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Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study

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Summary

Heterogeneous catalysis is of paramount importance in industrial processes such as the formation of ammonia, the formation of syngas, the catalytic cracking of oil, the formation of sulfuric acid and the formation of nitric acid, among many others. However, these processes require high temperature and pressure to achieve an efficient conversion. In addition, some of these processes lead to undesirable side products which can be environmentally damaging or can affect the catalyst, deteriorating it and thus leading to rapid efficiency loss.

A reasonable alternative for high-temperature industrial processes would be the use of electrocatalysis, which presents several advantages over conventional catalysis. First of all, electrons as reducing/oxidant agents contribute to cleaner processes. Secondly, the use of mild process conditions such as lower temperatures and pressures potentially leads to a higher stability of the starting material or products. Moreover, since the product distribution depends on the applied potential, controlling the potential would in principle allow for the selective formation of the aimed products avoiding harmful and/or undesired by-products. However, the electrochemical synthesis of chemicals is not widespread in industry. The reasons for this limited use of electrochemical techniques can be attributed to a lack of electrochemistry education, a lack of resources for the construction of electrochemical cells and especially to the high costs of electricity and electrochemical cells. The high energy input can be overcome by the use of cheap and abundant catalysts and electricity from renewable sources. Nevertheless, an efficient process must be developed before it has an industrial application. For this purpose, an exhaustive study of the electrochemical reaction must be performed first, in order to understand and control all the different parameters that affect the reaction, its product distribution, selectivity and efficiency.

In this thesis, we have discussed several parameters that affect the electrochemical conversion of environmentally harmful molecules such as nitrates and carbon dioxide to more valuable and less deleterious compounds, in order to cast light onto the mechanism of the reaction to achieve an efficient and selective system.

This thesis is divided in two main parts, the reduction of nitrates (chapter 2) and the mechanistic study of CO₂ conversion to different products such as ethanol (chapter 3), ethylene (chapter 4 and 5) and propylene carbonate (chapter 6).

Numerous previous works have studied the difference in product distribution during the reduction of nitrate on several metals and at several pH's. In chapter 2 of this thesis, we studied the electrocatalytic reduction of nitrate on copper electrodes. The influence of the electrode surface morphology was studied by employing two different copper single crystals, namely Cu(100) and Cu(111). In addition, the experiments were performed in acidic and in alkaline media, providing then a study of the influence of the pH in this reaction. The experiments have shown that the product distribution varies depending on the pH of the electrolyte. While in acidic media the products formed are NO and ammonia, in alkaline media the main product is hydroxylamine. In addition, the reduction of nitrate is structure sensitive only in basic media, with the formation of hydroxylamine favoured on Cu(100).

On the other hand, the electrochemical reduction of carbon dioxide has received considerable attention in the last decades due to the capability of copper to convert CO₂ into fuels such as methane, ethylene and ethanol. Although this process was discovered in the 1980's, the mechanism of the reaction is still under debate.

The reduction of carbon dioxide on copper has ethylene as its main C₂ product. Nevertheless, trace amounts of ethanol and acetaldehyde have been also observed. Since acetaldehyde has been confirmed as an intermediary for ethanol formation during the reduction of carbon monoxide, in chapter 3 we discuss the mechanistic implications of

acetaldehyde reduction to ethanol during CO₂ reduction. It is believed that these three compounds share a common intermediate at the early stages of CO₂ reduction. However, the pathway for ethylene and ethanol formation must bifurcate at later stages of the reaction. Our results have shown that the selectivity-determining intermediate is the product of the fifth protonation (CH₂CHO*). The protonation of this intermediate favours ethanol formation on undercoordinated sites. In contrast, square symmetry sites favour the formation of ethylene. Despite the higher energetic barriers found for ethanol compared to ethylene, the selectivity for ethanol can be increased by making use of the structure selectivity of the reaction.

Another interesting step in the mechanism of CO₂ reduction is related to the formation of ethylene. The only intermediate experimentally confirmed during the reduction of CO₂ to ethylene has been CO. Computational studies have hypothesized that the C-C bond formation in the ethylene pathway occurs via a reductive dimerization step and further hydrogenation. In chapter 4 we provided spectroscopic evidence for the formation of a CO hydrogenated intermediate (OCCOH) in the ethylene pathway. The formation of this intermediate has been confirmed to be structure sensitive, being favourable mostly on square symmetry sites.

Several factors such as the pH of the electrolyte, the chemical nature of cations or anions and the morphology of the electrode surface have been previously studied for the reduction of CO₂. All these parameters lead to significant changes in product distribution, selectivity and conversion rate. In chapter 5 we analyse the combined effect of electrode morphology, alkaline cation size and applied potential during CO reduction. In general, larger cations enhance the formation of ethylene at potentials more positive than -0.45V, whereas larger cations enhance the formation of methane at more negative potentials. We suggested that the ethylene pathway shuts down by the enhancement of the methane pathway, this correlation also being dependent on the cation size. Larger cations enhance the ethylene selectivity over a wider

potential range. We suggested that the cations act as catalytic promoters stabilizing intermediates with a favourable electrostatic interaction with the cation. In addition, the formation of the CO hydrogenated dimer explained in chapter 4 (OCCOH) has been found to be dependent on the cation size. Whereas the hydrogenated dimer is observable in FTIR when Li^+ , Na^+ and K^+ are present, it is not observable in the presence of Rb^+ or Cs^+ . DFT calculations describe the formation of $^*\text{OCCOH}$ as less favourable in presence of larger cations compared to smaller cations.

Finally, we studied in chapter 6 the conversion of carbon dioxide into larger organic molecules, specifically into cyclic carbonates. We analyzed the mechanism of the formation of propylene carbonate from carbon dioxide and propylene oxide on copper electrodes. We excluded carbon monoxide and (bi)carbonate as possible carboxylation agents. Moreover, we discarded the activation of propylene oxide via ring opening as the key step for this reaction. Our experiments suggest that the electrochemical reaction is initiated by the activation of CO_2 to CO_2^- , which attacks propylene oxide to ultimately form propylene carbonate.

In general terms, this thesis has stressed the importance of exhaustive mechanistic studies in order to gain knowledge of all the steps involved in an electrochemical reaction. The understanding of how different factors affect the selectivity and conversion towards a certain product can help in achieving more efficient processes, which can be steered to the formation of desired products by adjusting different parameters involved in the reaction.