Review

Carbon Dioxide as a Carbon Resource – Recent Trends and Perspectives

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

With the growing perception of industrialized societies that fossil raw materials are limited resources, academic chemical research and chemical industry have started to introduce novel catalytic technologies which aim at the development of economically competitive processes relying much more strongly on the use of alternative carbon feedstocks. Great interest is given world-wide to carbon dioxide (CO_2) as it is part of the global carbon cycle, nontoxic, easily available in sufficient quantities anywhere in the industrialized world, and can be managed technically with ease, and at low cost. In principle carbon dioxide can be used to generate a large variety of synthetic products ranging from bulk chemicals like methanol and formic acid, through polymeric materials, to fine chemicals like aromatic acids useful in the pharmaceutical industry. Owing to the high thermodynamic stability of CO_2, the energy constraints of chemical reactions have to be carefully analyzed to select promising processes. Furthermore, the high kinetic barriers for incorporation of CO_2 into C–H or C–C bond forming reactions require that any novel transformation of CO_2 must inevitably be associated with a novel catalytic technology. This short review comprises a selection of the most recent academic and industrial research developments mainly with regard to innovations in CO_2 chemistry in the field of homogeneous catalysis and processes.

Key words: CO_2, Homogeneous Catalysis, Renewable Energy, Methanol, Formic Acid

Table of Contents

1. Introduction

For more than a century value creation in the organic chemical industry has been based mostly on the steady and reliable supply of fossile carbon sources with petrochemistry dominating the last six decades. A notable exception is the generation of certain basic

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chemicals *via* biomass pyrolysis in parts of the German chemical industry in the early 20th century. In fact, the implementation of chemical technologies in the 20th century strongly reflected the general perception that fossil resources will remain available in sufficient quantities as the most economically feasible option. The same observation can be made for the production and usage of energy. A tremendous amount of fossil resources is currently used for the generation of electricity and heat for private and industrial applications and to generate liquid fuels for transportation systems. In 2011, *ca.* 33 % of the global energy consumption was satisfied by oil, while the amount of non-energetic use of oil in North America and Europe amounts to *ca.* 20 % only [1]. The total amount of carbon-based raw materials used in 2006 in Germany was equivalent to *ca.* 498 million tons stone coal energy equivalents from which only *ca.* 35 Mio t or 7 % were used non-energetically [2].

Inevitably, the use of fossil raw materials for energy production leads to the formation of carbon dioxide (CO_2). Even under the most optimistic scenarios for the replacement of fossil-based technologies, the above numbers clearly indicate that CO_2 will be generated as waste material from the energy sector in more than sufficient quantities to constitute an attractive carbon source for the chemical supply chain in the foreseeable future. The technologies to isolate CO_2 from such sources have reached a very mature state in the development of carbon capture and storage (CCS) [3]. It should be noted that also other highly concentrated streams of CO_2 are available from industrial as well as even natural sources [4].

With regard to the correlation between a rising CO_2 concentration in the atmosphere and currently observed changes in the global climate it should be noted at this point that the increased usage of CO_2 as a building block for carbon-based compounds and materials cannot provide a „silver bullet" to solve the problem of the world-wide CO_2 emissions. The anthropogenic annual CO_2 emissions in 2010 were estimated to be 29 billion tons [5]. The current utilization of CO_2 as an industry gas amounts to *ca.* 20 million tons while CO_2 usage as a raw material for chemical production reaches *ca.* 110 million tons, largely dominated by the synthesis of urea as fertilizer [6–9]. The annual production of urea amounted to 153 million metric tons in 2011 with a usage of *ca.* 112 million tonnes of CO_2 as a feedstock [6]. The largest fraction of urea is used as agricultural fertilizer, and smaller amounts are consumed for the production of fine chemicals, in polymer synthesis (*e. g.* as a starting material for urea-formaldehyde or urea-melamin resins) or for emission control in automotives. Given the typical scale of chemical products, urea is clearly an exception, and the range of $10^2 - 10^3$ Mio tons defines more or less the upper limit of the amount of CO_2 that could possibly be exploited for chemical products.

Nevertheless, the increased valorization of CO_2 can contribute significantly to the development of sustainable production processes: The compound is the most abundant C1 building block, available in sufficient quantities practically anywhere in the industrialized world. It is non-toxic, and can be handled readily and safely on a technical scale. With the increasing price of other carbon sources and the recent improvement of CO_2 capture technologies, it is also becoming more and more economically attractive. This opens new opportunities for the chemical synthesis of high-quality goods and can furthermore support the introduction of even safer production technologies in usually densely populated areas.

In this context it may be justified to explicitly name the at the time visionary publication by Friedrich Asinger (Chair of Technical Chemistry at RWTH Aachen University from 1959 to 1972), who pointed out already in 1986 that the use of CO_2 as feedstock for the production of methanol could contribute significantly to an alternative way of storing energy and producing chemical goods [10]. These arguments were reiterated and strengthened by Keim and Offermans in 2010 [11]. Whereas the ecologic, economic and societal drivers for the interest in CO_2 utilization have seen various changes in the more than 25 years since then, the scientific challenges for chemistry and chemical engineering remain the same: To address the thermodynamic constraints and the kinetic limitations of the transformations of the carbon dioxide molecule!

Various research activities for CO_2 utilization using catalytic technologies have been undertaken, and in the past years the field has seen re-newed dynamics resulting in impressive progress based on the ever increasing insight into the molecular basis of catalysis and novel reaction engineering concepts [12–15]. In particular, homogeneous catalysts have played an important role ever since the early years of CO_2 chemistry.

The group of Wilhelm Keim at the Institut für Technische Chemie und Petrolchemie at RWTH Aachen

University studied the telomerization of dienes with CO_2 already in the mid 1970's [16, 17]. Stoichiometric [18, 19] as well as catalytic [20] reactions leading to C–C bonds under CO_2 incorporation evolved in the following years. As a result of his early studies in Aachen Arno Behr published a monograph that formed the leading reference in the field for many years to come [12]. Also the work of Dieter Vogt on the insertion of CO_2 originated from this school [21].

Much research has been devoted to the synthesis of a variety of intermediate chemicals like acids, lactones, carbonates, as well as polymeric materials. Very recently a number of promising contributions were made in these areas. On the side of fundamental research, they address for example the direct synthesis of carboxylic acids from CO_2, based on different mechanistic principles such as oxidative coupling or CO_2 insertion to form new C–C bonds. Much closer to industrial application is the synthesis of polycarbonates and polyurethanes which incorporate substantial amounts of CO_2 *via* the formation of C–O bonds. Somewhere in between is the formation of C–H bonds by hydrogenation of CO_2, leading for example to methanol or formic acid as possible large-volume products. It is the aim of this short review to summarize some of the latest developments in homogeneous catalysis for the utilization of CO_2 in the chemical value chain on the basis of representative examples from these areas.

2. Synthetic Transformations of CO_2 Using Metal Complexes as Catalysts

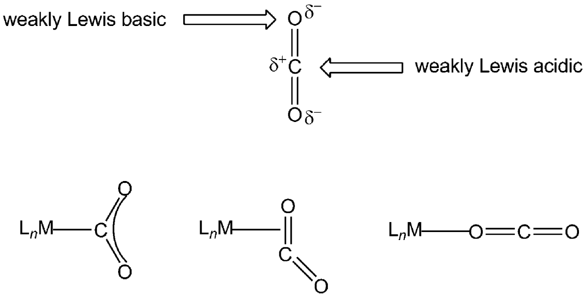
2.1 Reactivity of CO_2 at metal centers

Much pioneering work on catalytic CO_2 chemistry was conducted around the world including the groups of Behr [22 – 27], Hoberg [28 – 35], Walther [36, 37], and Dinjus [38 – 42], as well as Inoue [43 – 47], Musco [48], Yamamoto [49, 50], Darensbourg [51, 52], and others [53 – 57]. These efforts have developed a fundamental understanding of the chemistry of metal complexes with CO_2 providing a sound basis for the rational development of catalytic transformations of this raw material. A most recent overview by Rieger, Herrmann, and Kühn and coworkers [58], who focus on important developments of transition metal-based CO_2 chemistry, provides an excellent entry into the field. A review involving some of the authors of this manuscript [59] discusses the current technological status and future trends for catalytic CO_2 utilization in industry, including some basic criteria for the evaluation of the implementation of such strategies.

Considering solely the interaction of carbon dioxide with a metal center, CO_2 can bind by three general coordination modes as depicted in Fig. 1. In addition to the mononuclear binding modes shown here, multinuclear complexes containing bridging CO_2 ligands are also known [14]. The ligand CO_2 comprises a weakly Lewis acidic C atom and two weakly Lewis basic O atoms, and the C=O double bonds as possible coordinative sites. Consequently, the electronic nature of the complex fragment will strongly influence the preferred binding mode. Electron-rich metal centers favor **1** and **2**, which can be isolated as stable complexes in many cases. More electron-deficient centers will lead to **3**, observed only as transient species.

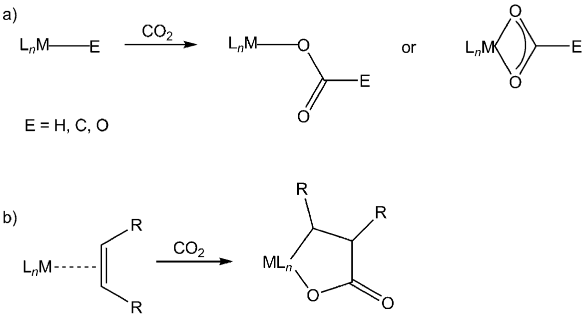
Although coordinated CO_2 molecules can undergo a variety of transformations, their involvement in catalytic processes is not a necessary prerequisite. The most obvious possibility for C–E (E = C,H,O,N) bond formation in catalytic cycles is the formal insertion of CO_2 into a M–E bond of a metal complex (Scheme 1). Alternatively, CO_2 can be incorporated into an organic framework *via* oxidative coupling with another unsaturated ligand as exemplified for an olefin in Scheme 1. Whereas the coordination of both coupling partners is typically assumed in oxidative coupling processes, the insertion reactions show often lower barriers for pathways without pre-coordination or only very weak interactions of CO_2 at the metal center.

These principal reactions comprise the most abundant types of currently known transformations of CO_2 at metal complexes. In the following sections some reactions which would be very interesting to be put into industrial practice or are close to being realized



1 **2** **3**

Fig. 1. Properties of CO_2 as a ligand (top) and coordination types of CO_2 in metal complexes (bottom) [14].



Scheme 1. Reactions of CO_2 with organometallic complexes: a) Insertion of CO_2 into a metal-element bond; b) Reaction of CO_2 with coordinated olefins.

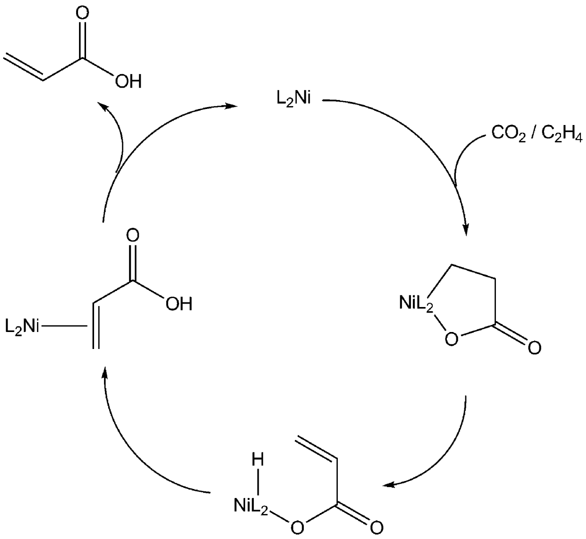
commercially are discussed. The order of the discussion is structured according to the underlying reaction principle.

2.2 Oxidative coupling of CO_2 and olefins – metallalactones as intermediates for the catalytic synthesis of acrylic acid

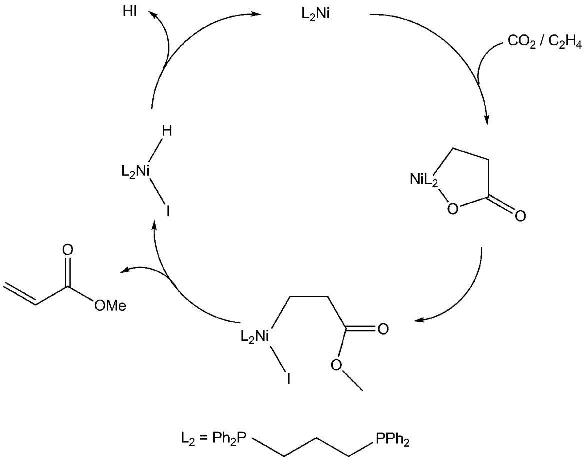
The oxidative coupling of CO_2 and olefins is a very interesting chapter of academic CO_2 chemistry, and it also has an important direct link to industrial production technologies for acrylic acid. Acrylic acid is a starting material for the production of polyacrylates. Currently acrylic acid is synthesized industrially by the SOHIO process on the 3×10^6 t/a scale *via* the oxidation of acroleine at heterogeneous molybdenum oxide-vanadium oxide catalysts at temperatures of 300 °C. As acroleine is produced by the oxidation of propylene oxide at bismuth-molybdenum oxide catalysts [60], it is obvious that the replacement of the high-energy two-step processes by a one-step low-energy pathway would be very interesting to enable a more sustainable overall route to acrylic acid. Given the increasing demand of propylene in the polyolefin industry, the use of ethylene as raw material would currently also be an attractive feature. Finally, a significant amount of CO_2 could be fixed in the polyacrylates for long time frames.

The group of Aresta published in 1975 that CO_2 reacts with $[Ni(cod)_2]$ (cod = *cis*,*cis*-1,5-cyclooctadiene) in the presence of 1,2-bis(dicyclohexylphosphanyl)-ethane (dcpe) yielding $[(\eta^2\text{-}CO_2)Ni(dcpe)]$ [61]. In the following years a lot of work was devoted to the oxidative coupling of CO_2 with olefins at nickel complexes [38] by many groups, with detailed fundamental knowledge resulting from the systematic work by Hoberg [62]. The nickelalactones undergo hydrolysis in the presence of mineral acids leading to the degradation of the nickel complex and formation of the free acrylic acid in a stoichiometric reaction. In principle, one can envisage to assemble a catalytic cycle as depicted in Scheme 2 on the basis of these observations. In this mechanism, CO_2 and ethylene can firstly be coupled to a metallalactone and subsequently be cleaved from the complex by β-hydride elimination to yield the corresponding unsaturated compound acrylic acid and retain the catalytically active species. Owing to the thermodynamics, the free acrylic acid would have to be stabilized in the form of a salt or another derivative to provide a driving force.

However, the β-hydride elimination from nickelalactones proved to be difficult. The reason is the steric hindrance induced by the rigidity of the planar metallalactone ring which makes it difficult for the β-hydrogen atom to come close enough to the nickel center. In a large number of experiments and theoretical investigations by many different groups it could be shown during the past decades that the β-hydride elimination for the production of acrylic acid from nickelalactones is only possible under very specific constraints preventing currently a direct route to acrylic acid.



Scheme 2. Hypothetical catalytic reaction of CO_2 with ethylene to yield acrylic acid using nickel(0) catalysts.



Scheme 3. Step-wise synthesis of methyl acrylate from CO_2, ethylene and methyl iodide at [(dppe)Ni] [64].

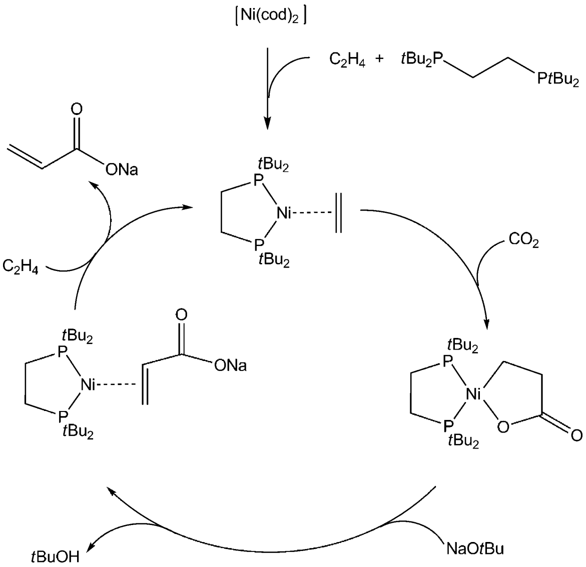
DFT computations have suggested that β-hydride elimination should be possible in principle when the Ni–O distance is extended, and in this way an agostic interaction between the nickel center and the β-hydrogen atom is enabled [63]. Accordingly, the opening of the metallalactone ring by breaking the Ni–O bond should favor the β-hydride elimination. The group of Rieger showed very recently that these predictions indeed allow for the formation of acrylic acid esters. They used the oxidative addition of MeI to open the dppp-complexed nickelalactone by oxidative addition of MeI as shown in Scheme 3 [64]. The resulting open chain species is flexible enough to undergo the β-hydride elimination, and methacrylate is produced as the thermodynamically favored product. The HI elimination resulting in the Ni(0) species would close a catalytic cycle, but this species cannot be converted to the metallalactone complex under the given reaction conditions. Accordingly, the reaction is not yet catalytic, and also substantial amounts of MeI (100 fold excess) are needed to obtain significant amounts of acrylate.

In 2012 the groups of Limbach and Hofmann reported on the catalytic formation of sodium methacrylate using [(dtbpe)Ni] (dtbpe = 1,2-bis-(di-*tert*-butylphosphanyl)ethane) in a two-step process for the reaction of CO_2 and ethylene. They used sodium *tert*-butylat (NaO*t*Bu) as a base to facilitate both the formal β-hydride elimination as well as the product stabilization [65]. The postulated reaction mechanism for the overall reaction sequence is depicted in Scheme 4.

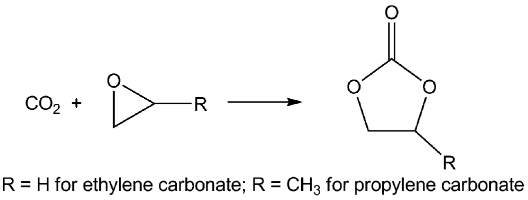
Although the amount of product formed per nickel center is currently equivalent to only 10 catalytic turnovers, this provides the first evidence for a catalytic production of sodium acrylate by a homogeneous catalyst. As such it serves as a nice example of a fruitful interplay between industrial needs and fundamental research.

2.3 Insertion of CO_2 into M–O bonds – synthesis of carbonates, polycarbonates and polyurethanes

Aliphatic and cyclic carbonates are valuable intermediate products in the chemical industry [66–70]. Dimethylcarbonate (DMC) for instance is used as a methylating agent in organic syntheses, for polymer fabrication and as a solvent and lubricant. The transesterifciation with phenol leads to diphenylcarbonate, which can be further reacted with Bisphenol A leading to the corresponding polycarbonate. Currently the reaction of phosgene with the corresponding alcohol is used for the synthesis of aliphatic carbonates [71], and alternatives based on more benign starting materials are the subject of many research efforts. The direct use of CO_2 remains a significant challenge, owing to the formation of water as the coupled by-product which imposes challenges on reaction engineering as well as catalyst design. Recent advances include the use



Scheme 4. Step-wise synthesis of sodium acrylate from ethylene and CO_2 with [Ni(dtbpe)] as mediator, resulting overall in a catalytic coupling of CO_2 and ethylene [65].



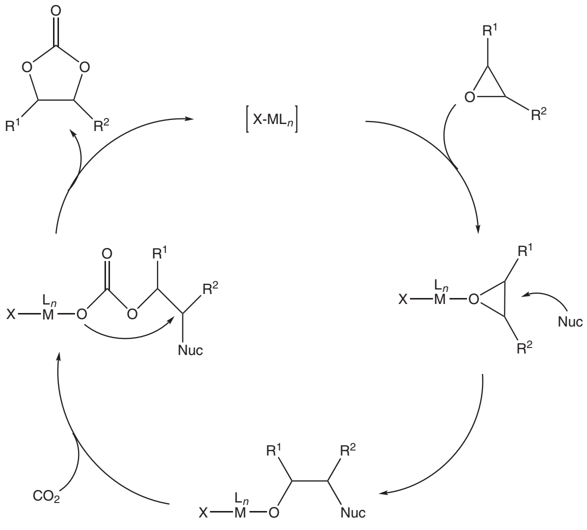
Scheme 5. Synthesis of cyclic carbonates from epoxides and CO_2.

of niobium-based systems described by Aresta for the synthesis of DMC and other carbonates [72 – 74]. Tin- and titanium-based mediators have been studied extensively by the groups of Ballivet-Tkatchenko [75 – 77] and Sakakura [78, 79], respectively.

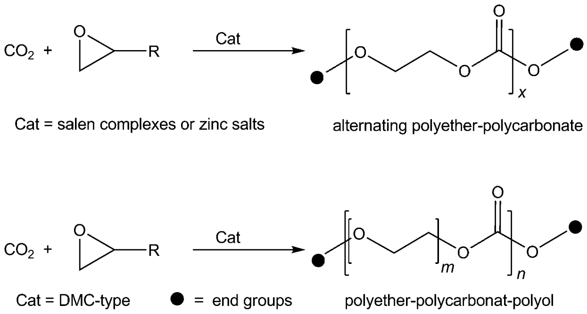
Five-ring carbonates can be obtained by the reaction of CO_2 with an epoxide in the presence of an appropriate catalyst (Scheme 5) [80 – 83]. The corresponding synthesis of ethylene and propylene carbonate is carried out on an industrial scale. Recent reviews by Sakakura [13, 67] summarize the current state of the art in industry and academia. Transition metal catalysts have been under investigation for more than three decades, and an initial report about the catalytic synthesis of (poly)-carbonates was published 1978 by Inoue and Takeda [84]. Currently mono- and binuclear salen complexes of aluminum, chromium and cobalt are studied predominantly [85 – 88], aiming mainly at an improved activity and at new synthetic applications including a stereocontrol at the chiral center.

The currently accepted catalytic cycle for the formation of cyclic carbonates from epoxides and CO_2 is depicted in Scheme 6. The initial step is the coordination of the epoxide *via* its oxygen atom to the metal center of the catalyst, resulting in an activation of the epoxide. Secondly the epoxide ring is opened by assistance of a halide or another nucleophile (Nuc) yielding an alkoxide. Subsequently, CO_2 inserts into the M–O bond, forming a carboxylate complex. Back-biting of the carboxylate under elimination of the nucleophile leads to the formation of the five-membered cycle. The intriguing interplay of Lewis-acid and Lewis-base activation is crucial for the development of bi-functional and bimetallic catalysts: One site binds the epoxide and the other coordinates CO_2, which then acts as a nucleophile and induces the ring opening of the epoxide.

Cyclic as well as open-chain aliphatic carbonates can be used as carriers for the carbonate unit in the synthesis of polycarbonates [89]. However,



Scheme 6. Simplified mechanism for the formation of cyclic carbonates from CO_2 and epoxides. Nuc = nucleophile.



Scheme 7. Co-polymerization of epoxides and CO_2.

polyalkylenecarbonates can also be obtained directly *via* catalytic co-polymerization of epoxides and CO_2 in high efficiency (Scheme 7) [13, 59]. Depending on the catalyst, the reaction can be controlled to produce either polyalkylenecarbonates of high molecular weight with fully alternating repetition units, or lower molecular weight materials with random incorporation of carbonate linkages. High molecular weight alternating polypropylenecarbonate is investigated intensively as a new polymer and for polymer blends in academia and industry [90, 91]. The shorter chain copolymers of propylene oxide and CO_2 show promising properties as polyol-building blocks in the production of polyurethanes, and pilot plant operations are currently under way at BayerMaterialScience in Leverkusen [92]. The development of the catalytic processes for the generation of the polyol building blocks was facilitated by the close collaboration between academia and industry at CAT Catalytic Centre, a joint research institution of RWTH Aachen University and the Bayer company. This successful approach provides an illustrative example for the innovation potential when fundamental research is applied to current challenges of industry in an appropriate research structure.

Polyether-polycarbonate-polyols bearing terminal alcohol groups are particularly interesting, as they provide entry to polyurethanes. Within the context of CO_2 utilization it is important to realize that the incorporation of CO_2 into these materials opens the way to industrial products which store CO_2 for long time frames. As polyurethanes constitute a market of *ca.* 14 million tons per year it becomes evident that a significant amount of CO_2 can be incorporated into these products. Furthermore, novel materials can be developed to extend the property portfolio of the existing products and in this way enrich the variety of polyurethane applications.

2.4 Insertion of CO_2 into M–H bonds – synthesis of methanol and formic acid

2.4.1 Hydrogenation of CO_2 to methanol

Methanol is produced on the 30 million ton scale [93] annually as one of the most important basic chemicals, as a widely used industrial solvent, and for fuel additives such as methyl *tert*-butylether (MTBE) [94]. Current industrial production of methanol is based on syngas (CO/H_2) which is mainly obtained from natural gas [95, 96]. CO_2 is sometimes present in the gas feed of these processes to balance the CO/H_2 ratio, and this is currently the second largest use of CO_2 in industrial synthesis after the urea processes, converting approximately 2 Mio t CO_2 per year. The direct synthesis of methanol by hydrogenation of pure CO_2 is possible in principle (Scheme 8) using heterogeneous-type catalysts. This has stimulated various concepts to use CO_2-based methanol as a sustainable carbon-based energy carrier and entry point into the chemical supply chain [11 – 13].

The use of CO_2 as an energy vector is closely related to the availability of hydrogen from non-fossil resources. A recent analysis [59] of the carbon footprint of the production process of methanol has shown that a net emission of 0.24 tons of CO_2 per ton of methanol is generated using syngas from steam reforming of natural gas. This value even increases drastically to 4.29 t(CO_2)/t(MeOH) when CO_2 is used as carbon source together with H_2 obtained by electrolysis of water using *e. g.* the current German power mix. However, if hydrogen production relies on electrolysis of water with electricity generated solely by renewable energy sources then the net CO_2 emission for methanol production would be negative, and 1.38 tons of CO_2 per ton of methanol could be fixed. In particular, electricity peaks from renewable power generators that cannot be accommodated in the grid might offer an attractive option to be coupled to CO_2 hydrogenation.

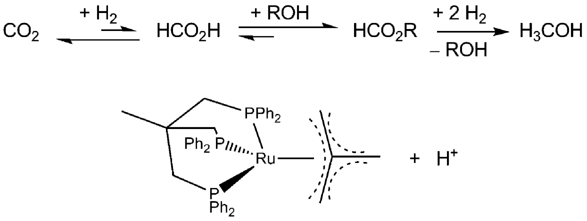
$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O$$

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Scheme 8. Generation of methanol by hydrogenation of carbon dioxide and carbon monoxide.

The prerequisite to make any of these scenarios viable is the availability of efficient catalysts for the hydrogenation of CO_2 to methanol. Heterogeneous catalysts have long been known for this reaction, and recent publications demonstrate the continuing interest [97 – 99]. Heterogeneous systems are currently already investigated for larger scale application [100]. In sharp contrast, no molecular catalyst has been known until recently to enable the multistep reduction sequence required for the hydrogenation of CO_2 to methanol. In groundbreaking studies, the group of Milstein reported ruthenium pincer compounds which successfully catalyze the hydrogenation of carbonic acid derivatives and even formates to methanol [101, 102]. This opened the possibility to hydrogenate CO_2 to methanol stepwise through such intermediates, if a catalyst could affect each of the steps. In a first approach, the group of Sanford used a cascade system of three different catalysts and observed the formation of methanol, albeit with very low turnover numbers [103].

Most recently, the first example for a single-site organometallic catalyst has finally been reported which allows the direct hydrogenation of CO_2 to methanol (Scheme 9) [104]. The catalyst precursor is a ruthenium triphos complex which bears the trimethylenemethane (TMM) ligand. Upon activation with catalytic amounts of acids with non-coordinating anions such as methanesulfonate or bis(trifluoromethanesulfon)amide (BTA) methanol



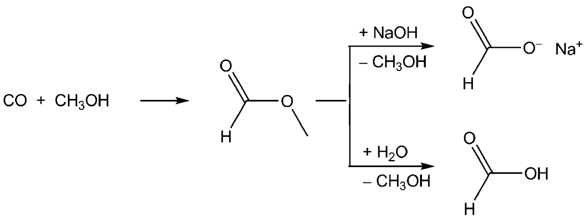
Scheme 9. Synthesis of methanol from CO_2 catalyzed by a ruthenium triphos complex.

was formed under relatively mild conditions with turnover numbers up to 220. Studies on the hydrogenation of formate esters and isotopic labeling experiments have confirmed a reaction sequence involving formate species as key intermediates. This opens new possibilities for rational catalyst development based on the molecular approach of organometallic chemistry which complements the development of multi-site heterogeneous catalysts in the synthesis of methanol from CO_2.

2.4.2 Hydrogenation of CO_2 to formic acid

The initial step of the hydrogenation sequence described above reduces CO_2 to the formate level. Formic acid itself is in fact also a very interesting target product with applications among others in agriculture (silage) and the leather industry, and as a commodity chemical. It is produced on the scale of several hundred thousand tons per year mainly by the reaction of carbon monoxide (CO) with methanol to yield the methylester of the acid [59]. Subsequently, the ester is cleaved with base or acid to yield the salts or free acid, respectively (Scheme 10).

Alternatively, CO_2 could be transformed into formic acid directly by simple addition of H_2. However, the thermodynamics of the reaction impose a major constraint on the feasibility of the reaction. The formation of formic acid from CO_2 and H_2 is an exothermic ($\Delta H = -31.6\,\mathrm{kJ\,mol^{-1}}$), though endergonic process ($\Delta G = +32.9\,\mathrm{kJ\,mol^{-1}}$), which makes the direct synthesis impossible [15]. To shift the equilibrium towards isolable amounts of the reduced species, the addition of appropriate stabilizers such as alkylamines or sodium hydroxide is necessary to form corresponding adducts or formate salts, thus establishing both exothermic and exoergic reactions (Scheme 11).



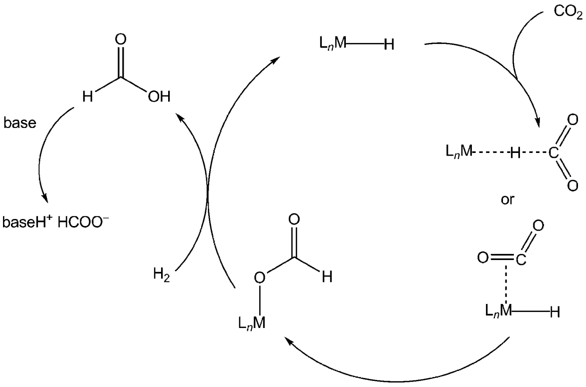
Scheme 10. Step-wise industrial synthesis of formic acid by carbonylation of methanol and hydrolysis.

$$CO_2 + H_2 \rightleftharpoons HCOOH \xrightarrow{NEt_3} HCOOH/NEt_3$$

Scheme 11. Reaction of carbon dioxide with hydrogen to formic acid and its stabilization by formation of the amine adduct.

Research for the development of catalysts for this reaction dates back to the mid 1970's, and nowadays there is a large variety of primarily rhodium, ruthenium, iridium and even iron catalysts with in some cases very high turnover frequencies and turnover numbers [58, 59]. The catalytic reaction relies on transition metal hydrides as catalytically active species, and the currently accepted reaction mechanism is depicted in Scheme 12.

The details of the hydride attack at the carbon center of CO_2 during the formal insertion and the hydrolytic cleavage of the resulting metal-oxygen bond depend strongly on the nature of the catalyst. For prototypical rhodium catalysts [105], the CO_2 molecule inserts into the M–H bond without the need for stable pre-coordination. Activation of the H–H bond during hydrogenolysis can occur either by oxidative addition or σ-bond metathesis, the latter pathway being preferred according to computational studies. Kinetic as well as computational studies consistently indicate



Scheme 12. General reaction mechanism for the catalytic hydrogenation of CO_2 to formic acid or formates.

that the rate-limiting barriers are in the later steps of the mechanism liberating the product and regenerating the active species. As this step is associated with the thermodynamically unfavorable formation of the free acid, the base is important to improve yields and rates of the reaction by deprotonation of the acid as soon as it is generated.

Although a large number of catalytic systems with high activity and productivity have been described, the above described interplay between catalyst and stabilizer prevents the production of the desired free acid in a simple way. Multi-step processes have been developed to enable the separation of the adduct from the catalyst and subsequent isolation of the free acid [106]. Several studies describe processes in which the adduct of formic acid and NEt_3 is transformed into a thermally cleavable salt by exchange of the base [107 – 110]. Furthermore, multiphase reaction systems were used to investigate the separation of the adduct from the catalyst. Very recently a novel process was introduced by BASF in which trihexylamine was used as the base together with a ruthenium catalyst in protic media [106, 110]. The corresponding adduct formed from formid acid and the amine could be separated form the aqueous phase and cleaved by distillation. Also immobilized ruthenium catalysts were used by the group of Zhang in combination wih ionic liquids (IL) carrying tertiary amino groups as basic functions and water [111, 112]. The chemical transformation took place at the solid catalyst that was removed by filtration to obtain an IL phase which contained the product. This phase was subsequently distilled which led to a cleavage of the acid/base adduct, and free formic acid was obtained.

Most recently, the first example of a fully integrated process scheme has been presented allowing production of free formic acid directly in a single process unit [113]. The concept relies on a continuous-flow process scheme where carbon dioxide plays a dual role as the reactant and as the mobile phase in the supercritical state ($scCO_2$). As depicted in Fig. 2, the catalyst and the stabilizing base are contained in the stationary phase consisting of an ionic liquid (IL) which is not miscible with $scCO_2$.

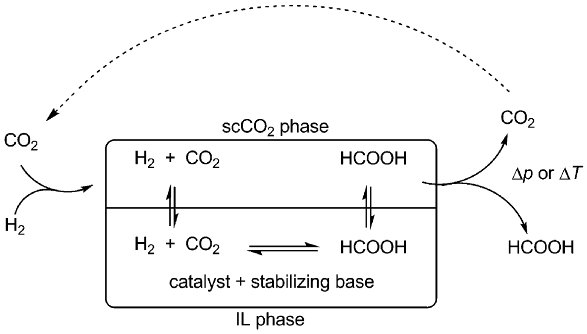


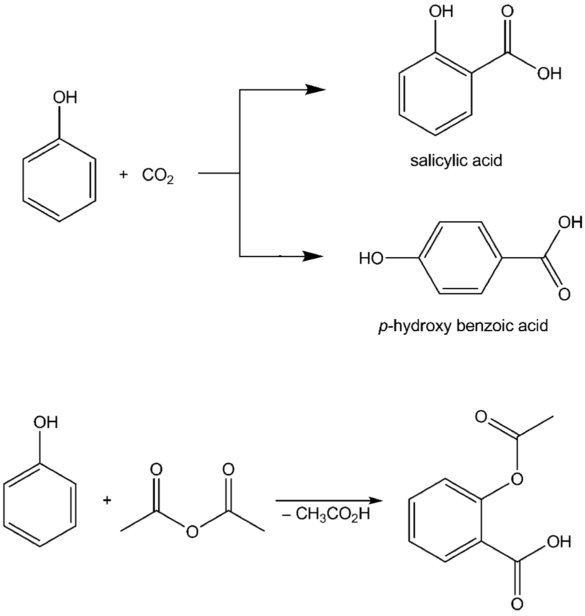
Fig. 2. Integrated process scheme for the catalytic hydrogenation of CO_2 to free formic acid under continouos flow conditions using $scCO_2$ as the extractive mobile phase and a stationary IL phase containing the catalyst and the base.

During the reaction the $scCO_2/H_2$ phase moves through the reactor, and CO_2 as well as H_2 can diffuse into the IL phase where they react to formic acid at the catalyst. The solid base present in the IL phase stabilizes the formic acid in form of the typical formate adduct. The flow of $scCO_2$ is able to extract part of the formic acid from the reaction mixture provided that its vapor pressure in the base adduct is sufficiently large to make it soluble in the $scCO_2$ phase. Stable performance over more than 200 hours on stream was observed for selected combinations of catalyst, IL, and base. This illustrates how rational process design can help to overcome limitations encountered in batchwise operation through continuous-flow systems based on advanced fluids as reaction and separation media.

2.5 Insertion of CO_2 into the M–C bond – direct synthesis of aromatic carboxylic acids

The stoichiometric reaction of CO_2 with alkali phenolates yielding hydroxy carboxylic acids dates back to the 1870's [114 – 120]. Today the process is known as the Kolbe-Schmitt reaction, and either salicylic acid or *p*-hydroxy benzoic acid can be obtained selectively by choosing either sodium or potassium ions, respectively, to balance the anionic charge of the phenolate (Scheme 13). The *ortho* selectivity in the presence of sodium (and also lithium) ions is a result of the chelate effect exerted by these cations [121], while the larger potassium ions drive the reaction selectively towards the *para*-substituted product [122, 123]. The synthesis of pharmaceuticals like acetyl salicylic acid (ASS, Aspirin), and of dyes and pesticides are the main applications for salicylic acid.

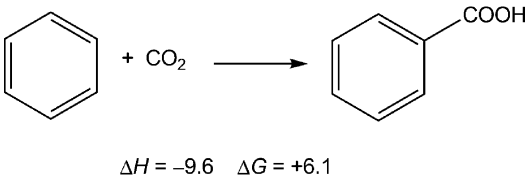
In general, aromatic carboxylic acids are important structural motifs in many pharmaceuticals, agrochemicals, and other fine chemicals and specialty products. The development of catalytic methods for the formal insertion of CO_2 into the C–H bonds of arenes would



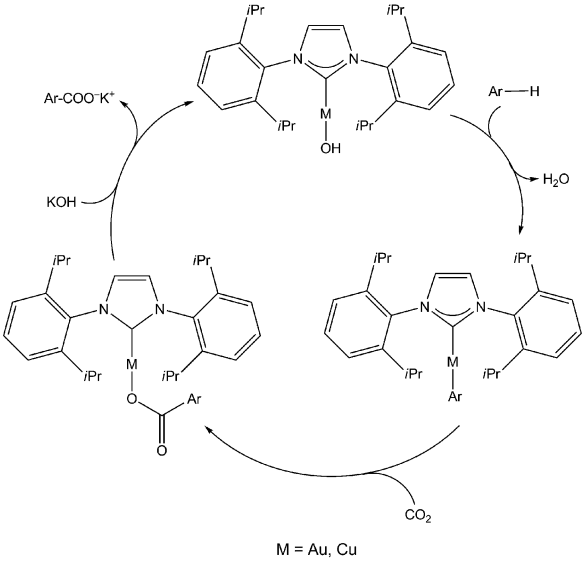
Scheme 13. Synthesis of *p*-hydroxybenzoic acid and salicylic acid, and further conversion to acetyl salicylic acid (ASS, Aspirin).

thus open a large field of possible synthetic applications. Despite significant recent progress this field is still in its infancy, and further fundamental academic research is needed to develop efficient systems. The insertion of CO_2 into the C–H bond of aromatic compounds suffers from the same thermodynamic limitations as the hydrogenation of CO_2 to formic acid making the utilization of an appropriate base inevitable. The carboxylation of benzene as a prototype reaction with the associated reaction enthalpy and the Gibbs free reaction energy is shown in Scheme 14.

Current synthetic techniques by which the CO_2 molecule can be introduced into arenes involve classical lithium or Grignard aryl compounds, aryl boronic esters [124, 125] or aryl halides [126, 127], which



Scheme 14. Synthesis of benzoic acid from benzene and CO_2 as a prototypical example for the direct carboxylation of arenes. Reaction energy and reaction Gibbs free energy in kcal mol^{-1}.



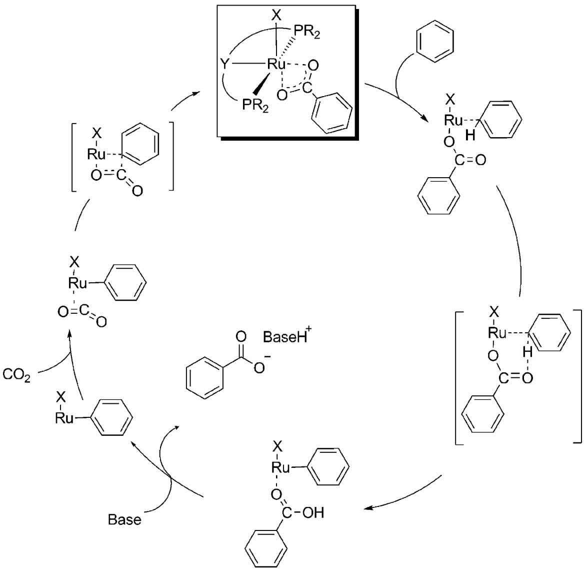
Scheme 15. Catalytic cycle of the insertion of CO_2 into the C–H bonds of arenes using gold and copper NHC catalysts.

makes the carboxylation an overall multistep process. An intriguing example for direct carboxylation of aromatic C–H bonds was presented recently by the group of Nolan who introduced gold hydroxy *N*-heterocyclic carbene (NHC) complexes as catalysts for the reaction of CO_2 with electron-deficient arenes [128 – 130]. Shortly after Nolan's report the group of Hou described similar insertions of CO_2 into such arenes using copper chloride NHC complexes [131]. The postulated reaction mechanism is shown in Scheme 15.

In the first step an acidic C–H group of the substrate reacts with the hydroxy group of the NHC complex liberating water. CO_2 subsequently inserts into the M–C bond with formation of the corresponding carboxylate, which is cleaved from the complex as its potassium salt regenerating the M–OH group at the metal complex. As stated above, the reaction relies on the acidity of the C–H bond, which is cleaved in the initial step and needs pK_A values of < 32, presenting a clear limitation in substrate scope.

The group of Iwasawa reported on the rhodium-catalyzed carboxylation of arenes with CO_2 initiated by directed metalation of substrates like 2-phenylpyridine or 1-phenylpyrazole [132]. Again, the insertion of CO_2 into the resulting Rh–C bond is believed to give the carboxylate intermediate. Regeneration of the active species by Rh–O cleavage and stabilization of the products in form of the thermodynamically favored esters requires two equivalents of aluminomethyl reagent per equivalent of substrate.

In order to assess systematically the various control factors that influence a potential catalytic cycle, a computational study investigating the potential of a series of ruthenium pincer complexes as catalysts in the direct carboxylation of benzene and related arenes was undertaken [133]. The study was based on a generally applicable catalytic cycle in which no special requirements as to the properties of the arene were made. The following assumptions guided the design of the catalytic cycle: Ruthenium phosphine complexes with coordinated benzoate ligands are available synthetically and have been characterized crystallographically. Such a benzoate complex should inevitably be present at some stage of the catalytic cycle if the formation of a C–C bond between CO_2 and a metal-bound arene does occur *via* an insertion mechanism. Ruthenium pincer complexes are widely known, and the typically observed meridional coordination mode allows within certain limits for a systematic variation of the electronic properties of the metal center. The starting point of the hypothetical catalytic cycle was therefore defined with a benzoate ligand coordinated bidentately at the metal center, while the third coordination site in the same plane is occupied by an anionic spectator ligand. The pincer ligand adopts the remaining three coordinations sites of an octahedrally coordinated ruthenium(II) center (Scheme 16).



Scheme 16. Postulated general mechanism for the direct carboxylation of benzene with CO_2 using ruthenium pincer catalysts. X = monodentate anionic ligand.

The first step of the catalytic process requires to open a coordination site by change from a bidentately coordinated benzoate to a monodentately coordinating one. The vacant coordination site is then filled by an incoming arene, which coordinates to the metal *via* the C–H bond. The first bond breaking/bond forming event consists of the H transfer from the arene in a σ-bond metathesis to a carboxylate oxygen atom. The carbon atom of the arene ring forms a covalent bond to the metal center, while the Ru–O linkage is changed from covalent to a simply coordinating mode. In the next step the trialkylamine base cleaves the benzoic acid from the complex and forms the typical ammonium benzoate adduct as product. The vacant coordination site at the metal is occupied at this stage by an incoming CO_2 molecule, which subsequently inserts into the Ru–C bond and in this way regenerates the catalytically active species.

Notably, the proposed catalytic cycle could be successfully modeled by location of all intermediates and transition states in a computational screening process for a large number of different ruthenium pincer catalysts. Predicted turnover frequencies were estimated following the analysis introduced recently by the group of Shaik [134–136] from computed catalytic cycles, allowing a detailed assessment of the relative changes in reaction rates associated with variations of individual components and parameters of the catalytic system. Based on these results, it was possible to identify catalyst lead structures which are predicted to generate TOFs high enough to yield benzoic acid derivatives under mild conditions. These results are expected to stimulate experimental work to synthesize such catalysts in order to validate the computational predictions.

3. Conclusion and Outlook

This short review highlighted current scientific developments in the utilization of CO_2 as a C1 building block for the industrial synthesis of chemical products. The following general conclusions can be drawn for the individual fields of potential application:

⇒ Very close to industrial realization or even in the state of becoming commercialized is the copolymerization of epoxides with CO_2 in the field of polycarbonate and polyurethane fabrication. The introduction of these new technologies into industrial processes would open a new chapter in the use of CO_2 as industrial feedstock on a large scale, resulting in improved carbon footprints for the production processes of these materials.

⇒ A significant impact on the carbon balance of the chemical and energetic supply chains could result from the combination of renewable hydrogen production with CO_2 reduction. For the CO_2-based production of methanol the development of a new catalyst technology is under way, and novel heterogeneous and homogeneous catalysts have provided new opportunities in this field. The synthesis of formic acid has reached a state where a large number of efficient catalysts are now available. The next level of innovation is expected to come from a process technology addressing the challenges of product separation and isolation resulting from the thermodynamic constraints of the transformation.

⇒ The direct catalytic carboxylation or aromatic substrates can offer a widely useful synthetic strategy ("catalytic Kolbe-Schmitt chemistry"), and first attempts to identify lead structures for catalysis development are providing promising results. However, large efforts in fundamental research are still required to arrive at synthetically useful and reliable methods of general applicability.

It is important to note that the rapid progress in this field in the last few years was based on three main pillars:

1) Strong dynamics initiated by significant funding schemes targeting the area in a strategic way.

2) Close interaction between academic research and industrial drivers brought together by open forms of collaboration in appropriate formats.

3) A strong basis in fundamental research in this field which has developed over decades, advancing largely by curiosity-driven and visionary endeavors.

Obviously, points 1 and 2 would not have been possible without the foundation of point 3. This should be taken as an important message to ensure sufficient room for fundamental academic research in modern science policy and funding, as it provides the grounds for technological and industrial innovation and will continue to lay the basis of sustainable solutions for current and future global challenges.

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[1] BP Statistical Review of Global Energy, **2012**; www.bp.com/statisticalreview (retrieved August 31, 2012).

[2] F . Schüth in *Die Zukunft der Energie*, (Eds.: P. Gruss, F. Schüth), C. H. Beck, München, **2008**, pp. 15 – 31.

[3] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, Th. E. Müller, *Energy Environ. Sci.* **2012**, *5*, 7281 – 7305.

[4] M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, **2010**.

[5] W. Kuckshinrichs, P. Markewitz, J. Linssen, P. Zapp, M. Peters, B. Köhler, Th. E. Müller, W. Leitner, *Weltweite Innovationen bei der Entwicklung von CCS-Technologien und Möglichkeiten der Nutzung und des Recyclings von CO_2*, Schriften des Forschungszentrums Jülich, Vol. 60, Jülich **2009**; ISBN 978-3-89336-617-0.

[6] P. Heffer, M. Prud'homme, 79th IFA Annual Conference, Montreal (Canada), 23 – 25 May **2011**.

[7] G. Pagani, *Hydrocarbon Process. Int. Ed.* **1982**, *61*, 87 – 91.

[8] J. A. Ritter, A. D. Ebner, *Sp. Sci. Technol.* **2007**, *42*, 1123 – 1193.

[9] M. Ahmadinejad, M. R. Desai, T. C. Watling, A. P. E. York, *Adv. Chem. Eng.* **2007**, *33*, 47 – 101.

[10] F. Asinger, *Methanol – Chemie und Energierohstoff. Die Mobilisation der Kohle*, Springer, Berlin **1986**.

[11] W. Keim, H. Offermanns, *Nachr. Chem.* **2010**, *58*, 434 – 435.

[12] A. Behr, *Carbon Dioxide Activation by Metal Complexes*, Wiley-VCH, Weinheim **1988**.

[13] T. Sakakura, J. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365 – 2387.

[14] W. Leitner, *Coord. Chem. Rev.* **1996**, *153*, 257 – 284.

[15] W. Leitner, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207 – 2221.

[16] W. Keim, A. Behr, H. Rzehak, *Tenside* **1979**, *3*, 113 – 116.

[17] J. P. Bianchini, B. Wegell, E. Gaydou, H. Rzehak, W. Keim, *J. Mol. Catal.* **1981**, *10*, 247 – 252.

[18] A. Behr, W. Keim, G. Thelen, *J. Organomet. Chem.* **1983**, *249*, C38–C40.

[19] A. Behr, E. Herdtweck, W. A. Herrmann, W. Keim, W. Kipshagen, *Chem. Commun.* **1986**, 4263.

[20] A. Behr, K. D. Juszak, W. Keim, *Synthesis* **1983**, 574.

[21] D. Vogt, Habilitation Thesis, RWTH Aachen, Aachen **1998**.
[22] A. Behr, G. Henze, *Green Chem.* **2011**, *13*, 25 – 39.
[23] A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski, S. Reyer, *Angew. Chem. Int. Ed.* **2009**, *48*, 3598 – 3614.
[24] A. Behr, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661 – 678.
[25] A. Behr, K.-D. Juszak, W. Keim, *Synthesis* **1983**, 574.
[26] A. Behr, K.-D. Juszak, *J. Organomet. Chem.* **1983**, *255*, 263 – 268.
[27] A. Behr, R. He, K.-D. Kuszak, C. Krüger, Y.-H. Tsay, *Chem. Ber.* **1986**, *119*, 991 – 1015.
[28] H. Hoberg, S. Schaefer, *J. Organomet. Chem.* **1982**, *236*, C28–C30.
[29] H. Hoberg, S. Schaefer, *J. Organomet. Chem.* **1983**, *251*, C51–C53.
[30] H. Hoberg, A. Ballestros, A. Sigan, C. Jegat, A. Milchereit, *Synthesis* **1991**, 395 – 398.
[31] H. Hoberg, S. Schaefer, G. Burkhart, C. Krüger, M. J. Romão, *J. Organomet. Chem.* **1984**, *266*, 203 – 224.
[32] H. Hoberg, D. Schaefer, B. W. Oster, *J. Organomet. Chem.* **1984**, *266*, 313 – 320.
[33] H. Hoberg, K. Jenni, C. Krüger, E. Raabe, *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 810 – 811.
[34] H. Hoberg, K. Jenni, *J. Organomet. Chem.* **1987**, *322*, 193 – 201.
[35] H. Hoberg, K. Jenni, K. Angermund, C. Krüger, *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 153 – 155.
[36] D. Walther, *Coord. Chem. Rev.* **1987**, *79*, 135 – 174.
[37] D. Walther, G. Bräunlich, R. Kempe, J. Sieler, *J. Organomet. Chem.* **1992**, *436*, 109 – 119.
[38] D. Walther, H. Schönberg, E. Dinjus, *J. Organomet. Chem.* **1987**, *334*, 377 – 388.
[39] D. Walther, E. Dinjus, J. Sieler, L. Andersen, O. Lindqvist, *J. Organomet. Chem.* **1984**, 395 – 398.
[40] E. Dinjus, J. Kaiser, J. Sieler, D. Walther, *Z. Anorg. Allg. Chem.* **1981**, *483*, 63 – 68.
[41] J. Kaiser, J. Sieler, U. Braun, L. Golic, E. Dinjus, D. Walther, *J. Organomet. Chem.* **1982**, *224*, 81 – 87.
[42] D. Walther, E. Dinjus, H. Görls, J. Sieler, O. Lindqvist, L. Andersen, *J. Organomet. Chem.* **1985**, *286*, 103 – 114.
[43] Y. Sakaki, Y. Inoue, H. Hashimoto, *J. Chem. Soc., Chem. Commun.* **1976**, 605 – 606.
[44] Y. Inoue, Y. Sasaki, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2375 – 2378.
[45] Y. Inoue, Y. Itho, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3320 – 3333.
[46] Y. Fukue, S. Oi, Y. Inoue, *J. Chem. Soc., Chem. Commun.* **1994**, 2091.
[47] Y. Inoue, H. Izumida, Y. Sasaki, H. Hashimoto, *Chem. Lett.* **1976**, 863 – 864.
[48] A. Musco, C. Perego, V. Tartiari, *Inorg. Chim. Acta* **1978**, *28*, L147–L148.
[49] T. Yamamoto, K. Igarashi, S. Komiya, A. Yamamoto, *J. Am. Chem. Soc.* **1980**, *102*, 7448 – 7456.
[50] S. Saito, S. Nakagawa, T. Koizumi, K. Hirayama, Y. Yamamoto, *J. Org. Chem.* **1999**, *64*, 3975 – 3978.
[51] D. J. Darensbourg, M. W. Holtkamp, *Coord. Chem. Rev.* **1996**, *153*, 155 – 174.
[52] D. J. Darensbourg, *Inorg. Chem.* **2010**, *49*, 10765 – 10780.
[53] D. A. Palmer, R. van Eldik, *Chem. Rev.* **1983**, *83*, 651 – 731.
[54] D. Gibson, *Chem. Rev.* **1996**, *96*, 2063 – 2095.
[55] D. H. Gibson, *Coord. Chem. Rev.* **1999**, 185 – 186, 335 – 355.
[56] X. Lin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27 – 59.
[57] C. Song, *Catal. Today* **2006**, *115*, 2 – 32.
[58] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510 – 8537.
[59] M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, Th. E. Müller, *ChemSusChem* **2011**, *4*, 1216 – 1240.
[60] W. A. Herrmann in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 3 (Eds.: B. Cornils, W. A. herrmann), 2nd ed., Wiley-VCH **2002**, pp. 1297 – 1304.
[61] M. Aresta, F. Nobile, V. G. Albano, E. Forni, M. Manasero, *J. Chem. Soc., Chem. Commun.* **1975**, 636 – 637.
[62] G. Burkhart, H. Hoberg, *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 76.
[63] M. Aresta, C. Pastore, P. Giannoccaro, G. Kovacs, A. Dibenedetto, I. Papai, *Chem. Eur. J.* **2007**, *13*, 9028 – 9034.
[64] C. Bruckmeier, M. W. Lehenmeier, R. Reichhardt, S. Vagin, B. Rieger, *Organometallics* **2010**, *29*, 2199 – 2202.
[65] M. L. Lejkowski, R. Lindner, T. Kageyama, G. E. Bodiz, P. N. Plessow, I. B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S. A Schunk, M. Limbach, *Chem. Eur. J.* **2012**, doi:10.1002/chem.201201757.
[66] D. Ballivet-Tkachenko, S. Sorokina in *Carbon Dioxide Recovery and Utilization* (Ed.: M. Aresta), Kluwer Academic Publishers, Dordrecht **2003**, 261 – 277.
[67] T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312 – 1330.
[68] F. Arico, P. Tundo, *Russ. Chem. Rev.* **2010**, *79*, 479 – 489.

[69] T. Sakakura, J.-C. Choi, H. Yasuda, T. Takahashi, K. Kohno, S. Kitazume, L.-N. He, *Prepr. - Am. Chem. Soc., Div. Pet. Chem.* **2010**, *55*, 49.

[70] S. Fujita, B. M. Bhanage, M. Arai in *Progress in Catalysis Research* (Ed.: L. P. Bevy), Nova Science, New York **2005**, pp. 57 – 79.

[71] R. Zevenhoven, S. Eloneva, S. Teir, *Catal. Today* **2006**, *115*, 73 – 79.

[72] M. Aresta, A. Dibenedetto, C. Pastore, *Inorg. Chem.* **2003**, *42*, 3256 – 3261.

[73] M. Aresta, A. Dibenedetto, L. Gianfrat, C. Pastore, *Appl. Catal. A* **2003**, *255*, 5 – 11.

[74] M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, *J. Mol. Catal. A* **2006**, *257*, 149 – 153.

[75] D. Ballivet-Tkatchenko, S. Chambrey, R. Keiski, R. Ligabue, L. Plasseraud, P. Richard, M. Turunen, *Catal. Today* **2006**, *115*, 80 – 87.

[76] M. P. Kalhor, H. Chermette, S. Chambrey, D. Ballivet-Tkatchenko, *Phys. Chem. Chem. Phys.* **2011**, *13*, 2401 – 2408.

[77] L. Plasseraud. D. Ballivet-Tkatchenko, H. Cattey, S. Chambrey, R. Ligabue, P. Richard, R. Willem, M. Biesemans, *J. Organomet. Chem.* **2010**, *695*, 1618 – 1626.

[78] K. Kohno, J.-C. Choi, Y. Ohshima, A. Yili, H. Yasuda, T. Sakakura, *J. Organomet. Chem.* **2008**, *693*, 1389 – 1392.

[79] K. Kohno, J.-C. Choi, Y. Ohshima, H. Yasuda, T. Sakakura, *ChemSusChem* **2008**, *1*, 186 – 188.

[80] T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, *11*, 1312 – 1330.

[81] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* **2006**, *15*, 1664 – 1666.

[82] J. E. Dengler, M. W. Lehenmeier, S. Klaus, C. E. Anderson, E. Herdtweck, B. Rieger, *Eur. J. Inorg. Chem.* **2011**, 336 – 343.

[83] S. Liang, H. Liu, S. J. Y. G. B. Han, *Chem. Commun.* **2011**, *47*, 2131 – 2133.

[84] N. Takeda, S. Inoue, *Makromol. Chem.* **1978**, *179*, 1377 – 1381.

[85] A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed.* **2010**, *49*, 9822 – 9837.

[86] L.-N. He, J.-Q. Wang, J.-L. Wang, *Pure Appl. Chem.* **2009**, *81*, 2069, 2080.

[87] J. Melendez, M. North, P. Villuendas, *Chem. Commun.* **2009**, 2577 – 2579.

[88] W. Clegg, R. W. Harrington, M. North, R. Pasquale, *Chem. Eur. J.* **2010**, *16*, 6828 – 6843.

[89] R. Schwalm, P. Ball, H. Fullmann, W. Heitz, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1984**, *25*, 272 – 273.

[90] www.novomer.com (retrieved August 31, 2012).

[91] www.basf.com (retrieved August 31, 2012).

[92] W. Leitner, T. E. Müller, C. Gürtler, *Bayer Magazine, Annual Report 2010* (Ed.: J. Schäfer); Bayer AG, Leverkusen, **2011**, pp. 32 – 37.

[93] H.-J. Althaus, R. Hischier, M. Osses, A. Primas, S. Hellweg, N. Jungbluth, M. Chudacoff, *Life Cycle Inventories of Chemicals*, Swiss Center for Life Cycle Inventories, Dübendorf, **2007**.

[94] T. Mokrani, M. Scurrell, *Catal. Rev. Sci. Eng.* **2009**, *51*, 1 – 145.

[95] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, Wiley-VCH, Weinheim **2003**, pp. 30 – 36.

[96] G. Olah, A. Coeppert, G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim **2006**.

[97] L. C. Grabow, M. Mavrikakis, *ACS Catal.* **2011**, *1*, 365 – 384.

[98] W. Wang, S. Wang, X. Ma, J. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703 – 3727.

[99] F. Liao, Y. Huang, J. Ge, W. Zheng, K. Tedsree, P. Collier, X. Hong, S. C. Tsang, *Angew. Chem. Int. Ed.* **2011**, *48*, 2162 – 2165.

[100] www.mitsuichem.com (retrieved August 31, 2012).

[101] E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609 – 614.

[102] E. Balaraman, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2011**, *50*, 11702 – 11705.

[103] C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18122 – 18125.

[104] S. Wesselbaum, T. v. Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2012**, *51*, 7499 – 7502.

[105] F. Hutschka, A. Dedieu, W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1742 – 1745.

[106] T. Schaub, R. A. Paciello, *Angew. Chem. Int. Ed.* **2011**, *50*, 7278 – 7282.

[107] D. Preti, C. Resta, S. Squarcialupi, G. Fachinetti, *Angew. Chem. Int. Ed.* **2011**, *50*, 12551 – 12554.

[108] J. J. Anderson, D. J. Drury, J. E. Hamlin, A. G. Kent, WO 8602066, **1986**.

[109] M. J. Green, A. R. Lucy, M. Kitson, S. J. Smith, EP 0329337.

[110] T. Schaub, R. Paciello, K.-D. Mohl, D. Schneider, M. Schäfer, S. Rittinger, WO 2010149507, **2010**.

[111] Z. Zhang, Y. Xie, W. Li, S. Hu, J. Song, T. Jiang, B. Han, *Angew. Chem. Int. Ed.* **2008**, *47*, 1127 – 1129.

[112] Z. Zhang, S. Hu, J. Song, W. Li, G. Yang, B. Han, *ChemSusChem* **2009**, *2*, 234 – 238.

[113] S. Wesselbaum, U. Hintermair, W. Leitner, *Angew. Chem. Int. Ed.* **2012**, *51*, 8585 – 8588.

[114] S. Walendy, G. Franciò, M. Hölscher, W. Leitner in *Exp. Green Sustainable Chem.*, (Eds.: H. W. Roesky, D. K. Kennepohl), Wiley-VCH, Weinheim 2009, pp. 275 – 277.

[115] Y. Kosugi, Y. Imaoka, F. Gotoh, M. A. Rahim, Y. Matsui, K. Sakanishi, *Org. Biomol. Chem.* **2003**, *1*, 817 – 821.
[116] H. Kolbe, E. Lautemann, *Liebigs Ann. Chem.* **1860**, *113*, 125 – 127.
[117] H. Kolbe, E. Lautemann, *Liebigs Ann. Chem.* **1860**, *115*, 157 – 206.
[118] H. Kolbe, E. Lautemann, *Liebigs Ann. Chem.* **1860**, *115*, 178.
[119] R. Schmitt, *German Patent 29939*, **1884**, 233.
[120] R. Schmitt, *J. Prakt. Chem.* **1885**, *31*, 397.
[121] J. Markovic, J. P. Engelbrecht, S. Markovic, *Z. Naturforsch. A: Phys. Sci.* **2002**, *57*, 812 – 818.
[122] S. E. Hunt, J. I. Jones, A. S. Lindsey, D. C. Killoh, H. S. Turner, *J. Chem. Soc.* **1958**, 3152 – 3160.
[123] Z. Markovic, S. Markovic, N. Manojlovic, J. Predojevic-Simovic, *J. Chem. Inf. Model.* **2007**, *47*, 1520 – 1525.
[124] K. Ukai, M. Aoki, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2006**, *128*, 8706 – 8707.
[125] T. Ohishi, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2008**, *47*, 5792 – 5795.
[126] A. Correa, R. Martín, *J. Am. Chem. Soc.* **2009**, *131*, 15974 – 15975.
[127] A. Correa, R. Martín, *Angew. Chem. Int. Ed.* **2009**, *48*, 6201 – 6204.
[128] I. I. F. Boogaerts, S. P. Nolan, *J. Am. Chem. Soc.* **2010**, *132*, 8858 – 8859.
[129] I. I. F. Boogaerts, G. C. Fortman, M. R. L. Furst, C. S. J. Cazin, S. P. Nolan, *Angew. Chem. Int. Ed.* **2010**, *49*, 8674 – 8677.
[130] I. I. F. Boogaerts, S. P. Nolan, *Chem. Commun.* **2011**, *47*, 3021 – 3024.
[131] L. Zhang, J. Cheng, T. Ohishi, Z. Hou, *Angew. Chem. Int. Ed.* **2010**, *49*, 8670 – 8673.
[132] H. Mizuno, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 1251 – 1253.
[133] A. Uhe, M. Hölscher, W. Leitner, *Chem. Eur. J.* **2012**, *18*, 170 – 177.
[134] S. Kozuch, S. Shaik, *J. Am. Chem. Soc.* **2006**, *128*, 3355 – 3365.
[135] S. Kozuch, S. Shaik, *J. Phys. Chem. A* **2008**, *112*, 6032 – 6041.
[136] A. Uhe, S. Kozuch, S. Shaik, *J. Comput. Chem.* **2011**, *32*, 978 – 985.