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Temperature and pressure effects on the electrochemical CO₂ reduction

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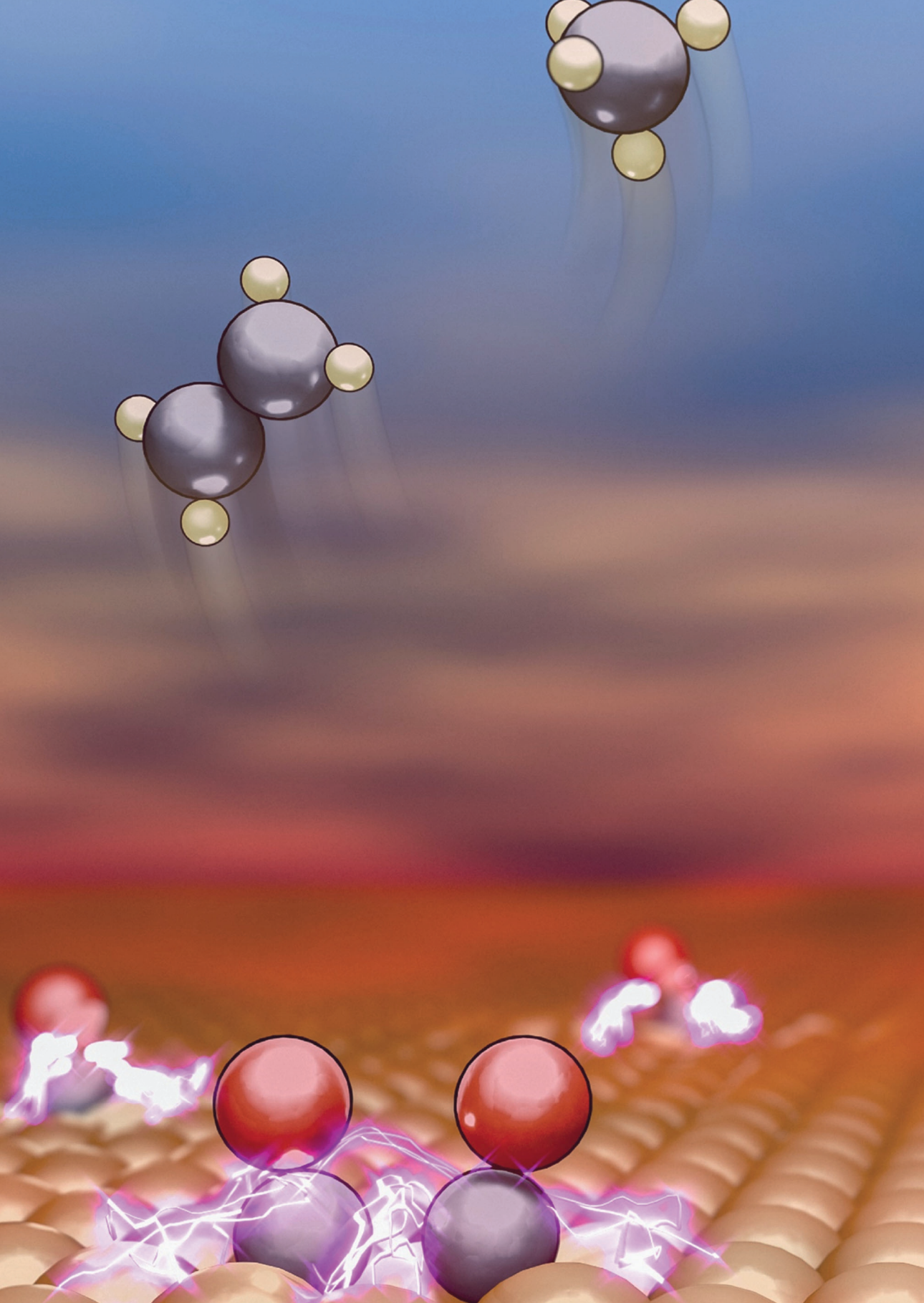
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Summary Outlook & Samenvatting



Summary

One of the largest and most pressing issues of this time is the changing climate due to manmade emissions of greenhouse gasses, most importantly CO_2 . To limit the effects of climate change, a rigorous change is needed in the way modern society uses energy and materials. A transition is needed from a world based on fossil fuels to a world based on renewable resources. Electrocatalysis can play a significant role in this transition as it can use renewable electricity to convert molecules as H_2O , CO_2 and N_2 into energy carriers or chemical building blocks such as hydrogen, CO, ethylene and ammonia. Electrochemical CO_2 reduction (CO₂RR) can be used to turn CO_2 from a pollutant into a resource by transforming it into valuable chemicals as CO, formic acid or ethylene. Therefore, in recent years the interest in this reaction has grown tremendously. Electrochemical research in general and CO₂RR studies specifically are often performed at ambient pressure and temperature and hence conclusions and fundamental insights are drawn at these conditions. However, for practical applications, ambient conditions might not be the most relevant, as industrial electrolyzers typically operate at elevated temperatures, for example due to thermal losses and/or hot feedstocks. Therefore, it is important to study the CO_2 reduction reaction at elevated temperatures and pressures to gain fundamental insights in the effects of these parameters.

Chapter 2 to 5 study the effect of temperature at ambient pressures on Au, Cu, Ag, CuAg alloy and Ni electrodes. Chapter 2 shows that on Au, in a rotating-ring-disk setup, the activity and selectivity of CO₂RR increases with temperature. We attribute this to the improved kinetics. We have performed partial pressure experiments to study the effect of temperature and CO_2 solubility independently and show that at high temperatures the reaction is limited by the CO_2 concentration. Moreover, we show that temperature experiments can be used to extract kinetic information such as the transfer coefficient and the apparent activation energy. The latter is influenced by the cation and therefore the magnitude of the temperature effect depends on the electrolyte used.

In Chapter 3, we investigate how reaction temperature affects the electrochemical CO_2 reduction on copper in the temperature range from 18-70 °C. We show that there are two distinct temperature regimes. From 18 up to ~ 48 °C, C₂+ products are produced with higher Faradaic Efficiency, while methane and formic acid selectivity decreases, and hydrogen selectivity stays approximately constant. From 48 to 70 °C, it was found that the Hydrogen Evolution Reaction (HER) dominates and the activity of CO₂RR decreases. Moreover, the CO₂RR products produced in this higher temperature range are mainly the C₁ products, namely CO and HCOOH. The observations in the first regime can be explained by an

increase in the CO coverage on the surface as evidenced by in situ Raman spectroscopy, in combination with increased local pH and faster kinetics with temperature. The second regime seems not to be related to any limited CO₂ mass transport, but rather due to changes in the copper surface as shown with lead underpotential deposition and double layer capacitance measurements, although a too high local pH could also be a factor.

Chapter 4 illustrates that the performance of Cu catalysts at elevated temperatures can be improved by alloying, in this case with Ag. By alloying, the hydrogen evolution can be significantly suppressed at elevated temperatures. However, at ambient pressures the optimum in C₂+ production with temperature remains, even at the different CuAg alloys. This chapter also demonstrates how intertwined the temperature effect is with other parameters. Temperature influences other parameters, such as the CO₂ solubility, and these should be deconvoluted where possible. In this case we deconvolute the effect of temperature and CO₂ solubility by partial pressure experiments. Moreover, the applied potential significantly influences the effect of temperature and both parameters should be studied simultaneously. Lastly, mass transport and temperature also influence each other's effect on the activity and selectivity of CO₂RR and therefore studies should combine the study of both parameters.

In Chapter 5, we investigate a nickel-derived catalyst for the electrochemical CO₂ reduction. Ni is an interesting electrocatalyst as it has recently been shown to have the unique ability to produce longer hydrocarbon chains via a chain growth mechanism in low but measurable amounts. However, the effect of the many parameters of this reaction remain to be studied in more detail. Here, we have investigated the effect of temperature, bulk CO₂ concentration, potential, the reactant, cations and anions on the formation of hydrocarbons via a chain growth mechanism on Ni. We show that temperature increases the activity but also the formation of coke, which deactivates the catalyst. The selectivity and thus the chain growth probability is mainly affected by the potential and the electrolyte composition. Remarkably, CO reduction shows lower activity, but higher chain growth probability than CO₂ reduction. Furthermore, we discuss that the rate determining step is most likely a hydrogenation step.

Chapter 6 to 8 discuss the development and application of a high-pressure high-temperature electrochemical cell, which is able to operate up to 140 bar and 200 °C. This setup allows the combined study of temperature and pressure. Moreover, it extends the temperature range that can be studied over 100 °C, even in aqueous electrolyte. Chapter 6 shows, as a the proof of concept of this high pressure cell, the temperature-dependent changes in the cyclic voltammograms of

polycrystalline gold up to 150 °C and 50 bar. Moreover, the catalytic performance of CO₂ reduction to CO on a rotating polycrystalline gold disk electrode was investigated under different pressure and temperature. At ambient pressures similar results were reached as in Chapter 2, but at elevated pressures the optimum in CO selectivity with temperature disappeared and CO reaches selectivities around 90%. In these conditions, temperature and pressure can still significantly enhance the activity of CO₂ reduction on gold.

Following the same order as the first chapters, we studied Cu in the high-pressure high-temperature electrochemical cell after studying Au. We show a change in the C-C coupling mechanism above 100 °C at pressures of 24 bar. Where at low temperatures most C-C bonds are formed via the traditional CO dimerization mechanism, at high temperatures the chain growth mechanism takes over and from 125 °C onwards this is the only mechanism making C-C bonds. We also show that temperature can improve the selectivity of the traditional CO dimerization mechanism at temperatures up to 75 °C, and that pressure helps to keep the system stable at these temperatures. Elevated pressures can reduce HER activity and selectivity dramatically, even at pressures of only a few bar. However, it is not pressure itself, but CO₂ pressure that enhances CO₂ reduction and C-C coupling specifically.

Chapter 8 extends the field of electrocatalysts for CO₂RR by screening 20 different metals for this reaction at different combinations of pressure and temperature at conditions up to 30 bar and 100 °C in aqueous electrolyte. We show that catalyst which are average at ambient conditions, can reach near 100% efficiency for CO₂RR at 30 bar and maintain this at high temperatures, because HER is significantly inhibited at elevated pressures. Both temperature and pressure can increase the CO₂RR activity significantly. However, if a catalyst does not perform CO₂RR at ambient conditions, increasing pressure and temperature will not turn this into a good CO₂RR catalyst and CO₂RR selectivity increases to maximum 30%. Nevertheless, some of these poor CO₂RR catalysts do show interesting products beyond CO and HCOOH, such as long chain hydrocarbons and methanol. Chapter 6 to 8 give a glimpse of what is possible and thereby open up new promising avenues for future investigations for electrochemical CO₂ reduction at high temperatures and high pressure in aqueous electrolytes.