallic catalyzed hydrogenation of ethylene glycol.[207]

glycol (EG) is produced by hydrolysis of ethylene carbonate, which is produced from ethylene oxide and CO_2 in the first step of the reaction. Ding and co-workers proposed replacing the hydrolysis step by a hydrogenation to produce methanol as the coupled by-product. A TON of up to 87000 and a TOF of up to 1200 h^{-1} could be obtained by using the Ru-PNP catalyst shown in Scheme 38. Interestingly, the hydrogenative degradation of poly(propylene carbonate) ($M_w = 100698$, $M_w/M_n = 1.77$, $>99\,\%$ carbonate linkages) to methanol and 1,2-propyleneglycol was also demonstrated in 99 % yield.

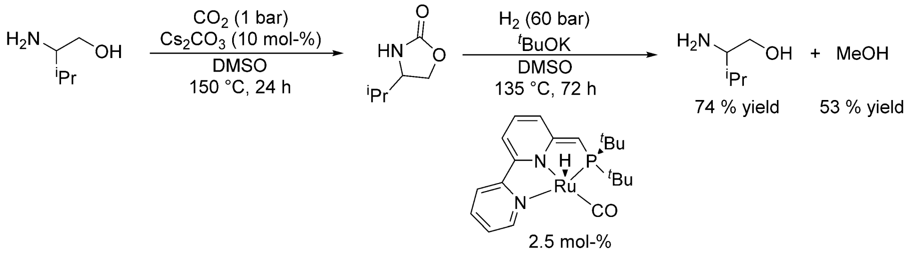


Scheme 39. Cascade reactions for the hydrogenation of CO_2 to methanol via alkyl formate (upper pathway) and DMF (lower pathway).[99,208]

In 2011, the Sanford group integrated the formate hydrogenation catalyst of Milstein into a one-pot cascade reaction:[99] They used it together with another Ru complex and a Lewis acid (Scheme 39, upper pathway) as a three-component catalyst system for the three steps of the cascade: a) hydrogenation of CO_2 to formic acid, b) esterification of formic acid to methyl formate, and c) hydrogenation of methyl formate to methanol. Adding the Lewis acid $Sc(OTf)_3$ as a co-catalyst to $[RuCl(OAc)(PMe_3)_4]$ gave a TON of 40 after 16 h and a TOF of 32 h^{-1} in the first hour for the combination of steps (a) and (b). By using a mixture of the three catalysts in CD_3OH at 135 °C, under a CO_2 pressure of 10 bar and a H_2 pressure of 30 bar, a TON of only 2.5 was achieved, which is significantly lower than expected from the performance of the Ru-PNN complex in the hydrogenation of formate (c). The main factors hampering higher TONs were found to be the inhibition/deactivation of the Ru-PNN catalyst by CO_2 and by $Sc(OTf)_3$. A higher TON of up to 21 could be obtained by spatial separation of the catalysts in separate vials inside the reactor.

In 2015, the same group described a similar cascade reaction process for the hydrogenation of CO_2 to methanol, whereby intermediate formation of dimethylformamide (DMF) was envisaged this time (Scheme 39, lower pathway).[208] The hydrogenation of CO_2 in the presence of $HNMe_2$ has been known to lead to the formation of DMF with very high activities and selectivities, as described in Section 2.3.2.[7a,33c] The last step of this cascade reaction, the hydrogenation of formamide to methanol, had much less precedent in the literature.[206,209] Sanford and co-workers showed that the Ru-MACHO-BH_4 complex together with 50 equivalents of the base K_3PO_4 is capable of selectively hydrogenating DMF to methanol at 50 bar H_2 pressure and 155 °C (Scheme 39, lower pathway). As catalyst deactivation became apparent at 155 °C, a temperature ramp as well as a large excess of H_2 was used to achieve high CO_2 conversions: hydrogenation of CO_2 to DMF was first carried out at 95 °C, and after 18 h the temperature was raised to 155 °C. A TON of up to 550 at overall CO_2 conversions of up to 96 % could be obtained by using this strategy. However, the selectivity to methanol was only about 30 %, with DMF and dimethylammonium formate (DMFA) as side products. Dimethylammonium dimethylcarbamate (DIMCARB), which was preformed from the reaction of $HNMe_2$ and CO_2, could also be used as a substrate by using the same method and the same catalytic system without additional CO_2. Based on this example, the combined capture of CO_2 in the form of compounds such as DIMCARB and conversion into methanol was proposed.

Another approach to combining low-pressure CO_2 capture with subsequent hydrogenation to methanol was also published by the Milstein group (Scheme 40).[210] In this approach, CO_2 is captured by an amino alcohol at low pressures (1–3 bar) at 150 °C in the presence of Cs_2CO_3 as a catalyst, which leads to the formation of the corresponding oxazolidone as an intermediate.[210,211] The resulting oxazolidone solution could be hydrogenated at 135 °C and 60 bar H_2

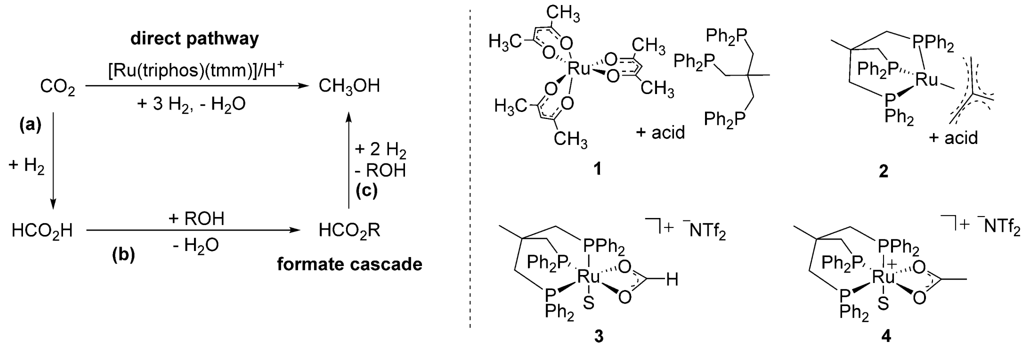


Scheme 40. Cascade reactions for the hydrogenation of CO_2 to methanol via oxazolidones obtained from CO_2 capture with amino alcohols.[210]

to give methanol and to restore the amino alcohol after addition of the Ru-PNN pincer complex (Scheme 40) and *tert*-BuOK (10 mol %). Excess CO_2 had to be removed after the CO_2 capture step, as the Ru-PNN pincer complex was deactivated by the presence of CO_2. By using valinol in DMSO as a capture medium, CO_2 could be converted into methanol in about 50 % yield by this procedure. The allure of these combined CO_2 capture/conversion concepts is that energy costs associated with CO_2 release from capture solutions could be avoided.

Most recently, Olah, Prakash, and co-workers have developed a homogeneous Ru-based catalyst for the synthesis of CH_3OH from CO_2 and H_2 by using a polyamine base to form carbamate adducts as the presumed actual substrate in solution. The polyamine could be used to capture CO_2 from very dilute gas mixtures containing about 400 ppm of CO_2. This allowed the CO_2 capture from air to be coupled with direct conversion into methanol using the homogeneous catalyst. It was reported that up to 79 % of the CO_2 captured from air could be converted into CH_3OH.[212]

In 2012, Klankermayer, Leitner, and co-workers reported the first example of a single organometallic catalyst which could integrate all reaction steps (a), (b), and (c) of the cascade reaction via alkyl formate (Scheme 41, lower pathway):[213] The catalyst system was based on a ruthenium center and the tridentate ligand triphos (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane). The catalyst was formed in situ from $[Ru(acac)_3]$ and triphos (**1**) or from [Ru(triphos)(tmm)] (tmm = trimethylenemethane; **2**), both in the presence of an acid co-catalyst (Scheme 41).[214] Combinations of ruthenium with triphos in the presence of different additives have been shown to form active catalysts for the hydrogenation of carboxylic esters to the corresponding alcohols,[214a,b,d–f,i] of amides to the corresponding alcohols and amines,[214c,g,i] of carboxylic acids to the corresponding alcohols,[214e,f,i] of carbonates to the corresponding alcohols,[214i] and of urea derivatives to the corresponding amines and methanol.[214i] Methyl formate and ethyl formate could also be hydrogenated to the corresponding alcohols using the catalyst systems $[Ru(acac)_3]$/triphos/organic acid (**1**) or [Ru(triphos)(tmm)]/organic acid (**2**).[213] Based on this finding, a catalyst (**2**) comprising [Ru(triphos)(tmm)] and one equivalent of $HNTf_2$ [$HNTf_2$ = bis(trifluoromethane)sulfonamide] was shown to enable the hydrogenation of CO_2 to methanol with a TON of up to 221 (20 bar CO_2 at RT, 60 bar H_2 at RT, 140 °C) in THF/EtOH as solvent. Ethyl formate was detected in trace amounts under these conditions, and lowering the reaction temperature to 90 °C caused the formation of methanol to slow down drastically (TON = 15) at the expense of ethyl formate (TON = 8).[213] A reaction system where only methanol was formed could be developed by using THF/MeOH as the solvent. Labeling experiments unequivocally demonstrated that methanol was produced catalytically from CO_2 and H_2 under these conditions and that the backward reaction corresponding to methanol reforming is also possible with this catalyst system.[213]



Scheme 41. Hydrogenation of CO_2 to methanol through a formate ester cascade and direct hydrogenation of CO_2 to methanol[213,215] with the ruthenium–triphos catalyst and structures of the corresponding catalyst precursors **1**, **2**, **4** (S = free coordination site or solvent), and the catalytically active formate intermediate **3**.

A detailed mechanistic study demonstrated that the multistep transformation of CO_2 to methanol can also occur directly on the Ru-triphos center without intermediate formation of alkyl formate, thus providing for the first time a molecularly defined catalyst for the selective formation of methanol directly from CO_2/H_2 (Scheme 41, upper pathway).[215] Methanol was obtained with a TON of up to 895 after 64 h when [Ru(triphos)(tmm)]/$HNTf_2$ (**2**) was used in the absence of an alcohol additive under optimized conditions (Figure 8; CO_2/H_2 = 1:3, 120 bar total pressure, kept constant by repressurizing, 140 °C). The initial TOF of 70 h^{-1} is in the range of the activity of the active sites in the classical heterogeneous Cu/ZnO-based catalysts (see above). Recycling the catalyst was possible by performing the reaction in 2-methyltetrahydrofuran (2-MTHF) and subsequent extraction of the formed methanol and water with additional water. In this way, the catalyst could be used four times, with 50 % of the initial productivity retained in the last cycle. Thus, process schemes involving liquid/liquid extraction rather than gas/solid reactor technology for the continuous production of MeOH can be envisaged.

High-pressure in situ NMR spectroscopy revealed the cationic formate complex $[Ru(\kappa^2\text{-}O_2CH)(triphos)(S)]NTf_2$ (**3**; S = solvent) to be a catalytically active intermediate in solution. Based on this finding, the analogous, robust acetate complex $[Ru(\kappa^2\text{-}OAc)(triphos)(S)]NTf_2$ (**4**; S = free coordination site or solvent) was developed as a precursor. The hydrogenation of CO_2 with a TON of 165 (20 bar CO_2, 60 bar H_2, 140 °C) was possible with catalyst precursor **4** in the absence of any acid and alcohol additives, thus indicating that the acid additive is only necessary to generate cationic active

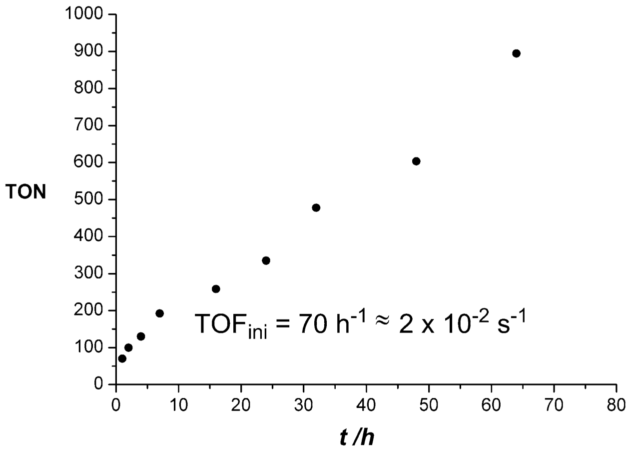


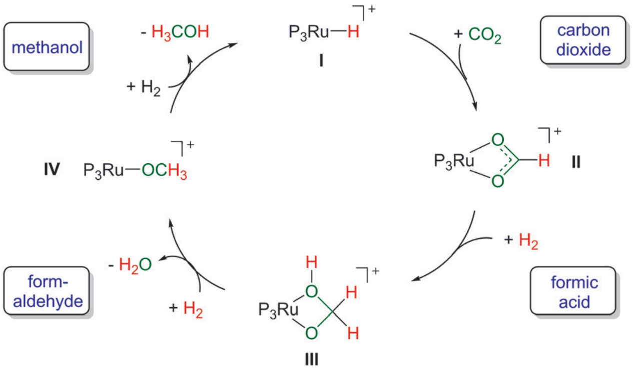
Figure 8. Evolution of the TON versus reaction time for the direct hydrogenation of CO_2 to methanol with system **2** in the absence of an alcohol additive (120 bar, pressure kept constant by re-pressurizing, $CO_2/H_2 = 1{:}3$, 140 °C).[215]

complexes such as the spectroscopically observed $[Ru(\kappa^2\text{-}O_2CH)(triphos)(S)]^+$ (**3**).

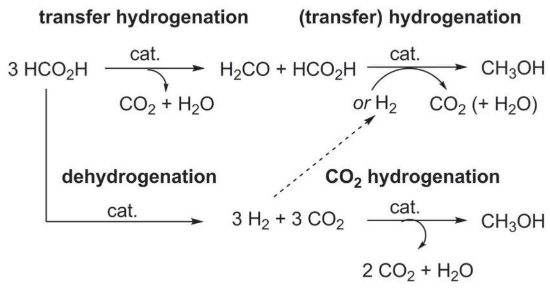
Based on earlier DFT studies concerning the hydrogenation of carboxylic esters and carboxylic acids with the catalyst system $[Ru(acac)_3]$/triphos/acid additive (**1**), Klankermayer, Leitner, and co-workers proposed that the cationic hydride complex $[Ru(H)(H_2)(triphos)(S)]^+$ (**I**) is a key intermediate that allows easy hydrogenation of carboxylate units.[214f] On the basis of **I** and the spectroscopically observed formate complex $[Ru(\kappa^2\text{-}O_2CH)(triphos)(S)]NTf_2$ (**3**; S = solvent), a catalytic cycle for the transformation of CO_2 to methanol within the coordination sphere of the Ru-triphos fragment could be established by DFT calculations.[215] The basic catalytic cycle shown in Scheme 42 provides a plausible picture for the formation of methanol, and is fully in line with experimental results and mechanistic proposals from recent work by other groups on the catalytic hydrogenation of CO_2/CO_2 derivatives, decomposition of formic acid, decomposition of formaldehyde, or methanol reforming.[99,166,182b,204,214f,216]

The intermediate coordination complexes have a striking similarity to the surface-bound species observed in heterogeneous catalysis, although the intimate mechanisms of their formation are quite different. Migratory insertion of CO_2 into the Ru-H complex (**I**) results in the formation of the spectroscopically observed formate complex (**II** = **3**). Reaction with one equivalent of H_2 reduces the carboxylate unit to form the Ru-hydroxymethanolate species (**III**). **III** is transformed into the Ru-methanolate complex (**IV**) with intermediate formation of formaldehyde and consumption of a second equivalent of hydrogen. The product methanol is liberated and the cycle is closed by hydrogenolysis of the Ru-OMe unit with a third equivalent of hydrogen. The transformation of CO_2 to methanol proceeds through a series of hydride-transfer and protonolysis steps: The reduction steps occur by migratory transfer of classical Ru-hydride ligands. Protonolysis of the Ru−O bonds occurs intramolecularly through heterolytic cleavage of coordinated H_2 molecules. The barriers for the proton transfer steps may be significantly lowered if assisted by the reaction medium. The specific reactivity of the Ru-triphos complex can be associated with the facial coordination of the triphos ligand, which imposes a favorable geometrical arrangement for transfer of the the hydride to carboxylate units, and with the high thermal stability of the Ru-triphos complexes.[214f,215]

In 2014, Cantat and co-workers showed that the catalyst system **1** introduced by Klankermayer, Leitner, and co-workers for the hydrogenation of CO_2 to methanol (Ru/triphos/acid additive), can also be used for the disproportionation of formic acid to methanol, CO_2, and water,[217] a reaction which was reported for the first time by Goldberg and co-workers in 2013.[218] Formic acid could be decomposed in the presence of $[Ru(cod)(methylallyl)_2]$/triphos/methylsulfonic acid at 150 °C to afford methanol with a yield of up to 50% (TON = 83). The ruthenium–triphos catalyst is apparently able to affect the decomposition of formic acid to CO_2 and H_2 and the hydrogenation of CO_2 to methanol, as well as the direct transfer hydrogenation of formic acid to form methanol. Thus, they compiled a network of reactions that could lead to the formation of methanol during the disproportionation process (Scheme 43).



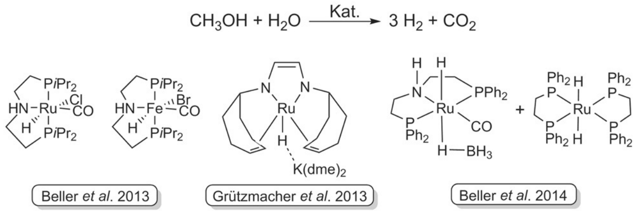
Scheme 42. Basic catalytic cycle for the hydrogenation of CO_2 to methanol at the Ru–triphos fragment. P_3-Ru denotes the Ru-triphos fragment with additional ligands to fill the coordination sphere.[215]



Scheme 43. Proposed reaction network for the disproportionation of formic acid to methanol.[217]

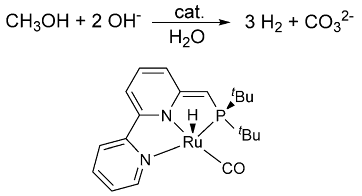
4.1.2.2. *Homogeneous Catalysis for Methanol Reforming*

The catalytic dehydrogenation of aqueous methanol to CO_2 and H_2 (methanol reforming) was reported for the first time in 1987 by Morton and Cole-Hamilton, who used homogeneous organometallic catalysts.[182a] They used [Rh(bipy)$_2$]Cl as a catalyst in the presence of NaOH at 120 °C to decompose a 95:5 v/v solution of methanol/H_2O at a TOF of 7 h^{-1}. In 2013, dehydrogenation catalysts for aqueous methanol were reported independently by the groups of Grützmacher and Beller (Scheme 44).[182b–d,219] Beller and co-workers group showed that methanol could be decomposed to CO_2 and three equivalents of H_2 with a TOF (based on moles of methanol) of up to 1573 h^{-1} by using the catalyst [RuHCl(CO)PNP] (PNP = HN($CH_2CH_2PiPr_2$)$_2$) in the presence of potassium hydroxide at 95 °C.[182b] A 3:2 mixture of methanol and water gave a TOF of up to 244 h^{-1}, while a highly diluted 9:1 MeOH/H_2O mixture still gave a TOF of 88 h^{-1}.[182b] In a long-term stability test, a 9:1 mixture of MeOH/H_2O was decomposed over a period of 23 days with a TON of > 116 000.[182b] Grützmacher and co-workers used [K(dme)$_2$][Ru(H)(trop$_2$dad)] (trop$_2$dad = 1,4-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene) for the decomposition of a 1:1.3 mixture of MeOH/D_2O at 90 °C in the presence of THF solvent under base-free conditions.[182c] After 10 h, 78 % of the methanol was decomposed to CO_2 and H_2 (TON = 156). During the catalytic cycle, the non-innocent azadiene ligands reversibly store molecular hydrogen. Shortly after, Beller and co-workers reported the use of an iron pincer complex [FeH(BH_4)(CO)(PNP)] (PNP = HN($CH_2CH_2PiPr_2$)$_2$) for methanol reforming (Scheme 44).[219] Pure methanol was decomposed to CO_2 and H_2 in the presence of KOH with a TOF of up to 245 h^{-1} at 91 °C. A mixture of 4:1 MeOH/H_2O was decomposed with a TOF of 137 h^{-1} under the same conditions. In 2014, the same group reported that aqueous methanol could be dehydrogenated in the absence of base by using a mixture of Ru-MACHO-BH_4 and [Ru(H)$_2$(dppe)$_2$] (dppe = 1,2-bis(diphenylphosphino)ethane; Scheme 44).[220] The catalysts were reported to operate in a synergistic manner, that is, their combined activity was higher than the sum of the activities of each single catalyst. An average TOF of 93 h^{-1} was obtained over 7 h at 94 °C, and a total TON of 4286 was obtained after 8 days.



Scheme 44. Organometallic catalysts used for reforming methanol.

In 2014, the Milstein group used the Ru-PNN pincer complex (Scheme 45), which had been employed before for the hydrogenation of alkyl formates to methanol, for methanol reforming to CO_2 and H_2 in the presence of NaOH or KOH and toluene solvent.[182d] The released CO_2 was trapped as carbonate. Methanol was converted with 77 % yield within 9 days with an average TOF of 14 h^{-1} based on methanol. Interestingly, the organic layer could be separated from the aqueous layer and reused without addition of new catalyst. The procedure could be repeated over a period of 1 month with a TON of around 9667 based on methanol.



Scheme 45. Methanol reforming to CO_2, which is trapped as carbonate in basic solution.[182d]

4.2. *Methylation Reactions*

Despite its simple reaction formula, the synthesis of methanol from CO_2 is a quite complex transformation involving a series of bond-breaking and bond-forming events that leaves only one C–O bond remaining from the CO_2 molecule. Conceptually, this can be taken even further by generating the CH_3 group and at the same time connecting it with other atoms such as nitrogen or carbon. This requires moving effectively in the horizontal and vertical directions on the catalytic chessboard and it is only very recently that chemists started to plan these combinations systematically.

4.2.1. *Catalytic N-Methylations*

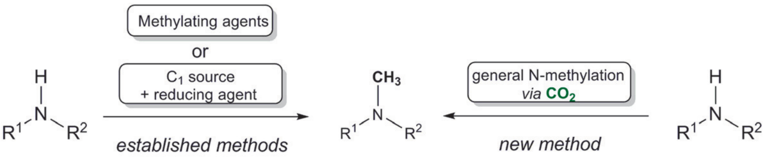
4.2.1.1. *Properties, Current Production, and Uses of N-Methylated Amines*

Synthetic methods for the preparation of amines are of paramount importance in organic chemistry.[221] *N*-Methylamines are key structural motifs in various biologically active natural compounds and consequently are an integral part of numerous pharmaceutical and agrochemical products.[222] For their synthesis, mono- or dimethylamine can be used as building blocks that already contain the N–CH_3 unit. In fact, the “methylamines” CH_3NH_2, (CH_3)$_2$NH, and (CH_3)$_3$N are important bulk chemicals with a high market value (production rate = 1 Mt year^{-1}; more than 4000 € t^{-1})[223] as they are commonly used as intermediates for a wide range of agricultural chemicals, animal nutrients, catalysts, electronics, dyes, explosives, fuel additives, as well as gas and oil treatments.[223a] Industrially, the methylamines are currently mainly produced from ammonia (NH_3) and methanol (CH_3OH) over heterogeneous dehydration catalysts.

Methods for the introduction of the methyl group at already existing N functionalities in more complex structures often involve the use of hazardous alkylating agents, such as methyl iodide or dimethyl sulfate, although dimethyl carbonate offers a greener alternative.[224] Another frequently used synthetic method for *N*-methylation employs formaldehyde and formic acid as the carbon source and reducing agent, respectively (Eschweiler–Clark methylation).[225]

4.2.1.2. Catalytic N-Methylation of Amines with CO_2

Despite the intensive efforts dedicated to the utilization of CO_2 for chemicals and polymers, CO_2 has only recently been considered a potential C_1 building block for the methylation of amines. It is noteworthy, however, that in 1988 Vaska and co-workers reported the formation of trimethylamine as a minor product in the Ru- or Os-catalyzed reaction of dimethylamine under CO_2/H_2 pressure to form dimethylformamide (DMF).[226] The formation of the third methyl group was presumed to arise from the hydrogenation of DMF,[112,226] but it was also suspected that exchange of a methyl group might be involved.[227] It was not until 25 years later that general methods of amine methylation using CO_2 as a C_1 source started to emerge rapidly (Scheme 46).[16a]

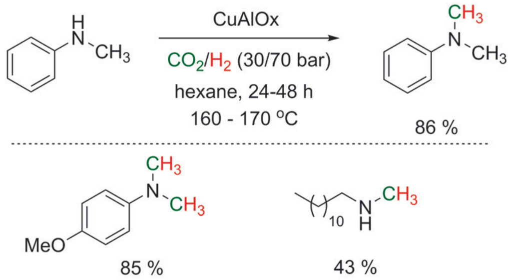


Scheme 46. General approaches for the *N*-methylation of amines.

Heterogeneous Catalysts

An early attempt to use CO_2 and H_2 for methylation was carried out with heterogeneous catalysts. In the mid-1990s, Baiker and co-workers[228] reported the Cu-catalyzed gas-phase methylation of NH_3 by CO_2 and H_2, but the system suffered from drawbacks, such as low yields, low selectivities, and the necessity of high temperatures (200–300 °C). For example, the maximum rate of production of methylamines from $NH_3/CO_2/H_2$ using Cu on alumina (46 wt %) was 1.21 mol$(kg_{cat}^{-1}h^{-1})$ at 280 °C, with the formation of CO (from the rWGS reaction) and H_2O as the main by-products. It was not until the first organometallic homogeneous systems demonstrated the possibility of selective methylation under mild conditions (see below) that similar solid catalysts were investigated for substrates other than ammonia. In 2014, Shi and co-workers reported a reusable Cu/alumina catalyst for the direct *N*-methylation of primary amines, secondary amines, nitrobenzene, and aromatic nitrile derivatives using CO_2 and H_2 (Scheme 47).[229] These substrates were efficiently and selectively transformed into the corresponding *N*-methyl or *N,N*-dimethyl products with excellent yields, although at very high loadings of the active metal (38 mol % Cu with respect to amine).

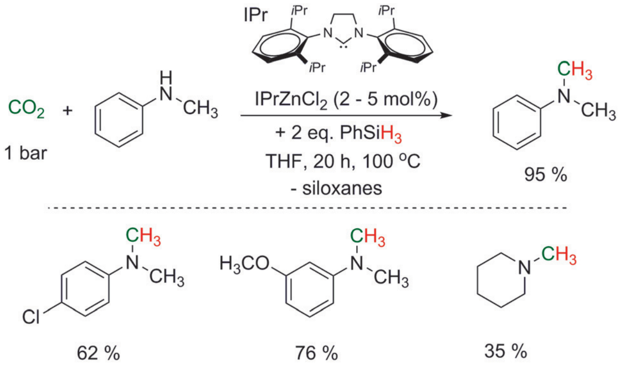
The same group developed an active Pd/ZrCuO$_x$ catalyst for the *N*-methylation of primary or secondary amines with CO_2/H_2.[230] The reaction afforded the *N*-methylated products in up to 97 % yield under relatively mild reaction conditions (10 bar CO_2, 25 bar H_2). In most of the primary amines examples, the monomethylated product was obtained with high selectivity. The N-methylation reactions generally required long reaction times (30–40 h), with *N*-formylation being the main reaction at shorter reaction times (15 h). Around the same time, Shimizu and co-workers reported the use of TiO_2 loaded with Pt and MoO_x as a highly effective catalytic system for the direct methylation of aliphatic and aromatic secondary amines by CO_2 and H_2 under solvent-free conditions.[231] The direct *N*-methylation of variable secondary amines under CO_2/H_2 pressure afforded the *N*-methylated product in up to 90 % yield. More recently, the direct methylation of amines under CO_2/H_2 pressure and using an alumina-supported gold catalyst was also reported to afford the *N*-methylated product in up to 99 % yield.[232]



Scheme 47. Heterogeneously catalyzed *N*-methylation of amines, nitrobenzene, and nitriles (not shown) with CO_2 and molecular hydrogen.[229]

Organometallic Catalysts

Initially, the homogeneously catalyzed *N*-methylation of amines with CO_2 was approached using silanes as the reducing agent. In 2013, Cantat and co-workers described the use of a Zn/NHC system for the direct methylation of aliphatic and aromatic amines from CO_2 (1 bar) and two equivalents of $PhSiH_3$. The *N*-methylated products were obtained in yields of up to 95 %.[233] The use of the sterically congested NHC ligand (IPr; Scheme 48), either as an external donor ligand for $ZnCl_2$ or using the isolated IPrZnCl$_2$ catalyst, resulted in significantly higher reactivity of this catalyst

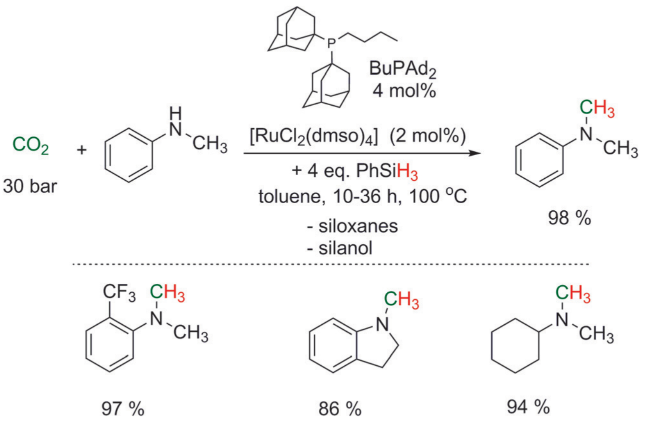


Scheme 48. IPrZnCl$_2$-catalyzed *N*-methylation of amines with CO_2 and $PhSiH_3$.[233]

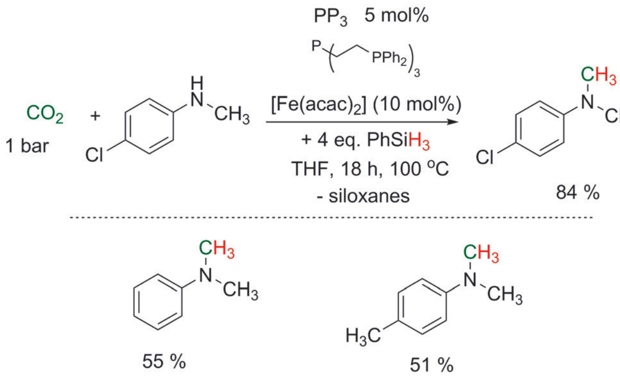
toward CO_2 reduction (Scheme 48). However, the *N*-methylation of primary amines afforded mixtures of mono- and dimethylated products with relatively moderate yields and poor selectivities. Most recently, Santoro et al. reported the use of a Cu/NHC catalyst and similar conditions for the direct methylation of amines using CO_2 and $PhSiH_3$ to afford the *N*-methylated products in yields of up to 99%.[234]

Liu and co-workers reported an immobilized version of these catalysts in the form of a fluoro-functionalized polymeric NHC-Zn complex (F-PNHC-Zn), which was synthesized from fluorous imidazolium salts as precursors. The catalyst was used for the formylation and methylation of amines using CO_2 as a C_1 building block and $PhSiH_3$ as the reducing agent instead of H_2.[235] This catalyst was found to significantly catalyze the formylation of amines to formamides, whereas the subsequent hydrogenation of the formamide was less reactive and the *N*-methylation only gave minor products in low yields of 8–35%. The F-PNHC-Zn catalyst showed high conversion (97%) for at least five cycles in the conversion of *N*-methylaniline into *N*-methylformanilidine and *N*,*N*-dimethylaniline.

The group of Beller developed a Ru-based catalyst for reductive methylation with silanes. They showed that $[RuCl_2(dmso)_4]$ in the presence of the bulky ligand $BuPAd_2$ (Ad = adamantyl) enabled the methylation of a large variety of anilines and aliphatic amines on using CO_2 (30 bar) and excess $PhSiH_3$ (4 equiv). The *N*-methylated products were afforded in yields of up to 98% (Scheme 49).[236] This catalyst system worked well for a variety of aromatic and aliphatic amines, whereas the $IPrZnCl_2$ catalyst used by Cantat and co-workers showed higher reactivity with aromatic amines. On the other hand, the Ru/L system used by Beller and co-workers requires the use of 30 bar of CO_2 compared to 1 bar for the $IPrZnCl_2$ system.



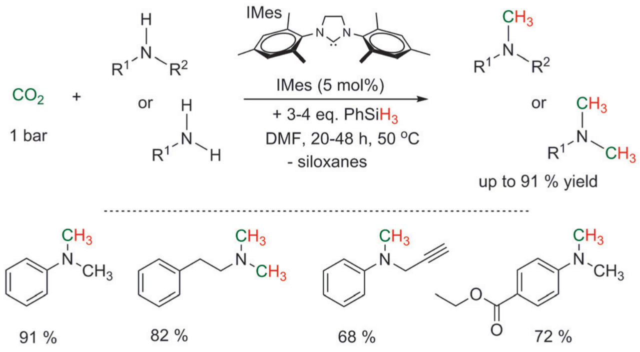
Scheme 49. $[RuCl_2(dmso)_4]/BuPAd_2$-catalyzed *N*-methylation of amines with CO_2 and $PhSiH_3$.[236]



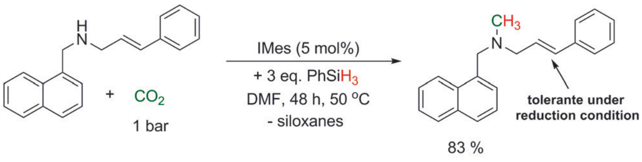
Scheme 50. Iron-catalyzed *N*-methylation of secondary amines with CO_2 and $PhSiH_3$.[237]

In general, the reduction using silanes appears to be catalyzed by a range of transition-metal complexes. Meanwhile, Cantat and co-workers demonstrated that the iron-based catalytic system $Fe(acac)_2/PP_3$ (acac = acetylacetonate; PP_3 = tris[2-(diphenylphosphino)ethyl]phosphine or tetraphos), which is known to catalyze the reduction of CO_2 to formamides in the presence of amines, can also be applied for the direct *N*-methylation of amines with CO_2 and excess $PhSiH_3$ (Scheme 50).[237] The activity of this system is promising (up to 66% yield of *N*-methylated product with 5 mol% Fe catalyst) and paves the way for the use of third-row transition metals. More recently, García and co-workers described the use of nickel-based catalysts for the direct *N*-methylation of primary and secondary aliphatic amines by using CO_2 and $PhSiH_3$. Two catalysts, $[(dippe)Ni(\mu\text{-}H)]_2$ and $[Ni(cod)_2]$/dcype (dippe = 1,2-bis(diisopropylphosphino)ethane; dcype = 1,2-bis(dicyclohexylphosphino)ethane), were used for the monomethylation of aliphatic primary amines.[238] The reaction proceeds under relatively mild conditions (1 bar CO_2) and affords the corresponding monomethylated products in moderate to good yields, with different nitrogen-containing species as significant side products.

Remarkably, metal-free systems have even been found to enable the catalytic *N*-methylation of amines with CO_2 and silanes, as disclosed by Dyson and co-workers by using NHCs[239] or by Liu and co-workers by using $B(C_6F_5)_3$[240] as catalysts. Earlier work by the group of Cantat had shown that NHC catalysts could be used for the reduction of CO_2 in the presence of amines to afford formamides, but only traces (<1%) of *N*-methylated products were detected in their system.[241] The procedure developed by Dyson and co-workers operates under ambient pressure at mild temperatures of 50 °C for a variety of mainly aromatic primary or secondary amines (Scheme 51). Interestingly, DMF is used as the solvent and the authors discuss the possibility of the solvent being involved in the CO_2 activation. The catalyst tolerates a broad range of substrates/functional groups including nitrile and nitro groups, double and triple bonds, as well as ether- and ester-substituted amines to provide the corresponding *N*-methylated amines in good to excellent yields (Scheme 51). To demonstrate the potential of this system, the NHC organocatalyst was used to prepare naftifine[242] (an antifungal drug), which was obtained in 83% yield with the alkene motif remaining intact (Scheme 52). The group of Dyson suggested that the reactivity of the NHC organocatalysts in this reaction is attributed to their nucleophilicity, which may activate CO_2 through the formation of imidazolium carboxylates.[201,241]



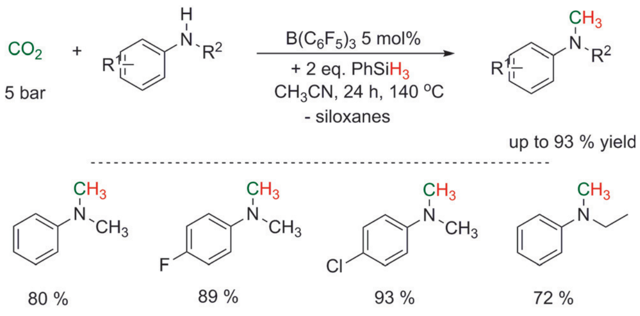
Scheme 51. Metal-free catalytic *N*-methylation of amines with CO_2 and $PhSiH_3$.[239a]



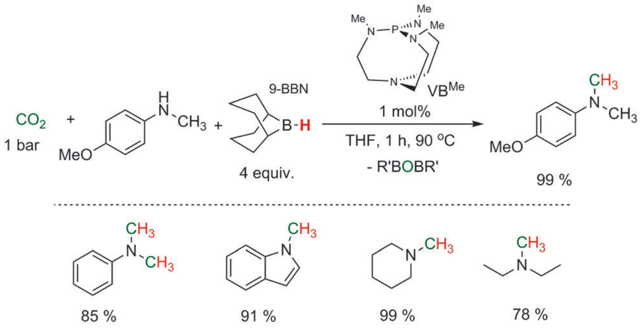
Scheme 52. Catalytic *N*-methylation of amines with CO_2 and $PhSiH_3$ for the synthesis of the antifungal agent naftifine.[239a]

In their studies, Liu and co-workers showed that the use of $B(C_6F_5)_3$ as a metal-free catalyst can efficiently catalyze the *N*-methylation of a broad range of anilines by using CO_2 as the carbon source in the presence of hydrosilane $PhSiH_3$.[240] The authors suggest a double role of the strong Lewis acidic catalytic boron center in $B(C_6F_5)_3$, which has a somewhat electron-deficient character as a transition-metal center for the activation of the Si–H bond as well as the activation of the amine substrate. With this catalyst, *N*-methylanilines with electron-donating and electron-withdrawing groups at the *ortho*-, *meta*, and *para*-positions of the benzene ring or other *N*-alkylanilines showed good reactivity, and resulted in the corresponding *N*-methylated products in yields of up to 93% (Scheme 53).

Cantat and co-workers showed that organocatalysts are also effective together with boranes as reducing agents for the *N*-methylation of amines on using CO_2 as a carbon source.[243] The use of 9-borabicyclo(3.3.1)nonane (9-BBN) as the reducing agent and NHCs as catalysts resulted in moderate to good yields of 50–80%. The use of Verkades superbases[244] provided high catalytic activity in the reductive functionalization of CO_2 with a broad range of substrates (Scheme 54). The reactions were performed under mild conditions of 90 °C and 1 bar of CO_2 pressure in short reaction times of typically less than 1 h. For example, the methylation of *N*-methylaniline to *N*,*N*-dimethylaniline was complete in just 10 min with a TON of 490 and a TOF of 2934 h^{-1}. The chemoselectivity of this system is also high, and anilines substituted with halogen, hydroxy, ester, and alkene substituents could be methylated, albeit with somewhat reduced activity.



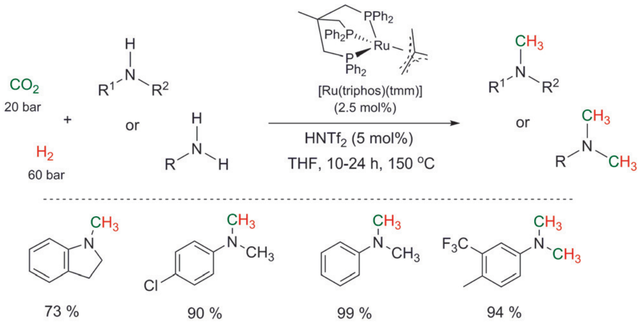
Scheme 53. Metal-free catalytic *N*-methylation of anilines with CO_2 and $PhSiH_3$ in the presence of $B(C_6F_5)_3$ as the catalyst.[240]



Scheme 54. Metal-free catalytic methylation of secondary amines with CO_2 and 9-BBN.[243]

Reductive methylation with CO_2 and reducing agents such as silanes or boranes is an attractive synthetic approach, especially if it can be carried out at ambient pressure in standard glassware apparatus. The functional-group tolerance can be an important factor in the synthesis of very complex molecules. However, the availability and energy requirements for the reducing reagents remain an issue, and, for example, other reagents containing Si-H groups may be more desirable than the standard $PhSiH_3$ reductant typically used in organic synthesis.[52] Furthermore, the coupled by-products add to the *E* factor and also require downstream separation and potential recycling. The use of CO_2 and H_2 clearly overcomes these limitations, although at the expense of needing the use of high-pressure reactor technology.

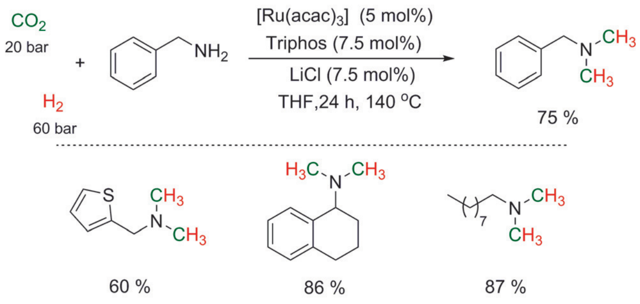
In 2013, the groups of Klankermayer and Leitner showed the first example of the direct *N*-methylation of primary and secondary amines with CO_2 and molecular hydrogen as the building blocks.[245] The key to the successful use of these simple and readily available reagents to construct the methyl group was again the triphos-based[246] ruthenium system. The choice of the catalyst was motivated by the catalytic reduction of CO_2 to methanol (see above) and the hydrogenation of amides pioneered by the group of Cole-Hamilton.[214c,g] In particular, the readily accessible complex [Ru(triphos)(tmm)][214h] showed very high reactivity for the direct *N*-methylation reaction in the presence of CO_2/H_2 and aromatic amines (Scheme 55). Activation of the precatalyst with two equivalents of an acid with a noncoordinating anion, such as $HNTf_2$, was found to give the highest activity. A range of primary and secondary aromatic amines could be methylated



Scheme 55. Ruthenium-catalyzed *N*-methylation of amines with CO_2 and molecular hydrogen.[245a]

to afford the di- or monomethylated amines in yields of >90% by employing CO_2/H_2 (20/60 bar) at 140–150 °C in THF as the solvent. Lower reactivity toward aliphatic amines was observed under these conditions.

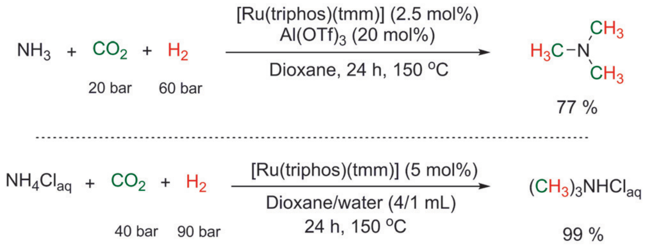
Subsequently, Beller and co-workers published a similar approach to the *N*-methylation of aromatic and aliphatic amines by using CO_2/H_2 in the presence of the closely related in situ catalyst [Ru(acac)$_3$]/triphos/H$^+$.[247] They were able to increase the activity of the catalytic system towards aliphatic amines by using LiCl as an additive (Scheme 56).



Scheme 56. Ruthenium-catalyzed *N*-methylation of amines with CO_2 and molecular hydrogen in the presence of LiCl as additive.[247]

Selective Synthesis of Trimethylamine from Ammonia or Ammonium Chloride

Recently, the groups of Klankermayer and Leitner showed that the [Ru(triphos)(tmm)] catalyst system can also be applied for the selective catalytic triple *N*-methylation of ammonia and ammonium chloride by using CO_2 as a C_1 source and molecular hydrogen as the reducing agent.[248] A Lewis and/or Brønsted acid is required as co-catalyst for the selective synthesis of trimethylamine from ammonia in organic solvents (Scheme 57, upper pathway). The efficient conversion of ammonium chloride system in aqueous solutions was achieved in a quantitative manner. The use of a biphasic aqueous/organic system enabled the separation and isolation of the product salt to be readily achieved. No co-catalyst is required in this latter case, probably because of the availability of the inherent proton from the substrate (Scheme 57, lower pathway).

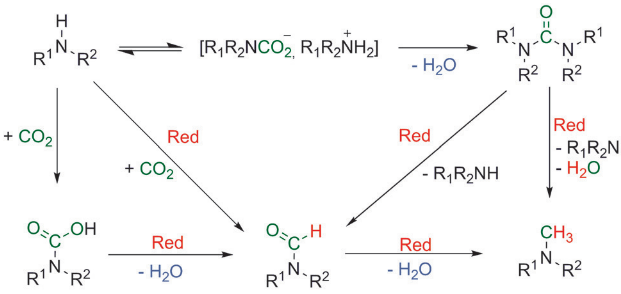


Scheme 57. Synthesis of trimethylamine TMA and its hydrochloride starting from NH_3 or NH_4Cl with CO_2/H_2.[248]

A salient feature of this new catalytic process is the use of ammonia, CO_2, and H_2 as the only reagents: all three components are readily available at ammonia production sites. At present, the hydrogen for the production of ammonia is formed from fossil feedstocks, which results in concomitant formation of CO_2 through the water-gas shift equilibrium. Whereas the current technology to produce methylamines requires an additional operation unit for the production of methanol, the catalytic process described here allows the potential direct utilization of the available gaseous production streams in a multicomponent combination for the synthesis of trimethylamine in a single step. Thus, the methylation based on CO_2/H_2 opens up new process options for the synthesis of methylamines in the area of high-volume products and bulk chemicals.

4.2.1.3. *Proposed Reaction Pathways for the Construction of the Methyl Group*

The construction of an *N*-bonded methyl group from CO_2 and H_2 involves numerous bond-breaking and bond-forming events, and a detailed picture of the mechanism is currently not yet available. Scheme 58 shows the reaction pathways that are currently mostly discussed for the overall transformation. Depending of the basicity of the amine substrate, either the equilibrium with CO_2 to form the carbamic acid or carbamte salt has to be considered. This equilibrium is strongly influenced by pressure and temperature.[249] Dehydration can lead to urea derivatives or—less favored—to isocyanates (not shown in Scheme 58). Upon reduction, any of these

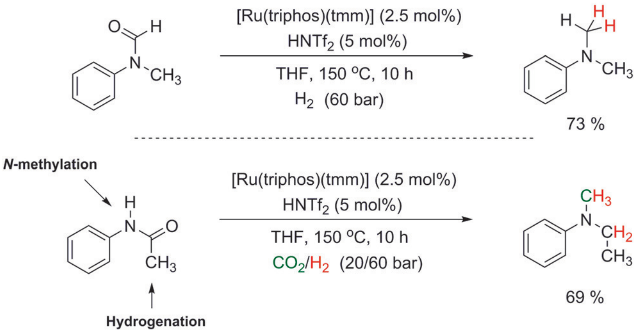


Scheme 58. Possible pathways for the catalytic *N*-methylation of amines by reduction of CO_2 after C–N bond formation. Alternatively, CO_2 can be hydrogenated to methanol followed by alkylation. Red = Reduction by H_2 or $PhSiH_3$.

species can be converted into formamides, which are generally believed to be intermediates on the way to the *N*-methyl group. This is supported by the detection of formamides in the product mixtures and by the ability of almost all the previously mentioned catalyst systems to reduce formamide substrates to the corresponding *N*-methylated products. However, no kinetic studies are currently available to demonstrate unequivocally that the formamides are true intermediates in a consecutive pathway. In cases where urea derivatives are detected under the reaction conditions, the direct reduction of *N*-methylated products by C−N bond cleavage cannot be ruled out. Other mechanisms such as the formation of methanol and subsequent alkylation are also conceivable. It may well be possible that different catalyst systems follow different channels in this complex network, or that a certain catalyst can simultaneously catalyze the reaction through parallel pathways.

4.2.1.4. *Catalytic N-Methylation of Amides with CO_2*

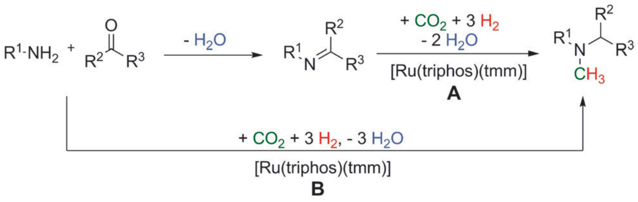
The [Ru(triphos)(tmm)]/$HNTf_2$ catalyst enabled the reduction of formamides under reaction conditions related to the established *N*-methylation reaction (Scheme 59, top). This initiated research on the sequential hydrogenation/methylation of amides as an access to unsymmetrical methyl/alkyl tertiary amines. Acetanilide was successfully transformed under standard reaction conditions and CO_2/H_2 pressure (20/60 bar) to *N*-ethyl-*N*-methylaniline in 69 % yield (Scheme 59, bottom).[245a] This unprecedented sequence offers an attractive synthetic method for the stepwise construction of unsymmetrical methyl/alkyl anilines.



Scheme 59. [Ru(triphos)(tmm)]-catalyzed hydrogenation of *N*-methylformanilide (top) and sequential hydrogenation/*N*-methylation of acetanilide (bottom).[245a]

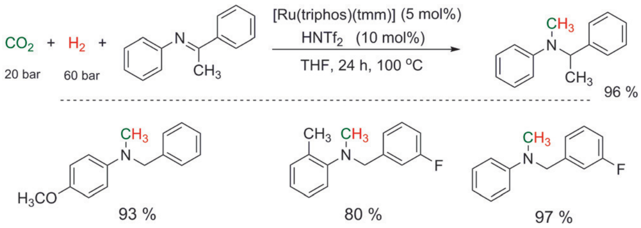
4.2.1.5. *Catalytic N-Methylation of Imines with CO_2*

Another approach to unsymmetric trialkyl amines is offered by the reductive methylation of imines. The [Ru(triphos)(tmm)]/$HNTf_2$ catalyst was found to allow the sequential reductive methylation of imines. For this transformation, isolated imines (Scheme 60, pathway A) as well as a mixture of aldehydes and amines (Scheme 60, pathway B) could be applied.[250] The multicomponent coupling is particularly intriguing considering the possible alternative pathways (hydrogenation of aldehyde, methylation of the amine) available in the system.



Scheme 60. Catalytic reductive methylation of imines with CO_2 and H_2 (A), and one-step synthesis of unsymmetrical tertiary *N*-methylamines by the three-component coupling of primary amines, aldehydes (R^2 = H) and CO_2 (B).[250]

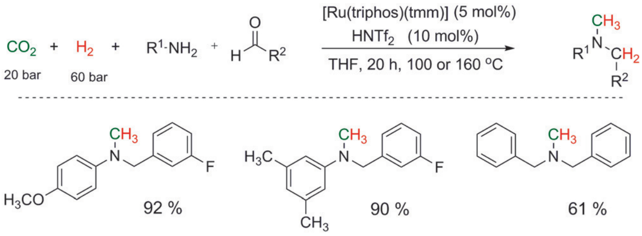
The reaction of *N*-(1-phenylethylidene)aniline proceeds smoothly at 100 °C and 5 mol % catalyst loading under otherwise standard *N*-methylation conditions to afford the corresponding *N*-methylated tertiary amine product (Scheme 61). In this case, the use of $HNTf_2$ as a co-catalyst is vital, as the use of other acids such as methanesulfonic acid (MSA) or *p*-toluenesulfonic acid (*p*-TsOH) led to the hydrolysis of the C=N bond of the imine and subsequent methylation of the aniline. The catalyst system provided excellent yields of up to 97 % for the unsymmetrical alkyl/methylanilines from the reductive methylation of a broad range of arylethylidenes and *N*-benzylideneanilines.



Scheme 61. Ruthenium-catalyzed reductive methylation of imines with CO_2 and molecular hydrogen.[250]

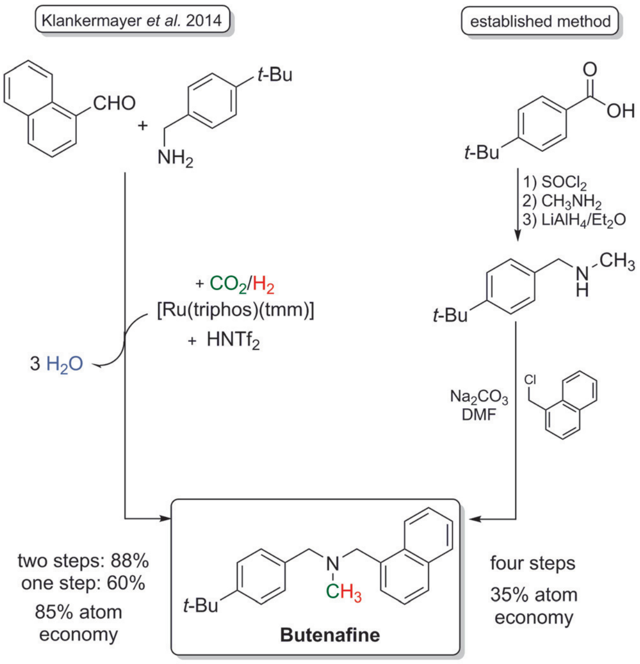
Comparable reaction conditions can be applied for the reductive three-component coupling of primary amines, carbonyl substrates, and CO_2. The unsymmetrical tertiary amines are obtained in fair to excellent yields from aniline derivatives and aromatic aldehydes under standard reaction conditions (Scheme 62). The use of more basic benzylamine as the substrate required higher reaction temperatures (160 °C), but also gave the desired products in moderate yields (Scheme 62).

To validate the new method for the synthesis of biologically active molecules, this Ru-catalyzed reductive methylation method was applied to the synthesis of butenafine (*N*-(4-*tert*-butylbenzyl)-*N*-methyl-1-naphthylamine), an antimycotic agent contained in many commercial fungicidal cremes.[242,251] The established method to prepare butenafine comprises a four-step synthesis that starts from *para-tert*-butylbenzoic acid[252] and produces large amounts of inorganic salts as by-products. The CO_2-based methylation route starts



Scheme 62. Ruthenium-catalyzed one-step preparation of *N*-methylated tertiary amines by three-component coupling of primary amines, aldehydes, and CO_2 with molecular hydrogen as reductant.[250]

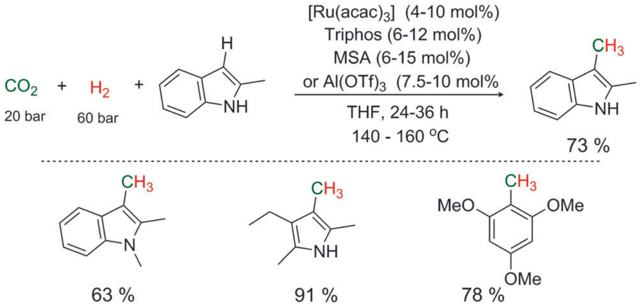
from 1-naphthaldehyde and 4-*tert*-butylbenzylamine as commercially available substrates (Scheme 63).[16a,250] Under the standard reaction conditions for the methylation of imines, butenafine was obtained in 88 % yield from the isolated imine and in 60 % yield from the one-step three-component coupling, even under these non-optimized conditions. This example demonstrates nicely the synthetic potential of CO_2/H_2 as a C_1 building block. It shows an improvement in terms of typical "Green Chemistry" metrics over the conventional process, irrespective of considerations about the CO_2 or H_2 source.



Scheme 63. Synthesis of antifungal agent butenafine by *N*-methylation with CO_2 and H_2 in comparison to established methods.[250]

4.2.2. Catalytic C–H Methylation

The construction of a methyl group from CO_2/H_2 can also be envisaged at reactive positions other than just N-H groups. A first example of the methylation of activated C–H bonds was provided by the group of Beller in 2014. They used the in situ ruthenium–triphos catalyst system to introduce methyl groups in the 3-position of pyrrolidones and indols.[253] The conditions employed in this reaction were comparable to those for *N*-methylation with the [Ru(acac)$_3$]/triphos/H^+ catalyst, with Al(OTf)$_3$ used as additional Lewis acid additive. This catalyst system worked mainly for the methylation of C–H bonds of electron-rich heteroaromatic compounds, in which the *C*-methylated products were generally afforded with moderate to high yields (Scheme 64).



Scheme 64. Ruthenium-catalyzed C–H methylation of heteroarenes with CO_2 and molecular hydrogen.[253]

5. Conclusion and Outlook

This Review highlights the synthetic potential of the combination CO_2/H_2 as a C_1 synthon in catalytic reactions and processes. The transformations are classified according to the reduction level and the bond-forming processes. From an application point of view, one can also distinguish crudely between high-volume and high-value products. The first class comprises the C_1 reduction products methanol, formaldehyde, and formic acid derivatives. These CO_2-based products can be used as base chemicals in the chemical supply chain, but additionally have potential as energy carriers or storage systems. In both cases, the input of "low-carbon" hydrogen from sustainable resources is essential to fully exploit the ecological benefits of this approach. Similar arguments apply to bulk chemicals or commodities that are obtained under C–C or carbon–heteroatom bond formation, such as saturated carboxylic acids or methylamines, although other aspects such as feedstock integration and process intensification may already provide benefits in today's value chains in this sector.

Importantly, the transformations introducing C_1 building blocks that emerge from this area open entirely new pathways to essential functional groups such as carboxylic acids, alcohols, or amines. These reactions enable novel synthetic methods for complex molecules including biologically active substances. The selective and clean introduction of methyl groups is an illustrative example where the use of CO_2/H_2 does not only replace less benign reagents, but also provides a completely new synthetic method. Although the direct impact on the anthropogenic carbon balance is arguably small for the individual applications in this area, these novel methods enable the resource efficiency of chemical production to be improved across the whole value chain and consequently have significant potential for the transition towards closed carbon cycles. As CO_2 and H_2 are relatively low-cost reagents, their targeted use can provide immediate economic drivers for sustainable production processes of higher value chemicals.

Despite the very dynamic progress made in the field during the last decade, the successful examples highlighted in this Review still only cover a small fraction of the chessboard that is laid out by this concept. At each of the reduction levels—which correspond to the C_1 compounds on the vertical line that have gained most interest so far—an array of molecular diversity addressing nearly every sector of the chemical industry can be assessed if C–C bonds and carbon–element bonds are formed selectively. As the understanding of the possible pathways and their underlying mechanistic principles increases, the ability of the catalysis community to master the strategic moves will equally improve, thereby allowing more complex, elegant, and efficient combinations. The key to this development is to derive design principles for catalysts that combine high selectivity in complex series of bond-breaking and bond-forming reactions with robustness and long-term stability, thereby moving the concepts of homogeneous and heterogeneous catalysis closer in a translational way. The ligand framework of transition-metal complexes provides a powerful strategic tool to impose particular coordination geometries that favor specific elementary steps and increase the stability of the active species at the same time. On the other hand, the detailed pictures of the active site and its environment that can be unraveled today for solid catalyst materials provide molecular insight into the catalytic cycle that rivals, and sometimes even surpasses, that of typical homogeneous catalysts.

Equally important—and in fact very closely interrelated—is the design of advanced reaction engineering solutions to provide suitable equipment and integrated process schemes across all scales of the value chain. For megaton volume processes such as methanol production, the continuous operation of gas/solid systems at elevated pressure and temperatures is favored today by the economy of scale provided at petrochemical sites. Alternative solutions are required if the logistics of the CO_2 and H_2 availability call for more diversified and smaller-scale production. The unprecedented thermally robust molecular catalysts allow operation in novel processing windows and, consequently, small-scale flexible flow reactor technology becomes increasingly attractive with these materials. This also provides, in particular, new opportunities for the synthesis of complex molecules, where the potential of "flow chemistry" is increasingly recognized. As CO_2-based reactions often require additional energy input for the downstream processing, because of thermodynamic constraints, integrated systems for reaction and separation become crucial. Minimizing the "thermodynamic penalty" remains a critical sustainability factor even for successful cases of coupling low-carbon energy systems with the abundant nonfossil feedstock.

In summary, groundbreaking studies and recent breakthroughs have demonstrated the potential of tailored catalysts to utilize the combination of CO_2 and H_2 as a C_1 synthon. Whereas some of these concepts can facilitate the transition of the energy system by harvesting renewable energy into chemical products, others provide options to reduce the environmental impact of chemical production already in today's petrochemical-based industry. Thus, interdisciplinary fundamental research from chemists and chemical engineers can make important contributions to the development of sustainable processes at the interface of the energetic and chemical value chain.

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