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Title: Electrocatalytic carbon dioxide reduction : a mechanistic study

Issue Date: 2013-10-08

Summary

Hydrocarbon-based fuels are worldwide the most important energy sources and energy carriers. The combustion of these hydrocarbons yields, apart from the desired energy, carbon dioxide (CO_2). This has led to significant increases of atmospheric CO_2 levels, which 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 sustainable energy, and without much additional CO_2 production.

Already in the 1980s it has been discovered in Japan that it is possible to reduce CO_2 to methane and ethylene using copper electrodes. The formation of methane and especially ethylene is surprising, and only takes place to a significant extent on copper electrodes. In spite of the extensive literature, the molecular mechanism is still unclear, in particular in relation to the carbon-carbon coupling step leading to the formation of ethylene. Understanding this C-C bond formation is important as it could open up routes to the production of high-energy fuels by the (photo-)electrochemical reduction of CO_2 . The research presented in this thesis is focused on the understanding of the molecular mechanism of the electrochemical reduction of carbon dioxide using copper electrodes. We have aimed to identify intermediates that determine the selectivity of the reaction to either methane or ethylene.

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In Chapter 2 we have aimed to obtain more insights in the key intermediates that determine the selectivity of CO₂ reduction to various products, by comparing the electrochemical reduction of CO₂ to the metal-catalyzed hydrogenation and reduction of CO₂ both homogeneously in solution and heterogeneously in the gas phase. Based on this comparison we have distinguished 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) CO₂ is inserted into existing carbon chains, close to the way CO₂ is fixed in nature.

In Chapter 3, we have identified key intermediates that determine if CO₂ is reduced to methane or ethylene by reducing C₁ and C₂ species containing oxygen, to investigate whether or not they can be reduced to either methane or ethylene on copper electrodes. For the the C₁ pathway to methane we have shown that it is very likely that CHO_{ads} is the key intermediate towards the breaking of the C-O bond and, therefore, the formation of methane. For the C₂ pathway to ethylene we have suggested that the first step is the formation of a CO dimer, followed by the formation of a surface-bonded enediol or enediolate, or the formation of an oxametallacycle. Both the enediol(ate) and the oxametallacycle would explain the selectivity of the C₂ pathway towards ethylene.

The formation and stabilization of these intermediates also depends on the atomic configuration of the electrode surface. We have used copper single crystals in order to study this structure dependence. 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. The adsorption of OH⁻ on copper electrodes in alkaline media appeared to be surface structure dependent, which allows for identification and characterization of the various single crystal facets.

In Chapter 5 we have compared the reduction of carbon monoxide (CO), a well known intermediate of CO₂ reduction on copper electrodes, on the single crystal surfaces Cu(111) and Cu(100). 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

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which CO is selectively reduced to ethylene at relatively low overpotentials. We have also shown in this chapter that the reduction of CO on polycrystalline copper is similar to the CO reduction on Cu(100), suggesting that the (100) facets seems to be the dominant crystal facet in polycrystalline copper. This could open up new routes to an affordable (photo-)electrochemical production of hydrocarbons from CO₂.

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 selective ethylene formation at low overpotentials was only observed on (100) terraces.

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) electrodes. The results supported our proposed reaction mechanism, in which two different reaction pathways to ethylene can be distinguished: a first, pH-dependent pathway that has a common intermediate (formyl) with the formation of methane that occurs mainly on Cu(111), and a second, pH-independent pathway via a carbon monoxide dimer. The latter pathway occurs on Cu(100) only.

