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Electrocatalytic CO₂ reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts

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Summary and Future Perspectives

Summary

Global energy challenges have received unprecedented attention and recognition in recent decades, which is associated with the increase in carbon dioxide emissions from fossil fuel combustion, global warming, climate change, and consequently the aim to decarbonize the current energy system. Electrification and renewable energy utilization are acknowledged to play an important role in future energy systems. In this respect, electrocatalysis is of paramount importance, since it facilitates the incorporation of renewable electricity in future energy systems. Renewable electricity is then stored in chemical bonds as fuels or commodity chemicals by sustainable processes. An additional advantage is the ability to tackle the intermittency problem of renewable energy sources. The production of energy carriers from CO₂ is a promising strategy to aid in the aforementioned energy and CO₂ related issues. Since the current energy infrastructure is optimized for liquid fuels, which are easier to handle and to store compared to gaseous fuels, the production of liquid products from CO₂ is preferred. This thesis focuses on the use of heterogeneous electrocatalysts and heterogenized molecular catalysts for the electrocatalytic conversion of CO₂ toward liquid products.

First, we give the conspectus from a broad perspective, briefly discussing the current status of the carbon cycle, and the role and relevance of electrocatalytic CO₂ reduction herein.

In chapter 2, we review recent breakthroughs and remaining obstacles in the research field of electrocatalytic CO₂ reduction. We highlight progress on important mechanistic topics such as the initial activation of CO₂, and carbon-carbon bond formation. Moreover, we discuss the influence of the electrode morphology and process- and reaction conditions such as mass transport, local pH gradients and cationic/anionic species on CO₂ electroreduction. Lastly, we discuss two important techniques often employed in electrochemical CO₂ reduction research: in situ spectroelectrochemistry and computational techniques.

In chapter 3, we shed light on local phenomena in the vicinity of the electrode surface, which influence the product spectrum of electrocatalytic CO₂ reduction. We demonstrate the involvement of disproportionation reactions, promoted by

the local alkaline environment near the electrode surface during electrocatalytic CO₂ reduction, caused by the concomitant hydrogen evolution reaction. These Cannizzaro-type reactions are found to be independent of the electrode material, and lead to disproportionation of aldehydes into acids and alcohols, which should be distinguished from those formed by direct CO₂ reduction. Especially for the formation of liquid products such as methanol and ethanol, where the corresponding aldehyde is often proposed as a reaction intermediate, one should keep the presence of these phenomena in mind, and be careful with the attribution of alcohols or acids observed. Lastly, we show that the occurrence of these disproportionation reactions is strongly influenced by the electrolyte pH and buffering strength.

We shift to electrochemical CO₂ reduction on molecular catalysts, which is introduced in chapter 4. First we give an overview of molecular catalysts often used for electrochemical CO₂ reduction. Next we briefly review the work done on metalloporphyrins for CO₂ reduction. We conclude this chapter with a discussion of heterogenized systems of molecular catalysts, since the remainder of this thesis is devoted to electrochemical CO₂ reduction on heterogenized metalloporphyrins.

In chapter 5, we study the electrocatalytic reduction of CO₂ toward formic acid on different metalloprotoporphyrins immobilized on pyrolytic graphite. We reveal the formic acid selectivity dependence on the metal center of metalloprotoporphyrins. Based on their metal center, we show that the investigated metalloprotoporphyrins can be divided in active (Rh, Sn, In centers), poorly active (Ni, Cu, Ga, Pd centers) and inactive (Cr, Mn, Fe, Co centers) porphyrins for formic acid formation. Moreover, we investigate the influence of the overpotential and electrolyte pH, which strongly affects the selectivity toward formic acid. Sn- and In-protoporphyrins are shown to be weakly coupled to the hydrogen evolution reaction, while Rh-protoporphyrin is strongly coupled to the hydrogen evolution reaction, leading to lower faradaic efficiency toward formic acid for rhodium protoporphyrin. Indium protoporphyrin was found to be the most active, the most stable, and most selective toward formic acid (faradaic efficiency up to $\approx 70\%$). Finally, an attempt was made to qualitatively study the influence of bicarbonate in formic acid formation.

Chapter 6 builds upon the findings of chapter 5, by studying immobilized indium protoporphyrins in more detail. Although heterogenized molecular catalysts have gained more attention recently, experimental procedures and choices are often still based on empirical considerations, without underlying mechanistic rationale. In this chapter, we made an attempt to gain insight into factors related to heterogenization of molecular catalysts. We investigate the influence of the nature of the substrate, its chemical functionality, and the catalyst chemical environment on the electrocatalytic CO₂ reduction performance. We show that there is a significant effect of the substrate, where pyrolytic graphite outperforms glassy carbon and boron doped diamond substrates with respect to the selectivity and activity of CO₂ electroreduction. This superior performance is ascribed to a combination of factors such as a more porous surface structure, leading to more efficient mass transport, an optimal interaction between substrate and catalyst, and a favorably low hydrogen evolution activity. Moreover, we modify the surface chemical functionality by plasma- and

electrochemical pretreatment of the pyrolytic graphite substrate. We show that hydrogenated functional groups negatively influence the selectivity, activity and stability of CO₂ electroreduction, while oxygen functionalization slightly improves the CO₂ reduction performance. Anodization of the pyrolytic graphite surface leads to a substantial enhancement in stability, which is associated with the formation of a thick graphite oxide layer with high edge plane density. Lastly, we immobilize the indium protoporphyrin in polymeric membranes. We show that encapsulation of the catalyst in polymeric membranes cannot be described simply by introducing a hydrophobic environment, which suppresses the hydrogen evolution. We found that dispersion in poly(4-vinylpyridine) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate improve the selectivity, activity and stability of CO₂ reduction, while encapsulation in nafion negatively impacts the CO₂ reduction. Although other molecular catalysts may behave differently, we strongly believe that there will be an influence of the substrate, its pretreatment, and catalyst encapsulation in polymers on the selectivity, reactivity and stability of CO₂ electroreduction. The insights obtained here, can be used to fine-tune and optimize heterogenized molecular systems for the electrocatalytic CO₂ reduction beyond the empirical level.

In chapter 7, we continue with the study of indium protoporphyrins immobilized on pyrolytic graphite for the electrochemical reduction of CO₂ toward formic acid. Herein, we investigate extrinsic factors to the porphyrin catalyst, which affect the CO₂ reduction performance. We focus on the effects of electrolyte composition on the activity and selectivity of CO₂ reduction, such as the influence of ionic species in solution, buffering strength and initial (bulk) pH of the electrolyte. Moreover, we look into the cause of instability observed for the heterogenized indium protoporphyrin system.

Future Perspectives

Electrochemical reduction of carbon dioxide will play a prominent role in future energy systems. However, in order to ultimately contribute to a more sustainable carbon cycle, simultaneous implementation of various processes is required. Most importantly, we need to move from laboratory scale to industrial scale, which leads to additional research topics that need to be addressed, not only from a fundamental point of view, but from an engineering perspective as well e.g. integration with a CO₂ capture system, large-scale production and regeneration of catalysts, product separation, and economic viability of the whole industrial system.

Zooming in on the electrocatalytic CO₂ reduction itself, to date, research has mostly focused on the fundamental and mechanistic aspects of electrochemical CO₂ reduction. Firstly, attention should also be given to the anode side of the system, since this can significantly affect the efficiency of the complete system. Moreover, instead of merely finding or improving highly active/selective electrocatalysts, CO₂ reduction research should be directed toward the inclusion of extrinsic factors

Summary and Future Perspectives

such as mass transport phenomena, fluid flow, electrode morphology, process- and reaction conditions, and catalyst stability.