1 | Introduction

1.1 Motivation

Carbon dioxide is the main product of the oxidation of hydrocarbons. Since hydrocarbon-based fuels are the world's most important energy source, the use of fossil fuels has lead to significant increases of atmospheric CO_2 levels, and they are not expected to level down in the coming decades unless drastic measures are taken.[1] The increasing presence of CO_2 in the atmosphere is causing a widespread concern about its possible consequences. On the other hand, from a more positive perspective, CO_2 is a vast and sustainable carbon feedstock, that could partly replace the widespread use of petroleum-based hydrocarbons as chemical building blocks. Therefore, converting carbon dioxide into hydrocarbons would not only limit the emission of carbon dioxide, but also supply us with a sustainable carbon feedstock, provided the conversion is performed using renewable energy, and without much additional CO_2 production. In this way, the re-usage of the carbon dioxide caused by human emissions would enable a sustainable carbon cycle. If the produced hydrocarbons can be used as fuels, a carbon energy cycle is created. Such a carbon-based energy cycle has two main advantages compared to other proposed energy cycles that are, for example, based on storing energy in hydrogen or batteries. First, hydrocarbons have a higher energy density, and second, storage is easier and there will be no need to change the existing fuel infrastructure, provided the generated fuel is a liquid.

In the Earth's natural carbon cycle, photosynthesis is one of the most important processes through which CO_2 is recycled. CO_2 is inserted in carbon

chains using the energy from sunlight to create carbohydrates, which are used in nature as chemical building blocks and energy carriers. Although these fuels used by nature are oxygen-rich, in contrast to fossil fuels that are oxygen poor and therefore more energy rich, mimicking photosynthesis would still be an attractive way to close our carbon-based energy loop, and to create a sustainable carbon energy cycle.

One of the promising ways to convert carbon dioxide into hydrocarbons is to do this electrochemically, and to ultimately integrate such a process in a photo-electrochemical device. An auspicious discovery in this area was made by Hori in 1985, who showed that CO_2 can be directly converted to hydrocarbons on copper electrodes.[2] Only copper electrodes catalyze this reaction to a significant extent, and the main carbon products are methane and ethylene.[3] Ample research has been performed to understand the electrochemical reduction on the molecular level, but in spite of the extensive literature, the molecular mechanism is still a matter of debate.[4,5] With the renewed interest in solar fuels and CO_2 reduction and recycling, the mechanistic details of the electrochemical CO_2 reduction have become a topical subject of interest again in recent years. Understanding the mechanism of this reaction is important as it would open up routes to the production of high energy fuels by the (photo-)electrochemical reduction of CO_2.

1.2 Outline of this thesis

The focus of this thesis is on the electrochemical reduction of CO_2 on copper electrodes, and in particular on the mechanistic aspects of this reaction. We start in Chapter 2 by comparing the reaction mechanisms of the electrochemical reduction of CO_2 to the reaction mechanisms of the metal-catalyzed hydrogenation and reduction of CO_2, both heterogeneously in the gas phase and homogeneously in solution, to obtain more insights in the key intermediates that determine the selectivity of CO_2 reduction to the various products.

In Chapter 3, we identify key intermediates that determine if CO_2 is reduced to methane or ethylene. Identification of intermediates could lead to new ways in which the reaction rate can be increased, or the selectivity of the reaction can be tuned towards desired products. We describe how we have identified new intermediates by reducing small organic species, to

investigate whether or not they can be reduced to either methane or ethylene on copper electrodes.

The formation and stabilization of these intermediates also depends on the atomic configuration of the electrode surface. Therefore, we have studied the reduction of CO, a well known intermediate of CO_2 reduction on copper electrodes, by using copper single crystals. The use of Cu single crystal electrodes requires a method to carefully characterize the surface structure. Therefore, we have developed a characterization method using blank voltammetry in alkaline media, which is presented in Chapter 4.

In Chapter 5 we have investigated the reduction of CO on two different Cu(*hkl*) basal planes, *viz.* Cu(100) and Cu(111). We have observed two different reaction mechanisms for ethylene formation: a first pathway that has a common intermediate with the formation of methane and that takes place preferentially at (111) facets or steps, and a second pathway at (100) facets in which CO is selectively reduced to ethylene at relatively low overpotentials.

Since the (100) orientation turned out to be very important for selective ethylene formation we have studied stepped Cu single crystals to compare the reactivity of a surface with (100) terraces to a surface with (100) steps, the results of which are presented in Chapter 6.

The pH is another important parameter in the reaction mechanism. In Chapter 7 we have investigated the influence of the pH by reducing carbon dioxide and carbon monoxide on Cu(111) and Cu(100) single crystal electrodes at different pH values.