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Electrocatalytic carbon dioxide reduction - A mechanistic study

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2 | Key intermediates in the hydrogenation and electrochemical reduction of CO_2

Abstract

Mimicking photosynthesis by (re)using carbon dioxide as a carbon feedstock for the production of hydrocarbons would enable a sustainable carbon cycle. Electrochemically, CO_2 can be reduced on copper electrodes to hydrocarbons, mainly methane and ethylene, and the integration of this process in a photo-electrochemical device could be a promising way to close the carbon cycle. Understanding the mechanism of this reaction is one of the keys to open up new, sustainable routes to carbon based fuels. In this chapter we aim to obtain more insights in the key intermediates that determine the selectivity of CO_2 reduction to various products, by comparing the electrochemical reduction of CO_2 to the metal-catalyzed hydrogenation and reduction of CO_2 both homogeneously in solution and heterogeneously in the gas phase. We distinguish four main pathways: (1) methane is formed via carboxyl (COOH) and carbon monoxide (CO), (2) methanol is formed via formate (HCOO) and formaldehyde, (3) ethylene is formed via the coupling of CO, leading to surface enolates, and (4) CO_2 is inserted into existing carbon chains, close to the way CO_2 is fixed in nature.

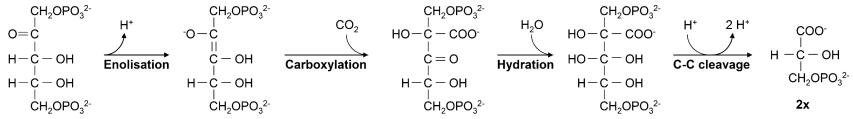

Figure 2.1 Carbon dioxide fixation in the Calvin cycle.

2.1 Introduction

To further our understanding of the mechanistic aspects of the electrochemical conversion of CO_2, it is worthwhile to compare this mechanism with other hydrogenation reactions of CO_2. Both homogeneous and heterogeneous catalysis have been used to convert CO_2 to various hydrocarbons, *i.a.* carbon monoxide, methanol, methane, and formic acid.[6]

This chapter will focus on the reaction mechanisms of CO_2 reduction on a molecular level using metal catalysts. We will compare the electrochemical reduction of CO_2, using copper and other metal electrodes in solution, with the metal-catalyzed hydrogenation and reduction of CO_2, both homogeneously with metal complexes in solution, and heterogeneously in the gas phase, to obtain more insights into the key intermediates that determine the selectivity of CO_2 reduction to the various products. We will not discuss the technical and economical feasibility studies of the various ways in which CO_2 can be converted, for such discussions we refer to other recent literature.[7–10]

We will start with a brief mechanistic overview of CO_2 fixation as it takes place in nature. Next we will give an overview of the reaction mechanisms for the various processes that are based on the hydrogenation of CO_2 including (I) the synthesis of carbon monoxide via the reverse water-gas shift (RWGS) reaction, (II) the methanation of CO_2, (III) methanol synthesis, (IV) hydrocarbon synthesis, and (V) the hydrogenation of CO_2 to formic acid using homogeneous catalysis. We will discuss the latest insights into the mechanisms of the electrochemical CO_2 reduction using metal electrodes and metal complexes, and will finally compare the various mechanisms in a concluding section.

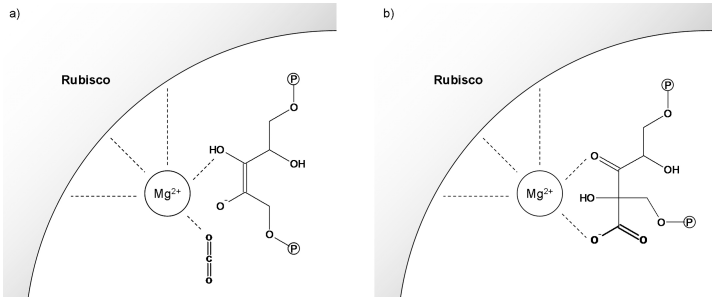

Figure 2.2 Carboxylation in the active site of Rubisco.

2.2 CO_2 fixation in the Calvin cycle

The conversion of CO_2 to carbohydrates in plants is called the Calvin cycle, named after Melvin Calvin who discovered the cycle in the 1950's (and who was awarded the Nobel Prize for Chemistry in 1961). In this cycle the energy of sunlight is used to fix CO_2 and convert it into triose phosphates.[11] The carbon fixation in the Calvin cycle can be broken down in four steps, as shown in Fig. 2.1. First, a proton is removed from ribulose-1,5-biphosphate, resulting in the formation of an enediolate intermediate. CO_2 binds to this enediolate to form a C_6 intermediate through a carboxylation reaction. This intermediate is hydrated in the next step, after which it breaks into two 3-phosphoglycerates.

After the carboxylation, the two 3-phosphoglycerates are converted into glyceraldehyde 3-phosphates, a three-carbon sugar phosphate. Five of these glyceraldehyde 3-phosphates are regenerated by converting them into three ribulose-1,5-biphosphates. So overall, three turns of the Calvin cycle yield one C_3 product, the glyceraldehyde 3-phosphate. These triose phosphates are used to synthesize hexose phosphates, which can be converted to (I) sucrose for transport, (II) starch for energy storage, (III) cellulose for cell wall synthesis, and (IV) pentose phosphates for metabolic intermediates.

The enzyme that catalyzes the carboxylation reaction is Ribulose-1,5-biphosphate carboxylase oxygenase (Rubisco). The active site of this enzyme contains an Mg^{2+} ion, that brings together and orients the reactants, as shown in Fig. 2.2.[12] Deprotonation of ribulose-1,5-biphosphate results in

the formation of the enediolate, shown in Fig. 2.2a. CO_2, polarized by the Mg^{2+} ion, is then added to the double C-C bond of the enediolate, resulting in the formation of a carboxylate, as shown in Fig. 2.2b.[11]

2.3 The mechanisms of CO_2 reduction using heterogeneous catalysis

2.3.1 Carbon monoxide synthesis via the reverse water-gas shift reaction

The formation of carbon monoxide from CO_2 via the reverse water-gas shift (RWGS) reaction,

$$CO_2 + H_2 \longrightarrow CO + H_2O \tag{2.1}$$

is one of the most promising ways to convert CO_2, for several reasons.[13] First, since the RWGS is an endothermic reaction, the reaction product CO is a way to store energy, *i.e.* the conversion of CO_2 to CO can be used to store hydrogen energy. Next, this reaction can be used to change the ratio of H_2/CO in syngas, allowing for selective hydrocarbon formation. Furthermore, the RWGS occurs as a side reaction in many processes where CO_2 and H_2 are present, for example in methanol synthesis. Finally, CO can be converted to various useful chemicals such as formic acid, methanol, formaldehyde, and long hydrocarbon chains.

Since the RWGS is a reversible reaction, catalysts active in the water-gas shift (WGS) reaction are often also active in the reverse reaction.[9]

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2.2}$$

Since Cu-based catalysts are the most studied for the WGS reaction, they are also applied for the RWGS reaction.[6] Examples of catalysts used for the RWGS are Cu-Ni/γ-Al_2O_3 and Cu-ZnO/Al_2O_3, the latter is used for methanol synthesis as well.[6] Cerium-based catalysts are also active in the (R)WGS reaction.[6,9]

The mechanism of the RWGS reaction is still controversial. According to two recent review articles, two main reaction mechanisms have been proposed: the redox-mechanism and the associative formate-mechanism.[6,9] In the redox-mechanism, the CO_2 dissociates directly to CO and O, followed

by the reduction of the oxide by hydrogen, resulting in the formation of water. On a Cu-based catalyst, this reaction can by modeled by:

$$CO_2 + 2\,Cu^0 \longrightarrow Cu_2O + CO \tag{2.3}$$

$$H_2 + Cu_2O \longrightarrow 2\,Cu^0 + H_2O \tag{2.4}$$

Both reaction 2.3 and 2.4 have been suggested as the rate determining step (RDS) for the (R)WGS.[14–17] Since it is a continuous process, the reduction of the oxidized Cu has to be faster than the oxidation process, and the RDS is probably the dissociation of CO_2.[6,16,18]

In the formate-mechanism, formate is formed by the association of hydrogen with CO_2. CO is subsequently formed by the decomposition of formate into CO and OH.

$$CO_2 \longrightarrow CO_{2,ads} \tag{2.5}$$

$$H_2 \longrightarrow 2\,H_{ads} \tag{2.6}$$

$$CO_{2,ads} + H_{ads} \longrightarrow HCO_{2,ads} \tag{2.7}$$

$$HCO_{2,ads} \longrightarrow CO + OH_{ads} \tag{2.8}$$

$$OH_{ads} + H_{ads} \longrightarrow H_2O \tag{2.9}$$

The dissociation of formate is assumed to be the RDS.[18] However, considering the mechanistic studies of the WGS reaction,[19,20] and taking into account the microscopic reversibility of the models used, it cannot be excluded that also in the RWGS carboxyl, COOH, is the intermediate to CO instead of formate. One indication why formate is unlikely as an intermediate to CO formation, is that formate binds bidentate with two O atoms to the surface, whereas CO binds with its C atom, which makes the reaction step from HCOO to CO + OH (reaction 2.8) very difficult.[19] Although adsorbed formate has been observed during the (R)WGS with several techniques, it could be only a spectator species.[19] Next to formate and carboxyl, carbonate has also been proposed as an intermediate for the RWGS reaction.[21]

2.3.2 Methanation of carbon dioxide

The hydrogenation of CO_2 to methane is an important process. This reaction, called the Sabatier reaction, can be used for the production of syngas

(via steam reforming), and is a way to store hydrogen energy and use this in the existing natural gas network.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \tag{2.10}$$

Supported Ni is the most studied catalyst material; other catalytic systems that are used for the Sabatier reaction are mainly based on Ru.[6,22]

Although differences in the rate and the selectivity for the methanation of CO_2 and CO are observed,[23] the general proposed mechanism of CO_2 hydrogenation is that CO_2 reacts to CO first, and subsequently follows the reaction mechanism of CO methanation.[6,22,24] For the first step, the formation of CO, it is proposed that, similar to the RWGS reaction and methanol synthesis, CO is formed via the decomposition of formate[6,22,25] or carboxyl.[24] Interestingly, it was proposed recently that the hydrogenation of CO_2 to formate (HCOO) is a dead-end in the reaction, and that only carboxyl (COOH) is leading to the formation of CO.[26]

The mechanism of CO methanation was proposed in the seventies to occur via an CH_xO intermediate,[27,28] but the generally accepted mechanism nowadays assumes the formation of surface carbon by CO dissociation via the Boudouard reaction, with subsequent hydrogenation.[6,22,24]

2.3.3 Methanol synthesis

The synthesis of methanol is an important industrial process, since methanol is an alternative fuel and an important building block for synthesis in the chemical industry; over 40 million tons of methanol are produced per year. Most methanol plants are fed by natural gas which is converted to syngas by steam reforming, and the syngas subsequently is converted to methanol using copper-based catalysts. It is a promising process since CO_2 and H_2 can be used as a starting material using the same catalysts.

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \tag{2.11}$$

The mechanistic details of the reaction of CO_2 to methanol are still a matter of debate. Two possible reaction pathways have been proposed for methanol synthesis from CO_2 and H_2 over Cu-based catalysts.[6,15,30] One pathway is the formate-pathway, in which the reaction to methanol proceeds through the formation of formate (HCOO), dioxomethylene (H_2COO), formaldehyde

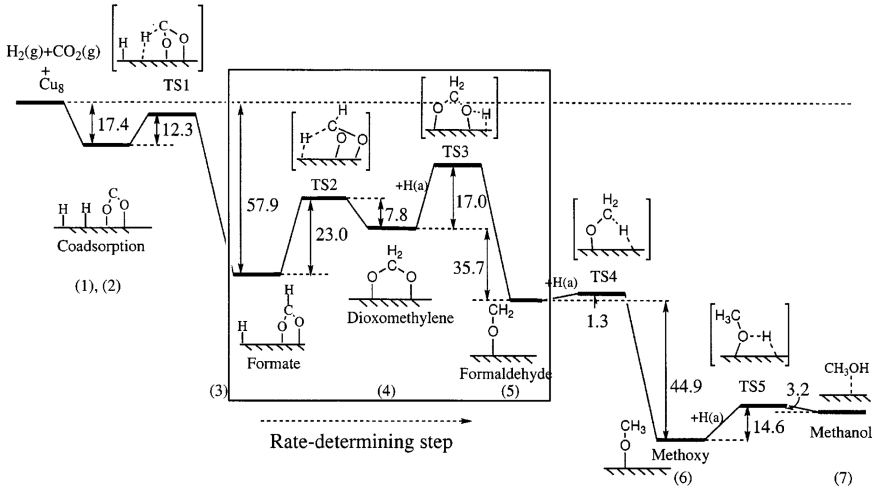

Figure 2.3 Hydrogenation of CO_2 to methanol via the formate-pathway on Cu(100). Reprinted with permission from Ref. 29. Copyright 2000 John Wiley & Sons, Inc.

(CH_2O), and methoxy (CH_3O). On Cu, this is usually considered as the predominant pathway.[15] An example of this pathway, calculated by Nakatsuji and Hu on Cu(100),[29] is shown in Fig. 2.3. There is no agreement in the literature on the RDS for this particular pathway. Usually the hydrogenation of adsorbed formate, as shown in Fig. 2.3, is considered to be the RDS,[29,31–34] but also the hydrogenation of dioxomethylene[15,35] or methoxy[36] have been proposed as the RDS.

The other pathway involves the RWGS reaction (2.1), where CO_2 is first converted to CO, which is then hydrogenated to form methanol.

$$CO + 2\,H_2 \longrightarrow CH_3OH \tag{2.12}$$

This RWGS-pathway can explain the formation of CO as the major byproduct during methanol synthesis from CO_2.[6,15,37] In this pathway, the CO will be hydrogenated to formyl (HCO) and formaldehyde (H_2CO) after which it will follow the same path as shown in Fig. 2.3. The overall RDS for the RWGS-pathway is the recombination of water from H and OH on the sur-

face.[15] Concerning the reduction of CO to methanol only, the hydrogenation of methoxy has the highest activation energy.[15,30,36]

To avoid undesired by-products, a highly selective catalyst is needed. Although many kinds of metal-based catalysts have been examined for the synthesis of methanol, modified Cu, in particular Cu/ZnO, remains the main active catalyst. Although this Cu/ZnO system has been studied extensively, there is no consensus in literature on the promotional role of ZnO, and on the active site of the catalyst. One proposition is that the active site is metallic Cu,[32,35] and that the ZnO improves the dispersion and stabilization of metallic copper.[6,15] On the other hand it has been proposed that the active site in methanol synthesis is a Cu^+ species, stabilized by the ZnO phase.[38–40] Recent work by Behrens *et al.* suggests that the active sites are steps at the Cu surface, alloyed with Zn.[41] The $Zn^{\delta+}$ at the steps increases the binding strength of oxygenated intermediates, which decreases the energy barriers in the reaction.

Other catalysts that have been used for methanol synthesis are Pd/β-Ga_2O_3, Cu/ZrO_2, and molybdenum sulfide.[6]

2.3.4 Synthesis of hydrocarbons

Hydrogenation of CO_2 to hydrocarbon chains would be the ultimate goal of CO_2 utilization. Investigations into this subject can be divided into two categories: methanol-mediated and non-methanol mediated.[6,42]

The hydrogenation of CO_2 via methanol is performed on a composite catalyst, a combination of the standard Cu-Zn catalyst used for methanol synthesis, with a zeolite used for the methanol-to-gasoline (MTG) process.[43,44] However, this method usually gives light alkanes as major hydrocarbon products because the methanol synthesis catalyst further hydrogenates the intermediate alkenes formed in the zeolites.[43,45]

The non-methanol mediated hydrogenation of CO_2 is usually performed using Fischer-Tropsch (FT) catalysts.[42] The most common metals in the FT process are cobalt and iron. Cobalt is the catalyst of choice in FT when long carbon chains are needed. However, when switching the feed gas from syngas to a gas mixture containing CO_2 and H_2, the product distribution changes significantly. In the presence of CO_2, cobalt acts as a methanation catalyst. Iron has a higher catalytic activity for the WGS reaction than cobalt, which means that under FT conditions CO_2 is formed from syngas,

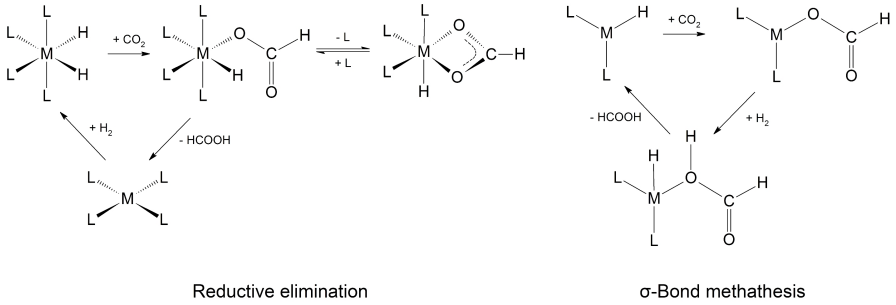

Figure 2.4 Reaction mechanisms of the hydrogenation of CO_2 to formic acid. 'M' represents a metal atom and 'L' a ligand group, which could also be the solvent.

making it often a less attractive FT catalyst. However, for the hydrogenation of CO_2 this is an advantage, since iron also catalyzes the RWGS reaction. CO_2 hydrogenation on Fe has been shown to occur in two steps: first CO_2 is converted to CO via the RWGS reaction, followed by chain propagation via the FT mechanism resulting in alkenes in the range C_2–C_5.[42,45]

It would go beyond the scope of this chapter to discuss the controversial FT mechanism in detail. Several different mechanisms have been proposed since the discovery in the 1920's.[46] Currently, the proposed mechanisms can be divided into two classes: according to the first class, CO or CH_xOH species are inserted into the growing hydrocarbon chain, after which the C-O or C-OH bond is broken. In the other class, the C-O or C-OH bond is broken first, leading to the formation of CH_x species that are incorporated into the growing chain. The currently generally accepted mechanism is the latter, where CO is dissociated first resulting in the formation of C_1 (CH_2) species, followed by FT chain growth.[46,47] The breaking of the C-O bond can be activated by the assistance of hydrogen, through the formation of adsorbed CHO or COH. Calculations on single-crystal surfaces have shown that this so-called "hydrogen assisted CO activation", is the optimum pathway on flat surfaces whereas at defects on the surface the direct dissociation of CO is favored.[47]

2.4 The mechanisms of CO_2 reduction using homogeneous catalysis

2.4.1 Synthesis of formic acid

The main product of CO_2 hydrogenation using homogeneous catalysis is formic acid. Formic acid has a wide range of applications in, for example, the leather industry and food preservation, and is a starting material for the production of various chemicals. Formic acid has also been proposed as a way to store hydrogen,[6,48] and as a fuel for formic acid fuel cells.[49] Complexes of several transition-metals are used to catalyze this reaction, *i.a.* rhodium, ruthenium and iridium.[6,50,51] Ru complexes often show the best activity and selectivity.[6]

$$CO_2 + H_2 \longrightarrow HCOOH \tag{2.13}$$

The key step in the reduction of CO_2 with H_2 to formic acid is the formation of the C-H bond. For the formation of this bond, formate has always been detected as an intermediate.[50] Formate is formed by the insertion of CO_2 into the metal-hydride bond. The binding of formate to the active site can be bidentate, ionic, or monodentate.[52,53] Various reaction mechanisms for the different metal complexes have been proposed,[6,51,52] but two fundamental different reaction mechanisms for the formation of formic acid are distinguished, as shown in Fig. 2.4.[54] In the mechanism shown in the left-hand panel of Fig. 2.4, the formate is formed upon oxidative addition of the CO_2, followed by reductive elimination of the formate by a hydride in the complex. On Rh, a different pathway is observed, with a smaller energy barrier compared with the reductive elimination mechanism, where the formic acid is formed from the formate directly from a dihydrogen complex by σ-bond metathesis.[52,54,55]

The reaction is often performed in organic solvents, but the addition of small amounts of water or alcohols has been shown to improve the catalytic hydrogenation of CO_2 to formic acid.[6,51,56] A proposed explanation is that hydrogen-bonding to the oxygen atom of CO_2 enhances the electrophilicity of carbon, thereby facilitating its insertion into the metal-hydride bond of the metal complex.[6,56]

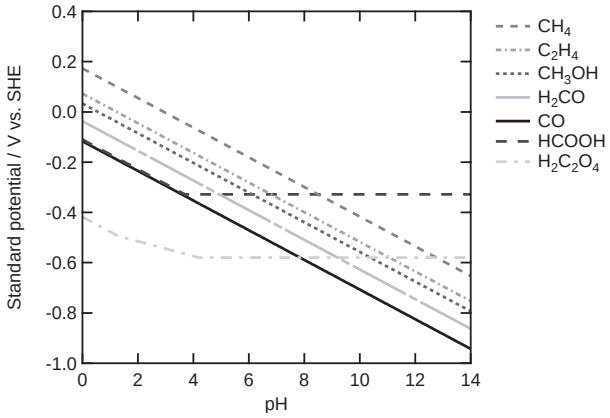

Figure 2.5 Standard potentials of various products of CO_2 reduction vs. pH.

2.4.2 Synthesis of other products

While active homogeneous catalysts for the production of formic acid have been discovered, there has only been a preliminary development of catalysts for the production of other products like methanol and CO.[51] The formation of CO is more thermodynamically favorable at elevated temperatures.[51] Using Ru complexes, the formation of CO, methanol and methane has been observed.[51,57] In this case, CO is observed as initial product, followed by the formation of methanol and methane, suggesting that methanol is formed from CO. For the formation of ethanol, a bimetallic catalyst of Ru and Co is used, where the Ru-complex is believed to be primarily responsible for the the reduction of CO_2 to CO and methanol, while the Co-complex is responsible for the formation of ethanol from methanol and CO.[51,57] Interestingly, the formation of ethanol was only observed in the presence of iodide.

2.5 Mechanisms of the electrochemical reduction of CO_2

The electrochemical reduction of carbon dioxide has attracted sustained attention in the past decades, for the synthesis of organic molecules as well as a possible means of energy storage, *e.g.* of high-energy electrons generated

by photo-excitation. The most common reaction products are those that require the transfer of 2 electrons,[58] *i.e.* formic acid, carbon monoxide, and oxalic acid, but examples of 6 and 8 electron conversions into *e.g.* methanol, ethylene and methane have also been reported:

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \tag{2.14}$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCO_2H \tag{2.15}$$

$$2CO_2 + 2H^+ + 2e^- \longrightarrow H_2C_2O_4 \tag{2.16}$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow H_2CO + H_2O \tag{2.17}$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \tag{2.18}$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \tag{2.19}$$

$$2CO_2 + 12H^+ + 12e^- \longrightarrow C_2H_4 + 4H_2O \tag{2.20}$$

Fig. 2.5 shows a Pourbaix diagram of the equilibrium potentials for the reduction of CO_2 to various products in water as a function of pH.[5,59,60] The formation of these products proceeds usually through proton-coupled multi-electron steps, that are generally more favorable than single electron reductions, since thermodynamically more stable molecules are formed.[59] The standard potential of the outer-sphere single electron reduction of CO_2 to $CO_2^{\cdot -}$ is -1.90 V vs. SHE in water, due to the large reorganizational energy needed for the formation of the bent radical anion.[59]

$$CO_2 + e^- \longrightarrow CO_2^{\cdot -} \tag{2.21}$$

Catalysts (partially) overcome the high overpotential for outer-sphere CO_2 reduction by binding and protonating the CO_2 species such that its stability is improved. Still, high overpotentials may lead to a broad product distribution, especially on heterogeneous catalysts. Therefore, considerable efforts have been made to find catalysts that not only lower the overpotential but also steer the selectivity of the reaction. Both homogeneous molecular catalysis and heterogeneous catalysis, mostly metals, have been investigated for these purposes.[61]

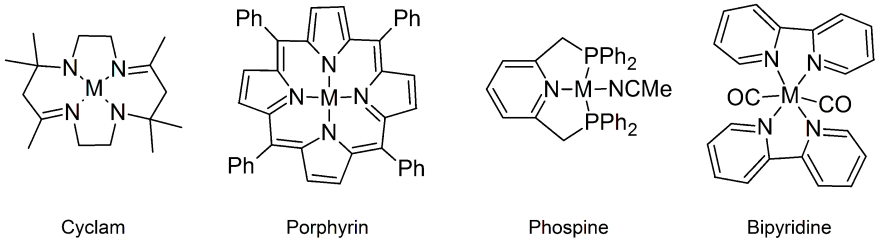

Figure 2.6 Examples of the types of metal complexes that are used to reduce CO_2.

2.5.1 Homogeneous electrocatalysis

The field of CO_2 (electro)reduction using transition metal complexes in non aqueous media started in the 1970's. In the homogeneously catalyzed reduction of CO_2, the reduced form of a reversible couple with an equilibrium potential negative to the reduction potential of CO_2 reacts with the CO_2 and generates the oxidized form. The reduction of the metal complex at the electrode starts a new catalytic cycle. With respect to homogeneous electrocatalysis, Savéant differentiates between redox catalysis and chemical catalysis.[60] In redox catalysis, the reduced form of the catalyst is only an outer-sphere electron donor, whereas in chemical catalysis the interactions between the catalyst and substrate are stronger, and involve the formation of an addition product between the catalyst and (a group of atoms initially belonging to) the substrate.[60]

Two families of transition metal complexes have been reported, namely Ag and Pd porphyrins, as well as some Ni macrocycles, that only form oxalate at potentials close to the $CO_2/CO_2^{\cdot -}$ couple, and therefore likely involve a redox or quasi-redox catalysis, in which electron transfer acts as a pre-equilibrium to the rate determining dimerization of $CO_2^{\cdot -}$. A quasi redox catalysis mechanism has also been reported for the reduction of CO_2 to oxalate by anion radicals of aromatic nitriles and esters.[60,62]

Electrocatalytic CO_2 reduction with metal complexes in solution typically proceeds through chemical catalysis.[60] The reported catalysts can be divided into different categories, as shown in Fig. 2.6: metal catalysts with macrocyclic ligands, which can be divided into cyclam-like and porphyrin-

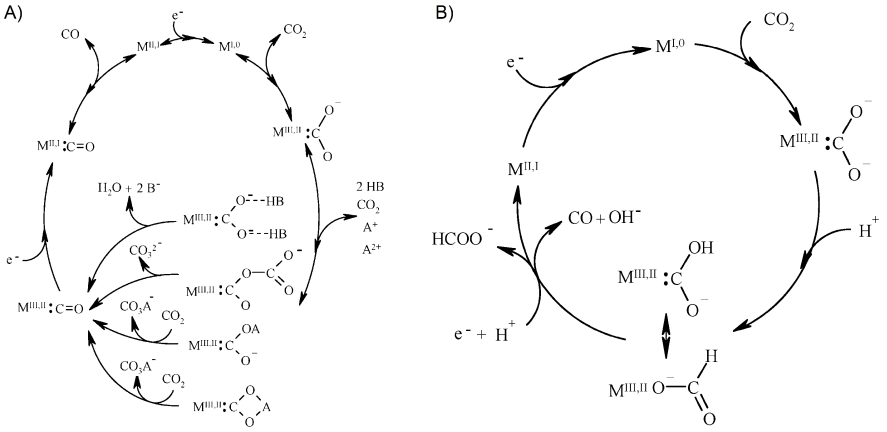

Figure 2.7 A) Various mechanisms for the reduction of CO_2 to CO in the presence of Lewis acids 'A' and weak Brønsted acids 'B'. B) Proposed mechanism for the reduction of CO_2 to CO and formate. Reprinted with permission from Ref. 60. Copyright 2008 American Chemical Society.

like complexes, metal catalysts with phosphine ligands, and metal catalysts with polypyridyl ligands.[59,60,63] The best efficiencies and/or selectivities are obtained with Ni (cyclams), Fe (porhyrins), Re and Ru (polypyridyls), and Pd (phosphines).

The most common reduction product using these catalysts is CO, at potentials much less negative than the $CO_2/CO_2^{\cdot -}$ couple, which clearly excludes a redox mechanism. Therefore, the first step in CO_2 reduction is most likely the coordination of CO_2 to the previously reduced metal complex.[60] On Ni cyclams this complexation has been shown to be stabilized by a strong back donation from Ni to CO_2. This causes an increase in negative charge at the O atoms of the CO_2, in a similar configuration to the $CO_2^{\cdot -}$ radical.[5,64] The presence of weak Brønsted acids and Lewis acids has been shown to stabilize the coordination of CO_2 and facilitate the breaking of the C-O bond to form CO, see Ref. 60 and references therein. Also water and CO_2 itself may have the same role as these acids. This has led to the proposed mechanisms for the formation of CO shown in Fig. 2.7A.[60,63,65,66]

The other common product obtained is formate. The suggested mechanism for the formation of formate, shown in Fig. 2.7B, is a proton-coupled electron transfer to the coordinated CO_2 that, depending on the catalyst, will lead to the formation of CO or formate.[60] Another mechanism, comparable to the reductive elimination reaction shown in Fig. 2.4, is via an internal hydride transfer to the coordinated CO_2.[63,67]

In some cases higher reduction products have been obtained with Ru complexes, *i.a.* formaldehyde, methanol, and even some C_2 species such as $CHOCO_2^-$ and $CH_2OHCO_2^-$.[68] These C_2 products, that are the result of 4 and 6 electron transfer reactions, are only possible if CO is a stable intermediate ligand that can be further reduced, and coupled with another CO_2. The nature of the catalyst is very important in this stabilization, and lower temperatures are used to stabilize the intermediates.[60,68] Interestingly, pyridinium has been shown to be able to reduce CO_2 to methanol through six sequential electron transfers.[69] This is probably the first case in which sequential one-electron transfers provide the low energy pathway for catalysis, in contrast to multi-electron transfer pathways. The mechanism of the reaction was studied on Pt electrodes with pyridinium in solution. Formic acid and formaldehyde were observed as intermediate products to the formation of methanol, and the reaction has been shown be first order in CO_2 and pyridinium.[69,70] The pyridinium radical is proposed as the actual catalyst[69,70] (although recent work by Keith and Carter suggests differently[71]). This radical can bind CO_2 and reduced intermediates through a coordinative interaction that stabilizes the intermediate species. The first step is the coordination of CO_2 to the pyridinium radical resulting in the formation of a carbamate species, suggesting a covalent N-C bond.[70] Subsequent electron transfer results in the formation of formic acid. Formic acid again is coordinated to a pyridinium radical and is, via the formyl-radical, reduced to formaldehyde. Coordination of formaldehyde results in hydroxymethyl, which is reduced to methanol. This mechanism suggests an inner-sphere-type electron transfer from the pyridinium radical to the intermediates for the various mechanistic steps, where the pyridinium radical is able to covalently bind the (radical) intermediate species and transfer the electron.

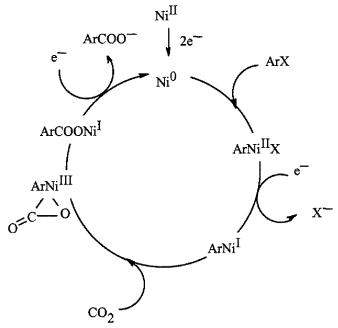

Figure 2.8 Mechanism of the carboxylation of aryl halides (ArX; X = Br, Cl, I). Reprinted with permission from Ref. 72. Copyright 2002 WILEY-VCH.

Electrochemical carboxylation

The application of CO_2 as a C_1 source in organic synthesis might be a way to CO_2 fixation, and could yield various useful carboxylic acids, including pharmaceuticals. In organic chemistry, low-valent Ni and Pd species are generated in situ from Ni^{II} or Pd^{II} precursors, and facilitate C-C coupling reactions.[72] Electrochemistry can provide an easy way to generate a desired oxidation state of a metal complex that becomes the active catalytic species for an organic reaction, at potentials that avoid the direct reduction of the organic compound. An example is the carboxylation of aryl halides.[72–74] The reaction was shown to proceed through Ni^0, Ni^I, Ni^{II} and Ni^{III} intermediates, as shown in Fig. 2.8. Another way of electrochemical carboxylation is the direct reduction of the organic compound, followed by the carboxylation.[74,75] An example is the carboxylation of α-chloroethylbenzene.[76] At the Pt cathode, the α-chloroethylbenzene is reduced, which effectively removes the chlorine. The reduced intermediate reacts with CO_2 to form the carboxylate. An Mg anode enhances the reaction, the created Mg^+ cations stabilize the carboxylate anions by producing an insoluble Mg salt that prevents oxidation or protonation.[76] Hindering the competing protonation reaction is also the reason why this direct carboxylation is usually performed in organic electrolytes or ionic liquids.

2.5.2 Heterogeneous electrocatalysis

The conversion of CO and CO_2 to hydrocarbons using heterogeneous catalysis is usually performed at elevated temperatures and pressures. The direct electrochemical conversion of CO_2 would allow a process that avoids high temperatures, and where the production rate can be controlled directly, depending on the availability of surplus electricity. Only a few metals are active in this process, and the product distribution is broad, depending heavily on the applied potential, the electrode material and electrolyte used.

Aqueous media

In aqueous media, metals can be divided roughly into 4 groups, based on the products formed during the electrochemical CO_2 reduction.[3,5] The first group includes the metals that evolve hydrogen at low potentials and with a high CO adsorption strength, such as Ni, Fe, Pt, and Ti. On these metals CO_2 is reduced to strongly bound CO that blocks further reduction. Therefore, the main product on these metals is hydrogen.

The second group of metals are those with a high hydrogen overvoltage and a very low CO adsorption strength, such as Sn, In, Tl, Pb, Hg, Bi, and Cd. Since the reduced intermediates are not, or very weakly adsorbed on the surface, these metals are not able to catalyze the breaking of the C-O bond in CO_2. These metals facilitate the conversion of CO_2 to formic acid with high current efficiencies. On Hg, formic acid is formed with 100% current efficiency. The first step in the formation of formic acid is the formation of $CO_2^{\cdot -}$. The formation of this radical is observed in aqueous and non aqueous solutions, and during its formation and subsequent reduction only a very small fraction of the electrode is covered by adsorbates (see Ref. 5 and references therein). The subsequent reduction and protonation of $CO_2^{\cdot -}$ to formate does not depend on pH, which shows that the proton donor is not H^+ but H_2O. This indicates a mechanism, in which CO_2 is reduced to $CO_2^{\cdot -}$ in solution, followed by the protonation by water to form $HCO_2^{\cdot}$ and its subsequent reduction to $HCOO^-$:

$$CO_2 + e^- \longrightarrow CO_2^{\cdot -} \tag{2.22}$$

$$CO_2^{\cdot -} + H_2O \longrightarrow HCO_2^{\cdot} + OH^- \tag{2.23}$$

$$HCO_2^{\cdot} + e^- \longrightarrow HCO_2^- \tag{2.24}$$

The third group of metals produces mainly CO. These include Au, Ag, Zn, and Ga, metals with a weak CO adsorption and a medium hydrogen overvoltage. The potentials at which CO is formed on these metals is less negative compared with the potentials where formic acid is formed, especially on Au.

Hori has shown that the heat of fusion of the various metal electrodes correlates well with the potentials of CO_2 reduction.[3] The heat of fusion is related to the *d*-electron contribution to the metallic bond, and may be taken as a measure of *d*-electron availability, which affects the strength of CO_2 adsorption. Therefore, metals with a higher heat of fusion adsorb CO_2 stronger, and reduce it at lower potentials. In this context, the CO and HCOOH forming metals are well separated; CO is formed at less negative potentials on metals with a higher heat of fusion. This suggests a different mechanism for the formation of CO, where the intermediate(s) are much more stabilized, *i.e.* adsorbed at the electrode.[5]

A similar relation between adsorption strength and overpotential has been suggested by Peterson and Nørskov, who investigated the correlation between the binding energies of the intermediates of CO_2 reduction vs. CO (for intermediates binding to the surface through carbon) and vs. OH (for intermediates binding to the surface through oxygen) for various transition metals.[77] From these binding energies, the limiting potential can be derived, at which each elementary step of a reaction becomes exergonic. The protonation of adsorbed CO is singled out as the most important step dictating the overpotential, with Cu having the lowest overpotential compared with other transition metals.

Hori suggested a mechanism for the formation of CO where the CO_2 is bound to the surface, coordinated in a similar way to the CO_2 shown in Fig. 2.7B,[5] as has has been calculated for the Ni cyclams discussed in section 2.5.1.[64] The negative charge on the O atoms then facilitates the protonation, and formation of adsorbed COOH. The next step is the breaking of the C-O bond, and the formation of CO and OH^-:

$$CO_2 + e^- \longrightarrow CO^-_{2,ads} \tag{2.25}$$

$$CO^-_{2,ads} + H_2O \longrightarrow COOH_{ads} + OH^- \tag{2.26}$$

$$COOH_{ads} + e^- \longrightarrow CO + OH^- \tag{2.27}$$

The fundamental possibility of the reversible conversion of CO_2 to CO and formate has been illustrated by Armstrong and Hirst.[78] They have discussed the immobilization of enzymes (carbon monoxide dehydrogenase (CODH) and formate dehydrogenase (FDH)) on electrodes and showed that the electrocatalytic conversion of CO_2 on these electrodes is reversible, *i.e.* they convert CO_2 to CO or formate and vice versa around the equilibrium potential of the corresponding redox couple. For the interconversion of CO_2 and CO by CODH, CO_2 binds at reducing potentials as a bridging ligand between the Ni and the dangling Fe atom in the [Ni4Fe-4S] active site. Then, CO migrates to Ni, and OH forms on Fe.[79] In contrast to metal surfaces, these highly efficient active sites can bind and stabilize the intermediate due to the precisely positioned functional groups and thereby lower the overpotential, or kinetically couple the formation and onward reaction of the intermediates. Moreover, enzymes seem to avoid the formation of poisons, such as CO, which frustrate the development of metallic formic acid oxidation catalysts.

Only a few metals can catalyze the conversion of CO_2 to hydrocarbons. The most interesting metal is Cu, with a moderate CO adsorption, where methane and even C_2 species such as ethylene are formed in significant amounts.[80] Some other metals such as Mo and Ru are able to convert CO_2 to methanol and methane, but with low efficiencies.[81,82]

Copper electrodes

In 1985, Hori discovered that on copper electrodes CO_2 can be reduced to hydrocarbons, mainly methane and ethylene.[2,80] Next to these hydrocarbons, also CO and formic acid are formed during CO_2 reduction. Also oxygenates such as ethanol and propanol are observed, although usually only in trace amounts.[4,5] Recently, up to 16 different reduction products have been observed.[83]

In spite of the extensive literature on carbon dioxide reduction on copper electrodes, the detailed mechanism of this reaction is still unclear.[4] It is known that ethylene and methane are formed through a different reaction mechanism and that carbon monoxide is a key intermediate in the formation of both ethylene and methane.[3,84,85] The exact reaction mechanism of carbon monoxide reduction to either ethylene or methane is still debated. Interestingly, methanol is not or produced only in very small amounts on a

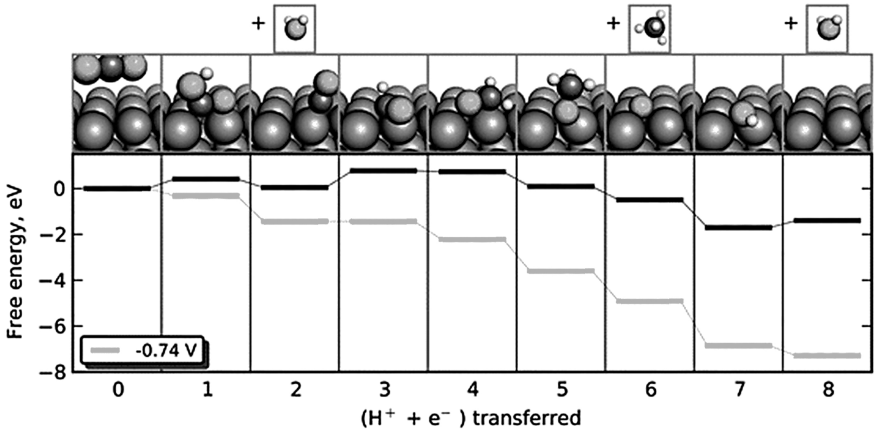

Figure 2.9 Free energy diagram for the lowest energy pathway to CH_4. The black pathway represents the free energy at 0 V vs. RHE and the gray pathway the free energy at the indicated potential. Reprinted with permission from ref. 86. Copyright 2010 Royal Society of Chemistry.

metallic Cu electrode, suggesting that the C-O bond is broken early in the reaction.[5]

The formation of methane from CO depends on pH, in such a way that the rate determining step must involve the transfer of a proton and an electron.[84] Recently, DFT calculations by Peterson *et al.* (see Fig. 2.9), as well as our own experiments presented in Chapter 3, suggested that the key intermediate to form methane is CHO_{ads}.[86] A similar path, but via adsorbed COH has been suggested by Hori.[84]

The formation of ethylene from CO, on the other hand, does not depend on pH.[84] Therefore, a dimer of carbon monoxide, whose formation does not involve the transfer of an hydrogen atom but does depend on potential (*i.e.* involves electron transfer), has been suggested as the key intermediate in the C-C coupling, see Chapter 3 for more details. A Fischer-Tropsch-like mechanism where CO is coupled to CH_x species cannot explain the observed selectivity to ethylene. We will show in Chapter 3 that the only C_2 species that can be reduced to ethylene is ethylene oxide, suggesting a shared oxametallacycle intermediate for the reduction reactions of CO_2 and ethylene

oxide. Enol-type species have also been proposed as key intermediates in the formation of C_2 species by Kuhl *et al.*[83]

Hori *et al.* showed that the extent of methane and ethylene formation sensitively depends on the surface orientation of the copper electrode.[87] On the (111) facet of the copper fcc crystal the formation of methane is favored, whereas on the (100) facet the formation of ethylene is dominant. Recent DFT calculations predicted that the limiting potential for the formation of the intermediates of the CO_2 reduction to CH_4 is lower on the Cu(211) surface compared with the Cu(111) and Cu(100) surface.[88]

Using Online Electrochemical Mass Spectrometry (OLEMS) we will show in Chapter 5 that on Cu(100), CO can be selectively reduced to ethylene at low overpotentials, whereas at higher potentials ethylene and methane are formed simultaneously both on Cu(100) and Cu(111), suggesting two different pathways for the formation of ethylene from CO.

Interestingly, methanol has been observed as a product of CO_2 reduction on intentionally oxidized Cu electrodes.[81,89] The electronic properties of Cu(I) in *p*-Cu_2O are thought to play an important role in the adsorption of CO_2, causing a stronger binding of CO_2 and CO on *p*-Cu_2O and other Cu(I) centers.[81] *p*-Cu_2O covered Cu has been shown to be able to absorb atomic O into the bulk Cu.[81] This might facilitate the dissociation of CO_2, but the exact mechanism leading to methanol is still unclear. Recently, Li and Kanan have shown that thick Cu_2O films catalyze the reduction of CO_2 to CO and HCOOH with high faradaic efficiencies at low overpotentials.[90]

Non aqueous media

The electrochemical reduction of CO_2 in non aqueous solutions, *e.g.* methanol, propylene carbonate or dimethyl sulfoxide, has several advantages compared with the reduction in water. The solubility of CO_2 is higher, and the hydrogen evolution is heavily suppressed. The main products are CO, HCOOH and $(COOH)_2$.[5] CO is the main product in non aqueous media on Cu, Ag, Au, Zn, In, Sn, Ni, and Pt. $(COOH)_2$ is formed on Cu, Sn, Ag, Zn, In and Au. Some metals form both CO and $(COOH)_2$, like Fe, Cr, Mo, Pd, and Cd. HCOOH is formed on Pt, Pb, Hg, Ag and Au. On Cu, hydrocarbons such as CH_4 and C_2H_4 have also been obtained.

The product selectivity is mainly determined by whether or not the reduced CO_2 is stabilized at the electrode surface. Metals like Hg and Pb

reduce CO_2 at potentials close to the potential of the $CO_2/CO_2^{\cdot-}$ couple (2.21).[5] The main product is oxalate or formate, depending on the concentration of water.[5,91] Therefore, Savéant *et al.* proposed that oxalate is formed by the dimerization of $CO_2^{\cdot-}$, similar to the oxalate formation in homogeneous catalysis.[91]

$$2\,CO_2^{\cdot-} \longrightarrow C_2O_4^{2-} \tag{2.28}$$

An alternative route to oxalate is the coupling of CO_2 to $CO_2^{\cdot-}$ resulting in the formation of $(CO_2)_2^{\cdot-}$, which is further reduced to oxalate.[5,92]

Formate is formed in a similar way as suggested for aqueous media and for homogeneous catalysis, where the small amount of water present reacts as a Lewis acid and protonate the $CO_2^{\cdot-}$ (2.23).[5,60,91] Increasing water concentrations in non-aqueous media lead to increasing formate, and decreasing oxalate formation.

On the metals that stabilize the reduced intermediates to a much greater extent, like Au, Zn and Ag, the main product is CO. In the absence of water, CO_2 reacts as a Lewis acid with adsorbed CO_2^- to form $OCOCO_2^-$, in a comparable way as occurs in homogeneous catalysis, depicted in Fig. 2.7A.[5,60] The breaking of the C-O bond then results in the formation of CO and CO_3^{2-}:

$$CO_2 + e^- \longrightarrow CO_{2,ads}^- \tag{2.29}$$

$$CO_{2,ads}^- + CO_2 \longrightarrow OCOCO_2^- \tag{2.30}$$

$$OCOCO_2^- + e^- \longrightarrow CO + CO_3^{2-} \tag{2.31}$$

2.5.3 Photoelectrochemical CO_2 reduction

The ultimate goal of CO_2 reduction would be to couple the CO_2 electrocatalyst to light harvesting by photo-excitation. This would yield a kind of artificial photosynthesis device to store the energy of sunlight in hydrocarbons. The basic steps always involve (I) the absorption of light to generate an excited state, (II) charge separation of the created electron-hole pair, (III) the energy of this charge separated state is used to reduce CO_2, (IV) catalyst regeneration.

The photoreduction of CO_2 can be divided into two general categories: the first category includes the homogeneous systems, which are entirely

molecule based.[93] The molecular light absorber and the catalyst could be the same molecule, or a molecular light absorber and a transition metal catalyst work in concert. In the second category, a semiconductor is used for the light absorption and charge separation steps, after which this energy is transfered to a homogeneous or heterogeneous catalyst.

The most frequently used photosensitizers in homogeneous systems are Ru(II) polypyridyl complexes, such as $[Ru(bpy)_3]^{2+}$. This photosensitizer (P) is irradiated by light and forms an excited state, P^*. This excited state is quenched by an electron donor (D), typically triethylamine, to P^-. The reduced photosensitizer in turn reduces the catalyst (cat), which then reduces the CO_2.[94]

$$P + h\nu \longrightarrow P^* \tag{2.32}$$

$$P^* + D \longrightarrow P^- + D^{\cdot+} \tag{2.33}$$

$$P^- + cat \longrightarrow P + cat^- \tag{2.34}$$

$$cat^- + CO_2 \longrightarrow cat + products \tag{2.35}$$

Cobalt and nickel macrocylic compounds are often used as catalysts. Sometimes the catalyst is linked to the photosensitizer in a supramolecular complex to increase the efficiency of the electron transfer to the catalyst.[94] Metalloporphyrins with Fe and Co can react both as a light absorber and a catalyst.[94] The obtained products are mainly CO and formate, in a similar way as described in section 2.5.1.[94,95]

Semiconductors have been shown to be efficient in the conversion of incident photon energy into electrical energy.[93] The semiconductor could be an electrode or a colloid. If the semiconductor surface is not electrocatalytically active, the separated charge has to be transfered to a catalytic species, which could be adsorbed on the surface or a species in solution. On these electrodes, not only the usual two-electron reduction products, formate and CO, are observed, but also formaldehyde and methanol.[95] A special case is *p*-GaAs. On the (111) facets of this electrode, the (photo)-electrochemical reduction of CO_2 to methanol with a current efficiency close to 100 % has been reported.[81,95] The mechanism for methanol formation is unclear. Even without applied potential and illumination, arsenic-rich surfaces of GaAs spontaneously produce CH_3OH, which is attributed to dissolution of the semiconductor in carbonic acid, resulting in the formation of Ga and As hydroxides and methanol.[96]

2.6 Discussion and conclusions

In this chapter, we have compared various mechanisms for the catalytic reduction of carbon dioxide, with particular emphasis on the low-temperature electrocatalytic reduction. The reduction of carbon dioxide may yield a variety of products, and most of these reactions tend to suffer from slow kinetics and/or poor selectivity. From the electrochemical point-of-view, only the conversion of carbon dioxide to carbon monoxide or to formic acid have been shown to be potentially reversible.[78] This is indeed expected for two-electron transfer reactions. In electrocatalysis, thus far this feat has only be accomplished with enzymes, whereas in heterogeneous catalysis the (reverse) water gas shift reaction is also known as a reversible catalytic reaction, though at higher temperature. No synthetic room-temperature electrocatalyst has yet been developed which can do the same. Such a catalyst would be extremely interesting for formic acid fuel cells, and its reversible counterpart, *i.e.* carbon dioxide and hydrogen storage in formic acid. Higher-energy fuels from carbon dioxide require the transfer of more than 2 electrons, and this invariably leads to overpotential losses.[58,77]

We believe that there are four main pathways for CO_2 reduction to high-energy fuels. The first pathway is methanation, which is the thermodynamically most favorable process. A key intermediate, not only in this pathway but also in the FT process and the electrochemical reduction of CO_2 on copper electrodes, is carbon monoxide. In all processes described in this chapter the intermediate leading to CO is carboxyl, COOH, with the only exception being the RWGS reaction for which a pathway via formate, HCOO, has been proposed. However, as argued in section 2.3.1, there is evidence that also in the RWGS carboxyl is the intermediate to CO, instead of formate. A next important step in the methanation is the breaking of the C-O bond in carbon monoxide. This dissociation can be either directly, forming surface carbon, or hydrogen assisted via the formation of CH_xO species. The latter has also been suggested for the electrochemical reduction of CO and CO_2, where CHO is considered to be the key intermediate in the formation of methane. It is not only the nature of the metal catalyst which determines whether or not CO can be dissociated. Cu and Ru are methanation catalysts, both under electrochemical and heterogeneous gas phase conditions. Under electrochemical conditions the methane formation rate is much higher on Cu, whereas under gas phase conditions Ru is far more active.[81] Frese has

attributed the higher activity of Ru in the gas phase to a higher hydrogen coverage compared with Cu, since the chemisorption of H_2 is more favorable on Ru, and to Ru being able to dissociate CO on defect sites whereas Cu binds CO normally in a non-dissociated form. The higher methanation rate on Cu under electrochemical conditions has been explained by the ability of Cu to allow large overpotentials without hydrogen evolution overwhelming the CO_2 reduction reaction. The high potential, in combination with the HCO formation, is here the driving force for the dissociation of CO.

The second pathway is the formation of methanol. It seems that methanol is always formed via the formate-formaldehyde route, as has been evidenced for methanol synthesis and for the (photo)-electrochemical reduction using pyridinium. Stabilization of the various intermediates, *e.g.* by adding ZnO to the Cu catalyst or as observed on the pyridinium by covalent bonding to the radical, seems to play an important role. Oxidized copper also seems to offer this (structural) stabilization, since on oxidized copper electrodes the formation of CO and HCOOH is enhanced,[90] and even the formation of methanol has been observed.[89] The formate-formaldehyde route also explains why methanol is not observed when CO_2 is reduced on metallic copper electrodes, as on copper formate cannot be further reduced.[4,5] On the other hand, C_2 oxygenates are, in low quantities, observed on copper electrodes. This is consistent with a reaction mechanism involving early breaking of the C-O bond, followed by C-C bond formation between CO or CO_2 and the reduced intermediate. Interestingly, heterogeneous gas phase catalysts which are effective for methanol synthesis are in general ineffective for C_2 oxygenate formation, and metals that are active in C_2 oxygenate formation are known to favor CO dissociation.[97]

The third pathway is the pathway that leads to ethylene, observed during the electrochemical reduction on copper electrodes. This reaction has been discovered and described in great detail by Hori, and is investigated further in this thesis. Ethylene is normally formed simultaneously with methane, although at lower overpotentials the formation of ethylene is favored, and formed via a carbon monoxide intermediate. In this thesis, its formation is suggested to involve reductive CO coupling and ene(di)ol(ate) intermediates. The dehydroxylation of enol-like surface species also explains the formation of C_2 and C_3 oxygenated species, such as ethanol. An enol is also the intermediate to the C-C bond formation in the Calvin cycle.

The fourth pathway is closest to the way CO_2 is fixated in nature through the Calvin cycle, namely through CO_2 insertion into an existing carbon chain, and subsequent carboxylate reduction. In electro-organic synthesis, this strategy is known as electrocarboxylation, but it has not gained much popularity yet as a sustainable solution for fuel production. It is interesting that the same Mg_2^+ ion that plays an important role in the active site of the carboxylation enzyme in the Calvin cycle, strongly enhances the electrocarboxylation reaction.[76]

In conclusion, the (electrochemical) reduction of CO_2 to interesting products, such as potential fuels, can take place through a variety of different pathways, and the pathway selected is highly sensitive to the catalyst material, electrode (over)potential, pH, electrolyte composition, solvent, etc. Although some common patterns can be observed, as discussed in some detail in this chapter, it appears that many pathways are similar in energy, involving intermediates with similar stability. This makes the search for or development of active and selective catalysts highly interesting but also highly challenging. Catalyst stability is an additional issue, that we have not touched upon in any detail, but that will clearly be crucial for any future deployment of this technology.