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**General Introduction**

## 1.1 Carbon dioxide emission and our fossil fuel ‘addiction’

Carbon dioxide plays a vital role in the biosphere and, in fact, life as we know it would not be possible without carbon dioxide, since carbon dioxide is the primary source of carbon in life on Earth. The main sources of carbon dioxide emitted into the atmosphere are either natural sources, including respiration, decay, volcano’s, geysers and hot springs, and man-made sources, including (fossil fuel) combustion and industrial processes. Processes that counteract the emission of carbon dioxide by removing it from the atmosphere include dissolution of carbon dioxide in the oceans, the growth of plants and micro-organisms and the formation of carbonate deposits in the Earth’s crust. For centuries these processes maintained a delicate balance in which an equilibrium concentration of 280 ppm carbon dioxide in the atmosphere was reached. After the Industrial Revolution, between 1760-1840, the concentration of carbon dioxide started to increase due to additional man-made emissions to 380 ppm in 2005.<sup>1</sup>

The noticeable increase in carbon dioxide concentration in the atmosphere is mostly due to the ever increasing consumption of fossil energy, which is speculated to account for >80% of the increase.<sup>2</sup> It has been estimated that amount of carbon dioxide that will be emitted in the 21<sup>st</sup> century will range anywhere from 3480 Gt to 8050 Gt, which is a huge amount compared to the 1100 Gt carbon dioxide that was emitted between 1850 and 2000.<sup>3</sup> Therefore the concentration of carbon dioxide in the atmosphere is projected to increase more heavily in the 21<sup>st</sup> century. Our dependency on the processes that emit carbon dioxide is clearly reflected in the way that our energy is generated. Over 75% of the energy is generated from fossil energy sources, such as coal, petroleum and natural gas.

The rising concentrations of carbon dioxide in the atmosphere can have serious consequences for the biosphere and the conditions on Earth. Since the oceans are the largest natural sink for carbon dioxide, storing carbon dioxide in the form of bicarbonate and carbonate ions, an increase in carbon dioxide concentration will lead to an increase in the amount of carbon dioxide that is dissolved in the oceans. This will lead to an increase in the acidity of ocean water, with unknown consequences for marine life. Furthermore, since carbon dioxide is

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a greenhouse gas, an increase in carbon dioxide concentration in the atmosphere can lead to a rise in global temperature. This rise in temperature is believed to cause the melting of glaciers and (sea) ice in the polar regions of the Earth. The melting of these icecaps will lead to a rise in sea level, potentially threatening the coastal populations.

## 1.2 Carbon dioxide utilization; closing the carbon cycle

Several options exist to control the rising emission of carbon dioxide. The first is to increase the energy efficiency and utilization of the existing processes that produce carbon dioxide. Secondly, the capture and sequestration of carbon dioxide is an option to mitigate rising carbon dioxide levels.<sup>2,4</sup> A third option is the development of techniques that can convert carbon dioxide in useful chemicals and fuels.<sup>5,6</sup> This last option of carbon dioxide conversion would be the most renewable solution on the long term, while the other options, such as carbon dioxide storage, would only enable the continued use of fossil fuels on the short term.

Nowadays carbon dioxide is already used as a chemical building block in the production of chemicals such as urea, salicylic acid and polycarbonates.<sup>5,6</sup> Unfortunately, the demand for these chemicals is low in comparison with the amount of carbon dioxide that is emitted from the consumption of fossil fuels. Furthermore, supercritical CO<sub>2</sub> is used as solvent in a number of applications, for instance in enhanced oil recovery (EOR), owing more to its physical properties than its chemical reactivity. Carbon dioxide can also be converted to carbon monoxide via the water gas shift reaction:



The produced carbon monoxide can then be converted to methanol by hydrogenation over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at elevated pressures and temperatures.<sup>7</sup> Furthermore, via the Fischer-Tropsch process CO can be hydrogenated to hydrocarbons at elevated pressures and temperatures. Both processes are commercially available from the technical point of view, however

the availability and costs of hydrogen, particularly if the requirement is production using renewable energy, is an issue.<sup>8</sup>

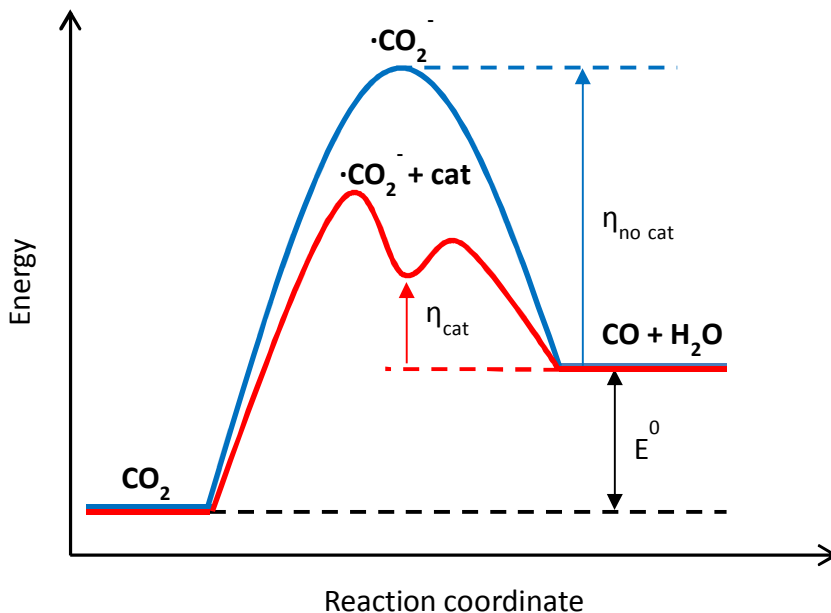
An alternative method for producing useful chemicals from CO<sub>2</sub> is the direct electrocatalytic reduction of CO<sub>2</sub> with renewable electrical energy.<sup>9,10</sup> A major advantage of this route is that only mild conditions are required, meaning no energy loss in the form of elevated temperatures or pressures. In addition, if the reduction of CO<sub>2</sub> could be steered towards the formation of products which can be used as fuels, one could close the anthropogenic CO<sub>2</sub> cycle by converting CO<sub>2</sub> into fuels which will release CO<sub>2</sub> upon use.

### 1.3 Electrocatalysis

Catalysis is defined as a chemical process in which the rate of reaction is enhanced by a substance, i.e. the catalyst, which is not consumed by the process.<sup>11</sup> A catalyst stabilizes reaction intermediates, thereby enhancing the rate of reaction (see Figure 1). Two main forms of catalysis are recognized: homogeneous catalysis, in which the catalyst is in the same phase as the reactants, and heterogeneous catalysis, where the reaction takes place at or near the interface between phases. The catalysis described in this thesis is heterogeneous electrocatalysis, meaning that the heterogeneous process that is catalyzed is an electrochemical process involving the transfer of electrons.

In electrocatalysis, an electrochemical half reaction is studied that takes place at the so-called working electrode. In the studies described in this thesis the working electrode is typically a solid metal electrode or a carbon electrode with nanoparticulate catalysts deposited on it. The working electrode is immersed in an electrolyte, in our case an aqueous salt solution, that is conductive and ensures that there is an electrical connection between the working electrode and the counter electrode. The potential on the working electrode is measured versus a standardized electrochemical reaction such as the  $2\text{H}^+ + 2\text{e}^- / \text{H}_2$  couple (called the reversible hydrogen electrode).

Every electrochemical half reaction has a standard equilibrium potential ( $E^0$ ), indicating the electrode potential of the reaction (referenced against the potential of the abovementioned hydrogen electrode), at which the reaction is theoretically in thermodynamic equilibrium. In practice often a potential very different from this equilibrium potential needs to be applied to ensure that the reactions proceeds in one or the other direction. This additional potential is denoted as the overpotential ( $\eta$ ) of a reaction. The overpotential of a reaction is typically caused by the existence of energetically unfavorable intermediates. For the electrocatalytic  $\text{CO}_2$  reduction such a limiting step is the formation of a  $\text{CO}_2^{\cdot-}$  radical intermediate, as is depicted in Figure 1.1, which is highly unstable. By offering a different, energetically more favorable, reaction pathway, the catalyst decreases the energy necessary to form this  $\text{CO}_2^{\cdot-}$  radical, thereby decreasing the necessary overpotential.



**Figure 1.1** A reaction scheme for the electrocatalytic reduction of  $\text{CO}_2$  to  $\text{CO}$ . A catalyst can change the energy of reaction intermediates, thereby changing the overpotential ( $\eta$ ) that is needed to drive the reaction and improving its energy efficiency.

Electrocatalysts are not only evaluated through the reduction of the overpotential that they can achieve for an electrochemical reaction, but also by comparing the current density, product distribution and the faradaic efficiency by which they form products. The current density that is observed for an catalyzed electrochemical reaction at a certain applied potential is the current normalized by the electrochemically active surface area of the catalyst. The current density is a measure for how fast an electrochemical reaction proceeds. Since the catalytic reactions take place on the surface of the heterogeneous catalyst, a normalization for the active surface area of the catalyst ensures that a fair comparison between catalysts is made.

Product distribution and the faradaic efficiency toward the formed products are important measures since they display the preference of a catalyst to form (desired) products. The product distribution on a catalyst shows which products are formed by the catalyst during the studied reaction. This can vary significantly between electrocatalysts, depending on the studied reaction. The faradaic efficiency for a certain product, sometimes also denoted as current efficiency, is the fraction of the total current, or transferred electrons, that is consumed in forming that product.<sup>12</sup>

Ultimately, a good and efficient electrocatalyst will thus display a high faradaic efficiency toward a desired product and will catalyze the reaction in such a way that a high current density is observed at low overpotential.

## 1.4 Scope and outline of this thesis

The focus of the research presented in this thesis lies on the development of selective and efficient nanostructured electrocatalysts for the reduction of CO<sub>2</sub> to valuable or useful chemicals.

In Chapter 2 we will give a review of heterogeneous and molecular electrocatalysts for the reduction of CO<sub>2</sub>, and discuss the reaction pathways through which they form various products. These mechanistic insights, together with mechanistic insights of CO<sub>2</sub> reduction on other metals and molecular

complexes, can provide crucial guidelines for the design of future catalyst materials able to efficiently and selectively reduce CO<sub>2</sub> to useful products.

Although the electrochemical reduction of CO<sub>2</sub> on copper electrodes is an intensively studied reaction, there has not been much attention for CO<sub>2</sub> reduction on copper in alkaline electrolytes, because this creates a carbonate buffer in which CO<sub>2</sub> is converted into bicarbonate (HCO<sub>3</sub><sup>-</sup>) and the pH of the electrolyte decreases. In Chapter 3, we show that electrolytes with phosphate buffers which start off in the alkaline region and, after saturation with CO<sub>2</sub>, end up in the neutral region, behave differently compared to CO<sub>2</sub> reduction in phosphate buffers which start off in the neutral region. In initially alkaline buffers a reduction peak is observed, which is not seen in neutral buffer solutions. In contrast with earlier literature reports we show that this peak is not due to the formation of a CO ad-layer on the electrode surface but due to the production of formate from bicarbonate reduction. The intensity of the reduction peak is influenced by electrode morphology and the identity of the cations and anions in solution.

In Chapter 4 we show that electrodeposited palladium on platinum, a good formic acid oxidation catalyst, has an onset potential for CO<sub>2</sub> reduction to formic acid that is dramatically reduced in comparison to bulk palladium. Two different reaction pathways are observed: a pathway at low overpotential in which formic acid is produced from either direct bicarbonate reduction or from the reduction of CO<sub>2</sub> generated from bicarbonate near the surface, and a pathway at more negative potentials where formic acid is produced from direct CO<sub>2</sub> reduction. Furthermore, we show that reversible formic acid oxidation and CO<sub>2</sub> reduction is possible on this catalyst, although unfortunately the processes are hindered by poisoning of the catalyst, most likely by CO.

In Chapter 5 we report on the synthesis of Pd<sub>x</sub>Pt<sub>(100-x)</sub>/C nanoparticles and their electrocatalytic properties for the reduction of CO<sub>2</sub> to formic acid, compared with their activity for the reverse oxidation of formic acid to CO<sub>2</sub>. We find that Pd<sub>x</sub>Pt<sub>(100-x)</sub>/C nanoparticles have a very low onset potential for the reduction of CO<sub>2</sub> to formic acid of ca. 0 V vs. RHE, which approaches the theoretical

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equilibrium potential of 0.02 V vs. RHE for this reaction. Furthermore, the Pd<sub>70</sub>Pt<sub>30</sub>/C catalyst shows a faradaic efficiency of 88% towards formic acid after 1 hour of electrolysis at -0.4 V vs. RHE with an average current density of ≈5 mA/cm<sup>2</sup>. Therefore this catalyst shows a competing or even better faradaic efficiency towards formic acid compared to recently reported catalysts, at a substantially lower overpotential, while avoiding the strong deactivation that was observed with the Pd-based catalysts reported in Chapter 4.

The electrochemical reduction of CO<sub>2</sub> to valuable products, especially hydrocarbons, is a reaction of considerable interest to both scientists and society since it is a potential reaction for energy storage and conversion. Copper has been long known to be a unique catalyst for CO<sub>2</sub> reduction, since it is the only catalyst able to produce methane, ethylene and ethane from CO<sub>2</sub> with decent faradaic efficiencies. The special catalytic properties of copper have recently been related to its ability to bind and protonate CO, a key intermediate for the production of hydrocarbons, efficiently. In Chapter 6 we report on the design and synthesis of a new non-copper-containing catalyst that is able to reduce CO<sub>2</sub> to C<sub>1</sub> to C<sub>5</sub> hydrocarbons. This catalyst was designed by combining a metal that binds CO too strongly, i.e. palladium, with a metal that binds CO too weakly, i.e. gold, in an effort to tune the binding energy of CO on this bimetallic catalyst.

The production of formic from electrochemical CO<sub>2</sub> reduction is especially relevant, since formic acid can be used as a fine chemical and fuel. In Chapter 7 we test Pd<sub>70</sub>Pt<sub>30</sub> nanoparticles, which have been shown in Chapter 5 to have great promise for formic acid production, on different support materials to study the effect of the support on the efficiency of formic acid production. A clear support effect can be seen for both the electro-oxidation of formic acid and the reduction of CO<sub>2</sub> to formic acid on these catalyst. In addition, we test the nanoparticles on different supports in a gas diffusion electrode setup in an effort to assess the applicability of this catalyst.

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