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Electrocatalytic reduction of CO₂ and nitrate on immobilized metal porphyrins

Shen, Jing

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Author: Jing Shen

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Chapter 1

Introduction

1.1. Electrochemical reduction of CO₂

The carbon cycle, along with nitrogen cycle and oxygen (water) cycle, comprises a sequence of events that are key to making the earth capable of sustaining life. However, human activities are altering the carbon cycle by adding more CO₂ to the atmosphere and influencing the ability of natural sinks, like forests and oceans, to remove CO₂ from the atmosphere, which will eventually jeopardize the living environment of humans. The main emission of CO₂ is from the combustion of fossil energy (coal, natural gas and oil) for energy and transportation. Since the industrial revolution, human related CO₂ emission has increased significantly, which is claimed to be one of the major contributors to the greenhouse effect and will result in a serious global warming issue^{1, 2}. As an abundant and problematic source in the atmosphere, we aspire to utilize CO₂. Mimicking natural photosynthesis, we would like to reduce CO₂ to valuable products using renewable energy, like sunlight and wind. Among different kinds of methods, the electrochemical reduction of CO₂ is a promising approach to achieve this goal. CO₂ is a very stable molecule, and its electrochemical reduction generally requires high overpotentials. On the other hand, the hydrogen evolution reaction (HER) is a competing reaction with the electrochemical reduction of CO₂, which leads to H₂ as a dominant product in many cases. In order to overcome these problems, different kinds of catalysts and solvents have been utilized. The equilibrium potential of the formation of each product is listed in Table 1³.

Table 1: The equilibrium potentials for the formation for various product from the electrochemical reduction of CO₂.

Reactions	E ⁰ /V vs NHE
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.28
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.37
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.24
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.14
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	0.04

As mentioned above, one of difficulties for the electrochemical reduction of CO₂ is the competition with the hydrogen evolution reaction. The hydrogen evolution reaction takes place close to its equilibrium potential of 0 V on many metal electrodes in aqueous electrolytes. Therefore, metal electrodes with high hydrogen overpotential have been utilized for the electrochemical reduction of CO₂ in early years, such as mercury and lead, to inhibit the hydrogen evolution reaction. Eyring and his coworkers showed that HCOO⁻ is produced with 100% faradaic efficiency from the CO₂ reduction in neutral aqueous electrolyte on a Hg electrode⁴. Later, other metal electrodes have been investigated for the CO₂ electrochemical reduction. Sakata et al. studied the electrochemical reduction of CO₂ on 32 metal electrodes in low-temperature aqueous KHCO₃ media. A periodic table for CO₂ reduction based on the dependence of reduction products on various metals, suggests the existence of a systematic rule for the electrocatalytic reduction of CO₂ on metal surfaces⁵. Hori et al have made comprehensive investigations on the electrochemical reduction of CO₂ on all different kinds of metal electrodes in 0.5 M KHCO₃⁶. They found that the purity of the metal electrodes and electrolyte solution significantly affects the product selectivity. They also conducted full chemical analysis of products. Based on the product selectivity from their studies, the metal electrodes have been divided into four groups: (i) formate ion as the major product, such as on Pb, Hg, In, Sn, Cd, Tl and Bi electrodes; (ii) CO formed as the main product, such as on Au, Ag, Zn, Pd and Ga electrodes; (iii) Cu electrode produces CH₄, C₂H₄ and alcohols; (iv) hydrogen is the only

product on electrodes such as Ni, Fe, Pt and Ti. The results from Hori et al have been confirmed later by other researchers⁷⁻¹¹.

From Hori's studies Cu is an exceptional electrode, as it is the only metal producing hydrocarbons and alcohols in a measurable quantity. Therefore, the Cu electrode has attracted intensive studies not only to increase the activity but also to reveal the mechanism for the CO₂ reduction. Recently, Jaramillo et al. observed 16 different products from the CO₂ reduction on Cu electrode, which makes it challenging to propose a mechanism¹². CO is a widely accepted key intermediate for the formation of hydrocarbons on Cu electrode from the reduction of CO₂¹³. Peterson et al. have studied 41 different intermediates on the Cu (211) surface by density functional theory calculations and proposed possible pathways for the electrochemical reduction of CO₂¹⁴. The adsorbed formate (*OCHO) is an alternative intermediate for the formation of formic acid, which is responsible for the formic acid production at more negative potential (-0.61 V). They also concluded that the key step in the formation of CH₄ and C₂H₄ is the hydrogenation of adsorbed CO to form adsorbed *CHO. The subsequent hydrogenation of *CHO leads to the formation of *H₂CO and *H₃CO, which will finally produce CH₄. The formation of ethylene requires of the creation of a C-C bond, which is a non-electrochemical step on the surface. Schouten et al. proposed a new reduction mechanism for CO₂ on Cu electrode¹⁵. The overall rate-determining step is the first electron transfer to form CO₂⁻_{ads}¹⁶. CO₂⁻_{ads} will further react to give CO and formic acid. Formic acid is a dead-end product^{16, 17}. CO is the intermediate for the formation of both CH₄ and C₂H₄. The rate-determining step for the formation of CH₄ is the breaking of the C-O bond in formyl intermediate (*CHO), while selectivity-determining step to C₁ and C₂ species is the formation of a CO dimer. Possible mechanistic pathways have been illustrated for the formation of C₁ and C₂ species on transition metals and molecular catalysts, as presented in Figure 1¹⁸.

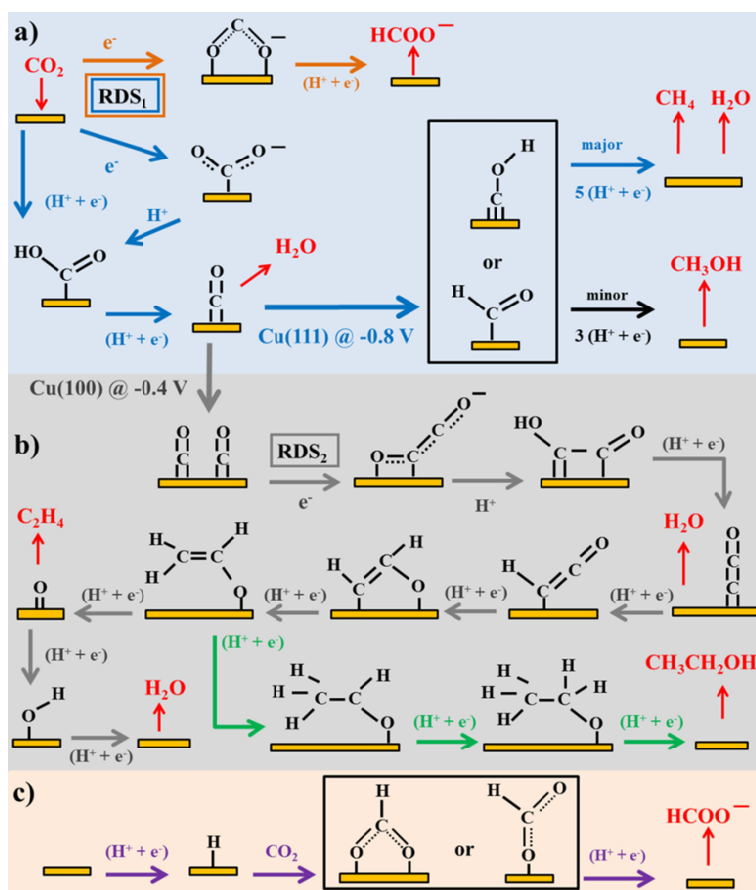


Figure 1. Possible reaction pathways for the electrocatalytic reduction of CO₂ to products on transition metals and molecular catalysts; a) pathways from CO₂ to CO, CH₄ (blue arrows), CH₃OH (black arrows), HCOO⁻ (orange arrows); b) pathways from CO₂ to ethylene (grey arrows) and ethanol (green arrows); c) pathway of CO₂ insertion into a metal-H bond yielding formate (purple arrows). Species in black are adsorbates, while those in red are reactants or products in solution. Potentials are reported versus RHE, while RDS indicates rate determining steps and (H⁺ + e⁻) indicate steps in which either concerted or separated proton-electron transfer takes place. Reprinted from Ref.18.

Molecular electrocatalysts are the other promising class of catalysts for the electrochemical reduction of CO₂. Molecular catalysts are primarily utilized as homogeneous catalysts, but they are more applicable when mobilized on an inert electrode acting as heterogeneous catalyst. The 2-electron transfer product CO is produced on a

cobalt porphyrin modified electrode from the electrochemical reduction of CO₂, such as a Co^{II}TPP (TPP= 5,10,15,20-tetraphenyl-21H, 23H-porphine) modified glass carbon electrode (with current efficiency of 92%)¹⁹, and 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinato cobalt(II) (CoTMPP) modified nanoporous activated carbon fiber electrode (with current efficiency up to 70%)²⁰. Formic acid is the other 2-electron transfer product formed on carbon-nanotubes supported iron-porphyrin (FeP) electrode²¹ and a cobalt- and nickel-phthalocyanine (CoPc and NiPc) coated graphite electrode²²⁻²⁴. Sende et al. have found that up to 87% formaldehyde, which is a 4-electron transfer product, is produced on a [Cr(4-v-tpy)₂]²⁺ (v-tpy = vinyl-terpyridine) film, which is higher than that of Co and Fe complexes, which produce 39% and 28% , respectively²⁵.

In order to suppress the hydrogen evolution reaction and increase the concentration of CO₂ in the electrolyte, non-aqueous solvents have been utilized for the CO₂ electrochemical reduction. Various solvent have been used, such as acetonitrile (AN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and propylene carbonate (PC). Ito and coworkers have investigated various metal electrodes for the electrolysis of CO₂ in PC with tetraethylammonium perchlorate (TEAP) as the electrolyte²⁶. The water content was 300 ppm. Metal electrodes have been divided into three groups based on the products. Pb, Hg and Tl give oxalate (C₂O₄²⁻) as the main product. With a small amount of water in the electrolyte, oxalic acid is partly reduced to glycolic acid and glyoxylic acid. CO is predominantly produced on Cu, Ag, Au, Zn, In, Sn, Ni and Pt from the reduction of CO₂. On Fe, Cr, Mo, Pd and Cd electrodes, C₂O₄²⁻ and CO are formed in comparable amount. The Faradaic efficiencies of products on all the metal electrodes were also evaluated. Haynes and Sawyer find CO and formate as the main product on Au and Hg electrodes in DMSO from the reduction of CO₂²⁷. Oxalic acid is exclusively formed on Hg electrode in DMF reported by Tyssee et al.²⁸. Oxalic acid is the main product at Pb electrode in nonaqueous electrolytes. It can be further reduced to higher carboxylic acids, glyoxylic acid, glycolic acid etc.²⁹. The reaction schemes of the CO₂ electrochemical reduction in H₂O-DMF solutions have been discussed by Savéant et al.³⁰. The CO₂^{•-} radical was assumed as an intermediate.

1.2. Nitrate electrochemical reduction

The nitrogen cycle is one of the most important nutrient cycles in terrestrial ecosystems. Everything that lives needs nitrogen. It is required for the building of proteins, DNA and enzymes. It is also essential for bacteria to produce ATP and gain energy for cell growth. 70% of the atmosphere consists of nitrogen gas. However, it is not directly available for use. Nitrate ions (NO_3^-) and ammonium ions (NH_4^+) are the only forms that can be utilized by plants. When present in excess, nitrogen compounds may pose risks both to environment and human health. Nitrate is commonly used as fertilizer in agriculture. The overuse of fertilizer leads to the excess of nitrate in the soil, which will be leached into groundwater. High level of nitrate in drinking water can cause methemoglobinemia or blue baby syndrome, which is a disease especially found in infants. The maximum contaminant level of nitrate in drinking water has therefore been set at 10 mg/L³¹.

The electrocatalytic reduction of nitrate is currently attracting much attention as one possible way to remove nitrate from ground- and waste-water. However, different kinds of products can be produced from the nitrate electrochemical reduction. The equilibrium potentials of the formation of various products are listed in Table 2³².

Table 2: The equilibrium potentials for the formation of various products from the electrochemical reduction of nitrate.

Reactions	E^0 /V vs NHE
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$	0.835
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	0.958
$2\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{N}_2\text{O}(\text{g}) + 5\text{H}_2\text{O}$	1.116
$2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2(\text{g}) + 6\text{H}_2\text{O}$	1.246
$\text{NO}_3^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{NH}_3\text{OH}^+ + 2\text{H}_2\text{O}$	0.727
$\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$	0.875

Platinum is the most studied electrode material for the nitrate reduction. The nitrate reduction on platinum follows a direct mechanistic pathway at moderate nitrate

concentration and acidity, while an indirect pathway applies to high nitrate concentrations (>1 M) and high acidity ($\text{pH} < 0$)³³. The electrochemical reduction of nitrate on polycrystalline platinum at low nitrate concentration and low pH has been studied intensively³⁴⁻³⁷. The cyclic voltammetry of the electrochemical reduction of nitrate on a polycrystalline platinum electrode in sulfuric and perchloric acid illustrates that the reaction is strongly hindered by the presence of specifically adsorbing anions, such as sulfate, as well as other anions^{35,36}. Investigations on the steady-state nitrate reduction in sulfuric acid show that the formation of adsorbed hydrogen (upd H) on the platinum surface inhibits the nitrate reduction^{37,38}. Nitric oxide (NO) is found to be the main surface-bonded intermediate by FTIR measurements and stripping experiments³⁹. Nakata et al. have argued that a chelating bidentate nitrate chemisorbs on the Pt surface instead of nitric oxide⁴⁰. Ammonia is the only product from the nitrate reduction on polycrystalline platinum electrode according to rotating ring-disk and online electrochemical mass spectrometry measurements⁴¹⁻⁴³.

The nitrate reduction on single-crystal platinum electrode offers more detailed mechanistic insights. Pt (110) is the most active platinum surface for the nitrate reduction in perchloric acid, while Pt (111) is more active than Pt (110) in sulfuric acid. Dima et al. have argued that the structure-sensitivity of the nitrate reduction on platinum single-crystal is due to the sensitivity of the adsorption of other species, such as hydrogen and anions⁴⁴. NO is found to accumulate at step sites of Pt (554) and Pt (553) electrode⁴⁴. Taguchi and Feliu presented a detailed study on the influence of step density on nitrate reduction on single-crystal platinum. They found that the electrocatalytic activity for nitrate reduction is non-linear with the step density⁴⁵. Based on the Tafel slopes, the conversion of nitrate to nitrite is considered to be the most difficult step. NO is considered to be the important intermediate, which is produced after nitrite formation.

Vijh was the first one to compare the activity of different metals for the nitrate electrochemical reduction. He found that metals with high overpotential for the nitrate reduction also tend to have a high overpotential for the hydrogen evolution reaction⁴⁶. Dima et al. investigated the activity of various transition-metal electrodes (Pt, Pd, Rh, Ru and Ir)

and coinage-metal electrodes (Cu, Ag and Au) toward the reduction of nitrate in acid solution⁴¹. The activity of transition-metal electrodes follows the order of Rh>Ru>Ir>Pt>Pd in sulfuric acid. The main products formed on a rhodium electrode are ammonia and nitrite. Among the coinage-metal electrodes, Cu is the most active one, followed by silver and gold. Pletcher and Poorabedi found that ammonia is the main product on copper electrode. NO is also found as a product on Cu electrodes⁴¹. “Poor metals” were also investigated for the reduction of nitrate in acid media, such as mercury⁴⁷, indium⁴⁸, cadmium⁴⁹ and tin^{50,51}. The high overpotential for the nitrate reduction on these metal electrodes is in agreement with the assertion of Vijh. The mechanism of the nitrate and nitrite reduction on noble-metal electrodes has been summarized by Duca et al. as shown in Figure 2.⁵²

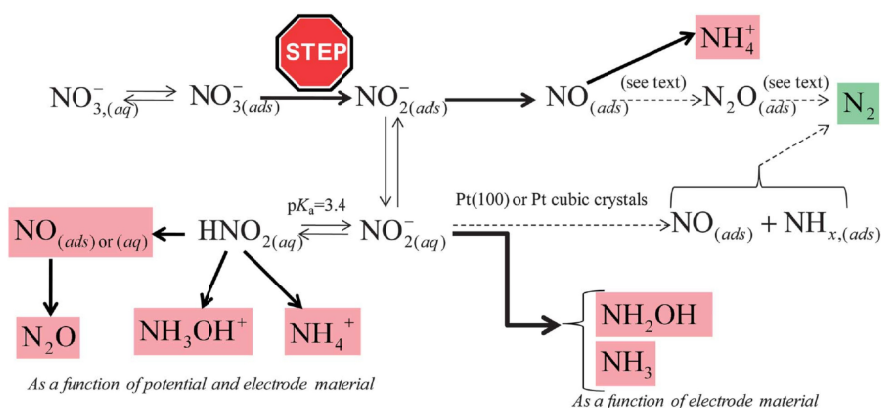


Figure 2. The major reaction pathways for nitrate and nitrite reduction on noble-metal electrodes. The ideal product, N₂, is highlighted in green, other products in red. The cartoon of the “STEP” sign highlights the rate-determining step. Thick lines emphasize those pathways that occur most often, where broken lines indicate reactions taking place under more specific conditions. Reprinted from Ref.52.

Besides metal electrodes, functionalized electrodes were also utilized for the electrochemical reduction of nitrate. Hydroxylamine (NH₂OH) and ammonia (NH₃) are the main products formed on the functionalized electrodes on different catalysts, such as metal cyclams and phthalocyanine modified electrodes⁵³⁻⁵⁵. In previous work, de Groot et al. have investigated the electrochemical reduction of NO by hemin (FePP) adsorbed at pyrolytic graphite⁵⁶. The formation of NH₂OH as main product was confirmed using rotating ring-disc electrode (RRDE), while N₂O was a minor product observed by on-line

electrochemical mass spectroscopy (OLEMS). They suggested pH-dependent competing pathways for the NO reduction, one of which leads to the formation of NH_3OH^+ (in acid media), the other one of which leads to N_2O formation (in alkaline media). In later work, the electrocatalytic nitrite reduction was studied at a hemin immobilized pyrolytic graphite electrode by Duca et al.⁵⁷. They concluded that NO is the substrate reduced by FePP in acidic media, which implies that the behavior of the nitrite reduction on FePP is closely related to that described for NO reduction by de Groot et al..

1.3. Experimental techniques

1.3.1 On-line electrochemical mass spectrometry (OLEMS)

Measurements of the volatile products have been conducted by combining the on-line electrochemical mass spectrometry (European Spectrometry systems Ltd) with the cyclic voltammetry (CV). These measurements allow the qualitative detection of various gaseous products formed during the reaction. In the electrochemical cell, cyclic voltammograms are collected from 0 V to -1.5 V with a scan rate of 1 mVs^{-1} by an Ivium A06075 potentiostat. The gaseous products formed at the working electrode enter into high-vacuum ($< 10^{-6}$ mbar) mass chamber through a porous Teflon tip (inner diameter, 0.5mm). Prior the experiment, the tip is cleaned by dipping into a 0.2 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 2 M H_2SO_4 solution for 15 minutes and rinsing thoroughly with MilliQ water. A 2400V SEM voltage is applied for all studied mass fragments, except for $m/z=2$ (corresponding to H_2) which has a SEM voltage of 1500 V to decrease the intensity of the signal. More details on the experimental setup can be found in Ref.⁵⁸.

1.3.2 Gas Chromatography (GC)

Quantitative measurements of the volatile products have been conducted by combining gas chromatography with long-term electrolysis. In a completely sealed two-compartment Teflon flow cell (with a volume of 12 mL for each compartment), the electrolysis is conducted at a given potential for 1h at atmospheric pressure. The reference electrode used in the flow cell is a Ag/AgCl electrode and the counter electrode is an Au

foil. A flow rate of CO_2 is first applied at 5 mL min^{-1} for 30 minutes to saturate the electrolyte and then decreased to 2 mL min^{-1} when the electrolysis started. The electrolysis was also conducted at high CO_2 pressure ($P=10 \text{ atm}$) in a stainless-steel autoclave for 2h. CO_2 is continuously purged through the autoclave before and during the electrolysis with a flow rate of 50 mL min^{-1} . The gaseous products are collected every 6 minutes. CO , CO_2 , H_2 and hydrocarbons are simultaneously separated using two columns in serie (a ShinCarbon 2 m micropacked column and a Rtx-1 column). A thermal conductivity detector is used for H_2 and CO , while a flame ionization detector is used for hydrocarbons. More details on the setup can be found in Ref.⁵⁹.

1.3.3 On-line high performance liquid Chromatography (HPLC)

The liquid products have been detected using high performance liquid chromatography (Prominence HPLC, Shimadzu) combined with linear voltammetry or electrolysis. Like in the OLEMS system, a Teflon tip (inner diameter: 0.38 mm) is positioned $\sim 10 \text{ }\mu\text{m}$ from the middle of the working electrode. Samples with a volume of $60 \text{ }\mu\text{L}$ are collected and stored in a 96-well microtiter plate ($270 \text{ }\mu\text{L}$ per well, Screening Device b.v.) using an automatic fraction collector (FRC-10A, Shimadzu). The flow rate of the sample collection is $60 \text{ }\mu\text{L min}^{-1}$ by using a Shimadzu pump (LC-20AT). The microtiter plate is then placed into an auto-sampler (SIL-20A) holder to analyze samples. $30 \text{ }\mu\text{L}$ of sample is injected into an Aminex HPX 87-H (Bio-Rad) column whose temperature is maintained at 85°C using a column oven (CTO-20A). The separated compounds are detected with a refractive index detector (RID-10A). Diluted sulfuric acid (5 mM) is used as the eluent with a flow rate of 0.6 mL min^{-1} . The linear voltammetry is conducted from 0 V to -1.5 V with a scan rate of 1 mV s^{-1} . More details on the setup can be found in Ref.⁶⁰.

1.3.4 On-line ion Chromatography (IC)

The ionic products are measured using on-line ion chromatography combined with linear voltammetry. The principle of on-line IC is similar as on-line HPLC. Samples are collected using a Teflon tip positioned in the center of the working electrode while the linear voltammetry is conducted from 0 V to -1.5 V at scan rate of 1 mVs^{-1} . A microtiter

plate with collected samples is placed onto an auto-sampler (SIL-20A) holder of an ion chromatography unit (Schimadzu, Prominence) with a conductivity detector (CCD-10Ap, Schimadzu). 20 μL of sample is injected and analyzed through two series of Shodex IC Y-521 columns, whose temperature is 30 $^{\circ}\text{C}$. A 2.5 mM nitric acid solution is used as an eluent at a flow rate of 8 mL min^{-1} .

1.4. Outline of this thesis

The focus of this thesis is on studying the catalytic activity of immobilized metal-porphyrin complexes toward the electrochemical reduction of small inorganic molecules, specifically CO_2 and nitrate, and in particular on the mechanistic aspects of the reactions. In general, pH and the nature of the metal center of the complexes play an important role on the selectivity. Therefore, the selectivity of both electrochemical reduction reaction of CO_2 and nitrate has been studied by varying pH and the metal centers of the complexes. We start in Chapter 2 by investigating the electrochemical reduction of CO_2 catalyzed by cobalt protoporphyrin immobilized on a pyrolytic graphite electrode in aqueous solution. New insights into the mechanism of the CO_2 electrochemical reduction on molecular catalysts will be proposed based on thorough investigations of the electrochemical reduction of possible intermediates as well as the influence of pH on CO_2 reduction.

In Chapter 3, we identify key intermediates of the CO_2 electrochemical reduction on a cobalt porphyrin using density functional theory (DFT) calculation. The most favorable pathways of the reaction are identified. The results of the theoretical investigation will be compared to the mechanistic conclusions from Chapter 2, to obtain a more comprehensive mechanistic understanding of the CO_2 electrochemical reduction on cobalt porphyrin complex.

The similarity of the requirements of electron and proton of the reduction of CO_2 and nitrate makes it interesting to study the catalysis of the nitrate reduction using metal-porphyrin complexes immobilized on pyrolytic graphite electrodes. Chapter 4 builds on previous work on de Groot and Duca on NO and nitrite reduction, respectively, by investigating the catalytic activity of various metal-porphyrin complexes for the nitrate

reduction. The cobalt porphyrin is shown to have the highest activity and selectivity toward hydroxylamine production, making it the most interesting catalyst. Furthermore, pH is shown to play a crucial role in determining the selectivity toward either hydroxylamine or ammonia, suggesting the sequential mechanism in which hydroxylamine is an important precursor for ammonia formation.

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