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Rational catalyst design for photo- and electrochemical hydrogenation reactions

by

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List of publications included in this thesis

- C. D. Sahm, A. Ciotti, E. Mates-Torres, V. Badiani, K. Sokołowski, G. Neri, A. J. Cowan, M. García-Melchor, E. Reisner. Tuning the local chemical environment of ZnSe quantum dots with dithiols towards photocatalytic CO₂ reduction. *Chem. Sci.* **2022**, *13*, 5988.
- A. Ciotti, M. García-Melchor. The importance of surface coverages in the rational design of electrocatalysts. *Curr. Opin. Electrochem.* **2023**, *42*, 101402.
- J. Sharp, A. Ciotti, H. Andrews, S. R. Udayasurian, M. García-Melchor, T. Li. Sustainable Electrosynthesis of Cyclohexanone Oxime through Nitrate Reduction on a Zn–Cu Alloy Catalyst. *ACS Catal.* **2024**, *14*, 3287.

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Abstract

Environmental pollution is an urgent threat to human health and the survival of life forms on land and in water. This crisis is fuelled by industrial, agricultural, and biomedical chemical waste, alongside the use of fossil fuels, which significantly contribute to greenhouse gas emissions. In addition to reducing pollutant discharge, transitioning from fossil fuels to renewable technologies is vital due to their finite nature. Heterogeneous catalysis offers a promising approach to valorise pollutants by converting them into valuable feedstocks, utilising mild reaction conditions in photo- and electrochemical processes, and minimising chemical waste. This waste reduction is enabled by the ease of catalyst separation and recycling, prevention of metal and organic contamination, and the use of water and alcohols as solvents. Accelerating catalyst discovery is crucial, and this is best achieved by integrating experimental and theoretical approaches. Computational studies, in particular, can elucidate the relationship between catalyst structure and efficiency, providing insights into how to tailor catalysts for improved performance.

This thesis investigates three heterogeneous catalytic reactions in collaboration with experimentalists. First, the photoreduction of CO_2 to CO was studied on ZnSe quantum dots functionalised with dithiol ligands of varying chain lengths, both with and without the Ni-cyclamphosphonate cocatalyst. Theoretical simulations revealed a correlation between ligand length and non-covalent interactions with reaction intermediates, resulting in a more favourable energy profile. Second, the electroreductions of acetophenone and NO_3^- were modelled on metal electrodes, including Ag, Au, Cu, In, Ni, Pt, Zn, and $\text{Zn}_{1-x}\text{Cu}_x$ alloys. Both studies confirmed the critical role of the hydrogen surface coverage in hydrogenations, particularly when the substrate cannot source protons from the solvent. The catalytic activity and selectivity in suppressing hydrogen evolution were found to be dictated by the density and binding strength of the hydrogen coverage. Specifically, while a hydrogen coverage is necessary for promoting hydrogenations, strong exergonic hydrogen binding raises the reaction energetics, and high coverage densities can drive hydrogen evolution via the Tafel mechanism. Lastly, the study on NO_3^- reduction demonstrated that complex reaction selectivities can be rationalised through the interplay of kinetic and thermodynamic factors. Overall, this thesis exemplifies how computational chemistry can effectively relate catalyst structure to performance, paving the way for optimising catalytic efficiency.

Summary

The ongoing climate crisis, driven by industrial, agriculture, and other anthropogenic activities, coupled with the finite availability of fossil fuels, demands a shift to renewable technologies and the valorisation of pollutants into valuable feedstocks. Heterogeneous catalysis offers a promising route to achieve both objectives by utilising green energy sources like light and electricity, enabling mild reaction conditions, and minimising chemical waste. Solid catalysts, in particular, are compatible with aqueous and alcoholic solvents and are easier to separate and recycle. Thus, accelerating catalyst discovery is crucial for mitigating environmental challenges. Integrating experimental and theoretical approaches can aid in the elucidation of relationships between catalyst structure and performance, guiding the rational design of more efficient materials.

This thesis discusses three heterogeneous catalytic reactions. In collaboration with Prof. Reisner's group (Cambridge University), the photoreduction of CO_2 to CO was studied using ZnSe quantum dots functionalised with dithiols of varying chain lengths, with and without a Ni-cyclamphosphonate cocatalyst. Functionalisation suppressed the competing hydrogen evolution reaction, with CO production maximised using 1,2-ethanedithiol and 1,6-hexanedithiol in the absence and presence of the cocatalyst, respectively. Periodic density functional theory simulations revealed that all dithiols anchored to Zn^{2+} sites on the quantum dot surface, the active site for hydrogen evolution. Modelling $^*\text{CO}_2^-$ on various functionalised ZnSe surfaces showed that only 1,2-ethanedithiol retained $^*\text{CO}_2^-$ via hydrogen bonding, while 1,6-hexanedithiol and 1,8-octanedithiol were too long to do so. The Ni-cyclamphosphonate cocatalyst demonstrated intrinsic activity, with $^*\text{COOH}$ as the highest energy intermediate, stabilised by hydrogen bonding in the presence of 1,6-hexanedithiol. These findings indicate that flexible dithiol ligands of suitable length promote CO_2 photoreduction through non-covalent interactions with intermediates.

The second study, also conducted with Prof. Reisner's group, investigated the electrochemical hydrogenation of acetophenone to 1-phenylethanol on Ag, Au, Cu, In, Ni, and Pt electrodes in an alkaline aqueous electrolyte, which minimises H_2 evolution. The project aimed to demonstrate that when organic substrates cannot hydrolyse H_2O , the electrode must source the required hydrogen atoms by reducing and retaining protons on its surface. Periodic DFT calculations of $^*\text{H}$ binding energy and coverage density on various cathodes revealed that metals with strongly endergonic (In) or exergonic (Ni, Pt) $^*\text{H}$ binding

perform poorly due to the lack of hydrogen atoms and high energy barriers associated with H-transfer steps, respectively. The dense hydrogen coverage predicted on Ni and Pt was also found to promote H₂ evolution via the Tafel mechanism. Conversely, metals with weak (Ag, Au) or slightly exergonic (Cu) *H binding performed best, suggesting that a moderate hydrogen coverage enhances cathode efficiency for alkaline hydrogenations. These theoretical findings were supported by experiments, confirming the efficiency of Cu, Ag, and Au in promoting the hydrogenation of a wide range of unsaturated compounds, including C=O, C=C, C≡C, and C≡N bonds, at low potentials with moderate to excellent conversion rates and chemoselectivities.

Lastly, the electroreduction of NO₃⁻ to NH₂OH for cyclohexanone oxime synthesis was explored in collaboration with Dr. Li's group (Manchester Metropolitan University), using Cu, Zn, and Zn_{1-x}Cu_x electrodes. Experimentally, Zn₉₃Cu₇ was the most efficient catalyst for oxime formation, although NH₃ was the dominant product. Cu mainly yielded NH₃, while Zn produced N₂, NH₃, and oxime in decreasing order. To rationalise these findings, the surface resting state of Cu, Zn, and Zn₉₃Cu₇ electrodes was assessed at the experimental conditions via periodic density functional theory calculations, followed by modelling the NO₃⁻ reduction mechanism starting from the *NO intermediate to avoid simulating charged species. Coherently with experiments, *NO hydrogenation at the oxygen, leading to atomic *N and *N-*N coupling to form N₂, was favoured on Zn. NH₃ and oxime formation resulted from *NO hydrogenation at the nitrogen, and their ratio in the product mixture was regulated by the *NH₂OH desorption energy and hydrogenation kinetics from the hydrogen coverage. Specifically, Cu and Zn₉₃Cu₇ displayed a moderate barrier for *NH₂OH hydrogenation, although its release was only exergonic on Zn₉₃Cu₇. NH₃ formation was instead kinetically impaired on Zn, explaining oxime formation despite the slightly endergonic *NH₂OH desorption.

Overall, these studies demonstrate how theoretical approaches can effectively elucidate complex catalytic selectivities observed experimentally, paving the way for optimising catalytic efficiency.

List of abbreviations

AP = acetophenone

APH₂ = 1-phenylethanol

APH⁺ = 1-phenylethyl cation

APH· = 1-phenylethyl radical

ASE = Atomic Simulation Environment

BDE = bond dissociation energy

BEEF-vdW = Bayesian error estimation functional with van der Waals dispersions

BM = Birch-Murnaghan

BenzDT = benzene-1,4-dithiol

BuDT = 1,4-butanedithiol

BuSH = 1-butanethiol

CHE = computational hydrogen electrode

COF = covalent organic framework

CO₂RR = CO₂ reduction reaction

D3 = third revision of the dispersion corrections by Grimme and co-workers

DFT = density functional theory

DMFC = direct methanol fuel cell

DT = dithiol

ECH = electrochemical hydrogenation

EDL = electric double-layer

EDT = 1,2-ethanedithiol

FE = faradic efficiency

GGA = generalised gradient approximation

HER = hydrogen evolution reaction

HexDT = 1,6-hexanedithiol

HexSH = 1-hexanethiol

HF = Hartree-Fock

HO-EtSH = 1,2-mercaptoethanol

HO-HexSH = 1,6-mercaptoethanol

LDA = local density approximation

LSDA = local spin density approximation

MCOF = metal covalent organic framework

ML = monolayer
MEMI = 3-(2-mercaptoethyl)-1-methyl-imidazolium halide
MOF = metal-organic framework
MPA = mercaptopropionic acid
NCI = non-covalent interaction
NEB = nudged elastic band
Ni(cycP) = Ni-cyclamphosphonate
NMR = nuclear magnetic resonance
NO₃RR = NO₃⁻ reduction reaction
OctDT = 1,8-octanedithiol
PBE = Perdew-Burke-Ernzerhof
PES = potential energy surface
PW91 = Perdew-Wang
p-XRD = X-ray powder diffraction
QD = quantum dot
QTAIM = quantum theory of atoms in molecules
RHE = reversible hydrogen electrode
SEM = scanning electron microscopy
SHE = standard hydrogen electrode
TON = turnover number
TS = transition state
VASP = Vienna Ab Initio Simulation Package
1D = unidimensional

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1. Introduction

1.1 The environmental crisis

Around 1800, the global population was approximately one billion. Since the industrial revolution in the 18th and 19th centuries, this number has been constantly growing, reaching its current peak of over seven billion.¹ The rising energy demands and the improvement in living standards have dramatically impacted the environment through overconsumption of resources and the release of pollutants into the air, water, and soil.

Air quality, in particular, has been mostly affected by the burning of fossil fuels and biomass, which are primary sources of greenhouse gases such as CO₂, CH₄, and NO_x.² Notably, CH₄ and N₂O are significantly more potent heat absorbers than CO₂ – about 21 and 310 times, respectively.² Furthermore, NO_x emissions are linked to severe health issues, including asthma and heart disease.³ As greenhouse gases accumulate in the atmosphere, global temperatures have risen by 1.4°C since the industrial revolution, with the past decade being the warmest on record.⁴ This has triggered a 103.3 mm rise in sea levels since 1993 due to melting ice sheets,⁴ and extreme weather events such as heavy rains, floods, droughts, and wildfires have increased in intensity and frequency.⁵

In response, 196 countries convened in France in 2015 to sign the Paris Agreement, which aims to limit global warming to 1.5°C with respect to pre-industrial levels.⁶ However, the European Commission's 2023 report on greenhouse gases emissions shows that these continue to rise, with China (29.16%), the United States (11.19%), India (7.33%), the European Union (6.67%), Russia (4.80%), and Brazil (2.44%) being the largest contributors.⁷ As a result, the atmospheric CO₂ concentration has increased by 50% since pre-industrial levels, now revolving around 420 ppm.^{8,9} At this rate, the carbon budget estimated to meet the targets of the Paris Agreement might be exceeded in seven years.⁹

In addition to greenhouse gases, the burning of fossil fuels also releases other harmful pollutants such as SO₂, volatile organic compounds, and CO.³ SO₂ is also naturally produced through the oxidation of (CH₃)₂S in oceans and volcanic activity.³ With an atmospheric residence time of days, it is oxidised to H₂SO₄ by OH radicals, H₂O₂, and O₃ in clouds.³ Along with HNO₃, formed by the atmospheric oxidation of NO_x, H₂SO₄ contributes to acid

rain, which severely impacts marine ecosystems and forest growth.³ Volatile organic compounds like formaldehyde, acrolein, furan, styrene, and benzene are instead mutagenic,³ and their oxidation, along with the fossil fuel combustion and CH₄ oxidation, produces CO, a toxic gas that is lethal in high concentrations (>1000 ppm) and still harmful at lower levels, causing symptoms like headaches, fatigue, and nausea.³

Other air pollutants include fluorinated and brominated hydrocarbons, which contribute to the depletion of the ozone layer in the stratosphere.¹⁰ Because this shields the Earth from the ultraviolet radiation from the sun, which in turn is a risk factor for skin cancer, cataracts and immune diseases, its thinning is harmful for animal and human life.¹⁰

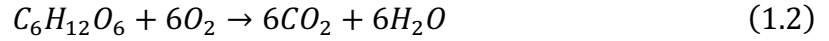
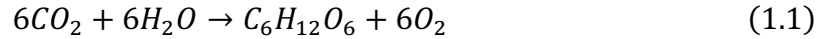
Soil and water pollution are instead largely driven by agricultural and domestic waste, such as personal care products, cleaning agents, and pharmaceuticals, particularly antibiotics, which contribute to bacterial resistance.¹¹ The runoff of pesticides and fertilisers into water basins promotes the growth of cyanobacteria and algae, leading to oxygen depletion and harming aquatic life, a process known as eutrophication.¹² Furthermore, persistent environmental contaminants such as per- and polyfluoroalkyls substances, used in water coatings and food packaging, resist degradation due to the inertness of the C–F bond.¹³ Additionally, non-biodegradable plastics, heavily used in agriculture for films, pipes, and other equipment, as well as in single-use items (*e.g.* fertiliser bags, and pesticide containers) are also a major source of pollution.¹³ Electronic waste, when not properly incinerated, releases particulate matter, phthalates, and brominated flame retardants, which negatively affect the endocrine and neurological systems.¹³ Lastly, soil contamination with toxic metals like Cr, Zn, Ni, Co, Cd, Cu, Mn, and Pb largely from mining, industrial activities, fossil fuel combustion, and improper disposal of electronic waste, also poses serious risks to food and human health.¹⁴

In the context of the environmental crisis outlined above, the following sections will focus on carbon and nitrogen-based waste.

1.2 The carbon cycle

In nature, carbon is exchanged between living organisms and the environment, as illustrated in **Figure 1.1**.¹ In this cycle, plants, plankton, and blue-green algae play a key role through photosynthesis, a process driven by sunlight that converts CO₂ and H₂O into glucose

($C_6H_{12}O_6$) and O_2 (Eq. 1.1). These products are then consumed during respiration by animals and plants, which releases CO_2 and H_2O (Eq. 1.2):



After the death of living organisms, their remains decompose in the soil and eventually form fossil fuels under anaerobic conditions, a process that takes millions of years. These are therefore a limited resource within the human timescale, and the point at which the consumption of fossil fuels exceeds their availability is referred to as Hubbert's peak.¹ The International Energy Agency (IEA) predicts that global oil demand may peak around 2028.¹⁵ In addition to depleting fossil fuel reserves, anthropogenic activities also contribute significantly to CO_2 emissions, as previously discussed. Of the anthropogenic CO_2 oceans currently absorb only about half.¹

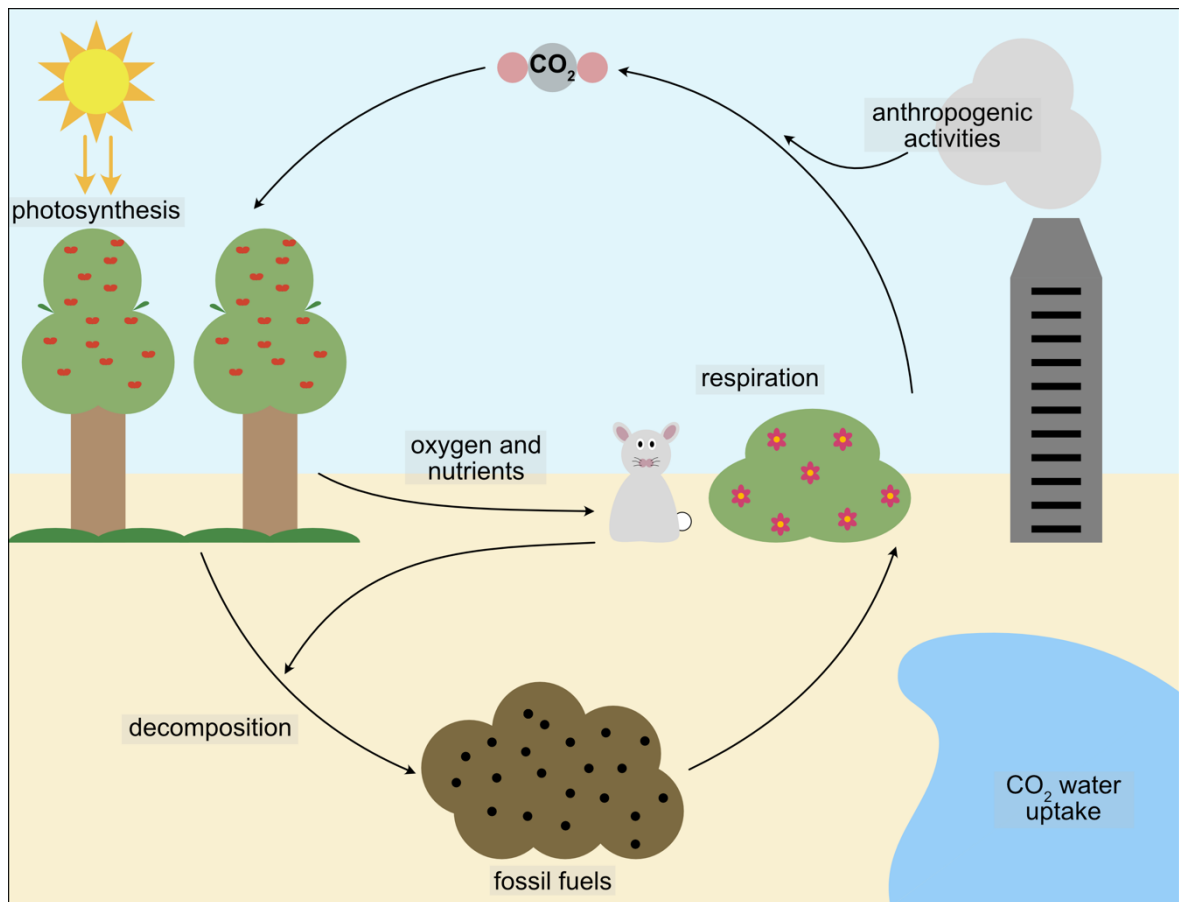


Figure 1.1 Schematic representation of the carbon cycle.

In this scenario, the scientific community is working to address two issues: the limited supply of fossil fuels and the accumulation of atmospheric CO₂ in the atmosphere. Thus, a possible approach is the adoption of renewable energy sources.¹ Furthermore, the CO₂ already present in the atmosphere can be captured, stored, and potentially converted into useful chemicals.¹⁶ To the aim of carbon capture, several strategies have been developed, including the use of alkaline solutions containing organic amines, NH₃, or NaOH.¹⁶ Alternatively, porous materials such as activated carbon, zeolites, and metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) can trap CO₂ through non-covalent interactions (NCIs).¹⁶ Another approach involves gas separation via selective membranes, such as organic polymers like chitosan derivatives or inorganic materials like ceramics.¹⁶ Alternatively, CO₂ can be physically separated at its desublimation temperature (−56.6°C) and collected as a high-purity liquid.¹⁶ The hydrate method instead envisions to trap CO₂ molecules in a crystal network of hydrogen-bonded water molecules, at low temperatures and high pressures.^{16,17} Lastly, autotrophic microorganisms such as microalgae can seize CO₂ directly from the atmosphere.¹⁶

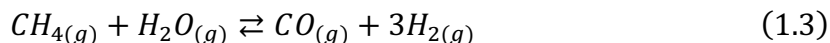
Once captured, CO₂ can be converted into valuable chemical feedstocks. The next Section provides a brief outline of the challenges of the CO₂ reduction reaction (CO₂RR) and details the potential products and their applications.

1.2.1 Overview of CO₂ reduction

Since carbon is in its highest oxidation state in CO₂ (+4), it can be reduced to an assortment of products depending on the number of electrons involved in the process, of variable chain length from one to three carbons.¹⁸ In order of decreasing oxygen content, CO₂ can be reduced to formic acid (HCOOH), acetic acid (CH₃COOH), carbon monoxide (CO), formaldehyde (HCOH), methanol (CH₃OH), ethanol (CH₃CH₂OH), methane (CH₄), ethylene (CH₂CH₂), and ethane (CH₃CH₃), all of which have applications across various industries. For example, organic acids are used in liquid fuel cells and, along with formaldehyde, in the synthesis of pharmaceuticals.^{19,20}

Additionally, the higher reactivity of CO compared to CO₂ facilitates its conversion into alcohols and hydrocarbons.¹⁹ Combined with H₂, it forms syngas, which is used both as a fuel and in the synthesis of NH₃ and CH₃OH.¹⁹ Furthermore, alcohols and hydrocarbons are also valuable fuels due to their high energy density.¹⁹ For instance, CH₃OH is used in direct methanol fuel cells (DMFCs), where CO₂ and H₂O are produced electrochemically by

oxidising CH_3OH at the anode and reducing O_2 at the cathode.²¹ The electric potential generated in this process enables DMFCs to serve as power sources in low-power and portable electronic devices, aided by the ease of CH_3OH transport and storage.²¹ Additionally, CH_4 plays a role in reforming processes to generate syngas, either via steam reforming with H_2O or dry reforming with CO_2 , as shown in Eq. 1.3 and 1.4:^{19,22}



Lastly, alcohols are common building blocks in chemical plants.¹⁹

Despite the numerous uses of the CO_2RR products, this process is faced with several challenges. First, the high stability of CO_2 , with a $\text{C}=\text{O}$ bond dissociation energy (BDE) of *ca.* 750 kJ/mol,²³ hinders its reduction. Moreover, the achievement of a high selectivity towards the desired feedstock is hindered by the numerous products of the CO_2RR itself, as well as the competition with the more facile hydrogen evolution (HER), discussed in greater detail in Section 1.2.6. Lastly, another challenge is the low solubility of CO_2 in water, around 30 mM at 1 bar and room temperature.¹⁹ This can be improved by applying higher pressures to increase the reactant flow and by replacing water with organic solvents like methanol and acetonitrile, or using more expensive alternatives like ionic liquids.¹⁹

1.3 The nitrogen cycle

Like carbon, nitrogen is exchanged between living organisms and the environment in the nitrogen cycle, shown in **Figure 1.2**.^{24,25} Molecular nitrogen (N_2) is the most abundant gas in the atmosphere (*ca.* 78%).²⁶ However, due to the strong $\text{N}\equiv\text{N}$ triple bond (BDE = 941 kJ/mol),²⁷ it is highly inert and not readily accessible to most plants and animals. Certain microbes, however, can fix it in the form of NH_3 , whose further conversion into nitrate (NO_3^-), mediated by bacteria, is known as nitrification. Both NH_3 and NO_3^- are taken up by plants and are eventually passed along to animals through the food chain. Then, upon the death of living organisms, nitrogen is returned to the soil as biomass decomposes. In a process called denitrification, bacteria in the soil convert nitrogen compounds like nitrite (NO_2^-), nitric oxide (NO), and nitrous oxide (N_2O) back to N_2 , releasing it into the atmosphere.

Human activities, much like in the carbon cycle, also interfere in the nitrogen cycle, since natural sources are insufficient to sustain the production of fertilisers needed to meet the global demand.²⁴ Thus, N_2 is artificially converted into chemicals for agricultural applications, particularly NH_3 , which also shows potential as a hydrogen carrier.²⁸ Currently, NH_3 is synthesised via the Haber-Bosch process (Eq. 1.5) under high temperatures and pressures (*ca.* 400°C and 150 bar), due to the stability of the $N\equiv N$ bond.²⁸



Other activities such as agriculture, manufacturing of explosives, metal finishing, fuel and wastewater treatment release NO_3^- .^{29,30,31,32} Due to its high water solubility, this is a widespread pollutant in groundwater basins, contributing to their eutrophication (Section 1.1.1).²⁹ In humans, exposure to high levels of NO_3^- can cause methemoglobinemia, a condition characterised by cyanosis, fatigue, shortness of breath, dizziness, headaches, and loss of consciousness.²⁹ It is caused by the reduction of NO_3^- to NO_2^- in the digestive system, which oxidises the Fe^{II} ions in haemoglobin, impairing O_2 transport. For this reason, the World Health Organization recommends maximum NO_3^- and NO_2^- levels of 10 and 0.03 mg/L, respectively, in drinking water.²⁹

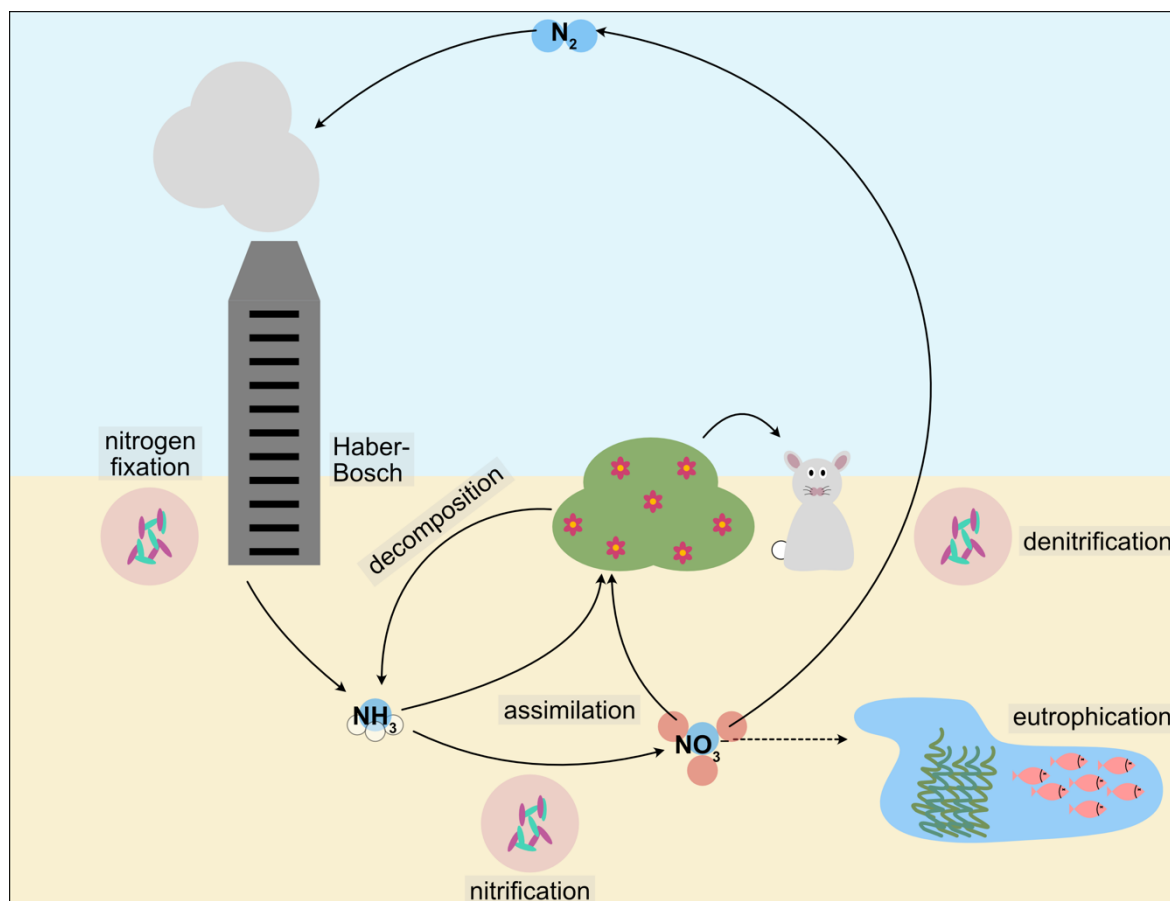


Figure 1.2 Schematic representation of the nitrogen cycle.

Like for CO₂, efforts are being directed to improve technologies for NO₃⁻ removal from the environment and its conversion into useful chemicals. For instance, one method involves reverse osmosis, where NO₃⁻ is filtered through a semipermeable membrane, although this process is energy intensive due to the required application of a driving force, *e.g.* pressure.³³ Biological remediation, involving bacteria that reduce NO₃⁻ under anaerobic conditions, faces challenges such as the generation of toxic by-products like NO₂⁻ and the sensitivity of the microorganisms to environmental conditions.^{33,34} Furthermore, adsorption techniques have been developed to capture NO₃⁻ using materials like activated carbon, zeolites, chitosan, cellulose polymers, and biochar.³⁵ Alternatively, resins functionalised with anions, typically chloride or bicarbonate, can replace them with the dissolved NO₃⁻.³³ These resins can then be regenerated by soaking them in concentrated saline solutions containing the original salts. Finally, electrodialysis can be used, where a potential difference between two electrodes drives ions through a series of ion-exchange membranes, selectively separating cations and anions into different compartments for collection.³³

The main challenges in converting NO₃⁻ into useful chemical feedstocks, along with potential products and their applications, will be discussed in the following section.

1.3.1 Overview of NO₃⁻ reduction

Since nitrogen is in its highest oxidation state in NO₃⁻ (+5), the nitrate reduction reaction (NO₃RR) can produce a wide variety of chemicals. As in the case of the CO₂RR, this diversity is both an advantage and a challenge, especially in terms of achieving product selectivity.

Thermodynamically, the most favourable end-products of the NO₃RR are N₂ and NH₃.²⁹ As discussed in the previous Section, at the industrial level NH₃ is primarily synthesised from N₂ via the Haber-Bosch process, which requires harsh conditions. Thus, given the lower bond dissociation energy of N=O in NO₃⁻ compared to N≡N in N₂ (204 kJ/mol vs 941 kJ/mol), the NO₃RR is considered a potentially more sustainable method for meeting the global NH₃ demand.²⁷ Another product of the NO₃RR is N₂O, a colourless gas widely used in the medical sector for sedation and pain relief.³⁶ It is also employed as a propellant in whipped cream dispensers, for leak detection in the oil industry, and to enhance the engine combustion in car racing.³⁶ Additionally, hydrazine (N₂H₄) is used for the detection of aldehydes and ketones in environmental, food, and industrial analyses.³⁷ Moreover, due to its high energy density and room temperature stability, it is utilised as a propellant in rocket

fuels.³⁸ Lastly, other products of the NO₃RR include NO₂⁻, NO, and hydroxylamine (NH₂OH).²⁹ The applications of NH₂OH are discussed in greater detail in Section 6.1.1, along with the coupling of NO₃RR with carbonate reduction for the synthesis of C–N products, such as urea, a widely used fertiliser.

Like the CO₂RR, the NO₃RR is primarily carried out electrochemically. However, the process is often hindered by competition with the more facile HER.²⁹

1.4 The role of catalysis

To improve the sustainability of the chemical industry, scientists are focusing on developing reactions that operate under environmentally friendly conditions, and on maximising the efficiency of pollutants processing. The field of chemistry that enables these objectives is known as catalysis. According to the International Union of Pure and Applied Chemistry (IUPAC), a catalyst is “*a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction*”.³⁹

In nature, most of the chemical processes essential to life are catalysed by enzymes, which are also applied in chemical synthesis.^{40,41} However, their industrial use is limited by their low throughput and the need of highly specific reaction conditions, and a detailed discussion of enzymatic catalysis is beyond the scope of this thesis. Beyond enzymes, catalysts can be divided into molecular species or solid state materials. Molecular catalysts usually share the same physical phase as the reactants, typically dissolved in solution. Thus, they are often known as homogeneous catalysts.⁴¹ In contrast, solid state materials, referred to as heterogeneous catalysts, exist in a different phase from the reactants, which are usually gaseous or dissolved molecules.⁴¹ Hybrid systems combine aspects of both homogeneous and heterogeneous catalysis by anchoring molecular catalysts, single metal atoms, or small metal clusters onto solid supports.⁴⁰

Catalysis can also be categorised based on the energy source used to drive the reaction, whether thermal energy (thermal catalysis), electrical energy (electrocatalysis), or electromagnetic radiation (photocatalysis). Combinations of these methods, such as photo-thermal and photo-electrocatalysis, also exist but are not discussed in this introduction.

The following Sections explore the advantages and challenges of homogeneous, heterogeneous, and hybrid catalysis, as well as their main industrial applications.

Additionally, the strengths and weaknesses of thermal, electro-, and photochemical processes are discussed in the context of heterogeneous and hybrid catalysis, along with commonly employed materials in each field.

1.4.1 Homogeneous catalysis

A prominent class of homogeneous catalysts is organometallic complexes, which consist of a transition metal centre surrounded by organic ligands. The metal centre is often a noble element such as Pd, Ir, Rh, or Ru, and the ligands can be highly sophisticated in structure, making organometallic catalysis costly.⁴² To address this issue, research efforts are focused on replacing noble metals with more earth-abundant elements such as Mn, Fe, Co, Ni, and Cu.⁴² Besides its cost, organometallic catalysis is also hindered by the environmental concerns associated with the disposal of metallic chemical waste and the toxicity of some metal catalysts. This is particularly problematic for products intended for biomedical applications, where the metal concentrations are governed by strict regulations.^{42,43} Additionally, the homogeneous nature of these systems complicates catalyst recovery and separation.^{41,44} For instance, in the synthesis of the herbicide (S)-metolachlor,⁴⁵ only the Ir metal centre is recuperated, while the Xyliphos ligand is lost. In light of these challenges, organocatalysis has emerged as a potentially more sustainable and less toxic alternative to organometallic catalysis. Organocatalysts, which include carbenes, phosphoric acids, amines, and alkaloids,⁴³ are fully organic and eliminate the concerns associated with metal toxicity. Lastly, another drawback of homogeneous catalysis in industrial applications is the difficulty in implementing continuous flow reactors.⁴⁴

Despite its limitations, homogeneous catalysis offers the significant advantage of controlling the catalyst structure. The well-defined, single site catalytic centres of organometallic and organocatalysts allow researchers to develop detailed structure-activity relationships and gain deep mechanistic insights.⁴⁴ This high level of control enables to refine chemo- and enantioselectivity through molecular modifications, making homogeneous catalysis invaluable for the synthesis of fine chemicals, pharmaceuticals, and bulk chemicals.^{43,45} A well-known example thereof is the Ziegler-Natta stereoselective synthesis of linear olefins, which can be conducted entirely in solution using a metallocene catalyst, typically based on Ti, and an organo-aluminium cocatalyst.⁴⁵

1.4.2 Heterogeneous catalysis

In heterogeneous catalysis, the fact that products and catalysts occupy different phases facilitates their separation and thus catalyst recycling.⁴⁶ Additionally, solid state materials typically exhibit higher stability under storage and operational conditions compared to molecular systems.^{47,48} The use of solid state metal catalysts in place of costly and often toxic organometallic complexes also reduces chemical waste and enhances reaction safety.⁴⁹ Furthermore, heterogeneous catalysis is well suited for continuous flow processes, which is particularly beneficial for industrial applications.⁴⁴

Nonetheless, heterogeneous catalysis remains less developed for complex organic synthesis, as it often exhibits lower chemo- and enantioselectivity than homogeneous systems.⁴⁴ For this reason, industrial applications of heterogeneous catalysis are primarily limited to the transformation of simple molecules, as discussed in more detail in Sections 1.4.3-1.4.4 and 1.4.7.⁴⁴

A key distinction between homogeneous and heterogeneous catalysis is the comparatively limited understanding of reaction mechanisms at solid interfaces, primarily due to the challenging identification of active sites.⁵⁰ This difficulty stems from the dynamic nature of catalyst surfaces under reaction conditions and their often complex morphology, which can be porous on the nanometer-to-micrometer scale. For example, undercoordinated atoms located at steps and edges have been shown to be more catalytically active than those on basal planes. As a result, nanomaterials often display superior catalytic performance compared to their bulkier counterparts. To study the dynamic processes occurring on catalyst surfaces, such as surface reconstruction and phase transitions, several techniques are employed. For instance, in-operando transmission and scanning electron microscopy are commonly used for these purposes.^{51,52} X-ray powder diffraction (p-XRD) is also widely applied to determine the crystal facets exposed by solid electrocatalysts.⁵³ Lastly, in-situ Raman and Fourier transform infrared spectroscopies are employed to identify reaction intermediates on catalyst surfaces.⁵³

The limitations of heterogeneous catalysis have led to the development of hybrid catalytic systems, which aim to combine the advantages of both homogeneous and heterogeneous approaches.

1.4.3 Hybrid catalysis

In hybrid catalytic systems, the presence of an anchored catalyst on a solid support is intended to enhance the activity and selectivity compared to unfunctionalised heterogeneous systems, possibly introducing stereochemical control.^{40,47} Additionally, such improvement in activity allows to adopt milder conditions compared to purely heterogeneous systems.⁴⁰ With respect to homogeneous catalysts, hybrid systems offer several advantages: they can be used in continuous processes, are easier to separate from products and recycle, and are more stable.⁴⁷

A recent computational study exemplifies the superior catalytic activity and stability of hybrid systems by investigating the oxygen evolution reaction on an Ir-based organometallic complex anchored to an IrO₂(110) surface.⁴⁸ This work showed no significant loss of catalytic activity after anchoring, while the enhanced stability of the hybrid system was attributed to the strong interaction between the catalyst and the surface. Ensuring optimal interplay between the components in hybrid setups is in fact paramount to prevent catalyst leaching, particularly under harsh conditions.⁴⁷ To this aim, both solid supports and catalysts can be functionalised to strengthen their interaction, as illustrated in **Figure 1.3**. For example, organometallic complexes often contain binding groups like thiols, amines, carboxylic acids, and phosphonic acids, which can establish NCIs or covalent bonds with the heterogeneous support, commonly a metal surface with undercoordinated atoms, a metal oxide, silica, alumina, or a polymer resin.^{40,47} Alternatively, molecular catalysts can be engineered with moieties that polymerise under an applied potential, forming a film of variable thickness.⁵⁴ Furthermore, single metal atoms and small metal clusters can be deposited on materials like graphene, carbon nitride, carbon nanotubes, and organic polymers, which present organic functional groups on their surfaces.⁴⁰ This approach is economically convenient when the active metal is a noble element, as it requires lower amounts of catalyst compared to traditional heterogeneous setups.⁴⁰ Moreover, hybrid catalysts can be incorporated into host materials with porous morphologies, such as zeolites, MOFs, and organic polymers.⁴⁷ Lastly, additional strategies for catalysts anchoring include supramolecular assembly within a guest structure on the heterogeneous surface, drop casting (*i.e.*, physisorbing the catalyst from solution and evaporating the solvent), and the electrostatic adsorption on charged thin films deposited on the support.⁵⁴

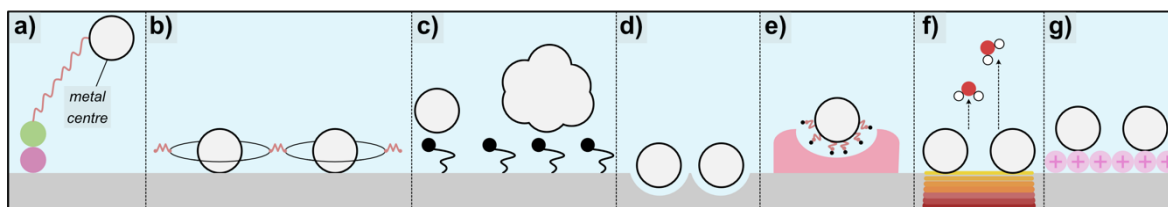


Figure 1.3 Illustration of the strategies to anchor catalysts on solid supports in hybrid systems: **a)** interactions via the ligand shell of a molecular complex, **b)** polymerization, **c)** deposition of a single metal atom and a small metal cluster, **d)** intercalation into surface pores, **e)** intercalation in supramolecular complexes, **f)** drop casting, and **g)** electrostatic adsorption on charged thin films.

Although hybrid catalysis is a more recent and less explored field compared to homogeneous and heterogeneous catalysis, its high tunability in catalyst design and interaction with solid supports makes it a very promising approach that is likely to gain increasing attention in the coming years.⁴⁸

1.4.4 Thermal catalysis

As discussed in Section 1.2, thermal processes use heat as the energy source to drive chemical reactions. Thus, they often necessitate extreme operating conditions, with temperatures reaching several hundreds of degrees Celsius, leading to high economic costs and environmental concerns.⁵⁵ Catalytic materials used in thermal catalysis must be highly resistant to heat, such as zeolites, transition metals, and metal oxides.⁵⁵ The high temperatures can also trigger many side reactions, reducing product selectivity.⁵⁵ Additionally, prolonged exposure to heat can deactivate catalysts through sintering –where catalyst particles agglomerate– or through phase changes caused by thermal degradation.^{56,55} Another common issue in thermal catalysis, especially in hydrocarbon transformations, is the formation of carbon deposits that can block active sites in a process known as coking.⁵⁵

Despite these disadvantages, thermal catalysis remains widely used in both industry and daily life. A notable example is the Haber-Bosch process for NH_3 synthesis, discussed in Section 1.1.4.^{28,57} Other key thermal processes include the large scale production of CH_3OH from syngas, which occurs on Zn and Cr oxides at *ca.* 400°C, and the Fischer-Tropsch synthesis of hydrocarbons, typically carried out at around 300°C.⁵⁷ Thermal catalysis also dominates the petrochemical sector, particularly in the cracking of hydrocarbons.⁵⁸ This can be performed in the absence of H_2 at temperatures between 800 and 900°C or in the presence of H_2 at slightly lower temperatures.⁵⁸ Another renowned thermal process is the reforming of CH_4 with H_2O (Eq. 1.3) or CO_2 (Eq. 1.4) for syngas production, reported in Section 1.1.3, which occurs at temperatures between 700 and 950°C.²² In non-industrial applications,

thermal catalysis is employed in catalytic converters in car engines to convert exhaust gases such as N_2O , CO , and unburned hydrocarbons into N_2 , CO_2 , and H_2O .^{55,56} Operating conditions span from 250-300°C (the minimum temperature required for activation) to 400-800°C (the optimal temperature range).⁵⁶ Common catalytic materials for this application include noble metals like Pt, Pd, and Rh, as well as alloys and more common elements like Cr.⁵⁶

1.4.5 Electrocatalysis

Redox processes involve the transfer of electrons between reactants. The species that gains electrons is said to be reduced, while the one that loses electrons is oxidised. Every reduction must be accompanied by an oxidation, and vice versa, but these processes can be physically separated.⁵⁹ One of the simplest setups involves two conducting plates, or electrodes, connected by a resistor and immersed in the reaction solution (**Figure 1.4a**).⁵⁹ The plate which promotes the reduction reaction is named cathode, while the plate promoting the oxidation is named anode. If the resulting redox process is spontaneous, it generates a current that flows from the anode to the cathode, creating a potential difference across the resistor. Such setup is known as galvanic or voltaic cell. If the redox process is not spontaneous, instead, an external potential must be applied to drive the reaction. This setup is called electrolytic cell.

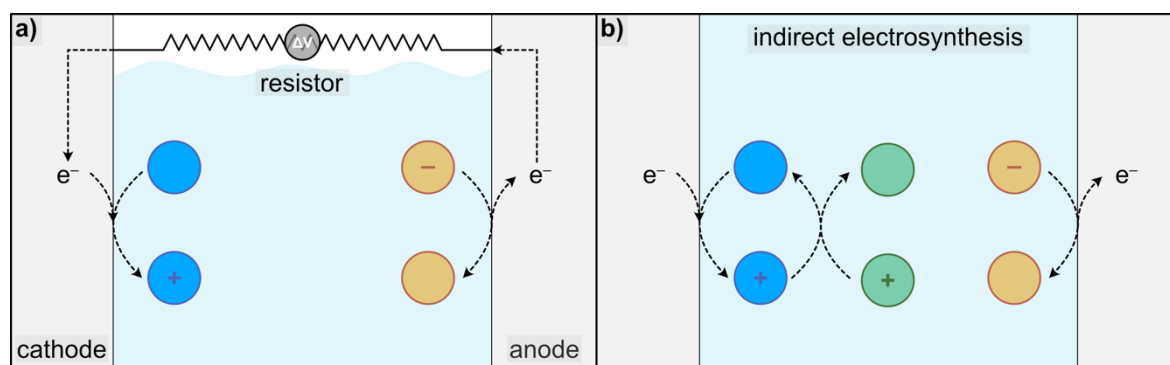


Figure 1.4 a) Illustration of an electrochemical cell composed by a cathode, anode, and resistor. **b)** Schematic representation of the indirect organic electrosynthesis approach using a mediator.

Compared to both homogeneous and thermal heterogeneous catalysis, heterogeneous electrocatalysis offers several advantages. For instance, metal electrodes replace organometallic catalysts and stoichiometric oxidants and reductants, lowering the chemical waste.⁴⁹ Moreover, the possibility of using electricity from renewable sources, and of adopting water and alcohols as solvents if compatible with the reactants, further enhances the sustainability of electrocatalysis for pollutant valorisation and organic synthesis.^{49,60,61}

Importantly, the use of water is not always viable in the presence of organocatalysts and organometallic complexes. Additionally, in some cases the reaction selectivity can be enhanced by tuning the applied potential, eliminating the need to functionalise the catalyst.^{49,60} Compared to thermal catalysis, electrocatalysis often operates under milder conditions, frequently at room temperature.⁶⁰ Finally, the ability to couple oxidation and reduction reactions in the same process is of industrial relevance.⁶⁰

Electrocatalysis finds practical application in environmental remediation and organic synthesis. For example, common water pollutants such as NO_3^- and NO_2^- from fertilisers, phenol from the chemical industry, cyanide from gold mining, and CH_3OH from the oil and gas industry can be treated electrochemically.⁶¹ In addition, electrocatalysis is used to convert greenhouse gases, such as CO_2 , into valuable products.¹⁸ To this aim, copper catalysts are among the most effective for hydrocarbon production, but the high stability of CO_2 , low reaction selectivity, and high overpotentials hinder the commercial applications of the electrochemical CO_2RR .¹⁸ In particular, the term overpotential refers to the discrepancy between the potential at which a reaction occurs in experiments, and the theoretical value at which the process is in equilibrium, determined via the Nernst equation reported below:⁵⁹

$$\Delta G^0 = -nFE^0 \quad (1.6)$$

where ΔG^0 is the Gibbs energy change associated with the reaction at standard conditions, n is the number of electrons exchanged in the electrochemical process and E^0 is the predicted voltage. While the Nernst equation is a thermodynamic relationship, a possible cause for an elevated overpotential is a high kinetic barrier for the electron transfer, as in the case of stable molecules like CO_2 .

In the context of organic electrosynthesis, functional groups are also interconverted through oxidation and reduction reactions. Organic oxidations driven by electricity include the transformation of alcohols into ketones, aldehydes, or carboxylic acids, aldehydes into carboxylic acids, and amines into aldehydes, ketones, or nitriles.⁵³ Common functional groups that can be hydrogenated electrochemically instead are $\text{C}=\text{N}$ and $\text{C}=\text{O}$ bonds, as well as $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds, especially when activated by electron-withdrawing groups.^{53,62} $\text{C}-\text{X}$ (where $\text{X} = \text{halogen}$) bonds have also been successfully hydrogenated and borylated via electroreductive pathways.⁶² Industrial examples of organic electrochemical processes include the dimerisation of acrylonitrile to adiponitrile for the production of Nylon-6,6,^{60,63} developed in the 1960s by Monsanto, the fluorination of hydrocarbons, developed by Simons

in 1949,^{60,63} and the oxidation of aromatics, such as toluene, to aldehydes.^{49,63} Fluorinated products are widely used as refrigerants and in the pharmaceutical and agricultural sectors, while aromatic aldehydes are employed as fragrances in perfumes and in the food industry.⁶³ Two primary approaches are employed for these transformations: a direct method, where the reactant is reduced or oxidised on the electrode surface, and an indirect method, where a mediator is reduced or oxidised at the electrode and then reacts with the substrate in solution (**Figure 1.4b**).⁶⁴ The chemical species used as mediators are numerous, ranging from metal salts, to aromatic compounds and organometallic complexes.⁶⁴ While these need to be separated from the products, adding to chemical waste, they improve stereoselectivity and chemoselectivity compared to direct approaches.⁶⁰

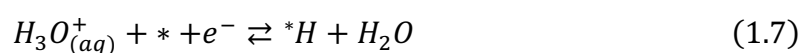
One of the key challenges in scaling up organic electrocatalysis is the competition with side reactions, such as the HER, which affects electroreduction processes.⁵³ The mechanism and optimal reaction conditions for HER will be discussed in detail in the next Section.

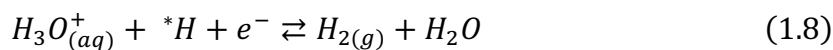
1.4.6 Hydrogen evolution reaction

As previously mentioned, an advantage of electrocatalysis is the ability to use water and alcohols as solvents. However, these contain protons, which can be reduced to H₂ at a thermodynamic potential of 0 V_{RHE}. This makes the HER an omnipresent competitor when a negative bias is applied.^{65,66}

The HER mechanism begins with the Volmer step, in which a proton is reduced to *H, with * denoting a surface active site, on the cathode surface.⁶⁷ When this occurs at more positive potentials than the equilibrium potential of the HER, hydrogen is said to be deposited underpotentially, a behaviour typical of noble metals such as Pt, Rh, Ru, Ir, and Pd, which adsorb it strongly.^{67,68} In contrast, if hydrogen is adsorbed at a potential below the thermodynamic value, it is deposited overpotentially and generally partakes in HER.^{67,69} The chemisorbed *H atoms can then either react with a proton from solution and an electron from the electrode, releasing H₂ in the Heyrovský step, or they can combine with each other in the Tafel step to form H₂ directly.⁶⁷

In acidic media, the proton source for the Volmer and Heyrovský reductions is H₃O⁺. These, along with the Tafel step, are described in Eq. 1.7, 1.8, and 1.9, respectively, and are illustrated in **Figure 1.5**:





Given this reaction mechanism, the binding energy of hydrogen, ΔG_{*H} , has been proposed as a key descriptor for the HER activity of cathode materials.^{70,71,68} According to the Sabatier principle, a highly exergonic ΔG_{*H} would hinder H–H coupling and H_2 desorption, while an endergonic ΔG_{*H} would impair the Volmer step.^{70,71,68,72} Thus, the optimal value of ΔG_{*H} is close to thermoneutral. This descriptor has been validated for a variety of different materials, including Ni, Mo, and Au surfaces, as well as the active sites in [Ni-Fe] hydrogenases.⁷² Another study successfully predicted variations in HER activity based on the concentration of sulphur vacancies in the basal plane of MoS_2 , which affected the ΔG_{*H} value.⁷³ In this context, the superior HER activity of Pt compared to other transition metals is attributed to its low overpotential for the Volmer step, resulting from its favourable ΔG_{*H} .⁶⁸

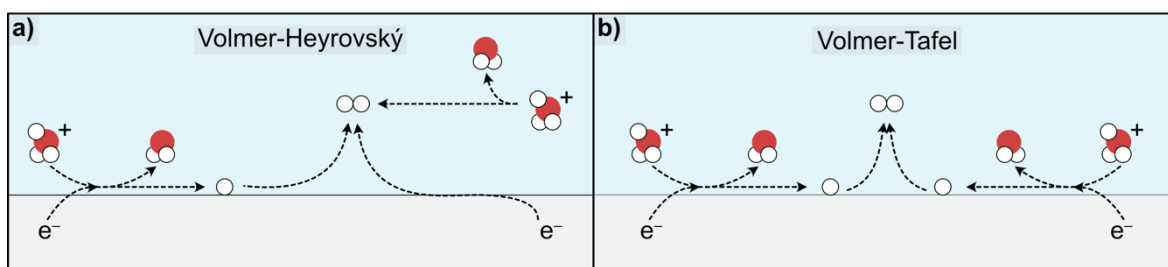
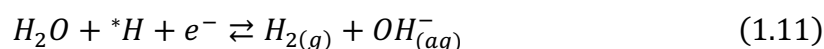
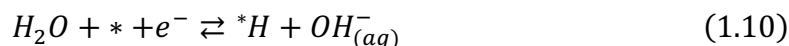


Figure 1.5 Schematic representation of the mechanism for the **a)** Volmer-Heyrovský and **b)** Volmer-Tafel HER in water under acidic conditions.

In alkaline media, the proton source for HER is water, which must be dissociated to provide protons (Eq. 1.10-12).^{67,70,71} For this reason, the Volmer step is generally considered the rate-determining step under basic conditions.⁶⁷



Due to the additional energy cost of water dissociation at the cathode, ΔG_{*H} alone can be insufficient to describe HER activity in alkaline media.⁶⁸ Instead, the water binding energy should also be assessed, since a favourable water adsorption can promote the Volmer step (Eq. 1.9).^{70,71} Experimentally, this was demonstrated by coating a Pt(111) electrode with

Ni(OH)₂ under basic conditions, which enhanced HER by improving the oxophilicity of the cathode, thereby promoting water adsorption and dissociation.⁷⁴

Besides pH, the applied bias also influences HER activity. Since the Volmer and Heyrovský steps involve a reduction at the cathode, they are promoted by increasingly negative potentials.⁶⁹ This results in progressively higher surface coverages of *H at more reducing biases, as described in a more quantitative fashion in Section 3.5.2. Furthermore, while the Tafel step is a chemical reaction that does not directly depend on the applied potential, the density of *H determines the availability of neighbouring atoms for H₂ formation.^{69,75} For this reason, the Tafel step can be indirectly affected by the electrode potential.

1.4.7 Photocatalysis

In photocatalysis, chemical reactions are promoted by exposure to electromagnetic radiation, typically ranging from ultraviolet (UV, 100-400 nm)⁷⁶ to visible (380-700 nm)⁷⁷ wavelengths. This excites an electron from the highest occupied to the lowest unoccupied orbital in a molecular photocatalyst or from the valence band to the conduction band in a semiconductor (**Figure 1.6**).⁷⁸ Semiconductors with larger band gaps require UV irradiation, while those with smaller band gaps can be activated by visible light.

The electron-hole pair generated during the excitation can drive oxidations via the filling of the hole or reductions via the electron transfer to a reactant. For an efficient charge transfer, the valence band maximum of the photocatalyst must be more positive than the oxidation potential of the substrate, while the conduction band minimum must be more negative than its reduction potential.⁷⁹

In the realm of heterogeneous photocatalysts, nanomaterials are widely studied. To qualify as such, at least one dimension of the material must range between 1 and 100 nm.⁸⁰ When all three dimensions fall within this range, the nanomaterial is referred to as zero-dimensional, like in the case of quantum dots (QDs).⁸⁰ In 2023, M. G. Bawendi, L. E. Brus, and A. Yekimov were awarded the Nobel prize in Chemistry for their work on QDs. When only two dimensions are under 100 nm, as in nanotubes and nanowires, the nanomaterial is regarded as one-dimensional.⁸⁰ Lastly, two-dimensional nanomaterials (*e.g.* nanosheets) have only one dimension within the nanometre range.⁸⁰ Their popularity as photocatalysts is due to the tunability of their band gap through size control, which can be tailored to specific reactions.⁸¹ In fact, at the nanoscale, the electronic energy levels are discrete, and their

spacing depends on the size of the material, with smaller dimensions leading to larger energy gaps.⁸⁰ Additionally, the high surface-to-volume ratio of nanosized materials increases the number of catalytic sites, enhancing their activity.⁸¹

In terms of composition, both inorganic compounds and organic polymers are used as photocatalysts.⁷⁸ Renowned inorganic photocatalysts include TiO_2 , SrTiO_3 , BiVO_4 , Ag_3PO_4 , TaON , Ta_3N_5 , CdS , and MoS_2 .⁸² TiO_2 has received significant attention due to its low cost, low toxicity, and chemical stability.⁸² Furthermore, it has been shown to successfully promote water splitting, generating H_2 without emitting greenhouse gases (**Figure 1.6**). However, the use of TiO_2 in its most stable phase (*i.e.* rutile) is limited by its large band gap (*ca.* 3 eV), which restricts the portion of the solar spectrum that can drive charge separation.⁸² To circumvent this issue, strategies like metal doping and the introduction of oxygen vacancies have been reported to narrow the band gap, by introducing defect states between the valence and the conduction band.^{82,78} In the realm of organic photocatalysts, instead, literature documents the use of graphitic carbon nitride, COFs, and metal covalent organic frameworks (MCOFs).⁸³ The band gaps of these materials can be tuned by altering the conjugation of organic linkers, adjusting the degree of polymerisation and crystallinity, and modifying the chemical composition (*e.g.* the C/N ratio in graphitic carbon nitride).⁷⁸ Thus, due to the significant structural variability offered by organic frameworks, their band gap is highly tunable. For example, the band gaps of MCOFs range from 1 to 5 eV, while graphitic carbon nitride has a more fixed band gap of approximately 2.7 eV.⁸³

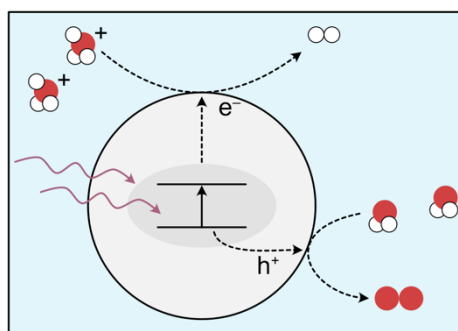


Figure 1.6 Schematic of photocatalytic water splitting on a semiconducting QD. This involves the reduction of two protons to H_2 , and the oxidation of two H_2O molecules to O_2 .

In addition to tuning the electronic properties, photocatalyst design focuses on minimising electron-hole recombination within the material, which hampers the charge transfer and reduces the catalytic activity. Hence, photocatalysts can be functionalised with cocatalysts that act as electron traps and improve reactant adsorption and reaction selectivity.^{84,85} To enable this, cocatalysts should facilitate the efficient charge transfer from the photocatalyst

to the substrate.⁸⁴ Examples include transition metal complexes and single element nanomaterials deposited on the catalyst surface, such as metals (Ag, Au, and Pt) and non-metals (*e.g.* carbon and black phosphorus).⁸⁵ To reduce the associated cost, noble metals can be alloyed with earth-abundant elements like Cu and Ni. Transition metal compounds, especially sulphides, carbides, phosphates, and borates, are also commonly used as cocatalysts.⁸⁵

Beyond water splitting, photocatalysis finds application in a variety of fields, like biomedicine. For instance, photocatalysts are used in photodynamic therapy for targeted cancer treatment, as well as in tissue engineering and antimicrobial applications.⁸³ Photocatalysis is also employed in the photodegradation of drugs and environmental pollutants, including small molecules (*e.g.* NO_x and CO₂), microplastics, and N₂ fixation.^{85,83} Similar to electrocatalysis, these processes can be carried out in aqueous solvents, and heterogeneous photocatalysts are easily separated from the substrates (Section 1.2.2). Another advantage is the potential use of solar radiation as a sustainable, low-cost energy source.⁸⁶ Yet, this presents several challenges. In fact, sunlight is unevenly distributed throughout the day, the seasons and across different parts of the globe.⁸⁶ Atmospheric gases also affect its intensity, which is variable within the spectral range. Additionally, the industrial scale up of photocatalytic processes is difficult due to the poor penetration of light in concentrated reaction media, the aggregation of the nanocatalysts on reactor surfaces, and the need for large catalytic surface areas. As a result, despite its numerous potential benefits, photocatalysis has yet to be widely implemented at an industrial scale.

2. Objectives

In light of the current climate crisis, catalysis plays a central role in the valorisation of organic reactants and the conversion of pollutants into relevant chemical feedstocks. To accelerate catalyst discovery, experiments must be combined with theoretical calculations that help unveil the underlying mechanism of action of catalytic materials. In this context, this thesis aims to rationalise the performance of heterogeneous catalysts for the photoreduction of CO₂ and the electrochemical reduction of acetophenone (AP) and NO₃⁻, to ultimately guide the design of more efficient catalytic systems. The results pertaining to each project are discussed in a separate chapter, whose specific objectives are outlined below.

2.1 Photochemical CO₂ reduction on ligand-functionalised ZnSe quantum dots

As discussed in the Introduction, the photoreduction of CO₂ is a sustainable strategy for its conversion into other valuable chemicals such as CO, which can be more easily transformed to alcohols and hydrocarbons.⁸⁷ In this scenario, the present study investigates the CO₂RR activity and selectivity towards CO of ZnSe QDs engineered with 1,2-ethanedithiol (EDT), 1,4-butanedithiol (BuDT), 1,6-hexanedithiol (HexDT) and 1,8-octanedithiol (OctDT), in the absence and in the presence of the Ni-cyclamphosphonate cocatalyst (Ni(cycP)). To rationalise the CO₂RR activity and selectivity observed experimentally, we set out to:

- Model the ZnSe bulk structure and surfaces indicated by p-XRD;
- Assess the adsorption of the EDT, HexDT and OctDT ligands and Ni(cycP) cocatalyst at the experimental coverage density;
- Verify the activity of the Zn²⁺ ions towards HER by calculating their hydrogen binding energy;
- Model CO₂ activation on the bare ZnSe and ZnSe | DT systems, also computing the NCIs between the DTs and the activated *CO₂⁻;⁸⁸
- Model the full CO₂RR mechanism in the ZnSe | Ni(cycP) and ZnSe | Ni(cycP) | DT set-ups, assessing the NCIs between the DTs and the most endergonic reaction intermediate.

This project was performed in close collaboration with the research group of Prof. Reisner, who carried out the experiments.

2.2 Electrochemical hydrogenation of acetophenone on transition metal electrodes

Electrochemical hydrogenations (ECHs) offer an alternative route to chemical reductions for the valorisation of organic compounds. While they are often impaired by the competition with HER, this can be hindered under alkaline pH.⁷⁰ Because not all organic substrates hydrolyse water at basic conditions, this work aims to demonstrate that, in such scenarios, the electrocatalyst itself must reduce and retain the *H atoms for the ECH reaction. Thus, the research group of Prof. Reisner performed the ECH of AP at alkaline pH on Ag, Au, Cu, In, Ni, and Pt metal electrodes. To explain their differential activity and selectivity, we proceeded to:

- Model the bulk cell and surfaces for the metal catalysts;
- Determine the surface coverage of the electrodes at the experimental conditions of potential and pH;
- Compute the thermodynamics of AP electroreduction on the metals, by sourcing the hydrogens from the catalyst surface coverage if available;
- Calculate the kinetics of AP hydrogenation mediated by the solvent;
- Explore the effect of different coverage configurations on the reaction energetics;
- Determine the kinetics and thermodynamics for HER via the Tafel mechanism.

2.3 NO₃⁻ electroreduction on Cu, Zn and Zn-Cu metal electrodes

As discussed in the Introduction, the scientific community is striving to convert NO₃⁻ ions into other chemicals of added value.²⁹ Specifically, this project aims at optimising hydroxylamine (NH₂OH) production for cyclohexanone oxime synthesis, a precursor in the preparation of Nylon-6. Experimentally, the electrochemical NO₃RR was conducted on Cu, Zn, and Zn_{1-x}Cu_x metal electrodes by the research group of Dr. Li. To rationalise the different activity and selectivity observed experimentally on the metal catalysts, we set forth to:

- Model the bulk cell and exposed surfaces of the Cu, Zn_{1-x}Cu_x and Zn electrodes indicated by p-XRD;
- Derive the catalyst surface coverage at experimental conditions of potential and pH;
- Explore the thermodynamics of the NO₃RR to N₂, NH₂OH and NH₃ as a series of PCETs, attempting all hydrogenations both at the nitrogen and oxygen to find the

most favoured reaction pathway, and modelling the binding of the intermediates in all available sites;

- Calculate the kinetic barrier for NH_2OH hydrogenation to NH_3 .

3. Methods

3.1 Foundations of quantum chemistry

In the 17th century, Newton formulated the laws of motion, establishing the foundation of classical mechanics, which remained undisputed until the 19th century. Then, experimental evidence such as the ultraviolet catastrophe and the structure of atomic and molecular spectra revealed the limitations of classical physics. In particular, it was determined that atoms, electrons and the electromagnetic radiation shared a dual nature, both as particles and waves, and exchanged energy in finite amounts, named *quanta*. Thus, a new field of physics emerged to study their properties, called quantum mechanics. With the advent of fast and efficient quantum mechanical simulations, made possible by the advances in computer science, quantum mechanics is now a central branch of Chemistry, capable of explaining and predicting the structural properties and reactivity of chemical systems at the nanoscale.

3.1.1 The Schrödinger equation

Quantum mechanics is based on the following five postulates:

- The properties of any physical system, called observables, can be described through a wavefunction $\Psi(r, t)$ whose value depends on space (r) and time (t);
- Any observable can be formulated through an operator $\hat{O}$ that is linear and Hermitian;
- The possible outcomes of its measurement are given by applying $\hat{O}$ to $\Psi(r, t)$;
- The average value $\langle o \rangle$ of multiple measurements of the same observable is:

$$\langle o \rangle = \frac{\int_{-\infty}^{+\infty} \Psi(r, t)^* \hat{O} \Psi(r, t) d\tau}{\int_{-\infty}^{+\infty} \Psi(r, t)^* \Psi(r, t) d\tau} \quad (3.1)$$

- $\Psi(r, t)$ evolves in time according to the time dependent Schrödinger equation, here reported, where the Hamiltonian operator $\hat{H}$ describes the energy (E) of the system:

$$\hat{H}\Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t} \quad (3.2)$$

If the potential energy is constant over time, it is possible to calculate E in terms of r only. This leads to the formulation of the time independent Schrödinger equation:

$$\hat{H}\Psi(r) = E\Psi(r) \quad (3.3)$$

where $\hat{H}$ captures the kinetic energy of the electrons ($\hat{T}_e$) and nuclei ($\hat{T}_N$), and the interelectronic ($\hat{V}_{ee}$), internuclear ($\hat{V}_{NN}$), and electronic-nuclear ($\hat{V}_{eN}$) interactions, as expressed in Eq. 3.4. Other terms are introduced when required (e.g. the presence of a magnetic field).

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN} \quad (3.4)$$

where, in atomic units:

$$\hat{T}_e = \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 \quad (3.5a)$$

$$\hat{T}_N = \sum_{A=1}^M -\frac{1}{2m_A} \nabla_A^2 \quad (3.5b)$$

$$\hat{V}_{ee} = \sum_{i<j}^N \frac{1}{r_{ij}} \quad (3.5c)$$

$$\hat{V}_{eN} = \sum_{i=1}^N \sum_{A=1}^M -\frac{Z_A}{r_{iA}} \quad (3.5d)$$

$$\hat{V}_{NN} = \sum_{A<B}^M \frac{Z_A Z_B}{r_{AB}} \quad (3.5e)$$

with N denoting the number of electrons, M the number of nuclei, m_A and Z_A the mass and atomic number of the nucleus A , respectively, r_{ij} the distance between electron i and j , r_{AB} the distance between nucleus A and B and r_{iA} the distance between electron i and nucleus A . Because $\hat{V}_{ee}$, $\hat{V}_{eN}$ and $\hat{V}_{NN}$ depend simultaneously on the relative position of different particles, the exact determination of $\Psi(r)$ is mathematically unfeasible. However, to partially circumvent this issue, it is possible to ignore the correlation between nuclei and electrons, due to the slower motion of the former compared to the latter, as envisioned by the Born-Oppenheimer approximation. Thus, the movement of the electrons is considered instantaneous with respect to that of the nuclei, and the time independent Schrödinger equation (Eq. 3.3) can be separated into a nuclear and an electronic component. The latter contains the terms $\hat{T}_e$, $\hat{V}_{ee}$ and $\hat{V}_{eN}$, while the internuclear energy V_{NN} is added as a constant

to the computed electronic energy, E_e . The solution to this equation renders the electronic wavefunction, $\Psi_e(r)$:

$$\hat{H}_e \Psi_e(r) = E_e \Psi_e(r) \quad (3.6)$$

For simplicity, the above terms will be referred to as $\hat{H}$, E , and Ψ .

3.1.2 The variational principle

Given N solutions Ψ_i to the Schrödinger equation, called basis set, an ensemble of N linear combinations (Φ) of Ψ_i can be derived, each characterised by a series of coefficients c_i :

$$\Phi = \sum_{i=1}^N c_i \Psi_i \quad (3.7)$$

It is possible to demonstrate that the energy of a trial wavefunction Φ , constructed from a certain set of c_i , can only be greater than, and at most equal to, the ground state energy, E_0 . This statement, called the variational principle, underlies many methods that are used to solve the Schrödinger equation for multi-electron and multi-nuclear systems. Its mathematical formulation is given by:

$$\frac{\int \Phi^* \hat{H} \Phi dr}{\int \Phi^* \Phi dr} \geq E_0 \quad (3.8)$$

3.1.3 The Hartree method

Due to the electron correlation (Section 3.1.1), solving Schrödinger equation for multi-electron systems is mathematically impossible. To get around this issue, Hartree proposed to average the electronic interactions as a mean field $\hat{V}_i$ for each electron i ,⁸⁹ as follows:

$$\hat{V}_i = \sum_{j>i}^N \int \frac{\Psi_j^2}{r_{ij}} dr \quad (3.9)$$

According to this definition, $\hat{V}_i$ represents the classical interaction between electrons i and j in all regions of space. For each i , j is taken to be of greater value, to avoid the double-counting of the same electron-electron interactions (*e.g.*, the repulsion given by $i = 1$ and $j = 2$, and $j = 1$ and $i = 2$, is the same, so the latter is discarded). Because $\hat{V}_i$ is

approximated as a mean field neglecting electron correlation, $\hat{H}$ can be separated into the sum of one-electron operators, $\hat{h}_i$, of the form:

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + V_i \quad (3.10)$$

Therefore, every monoelectronic wavefunction Ψ_i can be computed by solving the following equation:

$$\hat{h}_i \Psi_i = \varepsilon_i \Psi_i \quad (3.11)$$

The bottleneck in this methodology is that, unless the monoelectronic wavefunctions Ψ_i are known, it is not possible to compute the average field operators $\hat{V}_i$ that appear in the individual $\hat{h}_i$. To circumvent this issue, a trial set of molecular orbitals Ψ_i can be devised, *i.e.* monoelectronic wavefunctions expressed as linear combinations of atomic orbitals ψ_k :

$$\Psi_i = \sum_k c_k \psi_k \quad (3.12)$$

where the coefficients c_k are arbitrarily chosen.

Additionally, the formulation of Ψ_i in Eq. 3.12 can be further elaborated to include spin, a purely quantum mechanical property of electrons. Its operator presents two eigenfunctions s_i , labelled as α when the eigenvalue is positive ($\hbar/2$) and β when negative ($-\hbar/2$), and they are orthonormal. Multiplication of the spatial part of the monoelectronic wavefunction (Eq. 3.12) by s_i yields a so-called spin-orbital:

$$\Psi_i = s_i \sum_k c_k \psi_k \quad (3.13)$$

From the Ψ_i , a set of trial $\hat{h}_i$ can be constructed, and Eq. 3.11 can be solved for each electron i , furnishing a new set of eigenfunctions Ψ_i and their corresponding eigenvalues ε_i . Because of the independent treatment of the electrons, Hartree proposed to calculate the total energy of the system E_{sys} as the sum of the individual ε_i :

$$E_{sys} = \sum_{i=1}^N \varepsilon_i \quad (3.14)$$

and to construct the ground-state wavefunction Ψ^H of the multi-electron system as the product of the monoelectronic wavefunctions Ψ_i , also known as Hartree product:

$$\Psi^H = \prod_{i=1}^N \Psi_i \quad (3.15)$$

This procedure is repeated iteratively and, thanks to the variational principle outlined in Section 3.1.2, the set of solutions Ψ_i can only get closer to E_0 at every cycle. Thus, the procedure is terminated when the difference between consecutive E_{sys} values, or coefficients in the wavefunction Ψ^H , lowers below an arbitrary threshold. For this reason, the Hartree approach is said to be a self-consistent field method.

3.1.4 The Slater determinant

The form of Ψ^H given in Eq. 3.15 presents a fundamental flaw in the description of multi-electron systems, namely, it does not satisfy Pauli's exclusion principle. This states that two electrons cannot be characterised by the same set of quantum numbers, *i.e.* they cannot occupy the same spin-orbital. Consequently, a multi-electron wavefunction needs to be antisymmetric with respect to the exchange of the coordinates of two electrons, which is not true for Ψ^H . An appropriate modification was proposed in the form of a Slater determinant, calculated from a matrix where the spin-orbitals are arranged in different columns and the electron coordinates in rows (or vice versa):

$$\Psi^{SD} = 1/\sqrt{N!} \begin{vmatrix} \varphi_1(1)s_1(1) & \dots & \varphi_1(N)s_1(N) \\ \dots & \dots & \dots \\ \varphi_N(1)s_N(1) & \dots & \varphi_N(N)s_N(N) \end{vmatrix} \quad (3.16)$$

where the pre-factor $1/\sqrt{N!}$ normalises Ψ^{SD} and φ_i indicates the spatial part of each molecular orbital Ψ_i (Eq. 3.13). In Eq. 3.16, all electrons appear in every spin-orbital, coherently with their indistinguishability. Since determinants change sign when two rows, or columns, are inverted, they are indeed antisymmetric with respect to the exchange of the coordinates of two electrons.

Importantly, application of the N -electron Hamiltonian (Eq. 3.5a-e) to a two-electron Slater determinant results in the following expression for the total energy of the system, E_{sys} :

$$E_{sys} = \sum_{i=1}^N \left\langle \Psi^{SD} \left| -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right| \Psi^{SD} \right\rangle + \sum_{i=1}^N \sum_{j>i}^N \left(\left\langle \Psi^{SD} \left| \frac{1}{r_{ij}} \right| \Psi^{SD} \right\rangle \right) \quad (3.17)$$

The first two terms represent the kinetic energy of the electrons and their energy of interaction with the nuclei, respectively, and are grouped into a one-electron operator. The third term represents the interelectronic repulsions and, for each pair of electrons, it comprises two contributions, namely the Coulomb and exchange energies:

$$J_{ij} = \iint \Psi_i^*(r_1) \Psi_j^*(r_2) \frac{1}{r_{12}} \Psi_i(r_1) \Psi_j(r_2) dr_1 dr_2 \quad (3.18)$$

and

$$K_{ij} = \iint \Psi_i^*(r_1) \Psi_j^*(r_2) \frac{1}{r_{12}} \Psi_i(r_2) \Psi_j(r_1) dr_1 dr_2 \quad (3.19)$$

where r_1 and r_2 indicate the coordinates of the two electrons, while i and j run over the spin-orbitals. J_{ij} is the Coulomb integral, representing the classical repulsion between an electron of coordinates r_1 in the spin-orbital Ψ_i and an electron of coordinates r_2 in the spin-orbital Ψ_j . On the other hand, K_{ij} is the exchange integral and has no classical counterpart.

Because the spin functions are orthonormal, if Ψ_i and Ψ_j are characterised by parallel spin, K_{ij} is positive, whereas if Ψ_i and Ψ_j are characterised by antiparallel spin, K_{ij} vanishes. The exchange energy is in fact a consequence of Pauli's exclusion principle, according to which electrons of the same spin are described by different spatial orbitals, and therefore present a lower repulsion energy than the value predicted classically.

3.1.5 The Hartree-Fock method

Hartree's methodology to solve the Schrödinger equation was further developed by Fock, who proposed to use Ψ^{SD} as multi-electron wavefunctions, and to average the interelectronic repulsions by accounting for both the Coulomb interactions and exchange energy. Thus, the $\hat{h}_i$ monoelectronic operators of the Hartree method presented in Eq. 3.10 are replaced by the Fock operators $\hat{f}_i$ as follows:

$$\hat{f}_i = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \hat{J}_i - \hat{K}_i \quad (3.20)$$

where the $\hat{J}_i$ operator represents the average Coulomb repulsion between electron i and all the others, while the $\hat{K}_i$ operator represents the average exchange energy between electron i and all the others of the same spin. Thus, in a closed-shell calculation where all electrons are paired, the number of J_{ij} contributions is double the number of K_{ij} contributions. Like the Hartree approach, the Hartree-Fock (HF) method is also self-consistent. Specifically, it envisions the recursive solution of monoelectronic Fock equations of the kind:

$$\hat{f}_i \Psi_i = \varepsilon_i \Psi_i \quad (3.21)$$

After every iteration, new sets of monoelectronic Ψ_i and ε_i are derived. Due to the variational principle, the corresponding Ψ^{SD} and E_{sys} get closer to their ground-state values, and the procedure is repeated until the difference in Ψ^{SD} or E_{sys} lowers below an arbitrary threshold.

While the HF method improves on the Hartree approach by including the exchange energy of electrons of the same spin, a major limitation is the total neglect of the correlation energy between electrons.

3.2 Density functional theory

3.2.1 The Hohenberg-Kohn theorems

If the multi-electron wavefunction Ψ of a system for N electrons were known, it would be possible to compute its exact electron density $\rho(r)$ as follows:

$$\rho(r) = N \int |\Psi(r_1, \dots, r_N)|^2 dr_2 \dots dr_N \quad (3.22)$$

With r_i being the coordinates of electron i . Hohenberg and Kohn were able to show that $\rho(r)$ is uniquely related to the potential field generated by the nuclei, named external potential $\hat{V}_{ext}$. Because $\hat{T}_e$ and $\hat{V}_{ee}$ do not depend on the chemical system under analysis, but rather are universal, $\rho(r)$ was proven to uniquely determine the full $\hat{H}$. This statement constitutes the first theorem by Hohenberg and Kohn.⁹⁰ The second theorem by Hohenberg and Kohn states that $\rho(r)$ obeys to the variational principle.⁹⁰ Together, the first and second theorems

by Hohenberg and Kohn contributed to the development of Density Functional Theory (DFT).

3.2.2 The Kohn-Sham DFT

Building upon the Hohenberg and Kohn theorems, Kohn and Sham presented a method to determine $\hat{H}$ from a trial $\rho(r)$. They hypothesised a system of non-interacting electrons endowed with the same $\rho(r)$ as the real system, amounting to the sum of the squared monoelectronic wavefunctions Ψ_i :

$$\rho(r) = \sum_{i=1}^N \langle \Psi_i | \Psi_i \rangle \quad (3.23)$$

Then, the energy of the real system was written as a functional of $\rho(r)$, $E[\rho(r)]$, divided into the following components:

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ee,ni}[\rho(r)] + V_{Ne,ni}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)] \quad (3.24)$$

where $T_{ni}[\rho(r)]$, $V_{ee,ni}[\rho(r)]$ and $V_{Ne,ni}[\rho(r)]$ are the electron kinetic energy, electron-electron repulsion, and nuclear-electron attraction energy for the non-interacting system, respectively, while $\Delta T[\rho(r)]$ and $\Delta V_{ee}[\rho(r)]$ are the corrections to the kinetic and electron-electron repulsion energies due to the electron exchange and correlation. Together, these constitute the exchange and correlation term, $E_{XC}[\rho(r)]$, whose form is unknown.

The non-interacting terms in Eq. 3.24 can be rewritten in their HF form and applied to the Ψ_i . Thus, the functional $E[\rho(r)]$ becomes:

$$\begin{aligned} E[\rho(r)] = & \sum_{i=1}^N \langle \Psi_i | \frac{1}{2} \nabla_i^2 | \Psi_i \rangle + \sum_{i=1}^N \langle \Psi_i | \int \frac{\rho(r')}{|r - r'|} dr' | \Psi_i \rangle - \sum_{i=1}^N \langle \Psi_i | \sum_{A=1}^M \frac{Z_A}{|r - r_A|} | \Psi_i \rangle \\ & + E_{XC}[\rho(r)] \end{aligned} \quad (3.25)$$

Because the HF terms are computed for a system of non-interacting electrons, whose energy is corrected for exchange and correlation through $E_{XC}[\rho(r)]$, a set of independent one-electron equations can be solved, with the general form:

$$h_i^{KS} \Psi_i = \varepsilon_i \Psi_i \quad (3.26)$$

with h_i^{KS} being the Kohn-Sham Hamiltonian operator:

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 + \int \frac{\rho(r')}{|r-r'|}dr' - \sum_{A=1}^M \frac{Z_A}{|r-r_A|} + V_{XC} \quad (3.27)$$

where V_{XC} is the functional derivative of $E_{XC}[\rho(r)]$. Thus, the total energy of the system is the sum of the one-electron energies ε_i , and $\Psi(r)$ is the Slater determinant of the monoelectronic Ψ_i .

Since a trial $\rho(r)$ must be known to derive V_{XC} and solve the Kohn-Sham equations (Eq. 3.26), a self-consistent approach is adopted. Specifically, a basis set is first chosen, which allows to express the spatial part of the monoelectronic Ψ_i as linear combinations of atomic orbitals ψ_k of hypothetical coefficients c_k (as in Eq. 3.13). Then, V_{XC} is computed from the corresponding $\rho(r)$, and each h_i^{KS} is applied to the trial Ψ_i . Determination of a new set of coefficients c_k in the expansions of each Ψ_i allows to compute a new ensemble of h_i^{KS} , to be introduced in a new system of Kohn-Sham equations. This procedure is terminated when convergence of the energy, or $\rho(r)$, is reached for a given arbitrary threshold.

As the form of $E_{XC}[\rho(r)]$ is unknown, it must be approximated. Therefore, although $\rho(r)$ has variational behaviour, it is possible to determine lower energy values than the true one.

3.2.3 The local spin density approximation

As outlined in Section 3.2.2, $E_{XC}[\rho(r)]$ functionals need to account for the corrections to both $V_{ee,ni}[\rho(r)]$ and $T_{e,ni}[\rho(r)]$, and their exact form is unknown. Notation wise, an energy density per particle $\varepsilon_{XC}[\rho(r)]$ can be introduced, which also depends on $\rho(r)$ in a functional form. This allows to express $E_{XC}[\rho(r)]$ as follows:

$$E_{XC}[\rho(r)] = \int \rho(r)\varepsilon_{XC}[\rho(r)]dr \quad (3.28)$$

where $\varepsilon_{XC}[\rho(r)]$ includes exchange and correlation effects, for which different formulations have been proposed that can be divided into classes based on their treatment of $\rho(r)$. Among these falls the local density approximation (LDA), which assumes $\varepsilon_{XC}[\rho(r)]$ to only depend on the value of $\rho(r)$ at a given position r . Thus, $\varepsilon_{XC}[\rho(r)]$ is constructed as if each point in space behaved like a uniform electron gas endowed with $\rho(r)$ at r . Following this approximation, $\varepsilon_X[\rho(r)]$ has the form:

$$\varepsilon_X[\rho(r)] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(r) \quad (3.29)$$

Because spin is not incorporated in $\rho(r)$, a limitation of the LDA approach is that it ignores its effect on the exchange energy. Therefore, a new model was proposed, giving rise to the local spin density approximation (LSDA). This introduces the degree of spin polarisation $\zeta(r)$ into $\varepsilon_X[\rho(r)]$, defined at any position of space r as:

$$\zeta(r) = \frac{\rho^\alpha(r) - \rho^\beta(r)}{\rho(r)} \quad (3.30)$$

and $\varepsilon_X[\rho(r), \zeta(r)]$ becomes:

$$\varepsilon_X[\rho(r), \zeta(r)] = \varepsilon_X^0[\rho(r)] + (\varepsilon_X^1[\rho(r)] - \varepsilon_X^0[\rho(r)]) \left[\frac{(1 + \zeta(r))^{\frac{4}{3}} + (1 - \zeta(r))^{\frac{4}{3}} - 2}{2(\sqrt[3]{2} - 1)} \right] \quad (3.31)$$

where $\varepsilon_X^0[\rho(r)]$ is given by Eq. 3.29, while $\varepsilon_X^1[\rho(r)]$ is the analogous expression for a system of electrons sharing the same spin. For unpolarised systems, $\zeta(r) = 0$ renders the numerator of the second term also zero, and $\varepsilon_X[\rho(r)]$ coincides with $\varepsilon_X^0[\rho(r)]$.

For the correlation component $\varepsilon_C[\rho(r)]$, instead, there is no analytical expression. Thus, Ceperley and Alder calculated the energy of uniform electron gases of different $\rho(r)$ via quantum Monte Carlo techniques, subtracting the classical and exchange contributions to obtain $\varepsilon_C[\rho(r)]$.⁹¹ Their results then served as foundation for the development of other LSDA functionals by Vosko, Wilk and Nusair.⁹²

3.2.4 The generalised gradient approximation

An improvement over the LSDA is represented by the generalised gradient approximation (GGA). This accounts for the deviations of $\rho(r)$ from its value at r by including the gradient of the electron density, $\nabla\rho(r)$, into the functional.

The GGA functional employed in this thesis is the one developed by Perdew, Burke, and Ernzerhof, known as PBE.⁹³ It expresses the correlation energy $E_{C,PBE}$ as:

$$E_{C,PBE} = \int \rho(r) [\varepsilon_C^{unif}(r_s, \zeta(r)) + H(r_s, \zeta(r), t)] dr \quad (3.32)$$

where $H(r_s, \zeta(r), t)$ is a function of the local Size radius, r_s (*i.e.* the radius of a sphere containing, on average, a free valence electron), the degree of spin polarisation $\zeta(r)$, and a dimensionless density gradient, t , of the form $\frac{|\nabla\rho(r)|}{2\phi k_s \rho(r)}$. In the formulation above, ϕ is itself a function of $\zeta(r)$, and k_s is the Thomas-Fermi screening wavenumber. This highlights that, in a solid, the screening of the positive potential of the nuclei by the negative charge accumulated in their vicinity becomes almost complete at a set distance from the ion cores.⁹⁴ The term ε_c^{unif} in Eq. 3.32 is the correlation energy per particle of a uniform electron gas.

The exchange contribution $E_{X,PBE}$ is written below:

$$E_{X,PBE} = \int \rho(r) \varepsilon_X^{unif}(\rho(r)) F_X(s) dr \quad (3.33)$$

where s is a reduced density gradient of shape $\frac{|\nabla\rho(r)|}{2k_F\rho(r)}$, with k_F being the Fermi wavevector. The function $F_X(s)$, known as enhancement factor, scales the exchange energy of the uniform electron gas as follows:

$$F_X(s) = 1 + k - \frac{k}{1 + \frac{\mu}{k} s^2} \quad (3.34)$$

with the k parameter amounting to 0.804 and μ being the gradient coefficient for the exchange energy.

3.2.5 Dispersion interactions

Because of electron correlation, non-bonded chemical species can display fluctuations in their polarisation that result in an attractive force between them, *i.e.* an NCI. Therefore, these would only be correctly described by DFT if the exact correlation functional were known. Moreover, because they are characterised by a long range of action, they are inherently non-local properties of $\rho(r)$, and are therefore poorly described by the semi-local GGA approximation discussed above. Among the approaches proposed to correct the DFT energy accounting for dispersion interactions, the third revision of the scheme developed by Grimme and co-workers (D3) was employed in this thesis.⁹⁵ While the D3 method is transferable between different functionals, its main drawback is that the electronic structure of the system remains untouched, and the dispersion forces are accounted for just by adding a correction term to the calculated DFT energies.

In the framework of Grimme's D3 method, the dispersion energy $E_{disp}^{(2)}$ due to two-body interactions is determined as:

$$E_{disp}^{(2)} = \sum_{AB} \sum_{n=6,8,\dots} s_n \frac{C_n^{AB}}{r_{AB}^n} f_{d,n}(r_{AB}) \quad (3.35)$$

where r_{AB} is the distance between the A and B atoms, n is the order of the dispersion correction, and C_n^{AB} is the dispersion coefficient between atoms A and B, which Grimme *et al.* derived for all elements presenting an atomic number of 1 to 94. Only the parameters pertaining to the dispersion corrections of the 6-th and 8-th order were optimised, since longer-range dispersions were found to lead to unstable expressions for $E_{disp}^{(2)}$. The term s_n is a scaling factor that adjusts the resulting $E_{disp}^{(2)}$ depending on the specific functional that is used. Lastly, $f_{d,n}(r_{AB})$ is a damping function which determines the extent of the correction depending on r_{AB} . In the D3 model, it has the following expression:

$$f_{d,n}(r_{AB}) = \frac{1}{1 + 6 \left(\frac{r_{AB}}{s_{r,n} R_0^{AB}} \right)^{-\alpha_n}} \quad (3.36)$$

with R_0^{AB} being the cut-off distance at which atoms A and B are considered to interact, $s_{r,n}$ a scaling factor of such cut-off distance which tunes it according to the order of the correction and the functional in use, and α_n a coefficient that is adjusted so that $f_{d,n}(r_{AB})$ decays fast close to the nuclei, in order for bond energies not to be corrected by $E_{disp}^{(2)}$.

Additionally, the D3 model includes three-body interactions through the equation:

$$E_{disp}^{(3)} = \sum_{ABC} f_{d,(3)}(\bar{r}_{AB}) E^{ABC} \quad (3.37)$$

where the sum is over all atom triplets A-B-C, $f_{d,(3)}$ is a damping function of similar shape to that shown in Eq. 3.36, wherein $\bar{r}_{AB}$ is the geometric average of the individual distances r_{AB} , r_{BC} , and r_{CA} , and the energy of interaction, E^{ABC} , is not calculated as the sum of the atom pairs but rather through perturbative theory as:

$$E^{ABC} = \frac{C_9^{ABC} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3} \quad (3.38)$$

with θ_a , θ_b and θ_c being the angles formed by r_{AB} , r_{BC} and r_{CA} , and C_9^{ABC} being the negative geometric mean of the pairwise dispersion coefficients C_6^{AB} , C_6^{BC} and C_6^{CA} . Because C_9^{ABC} is negative, and the cosine function of θ_x can either be positive or negative, it is possible that the three-body term displays repulsive character.

3.2.6 The Bayesian error estimation functional

Another functional adopted in this thesis is the Bayesian error estimation functional with van der Waals dispersions (BEEF-vdW), developed by Wellendorff *et al.*⁹⁶ The authors first separated E_{XC} into parametrised expressions for the exchange and correlation contributions. In particular, $E_{C,BEEF}$ was written as a linear combination of local contributions from the Perdew and Wang correlation (PW91),⁹⁷ semi-local contributions from PBE, and non-local contributions from the vdW-DF2 method,⁹⁸ as reported in Eq. 3.39:

$$E_{C,BEEF} = \alpha_C E_{C,PW91} + (1 - \alpha_C) E_{C,PBE} + E_{C,DF} \quad (3.39)$$

where α_C is an unknown coefficient.

$E_{X,BEEF}$ was defined as in Eq. 3.33, and the enhancement factor $F_{X,BEEF}$ was expanded as a series of Legendre polynomials $B_m[t(s)]$ of a transformed reduced density gradient $t(s)$ of unknown coefficients a_m :

$$F_{X,BEEF} = \sum_m a_m B_m[t(s)] \quad (3.40)$$

with m being the order of the polynomial. The parameters in the formulation of $E_{X,BEEF}$ and $E_{C,BEEF}$ were then fitted with machine learning models to a computational and experimental dataset in order to predict molecular formation energies,^{99,100} gas phase reaction energetics,⁹⁹ kinetic barriers,¹⁰¹ NCIs,^{102,103} solid state properties,^{104,105} and chemisorption energies at solid interfaces.^{106,107,108,109,110,111,112,113,114} Bayesian statistics was subsequently employed to estimate the errors introduced by the aforementioned parametrisation in the calculation of the above properties. After fitting, the correlation coefficient α_C was set to 0.6001664769, while the a_m coefficients determined through machine learning are summarised in Table 3.1.

Table 3.1 a_m coefficients obtained by fitting the enhancement function $F_{X,BEEF}$, expressed as sum of the Legendre polynomials $B_m[t(s)]$ of order m (Eq. 3.40), to describe molecular formation energies,^{99,100} gas phase reaction energetics,⁹⁹ kinetic barriers,¹⁰¹ NCIs,^{102,103} solid state properties^{104,105} and chemisorption energies at solid interfaces.^{106,107,108,109,110,111,112,113,114}

m	a_m	m	a_m
0	1.516501714×10^0	15	$-8.018718848 \times 10^{-4}$
1	$4.413532099 \times 10^{-1}$	16	$-6.688078723 \times 10^{-4}$
2	$-9.182135241 \times 10^{-2}$	17	$1.030936331 \times 10^{-3}$
3	$-3.352754331 \times 10^{-2}$	18	$-3.673838660 \times 10^{-4}$
4	$3.418828455 \times 10^{-2}$	19	$-4.213635394 \times 10^{-4}$
5	$3.411870076 \times 10^{-3}$	20	$5.761607992 \times 10^{-4}$
6	$-1.416381352 \times 10^{-2}$	21	$-8.346503735 \times 10^{-5}$
7	$6.975895581 \times 10^{-4}$	22	$-4.458447585 \times 10^{-4}$
8	$9.859205137 \times 10^{-3}$	23	$4.601290092 \times 10^{-4}$
9	$-6.737855051 \times 10^{-3}$	24	$-5.231775398 \times 10^{-6}$
10	$-1.573330824 \times 10^{-3}$	25	$-4.239570471 \times 10^{-4}$
11	$5.036146253 \times 10^{-3}$	26	$3.750190679 \times 10^{-4}$
12	$-3.569472453 \times 10^{-3}$	27	$3.114938125 \times 10^{-5}$
13	$-9.874953976 \times 10^{-4}$	28	$-1.904911565 \times 10^{-4}$
14	$3.033722895 \times 10^{-3}$	29	$7.384362421 \times 10^{-5}$

3.2.7 Non-covalent interaction analysis

The qualitative analysis of NCIs relies on the quantum theory of atoms in molecules (QTAIM), developed by Bader.¹¹⁵ This aims at separating molecular space into regions corresponding to different atoms according to the properties of $\rho(r)$, as follows. At each position in space, it is possible to define the trajectory of $\nabla\rho(r)$, which is perpendicular to the isosurfaces of $\rho(r)$, named gradient vector path. Gradient paths always originate from and terminate at stationary points in $\rho(r)$, such as minima located at infinite distance from the molecule, maxima exclusively located at the nuclei or saddle points generated by covalent bonds. The latter exhibit a maximum in the directions perpendicular to the one connecting the bonded atoms, and a minimum along the internuclear axis. This causes the Laplacian of $\rho(r)$, $\nabla^2\rho(r)$, to be largely dominated by its negative components. As a result, space can be compartmentalised into different volumes by grouping together all the $\nabla\rho(r)$ trajectories which lead from a bond critical point or from infinity to the same nucleus, as exemplified in **Figure 3.1** for an ethylene molecule. The regions of space associated with

the same nucleus are called atomic basins, and the boundaries between them are called interatomic surfaces.

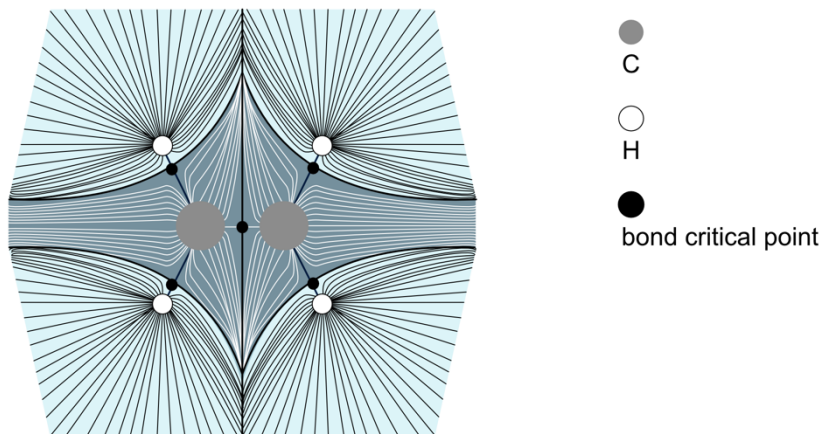


Figure 3.1 Compartmentalisation of an ethylene molecule into atomic basins by grouping all trajectories of $\nabla\rho(r)$ which lead to the same nucleus. The areas of space containing the gradient paths connected to H are highlighted in light blue, and those leading to C in grey.

While the QTAIM easily allows to locate the position of the bonds and the nuclei, the critical points pertaining to NCIs are less straightforward to identify.¹¹⁶ Because these are characterised by low values of $\rho(r)$, the main difficulty lies in discriminating them from the tails of $\rho(r)$. The property that allows to discern the two is the magnitude of $\nabla\rho(r)$, which is high in the tails due to their exponential decay and low in the regions where NCIs are present. Thus, the distinction between NCIs and tails of $\rho(r)$ must rely on the inspection of a reduced density gradient of the kind $|\nabla\rho(r)|/\rho^n(r)$, which in this thesis has the form:

$$s = \frac{1}{2(3\pi^2)^{1/3}\rho^{4/3}(r)} |\nabla\rho(r)| \quad (3.41)$$

In the critical points generated by NCIs, the sign of $\nabla^2\rho(r)$ is typically positive, regardless of their bonding or non-bonding character. Attractions and repulsions can be differentiated by inspecting the sign of the second eigenvalue (λ_2) in the Hessian matrix of $\rho(r)$: a positive λ_2 reveals a repulsion, while a negative λ_2 reveals an attraction. Lastly, the strength of the NCI is proportional to $\rho(r)$ at the critical point.

In this thesis, NCIs are represented by plotting s against $\rho(r)$ multiplied by the sign of λ_2 . Peaks at negative values of $\lambda_2\rho(r)$ are indicative of attractive interactions, while those at positive values denote repulsive interactions. The more negative (positive) the value, the more attractive (repulsive) the interaction.

3.3 Modelling chemical reactions

3.3.1 The potential energy surface

The concept of potential energy surface (PES) plays a central role in conformational and reactivity studies performed with computational techniques. Given a collection of N atoms, their positions can be described by their $3N$ atomic coordinates, which can be linearly combined in $3N$ different ways. Of these, the three combinations corresponding to translations and the three corresponding to rotations of the whole system along the x , y , and z axes do not affect the internal configuration. Thus, the number of internal coordinates that are used to specify the atomic arrangement of a chemical system is $3N - 6$, and the PES features $3N - 5$ dimensions. The $3N - 6$ internal coordinates are combinations of bond lengths, and planar and dihedral angles.

By definition, the minimum of a function is characterised by a null first derivative. On a PES, this implies that the derivative of the energy with respect to a spatial coordinate, *i.e.* the force acting in such direction, is null. Hence, minima on the PES are equilibrium geometries. Transition states (TSs) are instead found at saddle points of first order. Thus, to identify the arrangement of a chemical system in the form of reactants, products, reaction intermediates or TSs, it is necessary to first individuate the stationary points on a PES, and then to calculate the Hessian matrix to characterise them as energy minima or saddle points. Along with indicating the nature of the stationary points on the PES, the eigenvalues in the Hessian matrix also possess a physical meaning. In fact, it is possible to expand the energy around a minimum on the PES as a Taylor series, and truncate it to the second order:

$$E = E(x_i - x_0) + \frac{\partial E}{\partial(x_i - x_0)}(x_i - x_0) + \frac{1}{2} \frac{\partial^2 E}{\partial(x_i - x_0)^2}(x_i - x_0)^2 \quad (3.42)$$

where x_0 is the value of the internal coordinate x at the stationary point, and x_i is the displacement with respect to the stationary point. Discarding the first two terms, the expression for E becomes that of a harmonic oscillator with respect to $(x_i - x_0)$, and the value of the second derivative becomes the force constant of the interactions along x . Thus, the eigenvalues in the Hessian matrix represent the strength of the bonds along the corresponding coordinate. It must be kept in mind that the present reasoning is valid as long as the PES features a parabolic behaviour around x_0 .

To simplify the representation of the PES, it is usually depicted as its bi-dimensional cross-section along the reaction coordinate, showing the energy of reactants, intermediates, products, and TSs, instead of displaying its dependence on all $3N - 6$ internal coordinates (Figure 3.2).

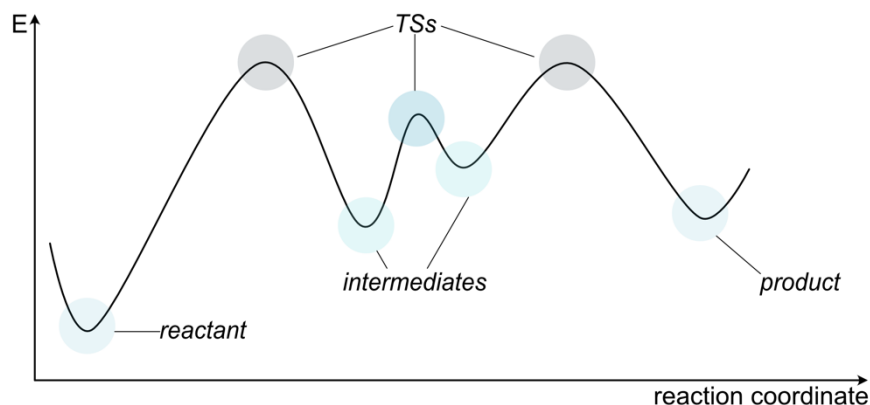


Figure 3.2 Cross-section of a PES along the reaction coordinate connecting reactant, TSs, intermediates and product stationary points.

It is clear from this discussion that, to describe a chemical process, it is necessary to employ algorithms that allow to identify energy minima and saddle points on the corresponding PES. Literature reports various methods to identify points of minimum energy. One example thereof, adopted in this thesis, is the conjugate gradient algorithm.¹¹⁷ After the construction of an initial configuration, the energy and the forces acting on the system are first calculated. The latter are used to predict the direction of the atomic displacements leading to the steepest descent in energy. The atoms are then moved along this vector by an arbitrary amount chosen by the user. This stage of the optimisation is named trial step. The energy and forces are calculated again and, based on their change with respect to the previous configuration, the energy of the closest minimum is estimated. The following step is called corrector step and envisions the displacement of the atoms towards such minimum. Thereafter, if the forces are still aligned with the search direction predicted to point to the minimum, another corrector step is taken. Otherwise, a new trial step is conducted along the direction of maximum decrease in energy. The procedure is repeated until convergence.

Another methodology to identify energy minima is the quasi-Newton algorithm.¹¹⁸ This relies on an approximate form of the Hessian matrix, updated at each iteration based on the forces from the current and previous geometries, guiding the atomic displacements towards the equilibrium. Because the Hessian matrix is not fully computed, the computational expense of quasi-Newton methods is reduced. However, since the approximate Hessian

matrix is built upon the forces acting on the atoms, if these are inaccurate (*e.g.* due to a poor initial structure) the quasi-Newton algorithm might fail to reach convergence.

3.3.2 Identification of transition states on the PES

The algorithms used in this thesis to identify TSs are the nudged elastic band (NEB)¹¹⁹ and the improved dimer¹²⁰ methods. The former generates a number of structures connecting the reactants and products, which are optimised by calculating the force acting on image i ($\vec{F}_i$):

$$\vec{F}_i = \vec{F}_{i,\parallel}^s - \vec{\nabla}E(R_i)_\perp \quad (3.43)$$

where $-\vec{\nabla}E(R_i)_\perp$ is the negative energy gradient in the directions orthogonal to the TS search, R_i the matrix of the atomic coordinates of structure i , and $\vec{F}_{i,\parallel}^s$ a spring force of the kind:

$$\vec{F}_i^s = k[(R_{i+1} - R_i) - (R_i - R_{i-1})] \cdot \hat{t}_\parallel \quad (3.44)$$

acting along the tangent of the reaction coordinate ($\hat{t}_\parallel$), with k being the spring constant. The latter dictates the distance between the images, while $-\vec{\nabla}E(R_i)_\perp$ maintains them on the reaction coordinate between reactants and products. Once the investigation is complete, the Hessian matrix is calculated on the highest image to confirm the presence of a single negative eigenvector, corresponding to an imaginary frequency along the reaction coordinate. An improvement over this procedure is the climbing-image NEB method,¹²¹ wherein the image of highest energy is not subject to the spring forces acting along the band. Instead, its energy is maximised along the direction of the TS search, and minimised in all the others, so that it converges to a TS structure.

In the improved dimer method, instead, a guess for the TS structure is provided along with a vector along the reaction coordinate decomposed along the x , y and z axes. This is the direction along which the real TS should be located. Then, the algorithm generates two structures, called dimer, characterised by atomic coordinates displaced by $\pm\Delta R$ relative to those of the TS guess. Their axes are then rotated towards the negative curvature of the energy. From here, a new TS guess is generated between the two images, thus minimising the energy with respect to all coordinates but the one of the dimer search. The procedure is repeated until convergence.

3.3.3 Thermodynamic corrections

Once the electronic energy E_e of a stationary point (Eq. 3.6) is determined with DFT, the energy of the nuclear motions is added by calculating the relevant thermodynamic contributions. In this thesis, the electronic energy of the atoms in solid bulks and surfaces is not corrected, since their vibrations are considered to be mostly unaffected by adsorption processes and can therefore be neglected when computing reaction energies. For adsorbates, instead, all $3N$ degrees of freedom (where N is the number of atoms) are treated as harmonic vibrations. Moreover, for a species bound to a solid support the product PV can be considered negligible, and the Gibbs energy $G(T)$ can be approximated to the Helmholtz energy $F(T)$:

$$G(T) = F(T) + PV \quad (3.45)$$

$$G(T) = F(T) = U(T) - TS(T) \quad (3.46)$$

where $U(T)$ is the internal energy and $S(T)$ the entropy at temperature T . The statistical formulations of $U(T)$ and the vibrational component to the total entropy are given in Eq. 3.47-48, respectively:

$$U(T) = E_e + E_{ZPE} + \sum_{i=1}^{3N} \frac{\varepsilon_i}{e^{\varepsilon_i/k_B T} - 1} \quad (3.47)$$

$$S(T) = k_B \sum_{i=1}^{3N} \left[\frac{\varepsilon_i}{k_B T (e^{\varepsilon_i/k_B T} - 1)} - \ln(1 - e^{-\varepsilon_i/k_B T}) \right] \quad (3.48)$$

where E_e is the electronic energy, E_{ZPE} the zero-point vibrational energy, ε_i the energy of vibration of each normal mode presented by the adsorbate, and k_B is Boltzmann's constant. Nuclear motions of gas molecules, instead, are described with the ideal gas model. At the conditions of standard pressure adopted in this thesis ($P^0 = 1$ atm), $G(T)$ is expressed as:

$$G(T) = H(T) - TS(T) \quad (3.49)$$

where the enthalpy, $H(T)$, is derived according to its statistical formulation:

$$H(T) = E_e + E_{ZPE} + \int_0^T C_P dT \quad (3.50)$$

with C_P being the heat capacity at constant pressure. This is determined by summing k_B to the translational, rotational, and vibrational heat capacities at constant volume:

$$C_P = k_B + C_{V,t} + C_{V,r} + C_{V,v} \quad (3.51)$$

with $C_{V,t}$ corresponding to $3/2 k_B$, $C_{V,r}$ corresponding to 0, k_B and $3/2 k_B$ for monoatomic, linear and non-linear gases, respectively, and $C_{V,v}$ corresponding to $k_B \left(\frac{\varepsilon_i}{k_B T} \right)^2 \frac{e^{\varepsilon_i/(k_B T)}}{(e^{\varepsilon_i/k_B T} - 1)^2}$ for each normal mode of vibration. In particular, non-linear and linear molecules present $3N - 6$ and $3N - 5$ vibrations, respectively. The electronic heat capacity $C_{V,e}$ is not included in Eq. 3.51, because excited states are usually not populated at room temperature. Lastly, $S(T)$ is calculated at P^0 as the sum of its translational, rotational and vibrational components, which in the ideal gas framework are:

$$S_t(T) = k_B \left\{ \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P^0} \right] + \frac{5}{2} \right\} \quad (3.52a)$$

$$S_{r,monoatomic}(T) = 0 \quad (3.52b)$$

$$S_{r,linear}(T) = k_B \left[\ln \left(\frac{8\pi^2 I k_B T}{\sigma h^2} \right) + 1 \right] \quad (3.52c)$$

$$S_{r,non-linear}(T) = k_B \left\{ \ln \left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} \right\} \quad (3.52d)$$

$$S_v(T) = k_B \sum_{i=1}^{N_{vib}} \left[\frac{\varepsilon_i}{k_B T (e^{\varepsilon_i/k_B T} - 1)} - \ln(1 - e^{-\varepsilon_i/k_B T}) \right] \quad (3.52e)$$

Where h is Planck's constant, M is the mass of the gas species, I is the moment of inertia of a linear molecule, I_X is the moment of inertia of a non-linear molecule around the axis of rotation X , σ is the symmetry number of the molecule, which expresses the number of rotations which bring it in a symmetrically equivalent position, and N_{vib} is the number of vibrational modes of the molecule.

3.4 Modelling crystalline solids

3.4.1 Real and reciprocal space

Solid state materials can be classified according to the presence, or absence, of long-range translational periodicity. In particular, amorphous materials are characterised by the lack of long-range order and can only be described in a statistical way. Crystalline solids, in general, are characterised by translational periodicity. The smallest repeating unit is named primitive cell, and is defined by the primitive lattice vectors, indicated as a_1 , a_2 and a_3 . It follows that any two equivalent atomic positions are connected by a translation vector R of the kind:

$$R = la_1 + ma_2 + na_3 \quad (3.53)$$

where l , m and n are integers. Because crystals are described by the periodic repetition of their primitive cell, all their properties are identical at r and $r + R$, and can in principle be evaluated exclusively within this space. Yet, since the symmetry of the macroscopic crystal lattice is not always apparent from the primitive cell, the latter can be replicated to generate the so-called conventional unit cell, which describes it more clearly. According to the Bravais classification, there are fourteen crystal packings which in turn can be grouped into seven classes (triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, rhombohedral and cubic), depicted in **Figure 3.3**. **Figure 3.4a-b** illustrates the difference between a face-centred cubic unit cell in the Bravais classification, and the primitive cell it originated from.

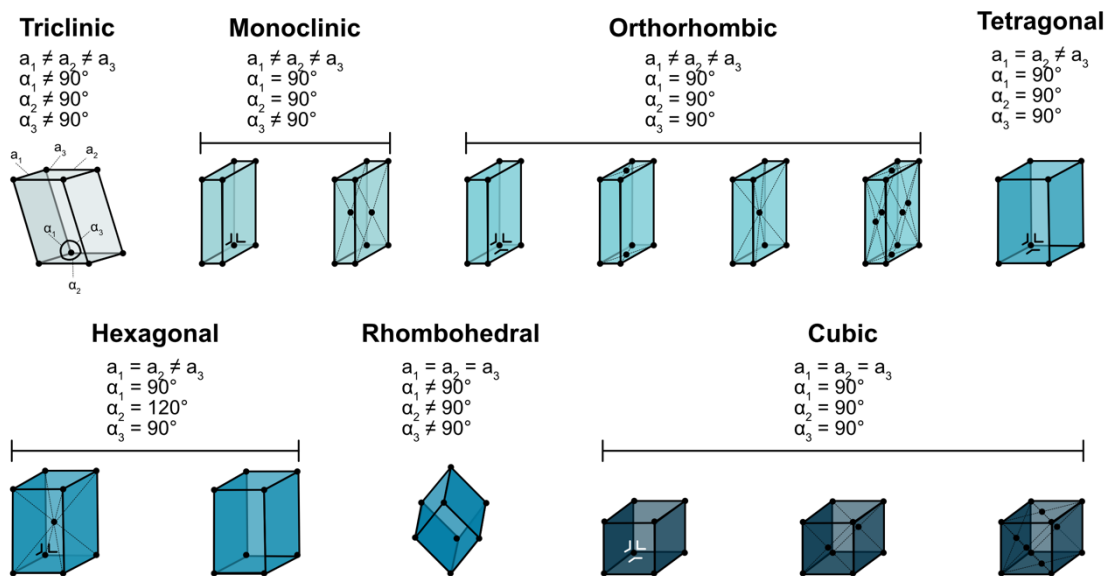


Figure 3.3 Packings in the Bravais classification. a_1 , a_2 and a_3 are the conventional lattice vectors, and α_1 , α_2 and α_3 their angles. Angles of 90° are indicated in the first structure for each of the seven symmetries.

For the discussion of the electronic properties of periodic solids addressed in the following Sections, it is convenient to introduce the concept of reciprocal lattice. The length and direction of the reciprocal lattice vectors b_1 , b_2 and b_3 are given by:

$$b_1 = \frac{2\pi(a_2 \times a_3)}{a_1 \cdot (a_2 \times a_3)}, b_2 = \frac{2\pi(a_3 \times a_1)}{a_2 \cdot (a_3 \times a_1)}, b_3 = \frac{2\pi(a_1 \times a_2)}{a_3 \cdot (a_1 \times a_2)} \quad (3.54)$$

where a_1 , a_2 and a_3 are the lattice vectors in real space. Thus, equivalent positions in reciprocal space are connected by a vector G expressed as:

$$G = ob_1 + pb_2 + qb_3 \quad (3.55)$$

where o , p and q are integers. The region of reciprocal space comprising all points that are closer to the origin than to any other reciprocal lattice point is known as the first Brillouin zone, exemplified in **Figure 3.4b** for a face-centred cubic cell.¹²²

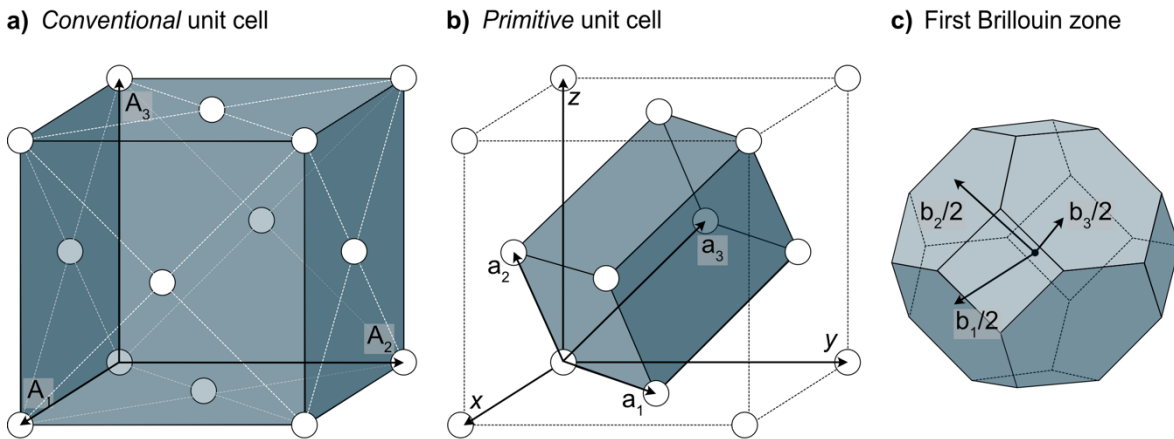


Figure 3.4 **a)** Conventional face-centred cubic cell, of lattice vectors A_1 , A_2 and A_3 . **b)** Primitive unit cell for a face-centred cubic lattice, of lattice vectors a_1 , a_2 and a_3 . **c)** First Brillouin zone and reciprocal lattice vectors b_1 , b_2 and b_3 for a face-centred cubic crystal.

3.4.2 Bloch's theorem

The potential $V(r)$ generated by the regular repetition of the nuclei in the solid must respect the periodicity of the lattice, as expressed by Eq. 3.56 and illustrated in **Figure 3.5**:

$$V(r) = V(r + R) \quad (3.56)$$

Consequently, it can be written as a Fourier expansion:

$$V(r) = \sum_G V_G e^{iG \cdot r} \quad (3.57)$$

Where G denotes the reciprocal lattice vectors and V_G the respective Fourier coefficients of the potential.

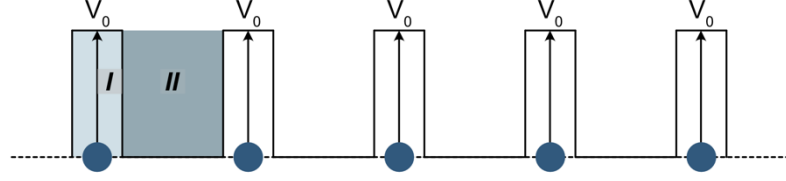


Figure 3.5 Graphical illustration of the periodicity of $V(r)$ along an array of atomic centres (blue circles). The potential assumes a value V_0 at the atomic centres (region I) and drops between them (region II).

In addition to the potential, the wavefunction itself must be periodic. Bloch was able to demonstrate that an appropriate form for the periodic wavefunction is:

$$\psi_k(r) = e^{ik \cdot r} u_k(r) \quad (3.58)$$

where k is a wavevector and r is the position in real space at which $\psi_k(r)$ is evaluated. $u_k(r)$ shares the same periodicity as the crystal lattice, and has the shape:

$$u_k(r) = \sum_G C_{k+G} e^{iG \cdot r} \quad (3.59)$$

By enforcing the periodic boundary conditions on $\psi_k(r)$, the allowed values for the reciprocal vectors k featuring in $\psi_k(r)$ can be determined. Mathematically, the equality between $\psi_k(r)$ at the position r and after a translation of Na_i is imposed, where N is the number of unit cells along the primitive vector a_i :

$$\psi_k(r + Na_i) = \psi_k(r) \quad (3.60)$$

Following Eq. 3.60, it is possible to demonstrate that the allowed values of k_i along each direction i in the first Brillouin zone of the material have the shape:

$$k_i = n \frac{2\pi}{Na_i} \quad (3.61)$$

With n ranging from 0 to $(N - 1)$. Since k_i can assume N discrete, non-degenerate values in the first Brillouin zone, the number of allowed combinations of k_1 , k_2 and k_3 in a three-

dimensional solid, and thus reciprocal vectors k , is N^3 . Outside the first Brillouin zone, k_i assumes values which are multiple of those in Eq. 3.61.

3.4.3 The electronic bands

To determine the electronic energy levels for an electron subject to a periodic potential, $V(r)$ and $\psi_k(r)$ (Eq. 3.57-58, respectively) are inserted in the time independent Schrödinger equation (Eq. 3.6). This leads to the formulation:

$$\sum_k e^{ik \cdot r} \left[\left(\frac{\hbar^2 k^2}{2m_e} - E_k \right) c_k + \sum_G V_G c_{k+G} \right] = 0 \quad (3.62)$$

where $\hbar$ is Planck's constant divided by 2π and m_e is the mass of the electron. For Eq. 3.62 to be null, the expression in square brackets must be zero for every k , giving rise to a set of so-called central equations. A common approximation that was devised for their solution is that of the nearly free electron. This assumes the potential due to the nuclei to be partially shielded by the core electrons, resulting in a small potential around the core regions of the atoms, which varies periodically as predicted by Eq. 3.57. Within this framework, E_k assumes a parabolic shape of the kind:

$$E_k = \frac{\hbar^2 k^2}{2m_e} \quad (3.63)$$

Because when N is large the number of allowed k vectors is high (Eq. 3.61), the energy levels E_k are closely packed. Therefore, the curve representing E_k as a function of k , also named band, is usually represented as continuous. At the Brillouin zone boundaries, however, E_k deviates from the parabolic shape predicted in Eq. 3.63. This is illustrated in **Figure 3.6a** for a unidimensional (1D) atom chain, representing the first Brillouin zone between $-\pi/a$ and $+\pi/a$. At $k = \pm\pi/a$, the energy levels become:

$$E_k = \frac{\hbar^2}{2m_e} \left(\frac{\pi}{a} \right)^2 \pm |V_G| \quad (3.64)$$

where V_G is the Fourier coefficient in the expansion of $V(r)$ associated with the Brillouin zone boundaries. The interval of forbidden energy values implied by Eq. 3.64 is called band gap, and has magnitude E_{BG} :

$$E_{BG} = 2|V_G| \quad (3.65)$$

The plot of E_k for the 1D array of atoms in **Figure 3.6a** can also be entirely displayed within the interval comprised between $-\pi/a$ and $+\pi/a$, by translating every point outside the first Brillouin zone by a reciprocal vector $n\pi/a$ (**Figure 3.6b**). Similar considerations hold for higher dimensional materials, although the band plot becomes more complex as each energy level is characterised by multiple values of k , one along every lattice vector of the crystal. Therefore, the graphical representation of the bands assumes three dimensions for a bidimensional solid, and four dimensions for a three-dimensional solid.

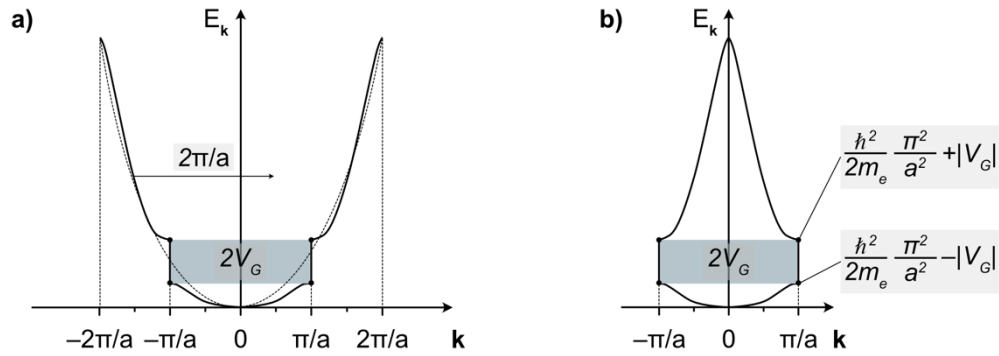


Figure 3.6 a) Extended representation of E_k between $-\pi/a$ and $2\pi/a$ in the nearly free electron model for a 1D chain of atoms. The vector $2\pi/a$, required to bring all E_k values into the first Brillouin zone, is depicted. b) Reduced zone representation of E_k from $-\pi/a$ to $+\pi/a$. The magnitude of the bandgap E_{BG} and the expression for E_k at $\pm\pi/a$ are also indicated.

Depending on the occupation of the electronic bands, materials can be classified as metallic, semiconducting or insulating. When the highest occupied energy level, *i.e.* the Fermi level, lies within a partially filled band, the material is called a metal. In this case, the excitation of the electrons is facile due to the small spacing of E_k . Instead, when an energy gap is present at 0 K between a completely filled band (valence band) and an empty one (conduction band) the material is an insulator. However, if the band gap is small enough to allow the thermal excitation of the electrons at finite temperatures, the material is called a semiconductor.⁹⁴

3.4.4 Plane waves and pseudopotentials

In principle, there is no upper limit to the number of terms that can be summed in the expansion for the plane waves reported in Eq. 3.58-59. However, while the inclusion of a higher number of terms improves the accuracy of the result, it also significantly raises the computational cost. Therefore, plane waves of higher energy than an arbitrary threshold,

called energy cut-off, are truncated, since they are considered to contribute minimally to the description of the electrons.

In addition to the expense of using several terms in the plane waves, treating all electrons explicitly also increases computational times. In fact, at the nuclei, wavefunctions present sharp features which would require the summation of a high number of plane waves to be reproduced. A possible approach to circumvent this issue is the frozen core approximation. This incorporates the potential due to the nuclear charges and the screening by the core electrons in the same term, named pseudopotential, which is specific of each element, and depends on the number of core electrons that it comprises. However, this method has the drawback that the full wavefunction is not described.¹²³ An alternative is therefore to define a spherical atomic volume for each element and write the wavefunctions inside the spheres as atom-like functions. This approach is called augmented plane wave method, and was further developed by Blöchl into the projector-augmented wave formalism.¹²⁴ The latter is based on the adoption of a smooth all-electron wavefunction, $\tilde{\varphi}_n$, where the subscript n describes the energy level and the k wavevector. This, in the vicinity of the nuclei, can be transformed into the desired oscillatory wavefunction φ_n through an operator $\hat{T}$ for which Blöchl proposed a formulation. Because $\tilde{\varphi}_n$ should be mainly corrected from its smooth behaviour in the region of space around the nuclei, a radius is defined for each element beyond which $\hat{T}$ has no action. Such mapping of the smooth $\tilde{\varphi}_n$ to φ_n through $\hat{T}$ proved computationally less expensive than the sum of plane waves in the core regions as required by Eq. 3.58-59. Moreover, the φ_n wavefunctions are usually calculated for each element and not derived for every simulation.

3.4.5 Smearing methods

As stated in the previous section, insulators feature fully occupied and unoccupied levels, while metals present a progressive depopulation of the energy levels with increasing E_k . In fact, for the latter, at any temperature above 0 K, the thermal excitation of the electrons is easy, due to the close spacing of the E_k values discussed in Section 3.4.3. Therefore, in metals, the electronic occupation of the energy levels should not be described by a step function that either assumes the value 0 or 1, but rather through a smearing function $f(\varepsilon_{i,k}, T_e)$, where i is the electronic energy level and T_e a fictitious electronic temperature, while respecting the condition reported in Eq. 3.66 that the overall number of electrons N must remain constant.¹²⁵

$$N = \sum_i \sum_k f(\varepsilon_{i,k}, T_e) \quad (3.66)$$

Because the number of states available to the electrons increases with T_e , this treatment introduces an entropic term $S_e(T_e)$ in the calculated electronic energy:

$$S_e(T_e) = -k_B \sum_i (f_i \ln f_i + (1 - f_i) \ln(1 - f_i)) \quad (3.67)$$

Thus, rather than obtaining a pure electronic energy $E_e(T_e)$, it results in a free electronic energy, $F_e(T)$:

$$F_e(T_e) = E_e(T_e) - T_e S_e(T_e) \quad (3.68)$$

The ground state energy at 0 K (E_0) is then obtained not as $E_e(T_e \rightarrow 0K)$, but by applying a correction scheme to $F_e(T_e)$. Consequently, although higher values of T_e result in a smoother smearing of the energy levels, they also introduce a larger error in the calculation of the ground state energy, E_0 . Hence, T_e must strike a balance between achieving the desired smoothness in the occupation of the energy levels and minimising the deviation from E_0 .

Another parameter that should be optimised to accurately describe the electronic behaviour is the width of the smearing function $f(\varepsilon_{i,k}, T_e)$. This term is usually labelled as σ , and determines the extent of the population of upper levels. Thus, insulating materials are usually assigned a small σ , whereas for metals it should be larger. To prevent significant deviations from E_0 due to an excessive electronic smearing, the Vienna Ab Initio Simulation Package (VASP),¹²⁶ the software employed in this thesis, recommends to set a σ value which lowers $S_e(T_e)$ below 1 meV/atom.

3.4.6 The Birch-Murnaghan equation of state

The first step in the modelling of solid state systems is the determination of the bulk unit cell of minimum energy. Because any change in the length of the lattice vectors reflects in the change of the reciprocal lattice vectors G in the sum of the plane waves (Eq. 3.59), relaxing the volume of a unit cell during a DFT calculation is not accurate. To avoid the simultaneous optimisation of the cell shape, energy, and volume, it is preferable to calculate a series of cell energies, each with different lattice parameters and at constant volume, and determine

the equilibrium lattice parameters by fitting the results to an equation of state. In this thesis, the relation adopted to correlate the Helmholtz energy E of the unit cells to their volume V is the Birch-Murnaghan (BM) equation of state, reported in Eq. 3.69 under isothermal conditions:

$$E = E_0 + \frac{9}{16} V_0 B_0 \left\{ \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^3 \left(\frac{\partial B}{\partial P} \right)_{P=0} + \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^2 + \left[6 - 4 \left(\frac{V_0}{V} \right)^{2/3} \right] \right\} \quad (3.69)$$

where P is the pressure of the unit cell, B is the isothermal bulk modulus defined as $-V(\partial V/\partial P)_T$, and V_0 and B_0 are the volume and isothermal bulk modulus of the equilibrium unit cell, respectively. Because B expresses the resistance of the material to compression, solids with a high B_0 are more difficult to deform, resulting in larger deviations of E from E_0 . After V_0 is extrapolated from the plot, the equilibrium lattice parameters a_0 , b_0 and c_0 can be determined. For cubic cells, these are directly calculated as the third root of V_0 , and the resulting unit cell is then relaxed at constant volume, allowing for shape changes. For non-cubic cells, it is necessary to carry out a separate BM fitting to optimise every lattice vector individually, while maintaining the others constant. This procedure is exemplified in **Figure 3.7**.

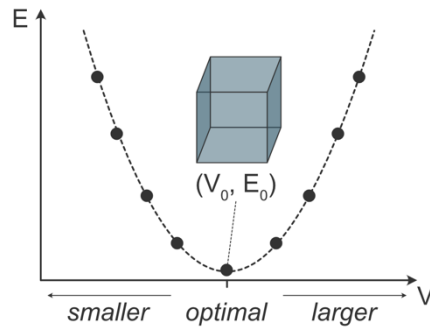


Figure 3.7 BM plot of the energy of a series of unit cells versus the corresponding volumes. The cell volume at equilibrium, V_0 , is extrapolated from the fitting.

3.4.7 The Wulff construction

Solid materials can expose different crystallographic planes, which correspond to distinct cuts through the bulk crystal structure. These are conventionally labelled with Miller indices (hkl) , defined as the reciprocals of the fractional intercepts that the plane makes with the lattice vectors of the bulk unit cell, as depicted in **Figure 3.8a**. Planes that do not intersect a lattice vector feature a Miller index of zero. From this definition, it also follows that Miller planes presenting indices related by a proportionality constant c are parallel. More

specifically, the interplanar distance, d_{hkl} , for planes with lower indices is equal to $c \times D_{hkl}$, where D_{hkl} is the interplanar distance for the corresponding family of planes with higher indices. This relationship is illustrated in **Figure 3.8b**.

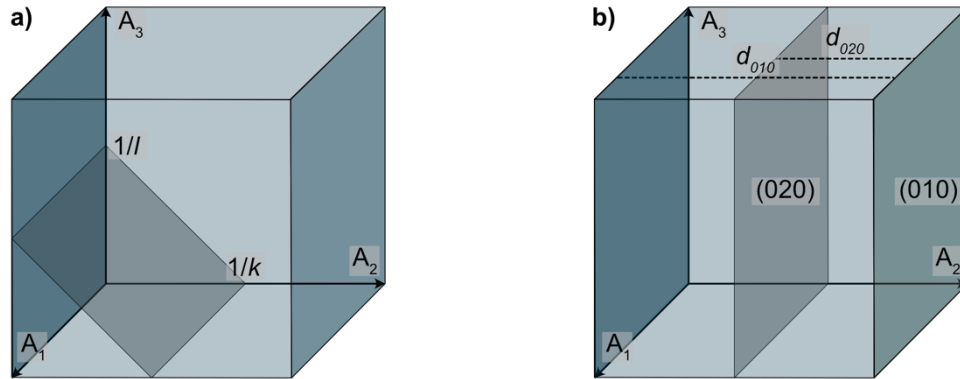


Figure 3.8 a) Example of $(0, k, l)$ Miller plane cleaved from a cubic crystal. **b)** Example of parallel (020) and (010) Miller planes, characterised by interplanar distances $d_{020} = 1/2 d_{010}$.

After optimisation of the bulk unit cell (Section 3.4.6), the most exposed facets presented by the material must be determined. In the case of nanoparticles, this corresponds to assessing their equilibrium shape. To this purpose, J.W. Gibbs hypothesised that any aggregate of matter would attain a shape that minimises its surface energy.¹²⁷ Years later, G. Wulff proposed a method to determine such shape, without proof.¹²⁸ This is based on the assumption that crystal particles are polyhedral structures exposing only Miller surfaces characterised by integer indices (hkl) , and the energy of the edges between said surfaces is neglected. The construct by Wulff consists of the following steps:

- Definition of an origin, O , and a constant, c ;
- Determination of the surface energies, E_{hkl} , for all the surfaces of interest;
- Calculation of their distance from the origin:

$$r_{hkl} = c \times E_{hkl} \quad (3.70)$$

- Generation of a plane at r_{hkl} for each surface under investigation.

The resulting shape contained by the planes, exemplified in **Figure 3.9**, is deemed to be the most stable shape for the nanocrystal, and it depends on the relative rather than absolute E_{hkl} values. Additionally, high-index surfaces are usually not exposed on the nanoparticle. In fact, assuming a low- and high-index facet exhibit the same E_{hkl} , the latter will be steeper, and therefore more internal than the low-index one (**Figure 3.9**). Thus, it will not appear on the surface of the nanocrystal.¹²⁹

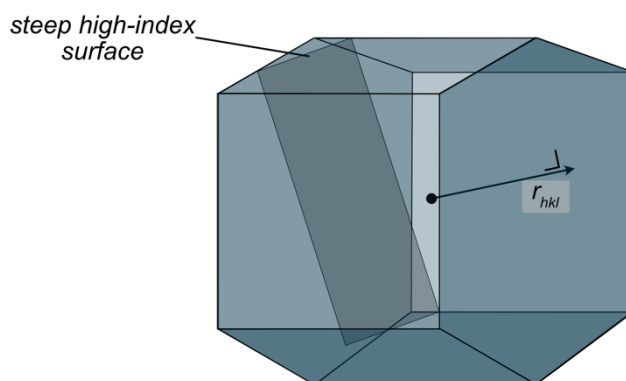


Figure 3.9 Nanoparticle shape obtained through a Wulff construction, based on the surface energies E_{hkl} of the exposed facets and the crystal packing of the bulk. A steep high-index facet is also depicted.

3.5 Modelling electrochemical processes

3.5.1 The electrochemical interface

The application of an electric potential to a metal electrode shifts the energy of its electrons by an amount equal to $-eV$, where e is the charge of the electron and V is the electrode potential against the reference of choice.⁶⁵ Moreover, the behaviour of the electrolyte ions and solvent molecules from the bulk solution to the electrochemical interface is also affected by the presence of a voltage.¹³⁰ In the 19th century, Helmholtz proposed that the electrolyte would form a double-layered structure, called electric double-layer (EDL) where cations (anions) would deposit at the cathode (anode), as illustrated in **Figure 3.10a**.¹³⁰ Gouy and Chapman then suggested to describe the EDL via a region of diffuse ions, where the potential decays in a non-linear fashion (**Figure 3.10b**).¹³⁰ Later, Stern combined the models above hypothesising a first region of space where the potential would be linearly decreasing and ions are chemisorbed, and a second region of space bearing diffuse ions, where the potential would be decreasing exponentially.¹³⁰

While it is desirable to compute the electronic charge distribution at the interface as accurately as possible, time independent DFT presents major shortcomings in the description of electrochemical interfaces.¹³¹ For instance, the arrangement of the water molecules and ions from the bulk solution to the interface features a liquid behaviour, *i.e.* high numbers of different configurations which are close in energy can be thermally accessible and statistically significant under reaction conditions. Such issues can be partially circumvented by recurring to ab-initio molecular dynamics simulations, although they fail to capture rare events such as chemical reactions that would require extended periods and are computationally very demanding.¹³¹ Classical molecular dynamic simulations, on the other

hand, are a much more cost-effective alternative for sampling and averaging statistically relevant configurations of solvent molecules and electrolyte ions. However, this approach sacrifices the detailed description of the electronic properties which could be achieved with quantum mechanical methods. Hence, it is not trivial to simultaneously capture the electronic charge distribution of the electrode atoms and the species at its surface, while also describing all the statistically relevant configurations of the solvent and the electrolyte ions.¹³¹

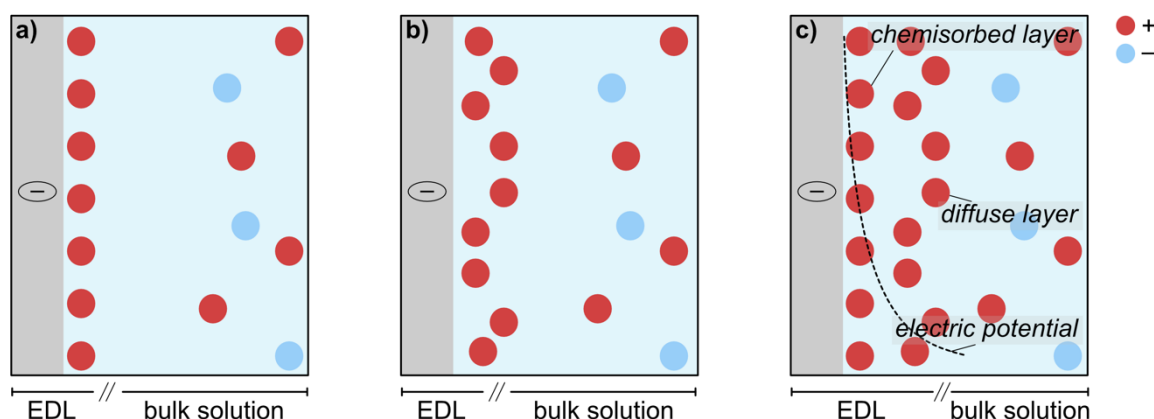


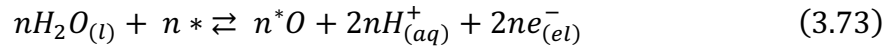
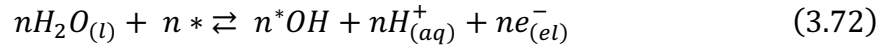
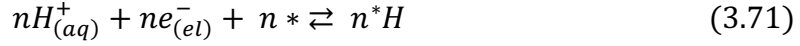
Figure 3.10 Depiction of the EDL at a cathode surface according to the **a)** Helmholtz, **b)** Gouy-Chapman and **c)** Stern model, with red and blue circles representing positive and negative ions, respectively. The steep decrease in potential close to the electrode and smooth decay in the bulk is also represented.

To the aim of this thesis, which is the modelling of reaction mechanisms, time independent DFT methods have been adopted, attempting to represent the density of coverage and stable configurations of the chemisorbed ions, as described in Section 3.5.3.

3.5.2 The computational hydrogen electrode

To model the effect of the electric potential, two are the main frameworks that are used in quantum-mechanical simulations, *i.e.* constant potential and constant charge. The former accounts for the application of the bias via the addition of a variable number of electrons in the simulation.¹³² The second instead does not vary the number of electrons in the system and accounts for the electric potential a posteriori, relying on the computational hydrogen electrode model (CHE).⁶⁵ Recently, it was shown that, for adsorption geometries that are stable both in the presence and absence of a voltage, the results in terms of Gibbs energy differences are identical.¹³² Nonetheless, the constant potential framework offers the further advantage of screening out adsorption geometries which are not stable under the application of the voltage.¹³² Yet, the optimisation of the number of electrons in the simulation cell for each reaction intermediate raises computational costs. Therefore, in this thesis, all calculations were performed at constant charge.

As reported in the previous Section, anions and cations can bind to the electrode surface, depending on the sign and on the amplitude of the applied electric potential. The most common ions in aqueous electrolytes are protons (H^+), hydroxy (OH^-) and oxy (O^{2-}) species. In acidic media, their adsorption is described by the following reactions:



where n is the number of ions and $*$ is a surface adsorption site. According to the definition of the reversible hydrogen electrode (RHE) reference, a solvated H^+ and an e^- are in chemical equilibrium with half a H_2 molecule at zero volts of applied potential:



Hence, $G_{H^++e^-}$ can be equated to half of the Gibbs energy of H_2 , G_{H_2} , and the Gibbs adsorption energies of $^*H$, $^*OH$, and $^*O$ at 0 V_{RHE} , $\Delta G_{nX,0V_{RHE}}$, can be written as:

$$\Delta G_{nH,0V_{RHE}} = G_{nH} - (G_* + n/2 G_{H_2}) \quad (3.75)$$

$$\Delta G_{nOH,0V_{RHE}} = G_{nOH} - (G_* + nG_{H_2O} - n/2 G_{H_2}) \quad (3.76)$$

$$\Delta G_{nO,0V_{RHE}} = G_{nO} - (G_* + nG_{H_2O} - nG_{H_2}) \quad (3.77)$$

where G_* is the Gibbs energy of the pristine electrode surface, G_{H_2O} the Gibbs energy of a H_2O molecule, and G_{nX} is the Gibbs energy of n adsorbed species X .

Because the application of an electric a potential raises the energy of the electrons by $-eV_{RHE}$, $G_{H^++e^-}$ and $\Delta G_{nX,0V_{RHE}}$ are corrected to account for V_{RHE} :

$$1/2 G_{H_2} = G_{H^++e^-} + eV_{RHE} \quad (3.78)$$

$$\Delta G_{nH,RHE} = \Delta G_{nH,0V_{RHE}} + neV_{RHE} \quad (3.79)$$

$$\Delta G_{nOH,RHE} = \Delta G_{nOH,0V_{RHE}} - neV_{RHE} \quad (3.80)$$

$$\Delta G_{nO,RHE} = \Delta G_{nO,0V_{RHE}} - 2neV_{RHE} \quad (3.81)$$

Eq. 3.79-81 are coherent with a favoured *H (*OH and *O) binding at negative (positive) V_{RHE} values.

If ΔG_{nX} values are to be referenced against the standard hydrogen electrode (SHE), the effect of pH on the energy of the solvated H^+ must be included in the formulation of $G_{H^+ + e^-}$. Specifically, G_{H^+} is expanded as follows:

$$G_{H^+}(pH) = G_{H^+}^0 + k_B T \ln[H_{(aq)}^+] \quad (3.82)$$

where $G_{H^+}^0$ is the chemical potential of a solvated H^+ and the activity coefficient of the proton is assumed to be unitary. Notably, this approximation is not always justified, especially in the presence of salts which can coordinate the H^+ ions. Converting the natural logarithm to base-10 and assuming a temperature of 298 K, $G_{H^+}(pH)$ becomes:

$$G_{H^+}(pH) = G_{H^+}^0 - 0.059pH \quad (3.83)$$

Thus, Eq. 3.79-81 are reformulated as:

$$\Delta G_{nH,SHE} = \Delta G_{nH,0V_{SHE}} + neV_{SHE} + n0.059pH \quad (3.84)$$

$$\Delta G_{nOH,SHE} = \Delta G_{nOH,0V_{SHE}} - neV_{SHE} - n0.059pH \quad (3.85)$$

$$\Delta G_{nO,SHE} = \Delta G_{nO,0V_{SHE}} - 2neV_{SHE} - n0.118pH \quad (3.86)$$

The above equations imply that higher values of pH favour *OH and *O binding, while *H adsorption is preferred at low pH, as expected.

3.5.3 Modelling of surface coverages

As stated in Section 3.5.1, electrode surfaces might exhibit absorbed ions from the electrolyte. For reactivity studies, it is therefore necessary to assess the resting state of the electrode surface under reaction conditions. This can be achieved by constructing surface coverage plots which represent the stability of different concentrations of absorbed species as a function of the applied voltage and pH. The following Section outlines the procedure adopted in this thesis.

First, the adsorption of a single $\ast\text{H}$, $\ast\text{OH}$ and $\ast\text{O}$ is modelled on all the possible surface sites *e.g.* *fcc*, *hcp*, *bridge*, and *top* for a face-centred cubic metal. Next, all the remaining sites are populated with the same adsorbate from the most to the least stable, calculating $\Delta G_{nX,0V_{RHE}}$ (Eq. 3.75-77) until H_2 or O_2 are evolved, or surface reconstruction occurs. $\Delta G_{nX,RHE}$ is then plotted versus V_{RHE} to construct a surface diagram like the one shown in **Figure 3.11a**, which shows the Gibbs energy of any surface state at a given V_{RHE} . Alternatively, only the lowest energy surface coverage is plotted for each potential and pH values, as exemplified in **Figure 3.11b**. The V_{SHE} values which correspond to a change in surface state can be translated to different pH, reported along the x axis, according to Eq. 3.87:

$$V_{SHE} = V_{RHE} - 0.059\text{pH} \quad (3.87)$$

At the boundary between different surface coverages, these are in equilibrium.

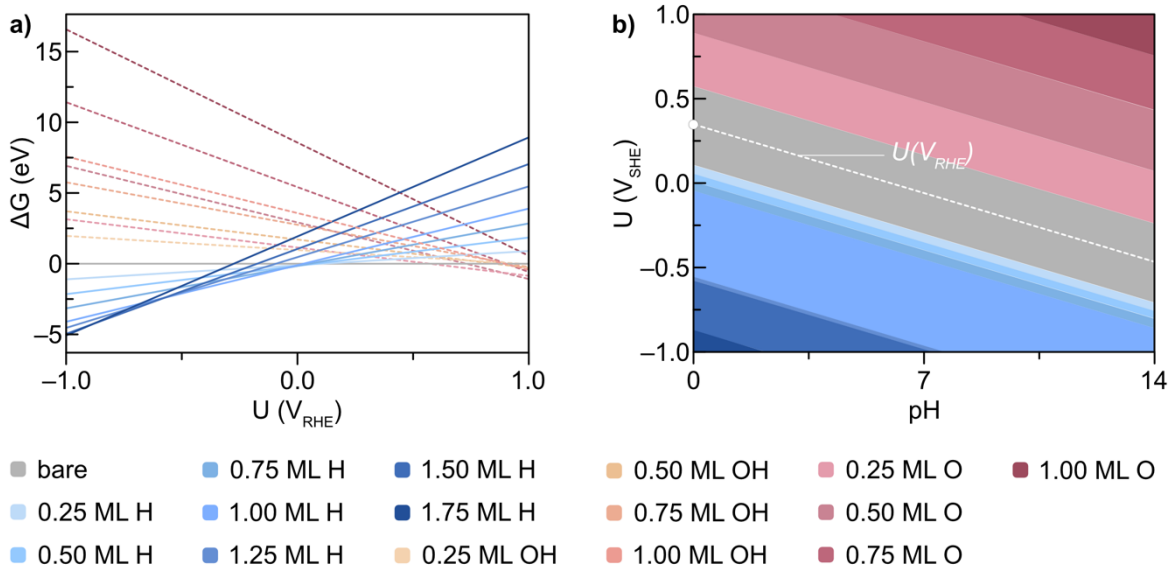


Figure 3.11 a) Plot of ΔG_{nX} for different surface coverages of a $p(2 \times 2)$ -Pt(111) supercell as a function of V_{RHE} . $\ast\text{H}$ coverages are illustrated in blue, while $\ast\text{OH}$ and $\ast\text{O}$ coverages are illustrated in purple and pink. The bare surface is indicated in grey. **b)** Pourbaix diagram illustrating the most stable coverage at each potential and pH values for the same $p(2 \times 2)$ -Pt(111) supercell.

4. Photochemical CO₂ reduction on ligand-functionalised ZnSe quantum dots

4.1 Introduction

4.1.1 Nanoparticle functionalisation for CO₂RR to CO

As discussed in the Introduction, the efficiency of CO₂RR is hampered by the low reactivity of CO₂, its low solubility, the plethora of products that can be generated, and the competition with HER.⁸⁷ In recent years, the functionalisation of catalyst nanoparticles is being explored as a viable strategy to overcome these issues, in the context of both electro- and photochemical CO₂RR. In this scenario, organic ligands are employed to create a hydrophobic environment which improves the affinity of QD surfaces towards CO₂ while also suppressing HER.⁸⁷ For example, Au nanoparticles engineered with alkylamines of different chain length have displayed enhanced CO₂ conversion and reduced HER with respect to the unfunctionalised catalysts.¹³³ At $-0.7\text{ V}_{\text{RHE}}$, the Au nanoparticles achieved a faradic efficiency (FE) for CO of around 55% and a current density of 5.5 mA/cm². Upon functionalisation with oleylamine, the FE increased to *ca.* 75% and the current density to 6.5 mA/cm² under the same conditions. Notably, the addition of a branched and bulkier chain like polyethyleneimine impaired CO₂RR, which was attributed to a higher ligand surface coverage that prevented CO₂ binding. In a different work, Ag nanoparticles were functionalised with imidazolium scaffolds bearing methyl, octyl, hexadecyl, and trityl side chains, revealing the best catalytic performance in the presence of the octyl chain.¹³⁴ The nanoparticles with the latter ligands displayed a FE for CO *ca.* 92% and a current density larger than 250 mA/cm² at $-1.2\text{ V}_{\text{RHE}}$. This excellent activity and selectivity were attributed to the optimal compromise between hydrophobicity and accessibility of the catalyst surface. In contrast, the longer chain ligands (*i.e.* hexadecyl and trityl chains) showed a poorer performance due to their steric hindrance, which prevented access of the reactants to the catalyst surface. The methyl side chain, on the other hand, did not create a sufficiently hydrophobic shell around the nanoparticles to efficiently promote CO₂ binding. Overall, these studies demonstrated that creating a hydrophobic environment with organic ligands while allowing CO₂ to reach the catalyst surface can enhance the electrochemical CO₂RR and suppress HER.

Similar principles have been applied to the functionalisation of QDs for the photocatalytic CO₂RR as well. In this context, transition metal chalcogenides like CdS, CuInSe₂ and ZnSe are typically used. Given their high affinity for thiol functional groups, a common ligand for engineering transition metal chalcogenides is mercaptopropionic acid (MPA). For example, CdS QDs functionalised with MPA have shown a selectivity of 82% for the photochemical CO₂RR to CO and a turnover number (TON, *i.e.* the maximum number of moles of reactants that a mole of catalyst can convert before deactivation) of 74.¹³⁵ Importantly, the bare nanoparticles displayed a selectivity around 3%, producing large amounts of H₂ and traces of CH₄. When a cobalt cocatalyst was added to the reaction mixture, the selectivity and the TON were raised to 95% and 942, respectively. Importantly, HER was minimised to traces of H₂. Similarly, CuInSe₂ QDs bearing MPA ligands and a Fe-based cocatalyst yielded CO with a TON of 450 and 99% selectivity, again impairing HER.¹³⁶ A more recent study assessed the performance of ZnSe QDs functionalised with 2-aminoethanethiol, which combined thiol and amino moieties in the same scaffold.¹³⁷ This system achieved a TON of around 4,000 for the photochemical CO₂RR to CO after 48 h, compared to a TON of 3,200 with nanoparticles engineered with MPA. This improved performance, however, came at the cost of catalyst stability. In fact, the production of CO in the presence of 2-aminoethanethiol plateaued after two days, while it continued to increase in the presence of MPA. This was explained by a larger aggregation of the nanoparticles promoted by 2-aminoethanethiol.

Metal cocatalysts are often employed alongside organic ligands to enhance the photocatalytic CO₂RR,^{135,136} as seen in some of the previous examples.^{135,136} They can be both metal clusters of noble (Pt, Pd, Ru, Rh and Au) and non-noble (Cu, Ni and Cd) metals, and oxides thereof,¹³⁸ or molecular complexes. In the latter case, Ni, Co, Fe, and Rh complexes have been reported. Importantly, both the metal centre and the ligand scaffold have been shown to determine the catalytic activity and selectivity of the QDs. In this context, CdS nanoparticles were functionalised with a terpyridine Ni complex, [Ni(terpy)₂]²⁺, bearing different anchoring groups.¹³⁹ When this presented a thiol moiety, the robust binding of the cocatalyst on the QDs allowed to reach selectivities over 90% and a TON of 20 toward CO in 8 h, after which HER prevailed. The decrease in HER was attributed to the surface coverage provided by the metal cocatalyst.^{140,139}

The following Section describes an example of functionalised ZnSe QDs for the photocatalytic CO₂RR to CO, which underlies the study reported in this chapter.

4.1.2 Photocatalytic CO₂RR on ZnSe QDs functionalised with imidazolium ligands

In collaboration with Prof. Reisner, our group investigated the performance of ZnSe QDs functionalised with 3-(2-mercaptoethyl)-1-methyl-imidazolium halide (MEMI) for the photocatalytic CO₂RR to CO.⁸⁸ As mentioned above, the thiol moiety provided an anchoring point for the ligands on the QD surface. The reaction was carried out in aqueous solution at room temperature and pH of 6.5, in the presence of 0.1 M ascorbic acid as sacrificial electron donor and a light source of above 400 nm. The ZnSe | MEMI system achieved a TON of 277 for CO formation with a selectivity of 18%, compared to *ca.* 1% with the bare ZnSe QDs. After 10 h of irradiation, however, the CO₂RR activity decreased, presumably due to the aggregation of the nanoparticles, degradation of the ligands, and accumulation of dehydroascorbic acid (oxidation product) on the surface. In an attempt to rationalise these findings, transient absorption spectroscopy revealed the Zn²⁺ surface ions as the active sites for both HER and CO₂RR. Coherently, DFT calculations indicated that the surface coverage by the MEMI ligands was responsible for suppressing HER. Moreover, the available Zn²⁺ sites were found to promote *CO₂^{δ-} formation, enhancing CO₂RR via the establishment of a hydrogen bond between the imidazolium scaffolds and *CO₂^{δ-} (**Figure 4.1**).

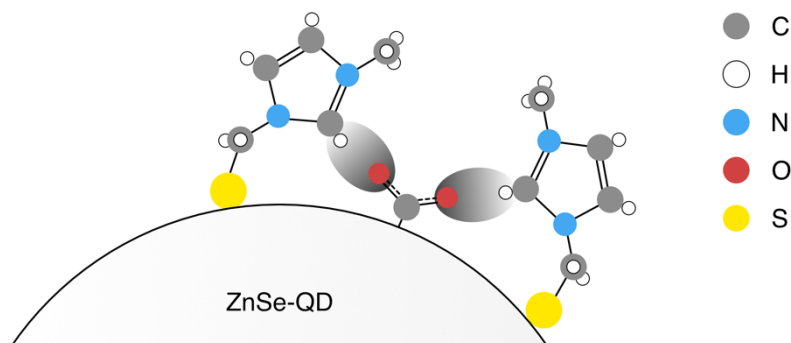


Figure 4.1 Activated *CO₂^{δ-} on MEMI-functionalised ZnSe QDs. The hydrogen bond between the MEMI ligands and the oxygen atom of *CO₂^{δ-} is highlighted.

4.2 Experimental results

ZnSe QDs were prepared by heating zinc stearate and selenium to 300°C in octadecene, and replacing the stearate anions with BF₄⁻ via ligand stripping. Transmission electron microscopy indicated the formation of spherical particles with diameter of 4.5 ± 0.7 nm. The ZnSe QDs were then functionalised with various dithiols (DTs) in aqueous solution, namely EDT, BuDT, HexDT and OctDT (**Figure 4.2a-d**). The binding of the DTs on the ZnSe QDs was confirmed via proton nuclear magnetic resonance (¹H-NMR) titration in D₂O at

concentrations of 25, 50, 75, 100, and 200 eq, through the broadening of the proton signals upon adsorption. Since free EDT was first observed at 200 eq, each ZnSe QD was deemed to accommodate on average at least 100 ligand molecules. In contrast, dissolved BuDT, HexDT and OctDT were detected at a loading of 50 eq. The performance of the bare and functionalised ZnSe QDs in the CO₂RR and HER was then assessed in aqueous solution of 0.1 M ascorbic acid under constant flow of CO₂ at a pH of 6.5, under irradiation above 400 nm. While HER prevailed on the bare ZnSe QDs, leading to a low selectivity of around 1% (Table 4.1), it was suppressed upon their functionalisation. Specifically, the DTs improved the selectivity towards CO₂RR from 1.7% (HexDT) to 15% (EDT). The best CO₂RR activity and selectivity were both displayed by EDT, as indicated in Table 4.1. Subsequently, the ZnSe QDs were functionalised with the Ni(cycP) cocatalyst (**Figure 4.2e**) at a pH of 5.5, previously optimised.¹⁴¹ The increase in HER compared to ZnSe and ZnSe | DT was attributed to the more acidic conditions, leading to a low selectivity of *ca.* 4%. Nevertheless, the CO yield obtained with ZnSe | Ni(cycP) was slightly larger than that of ZnSe | EDT. The ZnSe QDs were then functionalised in the presence of 20 and 50 eq of the Ni(cycP) cocatalyst and DT ligands, respectively. The best CO₂RR performance was achieved with HexDT, leading to a four-fold increase in activity compared to ZnSe | Ni(cycP). Importantly, the ZnSe | Ni(cycP) | DT setup also exhibited the highest selectivity towards CO₂RR of all the investigated systems, ranging from 25% (EDT) to 40% (HexDT). Again, the increase in H₂ production was attributed to the more acidic pH and the lower loading of DTs with respect to ZnSe | DT.

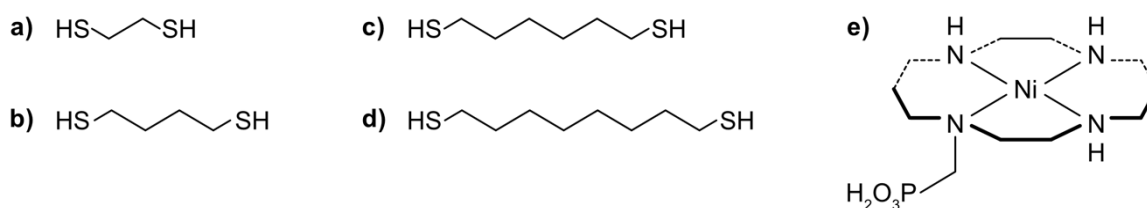


Figure 4.2 a) EDT, b) BuDT, c) HexDT, d) OctDT and e) Ni(cycP) cocatalyst adopted in this work to functionalise the ZnSe QDs for the photochemical CO₂RR.

Control experiments were run to compare the performance of the thiol moieties with other hydrogen bond donors such as the hydroxy group. Specifically, the ZnSe QDs were functionalised with 1,2-mercaptoethanol (HO-EtSH) and 1,6-mercaptoethanol (HO-HexSH) in the presence of the Ni(cycP) cocatalyst. ZnSe | HO-EtSH exhibited roughly half the activity and a third of the selectivity for CO₂RR compared to ZnSe | EDT. Similarly, ZnSe | Ni(cycP) | HexSH displayed a slightly lower CO₂RR activity and a third of the

selectivity of ZnSe | Ni(cycP) | HexDT. These findings proved the superior efficiency of the thiol group over the alcohol in promoting CO₂RR to CO on the ZnSe QDs.

The requisite of two thiol moieties was then tested using the 1-butanethiol (BuSH) and 1-hexanethiol (HexSH) ligands in the absence and in the presence of the Ni(cycP) cocatalyst, respectively. The CO₂RR activity of ZnSe | BuSH and ZnSe | Ni(cycP) | HexSH was approximatively a third of that displayed by ZnSe | BuDT and ZnSe | Ni(cycP) | HexDT, respectively, and their selectivity was significantly lower. Thus, two thiol moieties were deemed necessary to effectively reduce CO₂ on the ZnSe QDs. Lastly, a rigid ligand such as benzene-1,4-dithiol (BenzDT), of chain length 6.4 Å, was compared to BuDT (6.8 Å), with and without the Ni(cycP) cocatalyst. BuDT was found to display between two and three times the CO yield and selectivity of BenzDT in both setups, highlighting the higher efficiency of flexible ligands.

Table 4.1 Yields of CO and H₂ obtained on ZnSe QDs bearing EDT, BuDT, HexDT, OctDT, HO-EtSH, HO-HexSH, BuSH, HexSH, and BenzDT ligands, with and without the Ni(cycP) cocatalyst. Experiments were carried out under irradiation above 400 nm in an aqueous solution of 0.1 M ascorbic acid at room temperature. The pH was 6.5 and 5.5 for the experiments in the absence and in the presence of the Ni(cycP) cocatalyst, respectively. The selectivity for CO is also reported.

QD System	n_{H_2} (μ M)	n_{CO} (μ M)	CO (%)
ZnSe	16.7 $\pm$ 4.60	0.15 $\pm$ 0.02	0.9 $\pm$ 0.1
ZnSe EDT	5.29 $\pm$ 0.79	0.95 $\pm$ 0.19	15.1 $\pm$ 2.6
ZnSe BuDT	5.84 $\pm$ 0.99	0.46 $\pm$ 0.06	7.4 $\pm$ 0.4
ZnSe HexDT	8.18 $\pm$ 1.23	0.14 $\pm$ 0.03	1.7 $\pm$ 0.3
ZnSe OctDT	4.21 $\pm$ 0.63	0.27 $\pm$ 0.04	5.9 $\pm$ 0.5
ZnSe HO-EtSH	7.49 $\pm$ 0.97	0.56 $\pm$ 0.06	4.5 $\pm$ 2.5
ZnSe BuSH	16.8 $\pm$ 6.38	0.17 $\pm$ 0.04	1.1 $\pm$ 0.6
ZnSe BenzDT	14.5 $\pm$ 7.89	0.19 $\pm$ 0.01	2.6 $\pm$ 0.3
ZnSe Ni(cycP)	25.7 $\pm$ 3.69	1.09 $\pm$ 0.18	4.0 $\pm$ 0.2
ZnSe Ni(cycP) EDT	17.6 $\pm$ 2.64	1.21 $\pm$ 0.18	6.4 $\pm$ 0.3
ZnSe Ni(cycP) BuDT	11.6 $\pm$ 1.74	3.78 $\pm$ 0.46	24.5 $\pm$ 2.0
ZnSe Ni(cycP) HexDT	6.19 $\pm$ 0.93	4.05 $\pm$ 0.25	39.6 $\pm$ 1.9
ZnSe Ni(cycP) OctDT	5.82 $\pm$ 0.87	2.97 $\pm$ 0.24	22.8 $\pm$ 1.8
ZnSe Ni(cycP) HO-HexSH	22.4 $\pm$ 1.51	3.10 $\pm$ 0.16	12.2 $\pm$ 0.6
ZnSe Ni(cycP) HexSH	17.9 $\pm$ 0.89	1.15 $\pm$ 0.06	6.0 $\pm$ 0.3
ZnSe Ni(cycP) BenzDT	11.7 $\pm$ 0.59	1.45 $\pm$ 0.07	10.9 $\pm$ 0.5

4.3 Computational details

Periodic DFT calculations were performed with the version 5.4.4 of VASP,¹²⁶ adopting the PBE functional⁹³ with the third revision of Grimme dispersion corrections.⁹⁵ Core electrons were described with projector-augmented wave pseudopotentials,¹²⁴ and valence electrons with plane waves of 500 eV energy cut-off, optimised through the BM fitting¹⁴² described below. The electronic occupancy of the energy levels was expressed through a Gaussian smearing of width 0.05 eV. Reciprocal space was sampled at the Γ -point for gas phase species, while a Γ -centred grid of ≈ 29 k -points $\times\text{\AA}$ was adopted for solids, also optimised through the BM fitting discussed below. Electronic steps were considered converged below a threshold of 10^{-6} eV.

Geometry relaxations were performed with the conjugated gradient algorithm, imposing a displacement of 0.1 $\text{\AA}$ and a force convergence criterion of 0.015 $\text{\AA}/\text{eV}$, without allowing the cell shape and volume to change. Subsequently, stationary points were characterised through a frequency calculation using the finite differences method and a step size of 0.02 $\text{\AA}$. Whenever imaginary frequencies below 100 cm^{-1} were found, these were replaced with real frequencies of 12 cm^{-1} .¹⁴³

The thermodynamic corrections to the electronic energy were computed at the temperature of 298 K and pressure of 1 atm, using the thermochemistry module of the Atomic Simulation Environment (ASE).¹⁴⁴ The ideal gas model was adopted for gas phase molecules, while the harmonic model was employed for adsorbates without vibrating the atoms in the surface slab, as their contribution to the Gibbs energy was assumed independent of the adsorbates, and therefore negligible in the computation of relative energies. Given the high computational expense of frequency calculations, the corrections obtained for the binding of the Ni(cycP) cocatalyst on ZnSe | Ni(cycP) were also applied to the ZnSe | Ni(cycP) | DT systems. Similarly, due to the high number of adsorption configurations for the DTs in the presence of the Ni(cycP) cocatalyst (Section 4.3.1), the Gibbs corrections calculated for the ZnSe | DT systems were extended to ZnSe | Ni(cycP) | DT. This approach was validated by comparing the Gibbs corrections for the binding of EDT in ZnSe | EDT and ZnSe | Ni(cycP) | EDT, which differed by only 0.01 eV in both mono- and bidentate modes.

Molecules were constructed with the graphical interface of ASE, imposing a 15 $\text{\AA}$ vacuum along all directions to avoid interactions between periodic images. Based on a pK_a of ≈ 10 in water,¹⁴⁵ it was determined that the thiol group would be in its neutral form at the

experimental pH of 5.5. The phosphonate group of the Ni(cycP) cocatalyst instead would exhibit an overall charge of -1 , being the pK_a for the first and second deprotonation around 2 and 7, respectively.¹⁴⁶ Considering that the Ni centre was in the oxidation state of $+2$, the cocatalyst was modelled as neutral to account for the presence of a photogenerated electron.

The bulk cell of ZnSe was downloaded from Materials Project,¹⁴⁷ selecting the structure with zero energy above Hull. This was a cubic packing ($F\bar{4}3m$) of lattice parameter 5.664 Å. The unit cell of minimum energy was then determined by increasing and reducing the lattice vectors by 1% five times and optimising the resulting cell without allowing the volume and shape to change. These calculations were run with energy cut-offs for the plane waves of 500, 600, and 700 eV, and with Γ -centred k -point grids of $3\times3\times3$, $5\times5\times5$, $7\times7\times7$, $9\times9\times9$, and $11\times11\times11$. The resulting energies and volumes were then fitted to the BM equation of state, and the corresponding minimum was optimised by allowing the cell shape to relax but not the volume. A threshold of accuracy of 1 meV/atom was adopted to identify the energy cut-off to the plane waves and k -point density that provided the best compromise between computational cost and accuracy of the results (Section 4.4.1).

Experimental p-XRD data pertaining to previous work on ZnSe QDs indicated the presence of the (111), (200), (220), and (311) facets.⁸⁸ Surface slab models along these planes were constructed with ASE, consisting of four ionic layers and a 15 Å vacuum along the direction perpendicular to the surface. The atoms belonging to one, two, and three bottom layers were constrained in their bulk positions for each slab. The surfaces were then optimised, and their surface energy, E_{surf} , was computed according to the equation:

$$E_{surf} = \frac{E_{slab} - \frac{n_{slab}}{n_{bulk}} E_{bulk}}{2A} \quad (4.1)$$

where E_{slab} is the DFT energy of each structure, E_{bulk} is the energy of the bulk unit cell, n_{slab} is the number of atoms in the slab cell, n_{bulk} is the number of atoms in the bulk cell, and A is the surface area of the slab, calculated as $A = ab \sin \alpha$, where a and b are the lattice vectors parallel to the surface and α is their angle. A threshold of accuracy of 1 meV/atom was imposed to establish the maximum number of layers that could be constrained in their bulk positions without compromising the accuracy of the results. To determine the most exposed facet, a Wulff construction was carried out with the WulffPack package.¹⁴⁸

To individuate the presence of NCIs between the DTs and the *COOH intermediates, single-point calculations with the Gaussian09¹⁴⁹ software were carried out for the corresponding fragments in order to determine their electron density. These were performed with the ωb97xd functional,¹⁵⁰ using the 6-31g(d,p) basis set for C and H atoms with the addition of a diffuse *p* function for S, N, P, and O, while Ni was described with the effective core potential Lanl2dz¹⁵¹ with an *f*-polarisation function (exponent = 3.130). The NCIs were then computed with the Critic2 software¹⁵² by another group member (Dr. Eric Mates-Torres).

4.3.1 Surface coverage analysis

The density *d* of adsorbed DT ligands and Ni(cycP) cocatalysts per unit area on the (220) surface slab was calculated as follows:

$$d = \frac{n_{ligands}}{4\pi r^2} = \frac{n_{ligands}(cell)}{a \times b} \quad (4.2)$$

where *r* is the average experimental radius of the QDs (2.25 nm), *n_{ligands}* is the number of ligands per nanoparticle determined via ¹H-NMR titration (Section 4.2), *n_{ligands}(cell)* is the corresponding number of ligands adsorbed in the surface unit cell, and *a* and *b* are the surface unit cell lattice parameters (5.746 and 4.063 Å, respectively, see Section 4.4.1). The ZnSe QDs were considered of spherical shape.

In the absence of the Ni(cycP) cocatalyst, *d* corresponded to one EDT ligand in a unit cell replicated twice, and a HexDT or OctDT ligand in a unit cell replicated six times. To determine the direction of the replication, the chain length of the molecules was compared to the Zn²⁺-Zn²⁺ and Se²⁻-Se²⁻ interatomic distances along the *a* or *b* axes. In fact, the similarity between these interatomic distances and the chain lengths was deemed to facilitate the bidentate binding. Specifically, EDT and HexDT (with lengths of 4.403 and 8.689 Å, respectively) best matched the interatomic distances along the *b* axis, and were bound in a *p*(1×2) and *p*(1×6)-ZnSe(220) supercell. On the other hand, OctDT (11.492 Å) best matched the interatomic distances along the *a* axis and was adsorbed in a *p*(3×2)-ZnSe(220) supercell.

After determining the appropriate dimensions of the supercell for the DT binding, the monodentate adsorptions of the various DTs in the ZnSe | DT systems were modelled between the proton of a thiol group and Se²⁻, and between the lone pairs of sulphur and Zn²⁺. Because the former resulted in the desorption of the DTs, the bidentate modes were only simulated considering the lone pairs of both sulphur atoms interacting with Zn²⁺ ions.

According to the Ni(cycP) loading obtained from Eq. 4.2, a single Ni(cycP) cocatalyst was placed in a $p(3\times4)$ -ZnSe(220) supercell. To model its binding, a deprotonated oxygen atom of Ni(cycP) was adsorbed on Zn^{2+} , while the hydroxyl group was rotated to hydrogen-bond the surrounding Se^{2-} anions. Two adsorption configurations were identified and labelled as A (equivalent to A') and B (equivalent to B'), as illustrated in **Figure 4.3a**.

In the simulation of the ZnSe | Ni(cycP) | DT systems, the $p(3\times4)$ -ZnSe(220) supercell with the adsorbed Ni(cycP) cocatalyst was expected to host two DTs. To identify the possible combinations for the binding modes of the two ligands, all available Zn^{2+} sites were labelled with a letter from A to H, as indicated in **Figure 4.3b**. In light of the results obtained with the ZnSe | DT systems (Section 4.4.2), at least one DT was deemed to bind bidentately along the a or b axis, or diagonally. It was then noted that, for the second DT to interact with the CO_2RR intermediates on the Ni centre, it must be monodentate. In the case of EDT, this was only feasible upon adsorption on site H. Due to their longer chain, HexDT and OctDT could instead could approach the Ni centre from all the neighbouring sites. Therefore, these DTs were modelled in all mono- and bidentate modes on Zn^{2+} ions A-G, excluding the H and the unlabelled ones, which were considered to be sterically hindered.

To compute the CO_2RR mechanism with the ZnSe | Ni(cycP) | DT systems, the bidentate DT hypothesised in the $p(3\times4)$ -ZnSe(220) supercell was removed from the calculation, as it was not envisioned to interact neither with the CO_2RR intermediates on the cocatalyst nor with the monodentate DT based on the Zn^{2+} - Zn^{2+} distance of *ca.* 5 Å along both the a and b axes. To prove this assumption, an HexDT chain was adsorbed bidentately on the E-G sites, along with a monodentate ligand on sites A, B, C and D. The adsorption energy of the compound system was then compared to the sum of the individual binding energies (Section 4.4.2).

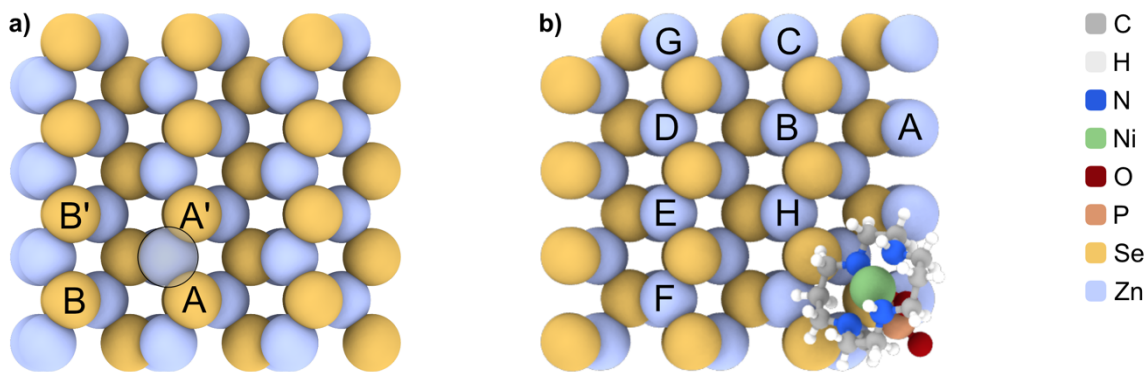


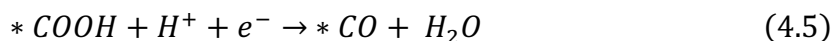
Figure 4.3 **a)** Top-view of bare $p(3\times4)$ -ZnSe(220). The Zn^{2+} site for the adsorption of the phosphonate group of Ni(cycP) is circled. The surrounding Se^{2-} ions are labelled as A, A', B and B'. **b)** Top-view of $p(3\times4)$ -

ZnSe(220) with the adsorbed Ni(cycP) cocatalyst. The Zn^{2+} sites available for DT adsorption are labelled with letters ranging from A to H.

4.3.2 Modelling the CO₂RR reaction mechanism

Previous work reporting the CO₂RR on ZnSe-QDs demonstrated that the Zn^{2+} ions are the surface active sites.⁸⁸ Additionally, CO₂ activation was shown to be the most endergonic step in the overall reaction, which could only be achieved upon the introduction of a negative charge in the simulation cell to account for the presence of a photogenerated electron. The subsequent hydrogenations were instead exergonic. Thus, to shed light on the CO₂RR activity of the DT-functionalised ZnSe-QDs, only the $*CO_2^-$ intermediate was optimised on the exposed Zn^{2+} sites, and the reaction mechanism was not further investigated.

Since the most endergonic step in the CO₂RR mechanism on the cocatalyst was instead unknown, the full reaction pathway was modelled following Eq. 4.3-6. Because the neutral form of Ni(cycP) was deemed to already account for the presence of the photogenerated electron (Section 4.3), no negative charge was included in the simulations of the CO₂RR mechanism on the ZnSe | Ni(cycP) and ZnSe | Ni(cycP) | DT systems.



where * denotes the resting state of the ZnSe | Ni(cycP) or ZnSe | Ni(cycP) | DT systems under examination, *i.e.* a $p(3 \times 4)$ -ZnSe(220) bearing the adsorbed Ni(cycP) cocatalyst, without and with a monodentate DT ligand, respectively. The Gibbs energy profile was calculated as follows, adopting the CHE⁶⁵ to account for the energetics of the hydrogenations:

$$\Delta G_{*CO_2} = G_{*CO_2} - (G_{CO_2} + G_*) \quad (4.7)$$

$$\Delta G_{*COOH} = G_{*COOH} - \left(G_{CO_2} + G_* + \frac{1}{2} G_{H_2} \right) \quad (4.8)$$

$$\Delta G_{*CO+H_2O} = G_{*CO} + G_{H_2O} - (G_{CO_2} + G_* + G_{H_2}) \quad (4.9)$$

$$\Delta G_{CO} = G_{CO} + G_{H_2O} + G_* - (G_{CO_2} + G_* + G_{H_2}) \quad (4.10)$$

where G_X represents the Gibbs energy of the species X . In the case of G_* , this includes the electronic energy of the ZnSe | Ni(cycP) or ZnSe | Ni(cycP) | DT system, as well as the thermodynamic corrections for the adsorbed Ni(cycP) and monodentate DT.

Lastly, the Gibbs adsorption energy of a hydrogen atom was calculated on the ZnSe | DT systems according to the CHE model as:

$$\Delta G_{*H} = G_{*H} - \left(\frac{1}{2} G_{H_2} + G_* \right) \quad (4.11)$$

Note: Dr. Eric Mates-Torres conducted the adsorption simulations of $*CO_2^-$ in the presence of the extra electron on ZnSe and ZnSe | DT, and of a hydrogen atom on ZnSe | DT.

4.4 Results

4.4.1 Modelling of the ZnSe bulk and surfaces

The bulk of the ZnSe crystal was optimised through a BM fitting, as detailed in Section 4.3. Table 4.2 reports the absolute bulk energies per atom obtained for the minimum of the BM plot during the assessment of the optimal k -point grids and cut-off energies to the plane waves. The $5 \times 5 \times 5$ k -point grid and a cut-off of 500 eV represented the best compromise between computational cost and precision of the results within 1 meV/atom. Relaxation of the corresponding minimum in the BM plot yielded a cubic cell of lattice parameter of 5.746 Å (**Figure 4.4a**), which compared well with the experimental value of 5.668 Å.¹⁵³

Table 4.2 Absolute electronic energy per atom, in eV, of the minimum predicted by the BM plot, adopting energy cut-offs of 500, 600, and 700 eV, and $3 \times 3 \times 3$, $5 \times 5 \times 5$, $7 \times 7 \times 7$, $9 \times 9 \times 9$, and $11 \times 11 \times 11$ k -point grids.

	3×3×3	5×5×5	7×7×7	9×9×9	11×11×11
500	−3.0858	−3.0894	−3.0895	−3.0895	−3.0895
600	−3.0862	−3.0898	−3.0899	−3.0899	−3.0899
700	−3.0848	−3.0883	−3.0885	−3.0885	−3.0885

To assess the most exposed surface on the ZnSe-QDs, the (111), (200), (220), and (311) facets were modelled as detailed in Section 4.3. **Figure 4.4b-e** reports the top and side-views

of these surfaces, while their E_{surf} were calculated as in Eq. 4.1 with one, two, and three bottom layers fixed (Table 4.3). The Wulff construction revealed that the (220) surface is the most exposed on the ZnSe-QDs, coherently with previous work.⁸⁸ Because the energy difference between relaxing the two and three uppermost layers was within 1 meV/atom, all subsequent reactivity studies were carried out on the (220) surface with the two bottom layers constrained in their bulk positions.

Table 4.3 Calculated E_{surf} values, in eV/Å², a and b lattice parameters, in Å, and α angle for the (111), (200), (220), and (311) surface slabs according to Eq. 4.1, with one, two, and three bottom layers fixed.

	(111)	(200)	(220)	(311)
one	0.054	0.114	0.029	0.054
two	0.056	0.115	0.030	0.056
three	0.058	0.114	0.031	0.056
a	8.126	5.746	5.746	14.075
b	8.126	5.746	4.063	8.126
α	120°	90°	90°	107°

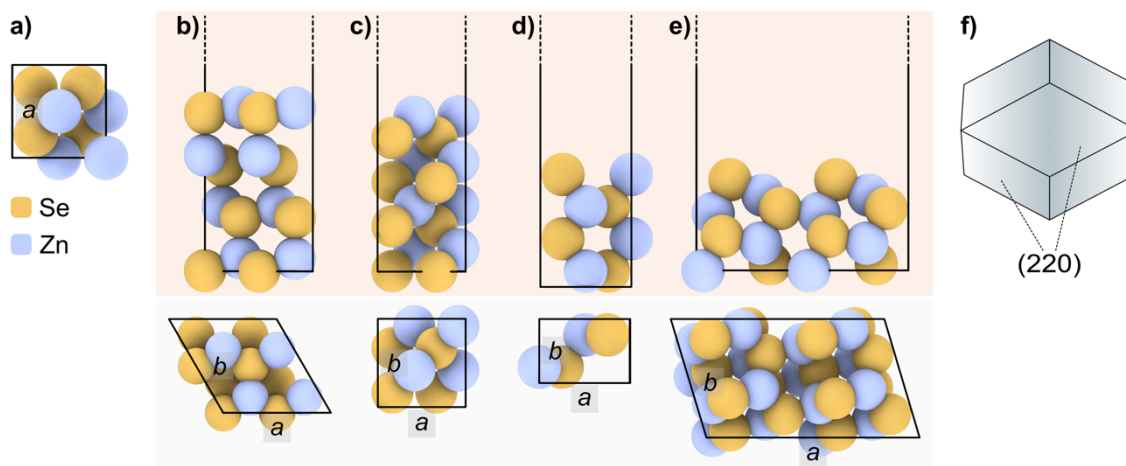


Figure 4.4 a) Bulk unit cell of ZnSe optimised through a BM fitting. Top and side-views of the b) (111), c) (200), d) (220), and e) (311) ZnSe surface slabs, modelled as four-layered slabs. f) Nanoparticle shape determined through Wulff construction.

4.4.2 Adsorption of the DT ligands and Ni(cycP) on the ZnSe QDs

The mono- and bidentate bindings of EDT, HexDT, and OctDT were modelled as detailed in Section 4.3.1. Their bidentate adsorption through the lone pairs of sulphur on Zn^{2+} , shown in **Figure 4.5**, resulted to be more stable than the monodentate by 0.15, 0.42, and 0.17 eV, respectively, as reported in Table 4.4.

Table 4.4 Binding energies of the monodentate (ΔG_{mono}) and bidentate (ΔG_{bi}) adsorption modes, and their energy difference $|\Delta\Delta G_{ads}|$, in eV, for an EDT, HexDT or OctDT ligand in a $p(1\times 2)$, $p(1\times 6)$ and $p(3\times 2)$ -ZnSe(220) supercell, respectively.

	ΔG_{mono}	ΔG_{bi}	$ \Delta\Delta G_{ads} $
ZnSe EDT	−0.12	−0.27	0.15
ZnSe HexDT	−0.56	−0.98	0.42
ZnSe OctDT	−0.55	−0.72	0.17

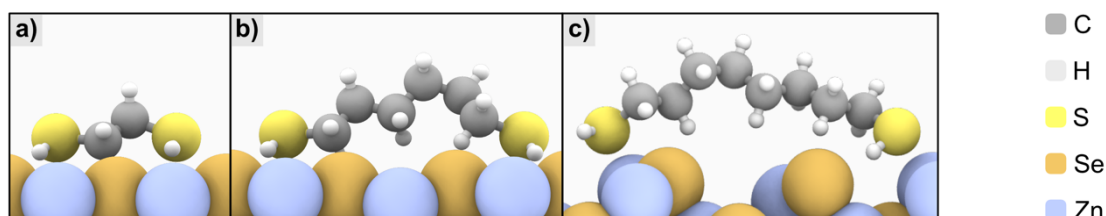


Figure 4.5 Side-view of the bidentate adsorption of an **a)** EDT **b)** HexDT, and **c)** OctDT ligand in a $p(1\times 2)$, $p(1\times 6)$ and $p(3\times 2)$ -ZnSe(220) supercell, respectively.

The Ni(cycP) cocatalyst was then modelled. Two orientations of the phosphonate group were identified, labelled in **Figure 4.6** as *OH-1* and *OH-2*. *OH-2* resulted to be more stable than *OH-1* by 0.10 eV, despite the slightly longer hydrogen bond highlighted in **Figure 4.6**. However, the latter featured a more exposed unprotonated oxygen, which could possibly interact stronger than the hydroxyl group with Zn^{2+} . Thus, the adsorption of the Ni(cycP) cocatalyst on $p(3\times 4)$ -ZnSe(220) was explored for both conformers on the A and B sites displayed in **Figure 4.3a**. The most stable adsorption mode was found to involve the Ni(cycP) cocatalyst in the *OH-2* configuration oriented on site A (Table 4.5).

Table 4.5 Electronic binding energies, in eV, of the Ni(cycP) cocatalyst in the *OH-1* (ΔE_1) and *OH-2* (ΔE_2) orientations of the phosphonate group (**Figure 4.3**), on the A and B adsorption sites (**Figure 4.1**).

	A	B
ΔE_1	−4.23	−4.21
ΔE_2	−4.33	−4.31

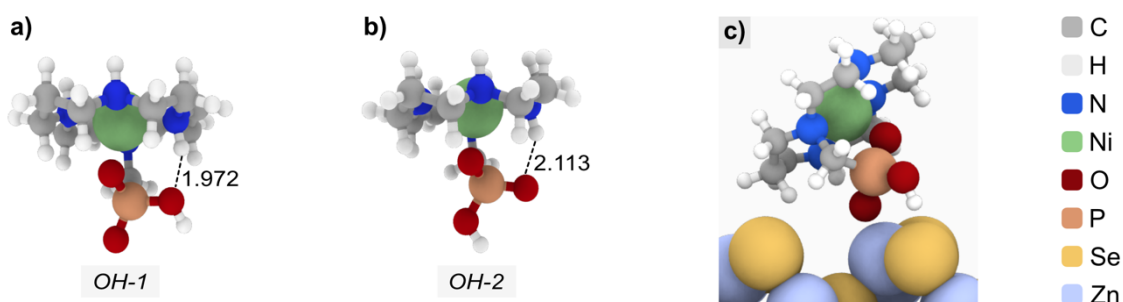


Figure 4.6 Depiction of the **a)** *OH-1* and **b)** *OH-2* conformers identified for the Ni(cycP) cocatalyst. **c)** Side-view of the adsorption of Ni(cycP) on $p(3\times 4)$ -ZnSe(220) in the *OH-2* orientation on site A.

Then, the mono- and bidentate binding modes of a single DT ligand on $p(3\times4)$ -ZnSe(220) with the adsorbed Ni(cycP) cocatalyst were investigated on the sites A-H illustrated in **Figure 4.3b** (Section 4.3.1). Table 4.6 shows that, in general, the bidentate binding was more favoured than the monodentate.

Table 4.6 Binding energies of monodentate (ΔG_{mono}) and bidentate (ΔG_{bi}) adsorptions, in eV, of EDT, HexDT, and OctDT, on sites A-H of $p(3\times4)$ -ZnSe(220) featuring the Ni(cycP) cocatalyst (**Figure 4.3b**).

System	Site	ΔG_{mono}	Sites	ΔG_{bi}
ZnSe Ni(cycP) EDT	H	-0.04	HB	-0.29
ZnSe Ni(cycP) HexDT	A	-0.64	AB	-0.83
	B	-0.66	AH	-0.64
	C	-0.52	BD	-0.77
	D	-0.49	BE	-0.86
	E	-0.46	CD	-0.64
	F	-0.37	CG	-0.73
	G	-0.53	CH	-0.96
	-	-	DF	-1.11
	-	-	EG	-1.15
	-	-	EH	-0.77
	-	-	FH	-0.87
ZnSe Ni(cycP) OctDT	A	-0.91	AB	-0.79
	B	-0.90	AD	-0.78
	C	-0.64	BF	-0.92
	D	-0.56	CE	-0.93
	E	-0.87	FG	-1.44
	F	-0.68	GH	-1.05
	G	-0.79	-	-

The presence of a second bidentate DT in the $p(3\times4)$ supercell was confirmed to not affect the adsorption of the first (Section 4.3.1). In fact, the energy difference between the sum of binding energies (ΔG_{sum}) in the presence of a single HexDT bidentate ligand on the E-G sites and a monodentate on the A, B, C or D site, and the overall binding energy ($\Delta G_{compound}$) of the system presenting both, was within 0.10 eV (Table 4.7). As mentioned in Section 4.3.1, the absence of interactions between the two DTs was attributed to the *ca.* 5 Å distance between the ligand chains, due to the spacing of the Zn^{2+} ions along the *a* and *b* directions.

Table 4.7 Gibbs adsorption energy of two HexDT ligands ($\Delta G_{compound}$), one bidentately adsorbed on the E-G sites and one monodentately adsorbed on the A, B, C or D site, sum of the Gibbs adsorption energies of a single HexDT ligand bound to those sites (ΔG_{sum}), and absolute difference of these values ($|\Delta\Delta G_{ads}|$).

	$\Delta G_{compound}$	ΔG_{sum}	$ \Delta\Delta G_{ads} $
EG + A	-1.73	-1.79	0.06
EG + B	-1.82	-1.81	0.01
EG + C	-1.64	-1.67	0.03
EG + D	-1.67	-1.64	0.03

4.4.3 CO₂RR on the ZnSe | DT systems

As reported in Section 4.3.2, the $^*\text{CO}_2^-$ intermediate was optimised on the available Zn^{2+} ions of the ZnSe and ZnSe | DT systems. It was observed that CO_2 desorbed into the gas phase on the bare ZnSe surface and in all ZnSe | DT systems except ZnSe | EDT. This finding was coherent with experiments, which indicated that EDT was the most efficient ligand in promoting the CO_2RR (Table 4.1). The capability of EDT in catalysing CO_2 activation was attributed to the establishment of a hydrogen bond between its dangling thiol group and an oxygen atom of $^*\text{CO}_2^-$, as revealed by the NCI analysis displayed in **Figure 4.7**.

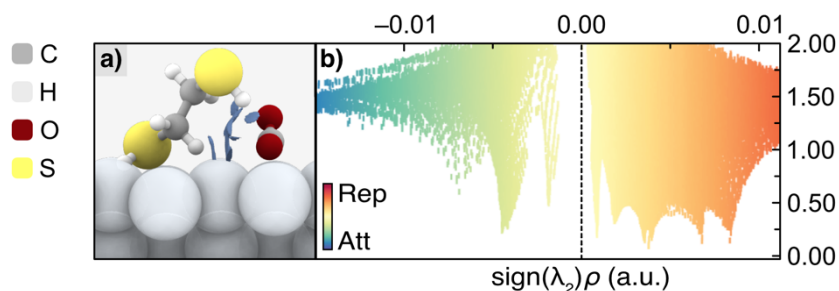


Figure 4.7 a) Optimised structure of $^*\text{CO}_2^-$ interacting with a monodentate EDT ligand on ZnSe | EDT. The NCI isosurfaces (isovalue = 0.5 a.u.) between the dangling thiol group of EDT and $^*\text{CO}_2^-$ are highlighted in blue. b) Plot of the reduced density gradient against $\text{sign}(\lambda_2)\rho(r)$. Attractive (repulsive) interactions are denoted by blue (red) shades; the stronger (weaker) the interaction, the darker (lighter) the shade.

4.4.4 CO₂RR on the ZnSe | Ni(cycP) | DT systems

After adsorbing the Ni(cycP) cocatalyst on $p(3\times 4)\text{-ZnSe}(220)$ (Section 4.4.2), the CO_2RR mechanism was modelled on the Ni centre. The most endergonic step was $^*\text{COOH}$ formation, as illustrated in **Figure 4.8** and reported in Table 4.8, while the subsequent hydrogenation to $^*\text{CO}$ and H_2O was energetically downhill. Specifically, the energy difference between the $^*\text{COOH}$ intermediate and the most exergonic step preceding it ($\Delta\Delta G_{^*\text{COOH}}$), *i.e.* $^*\text{CO}_2$ adsorption, was of 0.51 eV. The stabilisation of CO_2 on Ni, along

with the moderate $\Delta\Delta G_{*COOH}$ value, compatible with reactivity at room temperature, were in agreement with the enhanced activity of ZnSe | Ni(cycP) compared to the bare ZnSe QDs.

The CO₂RR was then modelled on all ZnSe | Ni(cycP) | DT systems bearing a monodentate ligand listed in Table 4.6. The adsorption of EDT on site H did not improve the thermodynamics of *COOH formation with respect to the bare Ni(cycP) cocatalyst, yielding a $\Delta\Delta G_{*COOH}$ value of 0.57 eV (Table 4.8). This was coherent with the similar performance of ZnSe | Ni(cycP) and ZnSe | Ni(cycP) | EDT observed experimentally (Table 4.1). Conversely, in the presence of HexDT and OctDT, $\Delta\Delta G_{*COOH}$ was dependent on the location of the monodentate ligand that interacts with the reaction intermediates adsorbed on the Ni centre. Specifically, the lowest $\Delta\Delta G_{*COOH}$ was achieved on site B for HexDT (0.36 eV) and site F for OctDT (0.54 eV). Notably, HexDT exhibited the largest decrease in $\Delta\Delta G_{*COOH}$, aligning with its enhanced CO₂RR activity reported (Table 4.1). In the case of OctDT, $\Delta\Delta G_{*COOH}$ was comparable to that obtained for the ZnSe | Ni(cycP) system, which did not explain the threefold increase in CO yield observed experimentally (Table 4.1).

Table 4.8 Relative Gibbs energies of the CO₂RR intermediates, and corresponding $\Delta\Delta G_{*COOH}$, on the ZnSe | Ni(cycP) and ZnSe | Ni(cycP) | DT systems bearing a monodentate DT (Table 4.6). The lowest $\Delta\Delta G_{*COOH}$ values for each system are highlighted in bold.

System	Site	ΔG_{*CO_2}	ΔG_{*COOH}	ΔG_{*CO}	$\Delta\Delta G_{*COOH}$
ZnSe Ni(cycP)	-	-0.26	0.25	-0.06	0.51
ZnSe Ni(cycP) EDT	H	-0.35	0.22	-0.10	0.57
ZnSe Ni(cycP) HexDT	A	0.05	0.41	0.14	0.41
	B	-0.04	0.32	0.20	0.36
	C	-0.36	0.48	-0.06	0.84
	D	-0.24	0.33	0.05	0.57
	E	-0.35	0.21	-0.04	0.56
	F	-0.37	0.20	-0.03	0.57
	G	-0.28	0.27	0.01	0.56
ZnSe Ni(cycP) OctDT	A	0.01	0.87	0.31	0.87
	B	0.01	0.59	0.30	0.59
	C	-0.30	0.60	-0.01	0.90
	D	-0.27	0.28	0.01	0.55
	E	0.21	0.75	0.50	0.75
	F	-0.04	0.50	0.27	0.54
	G	-0.02	0.79	0.22	0.81

To shed light on the different effect displayed by the DTs on the calculated $\Delta\Delta G_{*COOH}$ values, the NCIs between the ligands and the $*COOH$ intermediate were computed. Due to its short chain length, the EDT ligand did not efficiently interact with $*COOH$. This was coherent with the similar $\Delta\Delta G_{*COOH}$ values obtained for ZnSe | Ni(cycP) and ZnSe | Ni(cycP) | EDT. On the other hand, HexDT and OctDT were able to hydrogen-bond $*COOH$. Importantly, these ligands required to adopt a bent configuration so that the thiol moiety could approach the $*COOH$ species, as illustrated in **Figure 4.8c-e**. Thus, their chain flexibility was deemed essential for effectively establishing such hydrogen bond, coherently with the scarcer performance of BenzDT (Table 4.1). Comparison of the NCIs calculated for HexDT on site B and OctDT on site F, indicated a smaller degree of attraction for the latter. This result was attributed to the longer OctDT chain, which was deemed less optimal for interacting with the CO_2RR intermediates on the Ni centre.

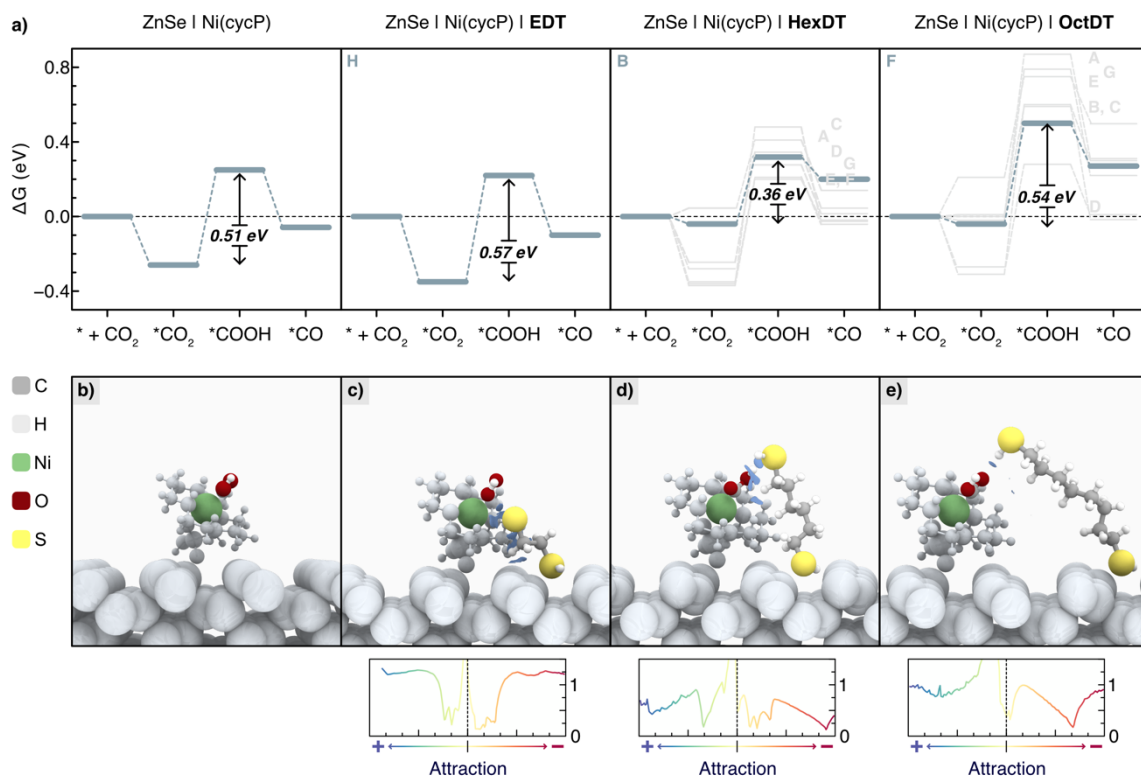


Figure 4.8 a) Gibbs energy profiles calculated for CO_2RR on the ZnSe | Ni(cycP) and ZnSe | Ni(cycP) | DT systems, adsorbing EDT, HexDT, and OctDT monodentately on the sites listed in Table 4.6. From left to right, optimised structure of $*COOH$ bound on the Ni centre of Ni(cycP) in the b) ZnSe | Ni(cycP), c) ZnSe | Ni(cycP) | EDT, d) ZnSe | Ni(cycP) | HexDT, and e) ZnSe | Ni(cycP) | OctDT systems. EDT, HexDT, and OctDT are bound on sites H, B, and F, respectively. The NCI isosurfaces (isovalue = 0.5 a.u.) between the dangling thiol groups and $*COOH$ are highlighted in blue. Plots of the reduced density gradient against $sign(\lambda_2)\rho(r)$ are provided in the insets. Attractive (repulsive) interactions are denoted by blue (red) shades; the stronger (weaker) the interaction, the darker (lighter) the shade.

4.4.5 Competition with HER

The Zn^{2+} surface ions on the ZnSe-QDs were shown in previous studies to be the active sites for HER.⁸⁸ Thus, to rationalise the different amounts of H_2 produced on the functionalised ZnSe-QDs, ΔG_{*H} was computed on the Zn^{2+} sites for the various ZnSe | DT systems (Eq. 4.11).¹⁵⁴ This amounted to -0.28 , 0.26 , and 0.06 eV in the presence of the EDT, HexDT, and OctDT ligands, respectively. The fact that all ΔG_{*H} values were close to thermoneutral was in agreement with the occurrence of HER at room temperature. Additionally, the observation of the bidentate binding as the most favoured mode for all DTs (Section 4.4.2) explained the decrease in HER on the ZnSe | DT systems with respect to the bare ZnSe-QDs (Table 4.1). In fact, this provided a more efficient blockage of the Zn^{2+} ions compared to the monodentate. It was also noted that EDT could cover neighbouring Zn^{2+} sites based on its chain length, which was not the case for HexDT and OctDT (**Figure 4.5**). This finding, along with its higher loading on the ZnSe QDs, suggested that the former was able to cover the Zn^{2+} surface ions more effectively. This was coherent with the higher H_2 yield of ZnSe | HexDT and ZnSe | OctDT compared to ZnSe | EDT (Table 4.1). Similarly, in the ZnSe | Ni(cycP) | DT systems, the enhancement of the selectivity towards CO_2RR with respect to the bare ZnSe surface and ZnSe | DT was attributed to the increased blockage of the Zn^{2+} surface sites. This result was in agreement with literature, as discussed in Section 4.1.1.^{140,139}

4.5 Conclusions

The photoreduction of CO_2 offers a green route for the production of versatile building blocks such as CO, which can be further converted into C_1 and C_2 feedstocks like alcohols and hydrocarbons. However, this process suffers from the competition with the more facile HER in aqueous electrolytes.¹⁸

In this work, experiments demonstrated the increase in the photocatalytic activity of ZnSe QDs for the CO_2RR to CO via functionalisation with DT ligands. Specifically, the largest enhancement was displayed by EDT, while longer-chain DTs exhibited a reduced performance. This observation was rationalised by modelling the $^*\text{CO}_2^-$ intermediate in the presence of the adsorbed DTs, which resulted in CO_2 desorption into the gas phase in the presence of HexDT and OctDT. On the other hand, the short chain of EDT allowed it to stabilize $^*\text{CO}_2^-$ binding via a hydrogen bond.

A larger increase in photocatalytic CO₂RR was achieved by introducing a Ni(cycP) cocatalyst into the reaction mixture. Assessment of the reaction mechanism on the Ni centre revealed *COOH formation as the most endergonic step, and its energetics were deemed coherent with the intrinsic Ni(cycP) activity seen in experiments conducted at room temperature. Further functionalisation of ZnSe | Ni(cycP) with DT ligands led to the best performance with HexDT, which enhanced the CO₂RR activity of the catalytic system four times compared to ZnSe | Ni(cycP) and ZnSe | EDT. Computational investigation of the NCIs between HexDT adsorbed in the vicinity of the cocatalyst and *COOH highlighted the presence of a hydrogen bond between the two. While EDT was too short to interact with the CO₂RR intermediates adsorbed on the Ni centre, OctDT displayed a qualitatively lower degree of attractive interactions. Thus, the superior behaviour of HexDT was attributed to its chain length, which was optimal to hydrogen bond the *COOH intermediate on the cocatalyst. Importantly, the flexibility of the ligands was proven as a necessary requirement to effectively interact with the reaction intermediates, in line with the poor experimental CO₂RR activity observed with a rigid DT such as BenzDT.

Lastly, the Zn²⁺ surface ions were confirmed to be active towards H₂ production by computing their ΔG_{*H} , which was close to thermoneutral. Thus, the suppression of HER was attributed to the coverage of the Zn²⁺ sites by the DT ligands and Ni(cycP) cocatalyst, in agreement with previous literature reports.⁸⁸ Specifically, the highest selectivity for CO of *ca.* 40% was displayed by ZnSe | Ni(cycP) | HexDT.

Overall, this project demonstrated that the photocatalytic CO₂RR on ZnSe QDs can be improved by minimising the competing HER through the functionalisation with flexible, hydrogen bond donor organic ligands, possibly in conjunction with metalorganic cocatalysts. These results represent a promising premise for further engineering semiconducting QDs through the exploration of different organic ligands and metal cocatalysts.

5. Electrochemical hydrogenation of acetophenone on transition metal electrodes

5.1 Introduction

As discussed in the Introduction, the chemical hydrogenation of organic substrates often requires high temperatures and pressures, organometallic catalysts, and organic solvents.⁴⁹ For instance, the hydrogenation of AP to 1-phenylethanol (APH₂), an intermediate in the synthesis of styrene and propylene oxide,¹⁵⁵ is typically performed under high H₂ pressures, which favour the hydrolysis step,¹⁵⁶ or via hydrogen transfer hydrogenation from an alcohol, usually 2-propanol, as shown in **Figure 5.1a**.¹⁵⁷ Both approaches rely on catalysts based on metals such as Ir,¹⁵⁸ Fe,¹⁵⁹ Mn,¹⁶⁰ and more frequently Ru^{156,157,161} functionalised with ligands such as phosphines, carbon monoxide, amines, and pyridine derivatives.^{156,158,161} Among these, Noyori-type catalysts with chiral diamine and diphosphine ligands have been shown to reduce AP to APH₂ with high enantioselectivity.¹⁶² Some examples are illustrated in **Figure 5.1b**, along with their reaction conditions and yields of APH₂.

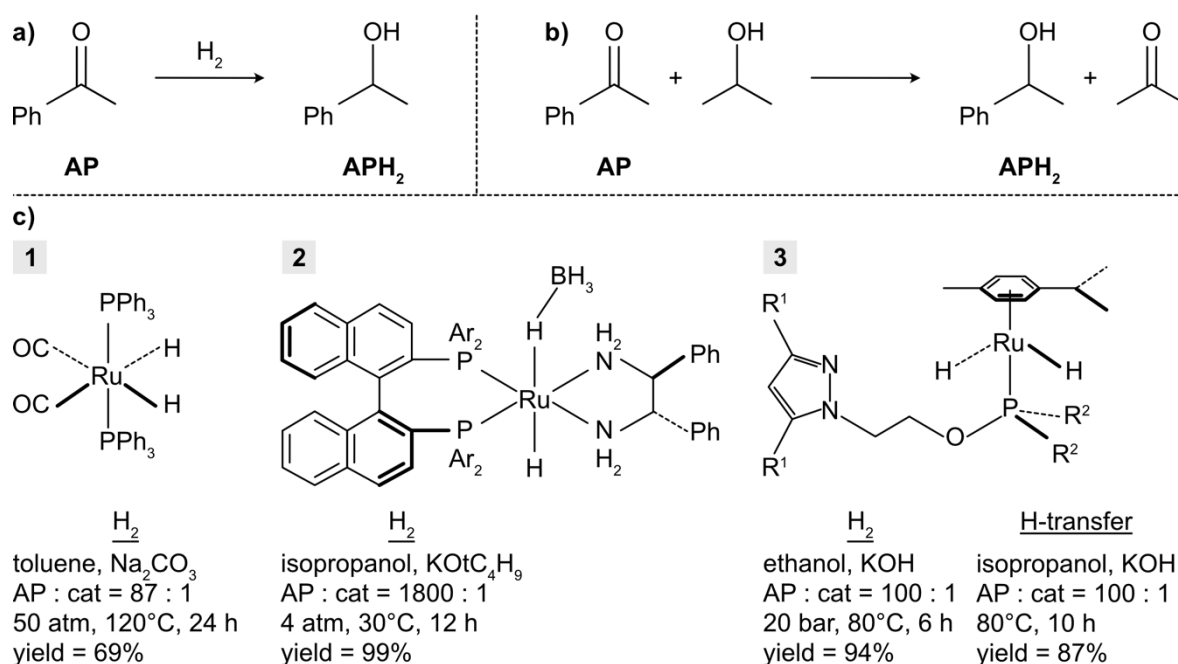
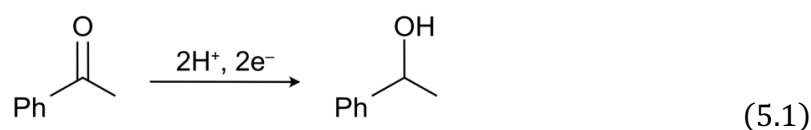


Figure 5.1 Reduction of AP to APH₂ via **a)** hydrogenation with H₂ and **b)** hydrogen transfer from 2-propanol. **c)** Examples of chemical reduction of AP to APH₂ both via H₂ and transfer hydrogenation (**1**,¹⁵⁶ **2**,¹⁶¹ **3**¹⁵⁷).

To avoid the use of organometallic complexes, H_2 , and harsh reaction conditions, AP reduction can be carried out electrochemically, potentially on non-precious metal catalysts using water or alcohols as solvents, as illustrated in Eq. 5.1:⁴⁹



Although HER competes with ECH processes in protic environments, it can be minimised under alkaline conditions, which require water to be hydrolysed on the catalyst surface to source the protons for the reaction (see Introduction).^{70,71} Thus, using a basic pH has been reported to enhance the selectivity of ECHs over HER. For example, the partial current density for the reduction of acetonitrile to ethylamine on Cu nanoparticles increased from 50 to over 600 mA/cm^2 at $-0.73 \text{ V}_{\text{RHE}}$ when switching from a 0.5 M H_2SO_4 solution to a 2 M NaOH solution.¹⁶³ Another study on the CO_2RR to ethylene on a Cu electrocatalyst showed that a 1 M KOH solution decreased the hydrogen coverage on the electrode, suppressing HER and achieving a FE of around 70% at $-0.55 \text{ V}_{\text{RHE}}$.¹⁶⁴

While alkaline conditions can mitigate HER, the ECH reaction still depends on the solvent as a proton source. In this context, organic substrates like AP may be inefficient at hydrolysing it, both in their non-reduced and reduced forms. In water, in fact, the 1-phenylethyl cation (APH^+) and radical ($\text{APH}\cdot$) feature a pK_a of -6.2 and 9.9 , respectively.^{165,166} Hence, the equilibrium of H_2O hydrolysis on the substrate is likely shifted towards the non-protonated intermediates at $\text{pH} > 10$ for both APH^+ and $\text{APH}\cdot$, as shown in **Figure 5.2**. Therefore, it was hypothesised in this work that, under alkaline conditions, the electrode would need to hydrolyse the solvent, reduce the protons, and retain them on its surface for the ECH reaction.

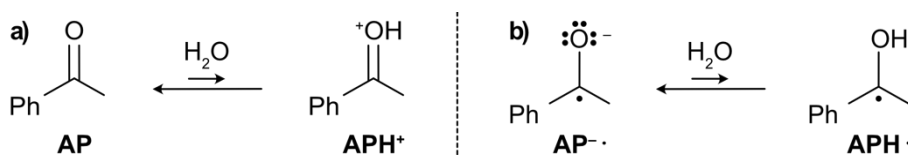


Figure 5.2 Equilibrium between the protonated and non-protonated form of **a)** AP and **b)** $\text{AP}^{\cdot-}$.

Importantly, experimental evidence supports the existence of reduction pathways involving chemisorbed hydrogen atoms on the electrode surface. An example thereof is the electroreduction of NO_3^- to NH_3 , where strained Ru nanoclusters were used as cathode materials.¹⁶⁷ A FE and a partial current density for NH_3 of *ca.* 100% and $125 \text{ mA}/\text{cm}^2$,

respectively, were obtained at $-0.2\text{ V}_{\text{RHE}}$. Both the adoption of alkaline conditions and the tensile strain of the catalysts, which impaired the coupling of surface hydrogens, were found to inhibit HER. Furthermore, the generation of hydrogen radicals was confirmed through electron spin resonance using 5,5-dimethyl-1-pyrroline-N-oxide as a scavenger, and their consumption during the NO_3RR was measured, indicating their role in NH_3 formation. Lastly, computational studies of the activation barriers for NO_3^- hydrogenation with and without hydrogen radicals also corroborated their involvement in the ECH reaction. Overall, it was concluded that the NO_3RR proceeded via hydrogen radicals generated on the catalyst rather than through electron transfer to the substrate followed by protonation in solution.

A second study investigated the reduction of furfural to furfuryl alcohol and 2-methylfuran on a Cu electrode to assess the role of adsorbed hydrogen atoms.¹⁶⁸ Kinetic measurements on a rotating disk electrode under alkaline conditions suggested that both HER and furfural ECH were limited by proton mass transport to the catalyst, which would not occur if the electron transfer to the substrate and its protonation happened at the electrode and in the bulk solution, respectively. Therefore, adsorbed hydrogen atoms were deemed responsible for furfural hydrogenation. This conclusion was further supported by comparing the ECH activity of Cu to that of Pd, which binds hydrogen weakly and only produced the hydrofuroin dimers, suppressing both HER and furfural hydrogenation. Additional evidence for chemisorbed hydrogen radicals was provided by kinetic measurements in deuterated solvents and by covering the Cu electrode with organic ligands.

In this work, the ECH of AP was performed under basic conditions on Ag, Au, Cu, In, Ni, and Pt metal catalysts, to investigate whether the protons for the reaction were indeed sourced from the solvent and retained on the electrode surfaces after their reduction.

5.2 Experimental results

A Cu metal electrode was prepared using dynamic hydrogen bubble templated electrodeposition¹⁶⁹ and characterised via scanning electron microscopy (SEM) and p-XRD. SEM confirmed the dendritic morphology expected from this synthetic method, and p-XRD indicated the presence of the (111), (200), and (220) facets. The electrochemical reduction of AP was investigated using a 0.05 M solution of AP dissolved in a 9:1 water-ethanol mixture, buffered to pH 11.8 via a 0.25 M $\text{KH}_2\text{PO}_4/\text{KOH}$ solution. The reaction was performed at constant potentials of -0.28 , -0.38 , -0.48 , -0.58 , and $-0.68\text{ V}_{\text{RHE}}$ for one hour. Gas chromatography and ^1H -NMR analysis of the reaction mixture indicated that the only

products formed were APH₂ and H₂. The highest FE and partial current density for APH₂ (J_{APH_2}) were achieved at $-0.48 \text{ V}_{\text{RHE}}$, with values of *ca.* 91% and 14 mA/cm^2 , respectively (**Figure 5.3a**). Accordingly, H₂ formation decreased between -0.28 and $-0.48 \text{ V}_{\text{RHE}}$, reached a minimum between -0.48 and $-0.58 \text{ V}_{\text{RHE}}$, and increased again at more cathodic potentials. Extending the reaction time to five hours at $-0.48 \text{ V}_{\text{RHE}}$ resulted in a APH₂ yield of $91 \pm 1\%$, although the FE decreased from 60% during the first three hours to $47 \pm 6\%$.

Next, Ag, Au, and In electrodes were prepared following the same synthetic approach used for Cu, while Ni was purchased as a commercial foam, and Pt as a foil. The ECH of AP was examined on these metals at $-0.48 \text{ V}_{\text{RHE}}$ under the same experimental conditions adopted for Cu. Ag and Au exhibited high FEs (80-90%) and J_{APH_2} values of $10\text{-}13 \text{ mA/cm}^2$, comparable to Cu. In contrast, In and Pt displayed lower FEs of around 20% and a J_{APH_2} values of *ca.* 2.5 mA/cm^2 (**Figure 5.3b**). Lastly, Ni was inactive for the ECH of AP. Overall, the activity and selectivity trend of the metals at $-0.48 \text{ V}_{\text{RHE}}$ was $\text{Cu} > \text{Ag} \approx \text{Au} > \text{In} \approx \text{Pt} > \text{Ni}$. Lastly, Ag and Au showed an increase in J_{APH_2} at more negative bias (**Figure 5.3c-d**).

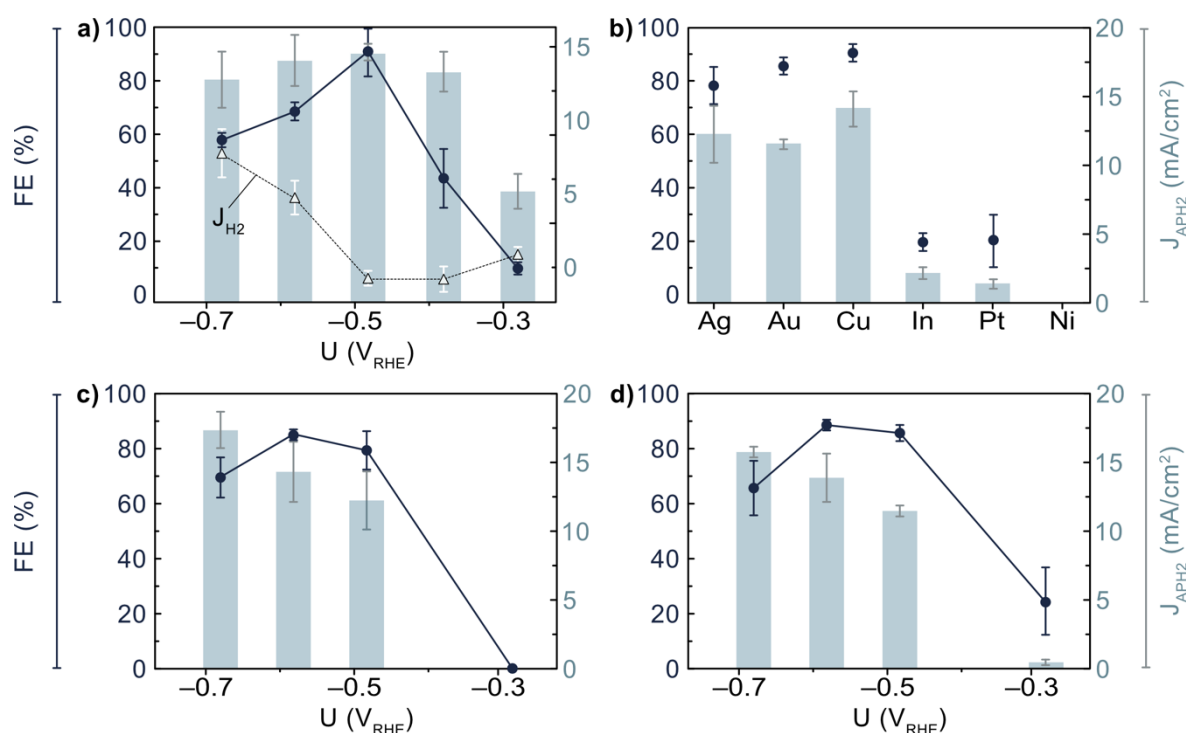


Figure 5.3 a) FE towards APH₂, J_{APH_2} and J_{H_2} on the Cu electrode at -0.28 , -0.38 , -0.48 , -0.58 and $-0.68 \text{ V}_{\text{RHE}}$. b) FE and J_{APH_2} on the Ag, Au, Cu, In, Pt and Ni electrodes at $-0.48 \text{ V}_{\text{RHE}}$. c) FE and J_{APH_2} on the Ag electrode at -0.28 , -0.48 , -0.58 and $-0.68 \text{ V}_{\text{RHE}}$. d) FE and J_{APH_2} on the Au electrode at -0.28 , -0.48 , -0.58 and $-0.68 \text{ V}_{\text{RHE}}$.

The activity and selectivity of the Cu electrode were then assessed for the ECH of organic substrates containing various unsaturated groups, including the C=O bond in benzaldehyde,

the C=C bond in maleic acid and cyclohexe-2-en-1-one, the C≡C bond in phenylpropionic acid, and the C≡N bond in acetonitrile, as displayed in **Figure 5.4**. In the reduction of the carbonyl C=O bond to –OH, the Cu electrode achieved similar conversions for benzaldehyde (85%) and AP. The C=C bonds of maleic acid and cyclohexe-2-en-1-one as well were hydrogenated with high conversions of 89% and 77%, respectively. Additionally, the C≡C triple bond of phenylpropionic acid was almost exclusively hydrogenated to a C=C double bond (76%), while the complete reduction to a C–C single bond was limited to 7%. Finally, the C≡N triple bond in acetonitrile was fully reduced to –NH₂ (86%). Overall, the Cu electrode demonstrated good performance for the ECH of C=O, C=C, C≡C, and C≡N bonds in a water-alcohol mixture, operating at potentials less negative than –0.60 V_{RHE}.

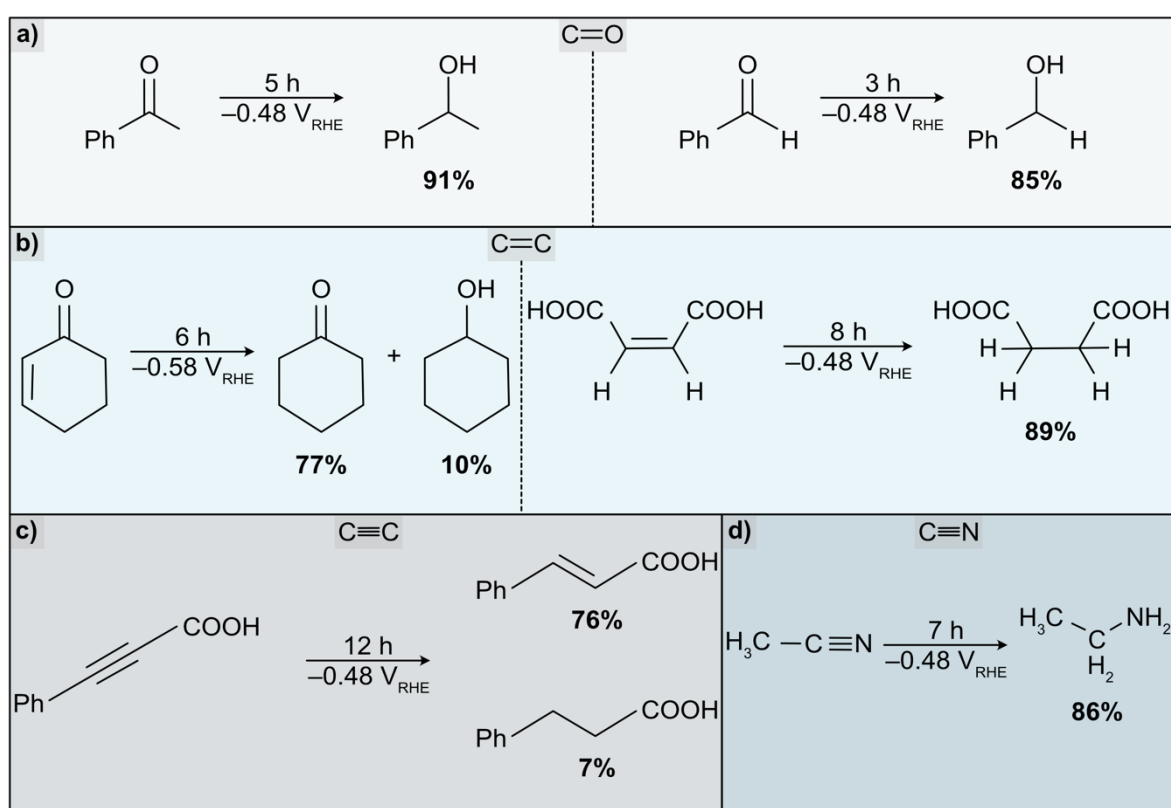


Figure 5.4 Conversion, applied potential and reaction time for the ECH on the Cu electrode of **a)** AP and benzaldehyde **b)** cyclohexe-2-en-1-one and maleic acid **c)** phenylpropionic acid and **d)** acetonitrile.

5.3 Computational details

Periodic DFT calculations were performed using VASP,¹²⁶ adopting the BEEF functional.⁹⁶ Core and valence electrons were described with projector-augmented wave pseudopotentials¹²⁴ and plane waves of energy cut-off of 500 eV, respectively. The electronic occupancy in molecular species was described with Gaussian smearing of width 0.05 eV, while the Methfessel-Paxton smearing of first order was used for metals, with a width of 0.2 eV. Reciprocal space was sampled at the Γ -point for molecular species, while solid-state simulations were carried out with a Γ -centred k -point grid of density *ca.* 40 k -points $\times\text{\AA}$, selected through a BM fitting¹⁴² performed by another group member on the Ag, Au, Cu, Ni and Pt metals. Electronic steps were considered converged within a threshold of 10^{-6} eV.

Geometry optimisations were performed with the conjugated gradient algorithm using a step size of 0.1 $\text{\AA}$, a force convergence criterion of 0.01 $\text{\AA}/\text{eV}$, and without allowing the cell shape and volume to change. To identify the TS in the hydrogenation of AP from the $\ast\text{H}$ surface coverage assisted by the solvent, the number of H_2O molecules to be introduced in the simulation was first benchmarked. To this aim, a trial TS structure for AP hydrogenation at the C on Ag(111) was set up with one, two and three H_2O molecules aiding the transfer, and optimised with the improved dimer method¹²⁰ imposing an energy convergence criterion for the ionic steps of 10^{-5} eV. Because two H_2O molecules resulted to furnish the largest decrease in the kinetic barrier (Section 5.4.4), they were employed in the subsequent TS searches for the $\ast\text{AP}$ hydrogenation at the O atom on the Ag(111), Au(111), and Cu(111) surfaces. For these, a preliminary NEB calculation¹¹⁹ using eight images was performed between the system featuring the $\ast\text{AP}$ and $\ast\text{APH}\cdot$ intermediates in the presence of water. This identified the presence of a TS for the hydrogen transfer from the surface to H_2O and another TS for the hydrogen transfer from H_2O to $\ast\text{AP}$. Because the former TS was higher in energy, it was refined with the improved dimer method as described above.¹²⁰

All optimised geometries were characterised through a frequency calculation using the finite differences method and a step size of 0.02 $\text{\AA}$. Whenever imaginary frequencies below 100 cm^{-1} were present, these were replaced with real frequencies of 12 cm^{-1} .¹⁷⁰ The thermodynamic corrections to the electronic energy were computed with the ASE thermochemistry module,¹⁴⁴ using the ideal gas model for the isolated molecules and the harmonic model for the adsorbates. For the correction to the electronic energy of adsorbates, the atoms in the surface slabs were not vibrated, as discussed in Section 4.3.

Molecular species were constructed with the graphical interface of ASE,¹⁴⁴ imposing a 15 Å vacuum along all directions to avoid interactions between periodic images. To represent bulk water, a cage of six water molecules hydrogen-bonded to each other was constructed in a cubic cell shape of side 5.862 Å along the *a* and *b* axes, and 5.034 Å along the *c* axis. This was first optimised by only allowing the atom positions to relax, followed by a second optimisation allowing the cell shape and volume to relax.

The bulk cell of In with lowest energy above Hull was downloaded from Materials Project.¹⁴⁷ This corresponded to a tetragonal packing of lattice parameters $a = b = 3.259$ Å and $c = 4.986$ Å. The unit cell of minimum energy was determined by enlarging and reducing the lattice parameters by 1% five times and optimising the corresponding cell without allowing the cell volume and shape to change. The resulting energies and volumes were fitted to the BM equation of state,¹⁴² and the unit cell with the volume of minimum energy was relaxed allowing the cell shape to relax but not the volume.

The various surface facets were cleaved as slabs of four layers, adding a vacuum of 15 Å along the direction perpendicular to the surface, and constraining the atoms in the two bottom layers in their bulk positions. For the face-centred cubic metals, the (111) facet was modelled.¹⁷¹ The most exposed surface of In instead was determined via a Wulff construction carried out with WulffPack.¹⁴⁸

5.3.1 Surface coverage analysis

The surface coverage analysis was performed on $p(2 \times 2)$ supercells for Ag(111), Au(111), Cu(111), Ni(111), and Pt(111), and on a $p(1 \times 2)$ cell for In(101). The face-centred cubic metals presented four *bridge*, *fcc*, *hcp*, and *top* sites, while In(101) featured four *bridge I*, *bridge II*, *hollow I*, *hollow II*, and *top* sites, as shown in **Figure 5.5a-b**. Thus, the addition of an adsorbate in these cells corresponded to an increase in coverage density by 6.25% for Ag(111), Au(111), Cu(111), Ni(111), and Pt(111), and by 5% for In(101). Although larger supercells would allow for a finer tuning of the coverage density, this was not expected to significantly impact the reactivity studies.

The binding of a single *H, *OH, and *O was first investigated for all aforementioned sites. Subsequently, the coverage density was gradually increased by adding a single adsorbate at a time to the most stable site. The clean surface was labelled as ‘bare’, and the covered slabs were labelled according to the adsorbate type (*i.e.* ‘H’, ‘OH’, ‘O’) and the coverage density.

Since the supercells presented four sites of each kind, the addition of a single adsorbate increased their population by 25%. The coverage density was therefore expressed as multiples of 0.25 monolayers (ML). For example, the label ‘0.25 ML X’ indicates 25% coverage of the most stable site for adsorbate X, corresponding to one adsorbate in a $p(2\times 2)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) supercell or in the $p(1\times 2)$ -In(101). The label ‘0.50 ML X’ denotes 50% of the coverage of the most stable site, corresponding to two adsorbates, as illustrated in **Figure 5.5c-d**. After filling the preferred sites, the second most favoured were incrementally populated, with labels such as ‘1.25 ML X’, ‘1.50 ML X’ and so on. The surface coverage analysis was terminated when surface reconstruction occurred, molecular species like H₂ evolved, or when the supercell could not accommodate additional adsorbates due to size constraints.

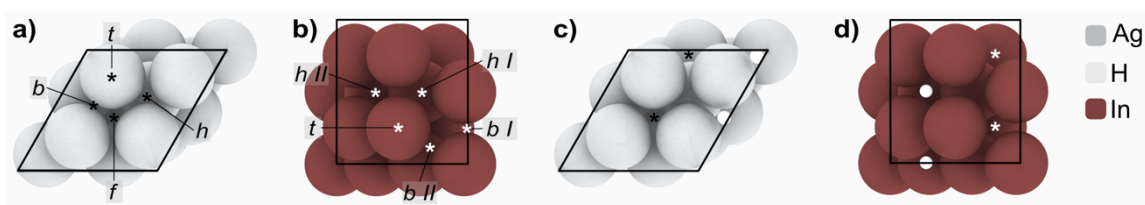


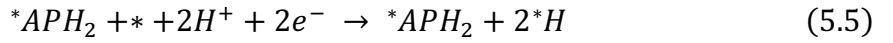
Figure 5.5 **a)** bridge (b), fcc (f), hcp (h) and top (t) sites on a $p(2\times 2)$ -Ag(111) supercell. **b)** bridge I (b I), bridge II (b II), hollow I (h I), hollow II (h II) and top (t) sites on a $p(1\times 2)$ -In(101) supercell. Exemplified 0.50 ML H coverage on **c)** $p(2\times 2)$ -Ag(111) and **d)** $p(1\times 2)$ -In(101).

5.3.2 Mechanistic study of AP electroreduction

For the mechanistic investigation of AP electroreduction, $p(6\times 4)$ -Ag(111), Au(111), Cu(111), Ni(111), and Pt(111) supercells were used to ensure a minimum distance of ≈ 8 Å between adsorbates in neighbouring periodic images. No reactivity studies were conducted on In(101), as discussed in Section 5.4.2.

The reaction mechanism was modelled by sourcing both protons and electrons from the catalyst surface coverage, considering two possible pathways. On Cu(111), Ni(111), and Pt(111), a $\ast\text{H}$ covered surface was predicted to be the most stable state under reaction conditions (-0.48 V_{RHE}), while Ag(111) and Au(111) were found to be stable in their bare states (Section 5.4.2). Thus, on Cu(111), Ni(111), and Pt(111), AP was adsorbed on the $\ast\text{H}$ covered slabs. The hydrogenation of AP via the surface $\ast\text{H}$ could then either proceed sequentially before replenishing the coverage vacancies created during the process, or each hydrogenation could be directly followed by vacancy refilling. Because no $\ast\text{H}$ was introduced into the simulation cell during the AP hydrogenation steps, these were treated as

chemical steps within the CHE framework. Hence, their energy differences should not be influenced by the applied bias. In contrast, the refilling of *H vacancies was an electrochemical step and thus should be lowered by a negative potential. For this reason, AP reduction and surface coverage regeneration were modelled as separated processes, with the reduction occurring first, followed by the replenishing of *H vacancies, as shown below:



where * denotes a surface site. The first hydrogenation (Eq. 5.3) was explored on all metals at both the carbonyl O and C atoms, leading to the second hydrogenation (Eq. 5.4) either at the C or O. The Gibbs energies for the reaction intermediates were calculated according to the CHE model as follows:

$$\Delta G_{*AP} = G_{*AP} - (G_{AP} + E_*) \quad (5.7)$$

$$\Delta G_{*APH \cdot} = G_{*APH \cdot} - (G_{AP} + E_* + G_{corr,*H}) \quad (5.8)$$

$$\Delta G_{*APH_2} = G_{*APH_2} - (G_{AP} + E_* + 2G_{corr,*H}) \quad (5.9)$$

$$\Delta G_{2*H} = G_{2*H} - (G_{AP} + E_* + G_{H_2}) + 2eU_{RHE} \quad (5.10)$$

$$\Delta G_{APH_2} = G_{APH_2} - (G_{AP} + E_* + G_{H_2}) + 2eU_{RHE} \quad (5.11)$$

where ΔG_X is the Gibbs energy associated with the formation of intermediate X , E_* is the electronic energy of the *H covered surface, ΔG_{2*H} is the Gibbs energy for replenishing the two *H vacancies on the catalyst, U_{RHE} the applied potential (-0.48 V_{RHE}), e is the electron charge, and $G_{corr,*H}$ is the the vibrational contribution to the energy of an adsorbed *H on the surface coverage.

On Ag(111) and Au(111), instead, the clean surface was used as the energy reference. The reaction mechanism was therefore modelled by first reducing two protons on the electrode surface before adsorbing and hydrogenating AP:



The reaction energetics were calculated using to the CHE model:

$$\Delta G_{2^*H} = G_{2^*H} - (E_* + G_{H_2}) + 2eU_{RHE} \quad (5.17)$$

$$\Delta G_{^*AP} = G_{^*AP} + 2G_{corr,*H} - (G_{AP} + E_* + G_{H_2}) + 2eU_{RHE} \quad (5.18)$$

$$\Delta G_{^*APH\cdot} = G_{^*APH\cdot} + G_{corr,*H} - (G_{AP} + E_* + G_{H_2}) + 2eU_{RHE} \quad (5.19)$$

$$\Delta G_{^*APH_2} = G_{^*APH_2} - (G_{AP} + E_* + G_{H_2}) + 2eU_{RHE} \quad (5.20)$$

$$\Delta G_{APH_2} = G_{APH_2} - (G_{AP} + E_* + G_{H_2}) + 2eU_{RHE} \quad (5.21)$$

Because the same potential correction was imposed to AP adsorption and its two reductions, the energy difference between them was not affected by the applied bias. Therefore, they were treated as chemical steps like on Cu(111), Ni(111), and Pt(111). Importantly, since the energies were referred to the clean slab, the vibrational Gibbs corrections to the adsorbed $^*H$ $G_{corr,*H}$ were added to $G_{^*AP}$ and $G_{^*APH\cdot}$ (Eq. 5.18-19). Additionally, it must also be noted that, in this framework, the values of $\Delta G_{^*AP}$, $\Delta G_{^*APH\cdot}$ and ΔG_{APH_2} also comprise the energy for the reduction of two protons on the catalyst surface.

The choice of the water reference for computing the activation barrier of AP hydrogenation from the surface coverage ($\Delta G^\ddagger$) was complex. In fact, using water monomers as a reference could fictitiously increase the number of hydrogen bonds in the TS. Furthermore, the corresponding thermodynamic corrections would pertain to the ideal gas model, which does

not conform to the behaviour of liquids. Similarly, the adoption of a H₂O cage would result in a deceitful decrease in the number of hydrogen bonds between the reference and the TS, and the thermodynamic corrections of bulk water would follow the harmonic model, which is also not devised to describe liquids. Thus, $\Delta G^\ddagger$ was calculated relative to the optimised $p(6\times 4)$ supercells with the adsorbed *AP and n H₂O molecules involved in the hydrogen transfer. Since *AP adsorption was endergonic (Section 5.4.3), ΔG_{*AP} (Eq. 5.7 and 5.18) was added to $G^\ddagger$ to compute $\Delta G^\ddagger$ relative to the surface resting states:

$$\Delta G^\ddagger = G^\ddagger - (G_{*AP+n*H_2O} + G_{corr,*H}) + \Delta G_{*AP} \quad (5.22)$$

5.3.3 Modelling H₂O binding

A H₂O molecule was bound through the oxygen lone pairs to the *bridge*, *top*, *hcp*, and *fcc* sites, as well as to a *H on the Ag(111), Au(111), Cu(111), Ni(111), and Pt(111) slabs used for *AP adsorption. Given the ambiguity in choosing the water reference as discussed previously, ΔG_{*H_2O} was computed relative to both a H₂O monomer in the gas phase and a cage of six H₂O molecules. On Cu(111), Ni(111), and Pt(111), Eq. 5.23a-b were used:

$$\Delta G_{*H_2O} = G_{*H_2O} - (E_* + G_{H_2O}) \quad (5.23a)$$

$$\Delta G_{*H_2O} = G_{*H_2O} - \left(E_* + \frac{1}{6} G_{H_2O-cage} \right) \quad (5.23b)$$

where G_{*H_2O} is the Gibbs energy of the adsorbed H₂O, E_* is the electronic energy of the *H covered surface, G_{H_2O} is the Gibbs energy of a gas phase H₂O molecule, and $G_{H_2O-cage}$ is the Gibbs energy of a cage consisting of six H₂O molecules. For Ag(111) and Au(111), instead, H₂O binding was expressed including the *H binding energy as:

$$\Delta G_{*H_2O} = G_{*H_2O} + 2G_{corr,*H} - (E_* + G_{H_2O} + G_{H_2}) + 2eU_{RHE} \quad (5.24a)$$

$$\Delta G_{*H_2O} = G_{*H_2O} + 2G_{corr,*H} - \left(E_* + \frac{1}{6} G_{H_2O-cage} + G_{H_2} \right) + 2eU_{RHE} \quad (5.24b)$$

Here, E_* is the electronic energy of the bare surface, and $G_{corr,*H}$ represents the Gibbs corrections for an adsorbed *H atom.

5.3.4 Mechanistic study of HER

To model HER via the Tafel mechanism on Ag(111), Cu(111), and Pt(111), the supercells should feature two adjacent $^*H$ atoms at the coverage densities predicted under experimental conditions. This requirement was already met by $p(2\times 2)$ -Cu(111) and Pt(111) at their expected coverage densities. Instead, for Ag(111), the least endergonic $^*H$ coverage at the applied potential of $-0.48 V_{RHE}$ was 0.25 H, which did not include adjacent $^*H$ atoms (Section 5.4.2). Thus, a $p(4\times 2)$ -Ag(111) supercell was employed for the HER study.

The $\Delta G^\ddagger$ for Tafel HER could vary depending on the active site for H_2 formation. To address this, combinations of neighbouring $^*H$ atoms at the aforementioned densities were first sampled. Since $\Delta G_{^*H}$ was found to be lowest on the *fcc* site (Table 5.2), one of the reactive atoms was assumed to occupy this site, next to a filled *bridge*, *hcp*, or *top* site. Then, $^*H_2$ adsorption was modelled on the *fcc*, *bridge*, *hcp*, and *top* sites. For these simulations, the quasi-Newton algorithm with a step size of 0.05 Å was used to prevent migration of $^*H$ to the *fcc* sites and desorption of H_2 into the gas phase. The thermodynamic corrections were not computed for these intermediates, as they only served to identify the possible initial and final states for the TS search in the Tafel HER.

On Pt(111), an NEB investigation¹¹⁹ of eight images was conducted between the stable configurations featuring neighbouring $^*H$ atoms and adsorbed $^*H_2$. The highest energy image was then optimised through an improved dimer calculation as previously described.¹²⁰ On the other hand, for Ag(111) and Cu(111), $^*H_2$ chemisorption failed, making it impossible to identify the TS using the NEB method. Consequently, an improved dimer calculation¹²⁰ was carried out on the TS-like structure that emerged from the optimisation of $^*H_2$ on a *bridge* site (Section 5.4.5).

The $\Delta G^\ddagger$ for HER relative to the surface resting states was computed for Cu(111) and Pt(111) using Eq. 5.24a, and for Ag(111) using Eq. 5.25b:

$$\Delta G^\ddagger = G^\ddagger - (E_* + 2G_{corr,^*H}) \quad (5.25a)$$

$$\Delta G^\ddagger = G^\ddagger - (E_* + G_{H_2}) + 2eU_{RHE} \quad (5.25b)$$

where E_* was the electronic energy of the *H covered surface for Cu(111) and Pt(111), and of the bare surface for Ag(111). In this way, the endergonic binding of hydrogen is included in the $\Delta G^\ddagger$ for H–H coupling on Ag.

5.4 Results

5.4.1 Modelling of the In bulk and surfaces

The equilibrium cell for bulk In, determined through the BM fitting (Section 5.3), was found to adopt a body-centred tetragonal packing with lattice parameters a and b equal to 3.351 Å, and c equal to 5.070 Å (**Figure 5.7a**). These compared well with the experimental parameters of 3.252 and 4.947 Å, respectively.¹ Following this, the (002), (101), (103), (110), (200), and (211) surface facets were cleaved, as suggested by experimental collaborators (**Figure 5.7b-g**). The corresponding lattice parameters (a and b) and the angle α for each facet are provided in Table 5.1, along with the surface energies (E_{surf}) calculated according to Eq. 4.1. A Wulff construction identified the (101) surface as the most exposed on In nanoparticles (**Figure 5.7h**).

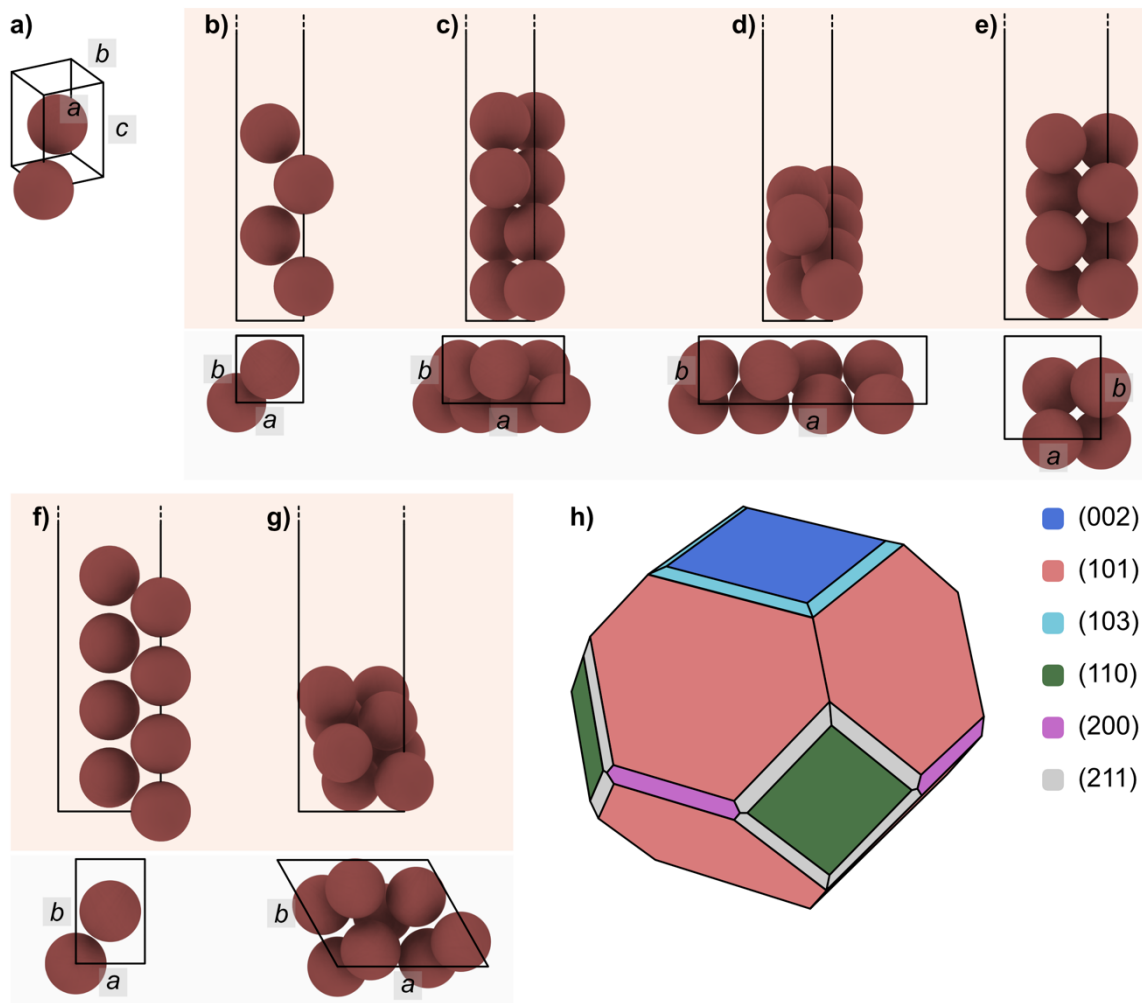


Figure 5.7 a) Bulk unit cell of In optimised through a BM fitting. Side and top-view of the b) (002), c) (101) d) (103), e) (110), f) (200) and g) (211) In surface facets, modelled as four-layered slabs. h) Nanoparticle shape determined through Wulff construction for In metal.

Table 5.1 E_{surf} , in $\text{eV}/\text{\AA}^2$, of the (004), (101), (103), (110), (200) and (211) surface slabs of In. The a and b lattice parameters, in $\text{\AA}$, and the α angle are also reported.

	(002)	(101)	(103)	(110)	(200)	(211)
E_{surf}	0.006	0.006	0.007	0.007	0.007	0.007
a	3.335	6.059	11.211	4.717	3.335	7.457
b	3.335	3.335	3.335	5.059	5.059	6.059
α	90°	90°	90°	90°	90°	120°

5.4.2 Surface coverage analysis

The $p(2 \times 2)$ supercells used for the surface coverage analysis of Ag(111), Au(111), Cu(111), Ni(111), and Pt(111) had lattice parameters a of 5.973, 5.979, 5.160, 5.013, and 5.667 $\text{\AA}$, respectively. The angle α between the lattice vectors parallel to the surface plane was of 60° for all metals, characteristic of the (111) facet for face-centred cubic packings.

Table 5.2 presents the Gibbs binding energies at 0 V_{RHE} for a single $^*H$, $^*OH$, and $^*O$, denoted as $\Delta G_{*X}(0V_{RHE})$, on the $p(2 \times 2)$ -Ag(111), Au(111), Cu(111), Ni(111), and Pt(111) supercells and on $p(1 \times 2)$ -In(101). On the face-centred cubic metals, the *fcc* site was the most stable binding site for all adsorbates, except for $^*OH$ on Pt(111), which preferentially bound to the *top* site. On In(101), the *hollow II* site was the preferred binding site for $^*H$, $^*OH$, and $^*O$. Table 5.3 details the energetics of the surface coverages obtained through the progressive addition of adsorbates to the most stable sites, $\Delta G_{*nX}(0V_{RHE})$, while **Figure 5.7** illustrates the corresponding plots derived by applying Eq. 3.79-81. This study indicated the limit for HER to occur at different coverage densities on the metals, *i.e.* six $^*H$ on Ag(111) and Cu(111), and nine on Ni(111) and Pt(111). On Au(111) and In(101), instead, the coverage analysis was interrupted upon addition of the fifth and fourth $^*H$ atom, respectively, which significantly reconstructed the surface. In contrast, the maximum coverage for $^*OH$ and $^*O$ was uniformly reached on all $p(2 \times 2)$ -Ag(111), Au(111), Cu(111), Ni(111), and Pt(111) supercells, each accommodating up to four adsorbates. Similarly, the $p(1 \times 2)$ -In(101) supercell could host up to four $^*OH$ groups, while the addition of a second $^*O$ caused significant surface reconstruction. Therefore, for this metal, no surface state was predicted at oxidising conditions beyond the 1.00 OH, which occupies the upper part of the Pourbaix diagram.

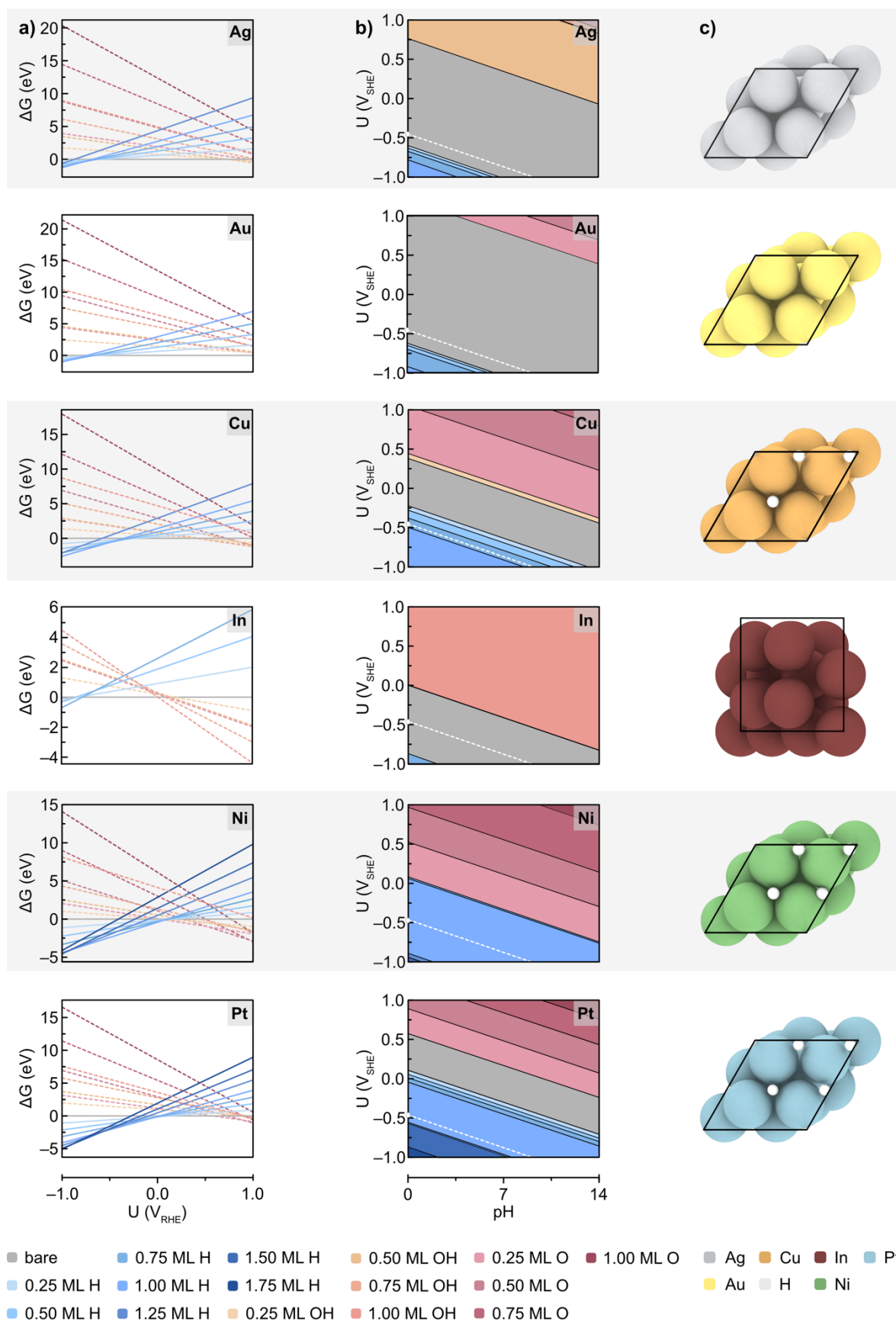


Figure 5.7 a) Plots of $\Delta G_{*nX}(U_{RHE})$ for $*H$, $*OH$ and $*O$ on the $p(2 \times 2)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) supercell and $p(1 \times 2)$ -In(101). **b)** Pourbaix diagram reporting the most stable surface states for the $p(2 \times 2)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) supercells and $p(1 \times 2)$ -In(101) as a function of

$U(V_{SHE})$ and pH, or $U(V_{RHE})$. The line corresponding to $-0.48 V_{RHE}$ is plotted in white. **c)** Top-view of the most stable surface states at the applied potential of $-0.48 V_{RHE}$.

Table 5.2 $\Delta G_{*X}(0V_{RHE})$, in eV, of a single *H, *OH and *O on $p(2\times 2)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) supercells and on $p(1\times 2)$ -In(101) in the sites highlighted in **Figure 5.5**. When an adsorbate moved to a different site or reconstruction occurred, this is indicated in place of $\Delta G_{*X}(0V_{RHE})$.

	<i>site</i>	$\Delta G_{*H}(0V_{RHE})$	$\Delta G_{*OH}(0V_{RHE})$	$\Delta G_{*O}(0V_{RHE})$
Ag(111)	<i>bridge</i>	<i>fcc</i>	<i>hcp</i>	<i>hcp</i>
	<i>fcc</i>	0.64	0.75	1.94
	<i>hcp</i>	0.65	0.77	2.02
	<i>top</i>	<i>fcc</i>	<i>fcc</i>	<i>fcc</i>
Au(111)	<i>bridge</i>	<i>fcc</i>	1.46	<i>hcp</i>
	<i>fcc</i>	0.64	1.43	2.41
	<i>hcp</i>	0.66	1.49	2.64
	<i>top</i>	0.77	1.55	<i>fcc</i>
Cu(111)	<i>bridge</i>	<i>fcc</i>	0.49	<i>hcp</i>
	<i>fcc</i>	0.25	0.37	0.81
	<i>hcp</i>	0.26	0.43	0.93
	<i>top</i>	<i>fcc</i>	<i>bridge</i>	<i>fcc</i>
In(101)	<i>bridge I</i>	<i>hollow II</i>	0.25	<i>hollow II</i>
	<i>bridge II</i>	<i>hollow II</i>	<i>hollow I</i>	reconstruction
	<i>hollow I</i>	<i>hollow II</i>	0.21	0.38
	<i>hollow II</i>	0.90	0.18	0.26
	<i>top</i>	0.95	<i>hollow II</i>	<i>hollow II</i>
Ni(111)	<i>bridge</i>	<i>fcc</i>	<i>hcp</i>	<i>hcp</i>
	<i>fcc</i>	-0.12	0.03	0.05
	<i>hcp</i>	-0.10	0.14	0.15
	<i>top</i>	<i>fcc</i>	<i>fcc</i>	<i>fcc</i>
Pt(111)	<i>bridge</i>	<i>fcc</i>	1.05	<i>hcp</i>
	<i>fcc</i>	-0.09	<i>top</i>	1.16
	<i>hcp</i>	-0.05	<i>top</i>	1.56
	<i>top</i>	-0.07	0.97	2.30

Table 5.3 $\Delta G_{*nX}(0V_{RHE})$, in eV, of n *H, *OH and *O on the $p(2\times 2)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) supercells and on $p(1\times 2)$ -In(101). The surface coverage analysis was interrupted upon surface reconstruction or evolution of molecular species.

	n	$\Delta G_{*nH}(0V_{RHE})$	$\Delta G_{*nOH}(0V_{RHE})$	$\Delta G_{*nO}(0V_{RHE})$
Ag(111)	2	1.26	1.49	4.82
	3	1.94	3.13	8.46
	4	2.74	4.96	12.39
	5	4.36	-	-
Au(111)	2	1.29	2.58	5.44
	3	2.00	4.51	9.26
	4	2.94	6.41	13.42
Cu(111)	2	0.52	0.89	2.90
	3	0.91	2.07	6.13
	4	1.42	4.71	9.93
	5	2.90	-	-
In(101)	2	1.82	0.26	reconstruction
	3	2.61	0.21	-
	4	-	0.02	-
Ni(111)	2	-0.25	0.54	1.10
	3	-0.34	1.36	3.03
	4	-0.41	3.73	6.16
	5	0.48	-	-
	6	1.42	-	-
	7	2.88	-	-
	8	4.50	-	-
Pt(111)	2	-0.15	1.72	2.94
	3	-0.16	2.77	5.44
	4	-0.11	3.60	8.60
	5	0.46	-	-
	6	1.04	-	-
	7	1.92	-	-
	8	3.21	-	-

The value of $\Delta G_{*H}(-0.48 V_{RHE})$, henceforth simply referred to as ΔG_{*H} , distinguished the metal electrodes into groups. Specifically, it was endergonic for In(101) (+0.42 eV), near thermoneutral for Ag(111) and Au(111) (+0.16 eV), exergonic for Cu(111) (-0.23 eV), and highly exergonic for Ni(111) and Pt(111) (-0.60 and -0.57 eV, respectively). Consequently,

the most stable state under experimental conditions was the bare surface for In(101), Ag(111), and Au(111), the coverage of 75% of the *fcc* sites with *H for Cu(111), and the full coverage of the *fcc* sites for Ni(111) and Pt(111) (**Figure 5.7c**).

5.4.3 AP and water adsorption on the metal electrodes

The first step in the ECH of AP involved its adsorption onto the electrode surface, either through the π -system of the phenyl ring or the carbonyl oxygen. These two orientations are illustrated in **Figure 5.8** for Cu(111). Table 5.4 summarises the values of ΔG_{*AP} for all metals, showing the binding to be slightly favoured via the phenyl ring. On all surfaces, *AP was adsorbed at an average distance of 3.9 Å from the metal electrode, with the aromatic ring oriented flat against the surface. While the values of ΔG_{*AP} in Table 5.4 for Ag(111) and Au(111) comprised the energy of reduction of two protons on the catalyst, these lowered to -0.01 and 0.07 eV via the phenyl ring, respectively, and 0.26 and 0.21 eV via the carbonyl O, if computed relative to the *H covered Ag(111) and Au(111) slabs.

Table 5.4 ΔG_{*AP} , in eV, for *AP adsorption on the metal electrodes through the phenyl ring and carbonylic O.

	Ag(111)	Au(111)	Cu(111)	Ni(111)	Pt(111)
Phenyl ring	0.19	0.20	0.14	0.04	0.06
Carbonylic O	0.46	0.36	0.13	0.32	Phenyl

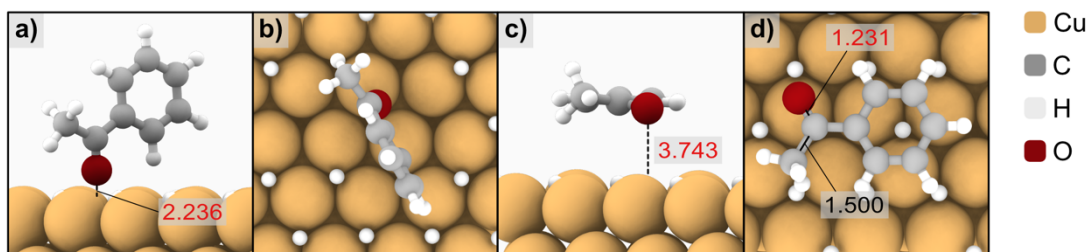


Figure 5.8 Side- and top-view for and adsorbed *AP on *p*(6×4)-Cu(111) featuring a 0.75 ML H coverage through the carbonylic O (panels **a**) and **b**), respectively) and the phenyl ring (panels **c**) and **d**), respectively). Relevant distances involving C and O atoms, in Å, are highlighted in black and red, respectively.

Subsequently, water binding was explored, revealing its physisorption at an average distance of 3 Å from the metal surfaces. The H₂O molecule adopted a slightly tilted orientation, with the oxygen lone pairs pointing towards the electrode for all metals except Ni, where the protons faced the surface (**Figure 5.9**). The values of ΔG_{*H_2O} were endergonic on all surfaces when referenced to both a gas phase water monomer and a water cage, with the difference between the two references falling within 0.06 eV (Table 5.5). Relative to the *H covered

surfaces and the water cage, ΔG_{*H_2O} was approximately 0.15 eV on Ag (0.16 eV), Au (0.15 eV), Ni (0.13 eV), and Pt (0.14 eV), and of 0.09 eV on Cu.

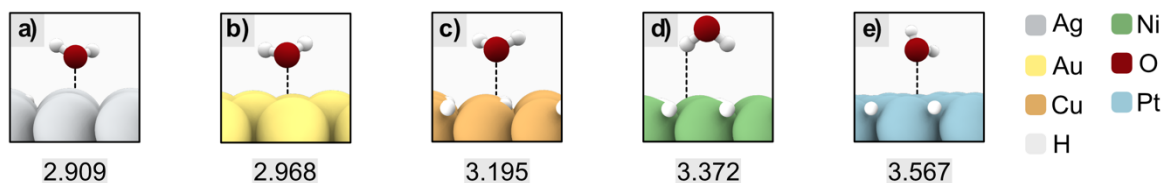


Figure 5.9 Side-view of a H₂O molecule bound on a **a)** Ag(111), **b)** Au(111), **c)** Cu(111), **d)** Ni(111), **e)** Pt(111) $p(6\times4)$ supercell featuring the *H coverage adopted for the AP mechanistic studies. Distances to the catalyst surfaces are reported in Å.

Table 5.5 ΔG_{*H_2O} , in eV, for the adsorption of the H₂O molecule on the *H covered $p(6\times4)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) supercells, relative to a gas phase H₂O molecule and a H₂O cage. The difference between the binding of AP and H₂O binding referred to the H₂O cage is also reported as $\Delta\Delta G$.

	Ag(111)	Au(111)	Cu(111)	Ni(111)	Pt(111)
$\Delta G_{*H_2O}(gas\ phase)$	0.41	0.35	0.16	0.19	0.19
$\Delta G_{*H_2O}(H_2O - cage)$	0.36	0.30	0.09	0.13	0.14
$\Delta\Delta G$	0.17	0.10	-0.05	0.06	0.08

Notably, AP and H₂O binding energies were approximately isoenergetic only on Cu. On the other metals, the preference for AP binding was of *ca.* 0.10-0.20 eV (Table 5.5). Furthermore, AP was expected to replace more than one H₂O molecule on the catalyst surface, due to its larger size. Therefore, on Ag(111), Au(111), Ni(111), and Pt(111), H₂O binding and hydrolysis were expected to be more significantly impaired by AP adsorption than on Cu(111). This finding was in alignment with experimental reports showing a decrease in the *H coverage on a Pt electrode in the presence of AP.⁶⁶

5.4.4 AP hydrogenation from the H surface coverage

As discussed in Section 5.3.2, the electroreduction of AP can proceed via two possible mechanisms: hydrogenation of the carbonyl C first, followed by the O, or vice versa. The ΔG_{*APH} values for these pathways are reported in Table 5.6. The hydrogenation at the C atom was found to be thermodynamically preferred on Ag(111) and, to a lesser extent, on Cu(111). However, the $\Delta G^\ddagger$ for the hydrogenation of *AP the C on Ag(111), assisted by the solvent, was calculated to be of 2.18, 1.57, and 1.84 eV with the assistance of one, two, and three H₂O molecules, respectively, relative to the surface resting state (**Figure 5.10a-c**). Such values were deemed incompatible with catalytic activity at room temperature, suggesting

that AP electroreduction via hydrogenation at the C first was not viable at ambient conditions.

Table 5.6 $\Delta G_{*APH\cdot}$, in eV, for the hydrogenation of *AP at the C or at the O from the *H surface coverage on $p(6\times4)$ -Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) slabs.

	Ag(111)	Au(111)	Cu(111)	Ni(111)	Pt(111)
$\Delta G_{*APH\cdot}(C)$	0.13	0.60	0.41	1.79	1.46
$\Delta G_{*APH\cdot}(O)$	0.68	0.28	0.49	0.79	0.52

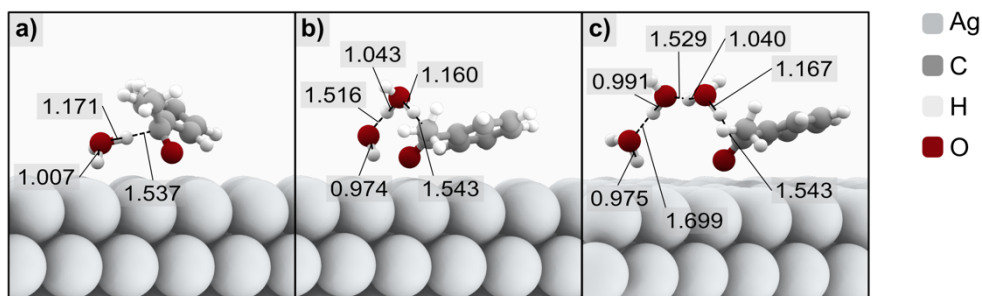


Figure 5.10 TS structures for *AP hydrogenation at the C from the surface coverage promoted by **a)** one, **b)** two and **c)** three H_2O molecules on Ag(111). Relevant distances are reported in Å.

Figure 5.11c illustrates the thermodynamics of the ECH of AP via hydrogenation at the O first. For all metals, this step was endergonic relative to the adsorbed *AP, following the trend: Au (+0.08 eV) < Cu (+0.35 eV) < Pt (+0.46 eV) < Ag (+0.49 eV) < Ni (+0.75 eV). This finding was consistent with the breaking of the carbonyl bond and the formation of a radical intermediate, as indicated by the magnetic moments. Specifically, on Cu, the O, the carbonyl C, the phenyl C bearing the C=O group, the ortho, the meta and the para positions displayed a radical character of 0.47, 0.19, 0.03, 0.05, 0.02 and 0.06 electrons, respectively, indicating a redistribution of electronic density upon radical formation. The subsequent hydrogenation of *APH $\cdot$ to *APH $_2$ was downhill in energy, following the trend Ag (−1.31 eV) < Au (−0.98 eV) < Cu (−0.89 eV) < Pt (−0.38 eV) < Ni (−0.24 eV). Notably, this order correlated with the ΔG_{*H} values on these surfaces (Ni < Pt < Cu < Ag $\approx$ Au). Finally, on Cu(111), Ni(111), and Pt(111), the *H surface coverage was regenerated ($2*H_{Cu-Ni-Pt}$).

Overall, the formation of *APH $\cdot$ was the most endergonic step in the reaction mechanism, which was particularly unfavourable on Ni(111). This finding was consistent with its poor experimental activity (**Figure 5.3b**) and its strong competition with HER.^{154,173} The superior HER activity of Pt likely explained its limited performance in the ECH of AP, as discussed in more detail in Section 5.4.5. Lastly, the energy profile of Ag(111), Au(111) and Cu(111) aligned with their catalytic activity at room temperature. Notably, on Cu(111), the $\Delta G_{*APH\cdot}$

decreased further upon diffusion of the surface $^*\text{H}$, which is reported to be accessible at room temperature.¹⁷⁴ More specifically, the configuration of the $^*\text{H}$ atoms displayed in **Figure 5.11d** rendered a $\Delta G_{^*\text{APH}}$ of 0.39 eV compared to 0.49 eV on the uniform coverage. Additionally, given the comparable energies of the 0.50 and 1.00 ML H coverages to the 0.75 H, the $\Delta G_{^*\text{APH}}$ was reassessed under these conditions, yielding values of 0.54, 0.59, and 0.39 eV, calculated relative to their own resting state, indicating similar catalytic activity (**Figure 5.11d**).

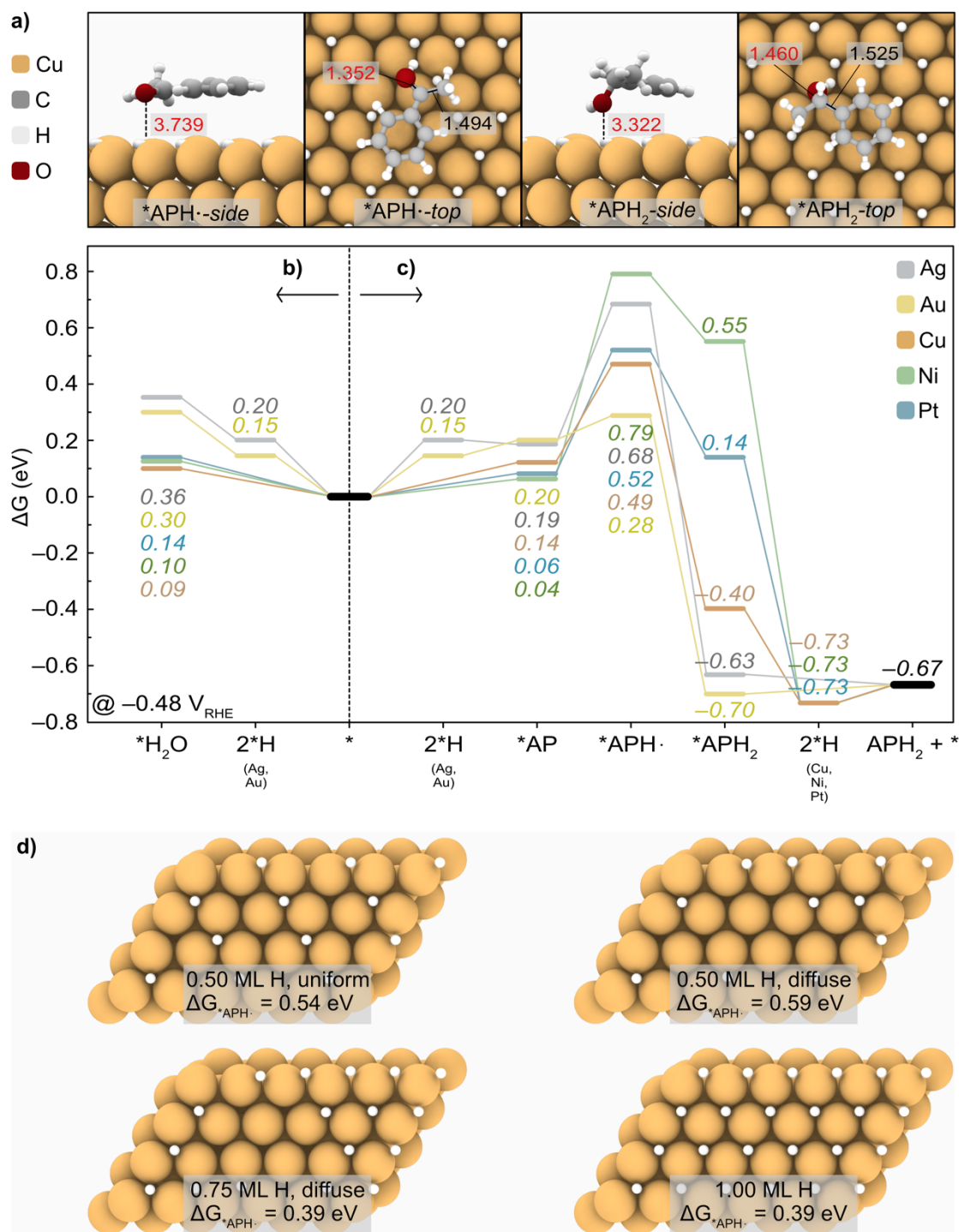


Figure 5.11 a) Top-view of the $^*\text{AP}$, $^*\text{APH}$ and $^*\text{APH}_2$ intermediates on $p(6\times4)\text{-Cu}(111)$ featuring a uniform

0.75 ML H coverage. Relevant distances involving C and O atoms, in Å, are highlighted in black and red, respectively. **b)** Gibbs energy of H₂O adsorption on *p*(6×4)-Ag(111), Au(111), Cu(111), Ni(111) and Pt(111). **c)** Gibbs energy of AP electroreduction sourcing the hydrogen from the electrode coverage, calculated on *p*(6×4)-Ag(111), Au(111), Cu(111), Ni(111) and Pt(111) at −0.48 V_{RHE}. **d)** Top-view of *p*(6×4)-Cu(111) slabs featuring uniform 0.50 H, diffuse 0.50 H, diffuse 0.75 ML H and 1.00 ML H coverages, with the respective $\Delta G_{*APH\cdot}$.

Subsequently, the $\Delta G^\ddagger$ for *AP hydrogenation at the O was calculated on Ag(111), Au(111), and the unevenly covered Cu(111) slab which lowered $\Delta G_{*APH\cdot}$ (**Figure 5.11d**) with the assistance of two H₂O molecules. The barriers were of 0.73, 0.48, and 0.76 eV, respectively, relative to the surface resting states, in alignment with the ECH activity observed at room temperature. The TS structures are depicted in **Figure 5.12**.

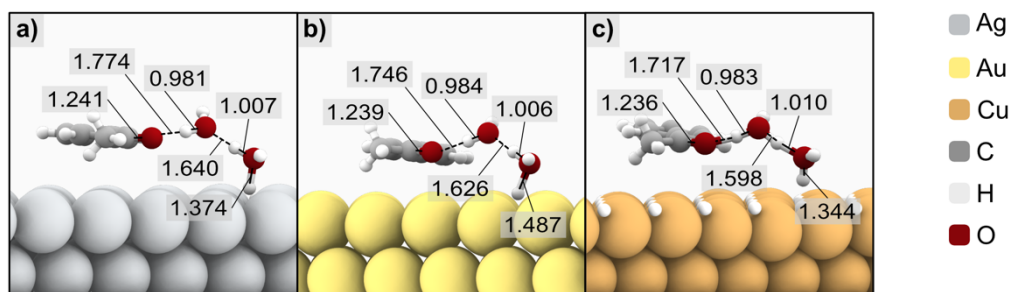


Figure 5.12 TS structures for AP hydrogenation at the O from the surface coverage promoted by two H₂O molecules, with relevant distances in Å, on **a)** Ag(111), **b)** Au(111) and **c)** Cu(111).

However, neither the $\Delta G_{*APH\cdot}$ nor the $\Delta G^\ddagger$ computed relative to *AP (Au: 0.28 eV < Ag: 0.54 eV < Cu: 0.62 eV) alone explained the experimental activity trend, *i.e.* Cu > Ag $\approx$ Au. However, as discussed in Section 5.4.3, the preference for AP binding over H₂O on Ag(111) and Au(111) was deemed to hinder water hydrolysis on the electrode surface, reducing the availability of adsorbed *H. Thus, while Ag and Au were envisioned to be active towards the ECH of AP once *H atoms were present, their performance was impacted by the competitive adsorption between AP and H₂O.

In conclusion, this study indicated that effective ECH catalysts feature moderate *H coverages that support the electroreduction of organic substrates. Along with a favourable ΔG_{*H} , they need to promote H₂O dissociation in the presence of the reactant by binding both with similar strength. Additionally, the diffusion of surface *H was found to enhance the formation of key reaction intermediates, such as *APH $\cdot$.

5.4.5 Hydrogen evolution

Following the assessment of the activity of the metal electrodes for the ECH of AP, their selectivity was analysed in relation to the competition with HER. On Cu, the decline in J_{H_2} between -0.28 and -0.48 V_{RHE} (**Figure 3a**) was attributed to the presence of a coverage of weakly bound $*H$ atoms that actively participated in AP electroreduction, as predicted by the computational coverage analysis (**Figure 5.7b**). At more cathodic potentials, instead, the full coverage of the *fcc* sites was hypothesised to favour HER via the Tafel mechanism by maximising the number of adjacent $*H$ atoms, consistent with literature reports.⁶⁹ This interpretation also aligned with the low FE of the Pt electrode, which was predicted to fill all *fcc* sites at reaction conditions. In this context, the high FE observed for the Ag and Au electrodes at -0.48 V_{RHE} was attributed to the scarcity of neighbouring $*H$ atoms, as predicted by the coverage analysis (**Figure 5.4c-d**).

To further interpret the trend in HER based on the $*H$ coverage density at the experimental potentials, the kinetics of the Tafel mechanism were explored. Due to its unfavourable ΔG_{*H} , the HER activity of In(101) was not investigated. Additionally, Au(111) and Ni(111) were hypothesised to exhibit a similar behaviour to Ag(111) and Pt(111), respectively, in light of the comparable ΔG_{*H} values and coverage densities. Therefore, the energetics for HER were only computed on the Ag(111), Cu(111), and Pt(111) surfaces, as outlined in Section 5.3.4. Tables 5.7 and 5.8 summarise the adsorption energies of two vicinal $*H$ atoms and of the H_2 molecule, respectively. In agreement with the coverage analysis, the *fcc* + *fcc* configuration was the preferred combination for two adjacent $*H$ atoms on all three metals. Additionally, $*H_2$ was stable on Pt(111) across the *bridge*, *fcc*, and *top* sites, whereas desorption was dominant on Ag(111) and Cu(111). However, on Cu, the attempt to bind $*H_2$ on the *bridge* site converged to a structure with a H–H distance of 1.104 Å and an imaginary frequency of 1182.83 cm⁻¹ in the coupling direction.

Table 5.7 ΔE , in eV, of all possible configurations of vicinal $*H$, calculated relative to the $*H$ covered surfaces as $(E_X - E_s)$, where E_X and E_s are the electronic energy of configuration X and the surface (*i.e.* a uniform 0.25 H, 0.75 ML H and 1.00 ML H coverage on $p(4\times 2)$ -Ag(111), $p(2\times 2)$ -Cu(111) and $p(2\times 2)$ -Pt(111)), respectively.

	<i>fcc</i> + <i>bridge</i>	<i>fcc</i> + <i>fcc</i>	<i>fcc</i> + <i>hcp</i>	<i>fcc</i> + <i>top</i>
Ag(111)	0.28	0.04	0.29	-
Cu(111)	0.16	0.00	0.14	-
Pt(111)	<i>fcc</i> + <i>fcc</i>	0.00	<i>fcc</i> + <i>fcc</i>	0.18

Table 5.8 ΔE , in eV, of $^*\text{H}_2$ adsorption in *bridge*, *fcc*, *hcp* and *top* sites, calculated relative to the $^*\text{H}$ covered surface as $(E_{^*\text{H}_2} - E_s)$, where $E_{^*\text{H}_2}$ is the electronic energy of adsorbed $^*\text{H}_2$. The label H–H indicates the stabilisation of a structure with internuclear distance of around 1.0 Å, not classified as a formed H_2 molecule.

	<i>bridge</i>	<i>fcc</i>	<i>hcp</i>	<i>top</i>
Ag(111)	$\text{H}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{H}_2(\text{g})$
Cu(111)	H–H	$\text{H}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{H}_2(\text{g})$
Pt(111)	1.20	1.26	<i>fcc</i> + <i>fcc</i>	0.66

The H–H structure obtained on the *bridge* site of Cu(111) was optimised to a TS and replicated on Ag(111). Both converged to a stationary point featuring an imaginary frequency in the direction of H–H coupling, resulting in $\Delta G^\ddagger$ values of 0.62 and 1.02 eV, respectively, relative to the surface resting states (**Figure 5.13a-b**). Given the desorption of H_2 from all other sites, no additional TS structures were searched for the HER via the Tafel mechanism on these two metals. On Pt(111), instead, both the *fcc* + *fcc* and *fcc* + *top* configurations were adopted as initial states for the TS search, while the final state was set as $^*\text{H}_2$ adsorbed on the *top* site, since this was the most stable site. Both TS searches converged to the same TS, depicted in **Figure 5.13c**, with a $\Delta G^\ddagger$ of 0.64 eV relative to the surface resting state.

Overall, these $\Delta G^\ddagger$ values confirmed HER as the competing process with the ECH of AP, in line with the experimental observations.

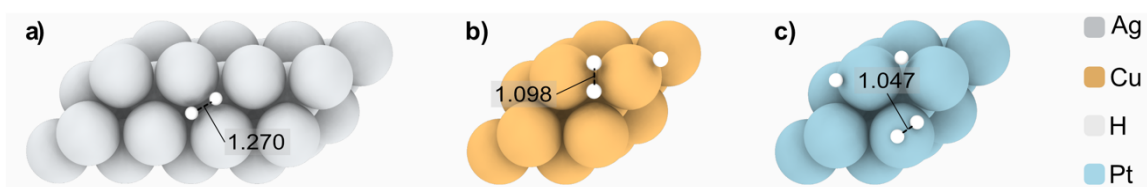


Figure 5.13 TS structure for HER via the Tafel mechanism on a *bridge* site of **a)** $p(4\times 2)$ -Ag(111) and **b)** $p(2\times 2)$ -Cu(111), and on the *top* site of **c)** $p(2\times 2)$ -Pt(111). Relevant distances are reported in Å.

5.5 Conclusions

ECH reactions are a promising, more sustainable alternative to traditional thermal hydrogenations. While alkaline electrolytes are known to suppress the competing HER, organic substrates might not efficiently source protons from the solvent under basic conditions. In this study, the ECH activity of Ag, Au, Cu, In, Ni, and Pt metal electrodes was investigated towards the ECH of AP to APH_2 , hypothesising that efficient cathode materials hydrolyse H_2O and retain $^*\text{H}$ atoms on their surfaces with moderate strength. In such scenario, a theoretical surface coverage analysis revealed that the $\Delta G_{^*\text{H}}$ of these metals

followed the trend $\text{In} < \text{Ag} \simeq \text{Au} < \text{Cu} < \text{Pt} \simeq \text{Ni}$, confirming them as a variable pool for exploring the relationship between ECH performance and $^*\text{H}$ coverage density and strength. Experimentally, optimisation of the reaction conditions on Cu identified $-0.48 \text{ V}_{\text{RHE}}$ as optimal potential, leading to a FE of *ca.* 91% and a J_{APH_2} of 14 mA/cm^2 at a pH of 11.8, while a more cathodic bias, favoured HER. Under such conditions, the performance of the metal electrodes followed the trend $\text{Cu} > \text{Ag} \simeq \text{Au} > \text{In} \simeq \text{Pt} > \text{Ni}$.

Theoretically, the $\Delta G_{^*\text{H}}$ and $^*\text{H}$ coverage density of In at the specific conditions adopted in this work suggested that its poor catalytic activity stemmed from its unfavourable $^*\text{H}$ binding and predicted lack of surface $^*\text{H}$, leading to its exclusion from further studies. In contrast, Ni and Pt featured a full coverage of the *fcc* sites with $^*\text{H}$ and an exergonic $\Delta G_{^*\text{H}}$ under operational settings. Cu showed 75% of its *fcc* sites occupied by $^*\text{H}$ with a moderate $\Delta G_{^*\text{H}}$, while Ag and Au were predicted to be mostly bare. Yet, since their $\Delta G_{^*\text{H}}$ was close to thermoneutral, the reduction of the two protons required for the ECH of AP was deemed feasible at room temperature. The ECH mechanism was then explored on the $^*\text{H}$ covered Ag, Au, Cu, Ni, and Pt surfaces by adsorbing and hydrogenating $^*\text{AP}$ at the O first and then at the C via two $^*\text{H}$ atoms, with $^*\text{APH}\cdot$ being the most endergonic intermediate. On Pt and Ni, the strongly bound $^*\text{H}$ coverage was found to increase the energy cost of $^*\text{AP}$ hydrogenation. Their low activity and selectivity in the ECH of AP were further attributed to the competition with HER, driven by their dense $^*\text{H}$ coverage and moderate $\Delta G^\ddagger$ for H–H coupling via the Tafel mechanism, computed on Pt. On Ag, Au, and Cu, both the thermodynamic and kinetic profiles were compatible with AP hydrogenation at room temperature. Notably, on Cu, $^*\text{H}$ diffusion further lowered the energy required for $^*\text{APH}\cdot$ formation. The reduced activity of Ag and Au compared to Cu was traced to their preferential binding of AP over H_2O , thereby hindering the reduction of the two protons necessary for the ECH process.

Importantly, the active role of a moderate $^*\text{H}$ surface coverage in the promotion of ECH reactions was further supported by exploring the reaction scope on the Cu electrode. In fact, this demonstrated moderate to excellent conversions and chemoselectivity (70-90%) toward the reduction of $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, and $\text{C}\equiv\text{N}$ functional groups under similar conditions to those adopted for AP.

Overall, this work indicates that reaction conditions can be optimised based on the pK_a of reaction intermediates and the $\Delta G_{^*\text{H}}$ of the electrode, to meet the criteria specified above: a coverage of moderately bound and well-spaced $^*\text{H}$ atoms, along with a similar binding affinity for H_2O and the reactant. Conversely, a highly exergonic $\Delta G_{^*\text{H}}$ increases the energy

cost of the ECH process, with dense coverages promoting HER via the Tafel mechanism. Instead, an unfavourable ΔG_{*H} , combined with a preference for reactant adsorption over H_2O , impairs the generation of the $*H$ coverage necessary for efficient ECH. Building upon these results, future theoretical and experimental research could focus on the rational design of earth abundant cathode materials, using computational methods to predict the optimal potential for ECH processes, tailored to the substrate and electrode composition.

6. NO₃[−] electroreduction on Cu, Zn and Zn-Cu metal electrodes for C–N coupling

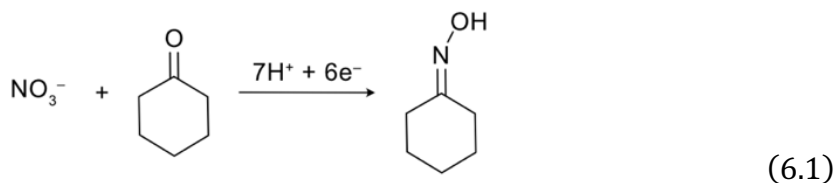
6.1 Introduction

6.1.1 C–N coupling via the NO₃RR

As addressed in the Introduction, NO₃[−] can be converted into a variety of building blocks, most importantly NH₃. A further step in NO₃[−] valorisation is the reaction of the NO₃RR products with carbon scaffolds via C–N coupling. Specifically, research efforts are being directed toward the co-electrolysis of carbonate and NO₃[−] streams for the synthesis of platform chemicals such as urea, acetamide, methylamine, formamide, and ethylamine. These products are used in explosives, fertilisers, pharmaceuticals, as well as in chemical industry.¹⁷⁵ In a recent work, a partial current density of *ca.* 6 mA/cm² and a FE of 60% were achieved for urea electrosynthesis from HCO₃[−] and NO₃[−] using a Zn-Cu hybrid catalyst at −0.7 V_{RHE}, with the synergistic interaction between the two metals promoting C–N coupling.¹⁷⁶ In contrast, the single component catalysts mainly reduced HCO₃[−] and NO₃[−] separately, with a lower FE towards urea of *ca.* 15%. Another recent study aimed at urea electrosynthesis reported a FE around 70% and a current density of 1 mA/cm² at −0.2 V_{RHE} on CuWO₄, demonstrating the cooperation between bimetallic sites in the C–N coupling.¹⁷⁷

Among the NO₃RR products that can partake in C–N coupling, NH₂OH is of great interest in light of its high nucleophilic character and versatile reactivity. Moreover, it finds application in pharmaceuticals, textiles, and electronics.¹⁷⁸ The chemical route for its synthesis, however, entails the hydrogenation of NO_x on Pd catalysts, which requires strongly acidic conditions and high temperatures and pressures. Furthermore, the reactant H₂ gas is dangerous to transport and store.¹⁷⁹ Alternatively, NH₃ can be oxidised to NH₂OH with O₂ and/or H₂O₂. Again, high temperatures are typically used, as well as strongly basic conditions and an excess of oxidant. Similarly to H₂, H₂O₂ is explosive, which poses a challenge to its storage and transportation.^{180,181} Lastly, NH₂OH itself is chemically unstable and can explode when heated. It also irritates the respiratory system, skin, and eyes.¹⁷⁸ A solution to these issues is offered by the one-pot electrochemical NO₃RR to NH₂OH followed by its reaction with C-containing compounds. Some examples include the synthesis

of artificial amino acids¹⁷⁸ and cyclohexanone oxime, an intermediate in the synthesis of Nylon-6,¹⁸² which process is summarized in Eq. 6.1.



For the synthesis of cyclohexanone oxime via the electrochemical NO₃RR, the reduction of NO has been reported on Fe and Pd electrodes.¹⁸² The catalytic performance of Pd was found to be impaired by the hydrogenation of cyclohexanone to cyclohexanol, while Fe resulted in the desired product with nearly 100% selectivity at $-0.30 \text{ V}_{\text{RHE}}$. These results highlight the need for a cathode material inert to the organic substrate.

In another study, the reduction of NO to NH₂OH was performed on Al nanofiber membranes for the synthesis of 2-pyridinealdoxime.¹⁷⁸ A FE of around 50% and a yield of 92% were achieved, with NH₃ being the main side product. Notably, the presence of the 2-formylpyridine reactant was observed to enhance the rate of reduction of NO to NH₂OH, presumably due to the fast and favourable C–N coupling.

To enhance the NO₃RR activity and selectivity towards NH₂OH production, composite materials combining the properties of different elements are being researched. In this context, Cu plays a pivotal role among the most efficient metals for NO₃RR, due to its abundance and low cost. Examples of Cu-based catalysts include oxides, nanomaterials and clusters on carbon and metal-organic framework supports, single crystals of different morphology, and alloys.¹⁸³ For instance, oxygen vacancies in a CuO cathode promoted NO₃RR to NH₃ due to their improved binding energy of NO₃[−] ions, achieving a FE of *ca.* 80% and a current density of 90 mA/cm² at $-0.6 \text{ V}_{\text{RHE}}$.¹⁸⁴ Another study investigated the NO₃RR activity and selectivity of Cu(111) and Cu(100) single crystals.¹⁸⁵ The former was shown to favour the reduction of NO₂[−] to NH₃, while the latter performed better in the reduction of NO₃[−] to NO₂[−]. Thus, the combination of the two facets in tandem allowed to reach a partial current density of 665 mA/cm² and a FE of *ca.* 80% towards NH₃ at $-0.59 \text{ V}_{\text{RHE}}$. In the realm of alloys, Ni is considered a suitable partner for Cu due to their similar size and favourable mixing. For example, a Cu₅₀Ni₅₀ alloy dispersed on carbon fibre in 0.5 M Na₂SO₄ and 0.1 M KNO₃ achieved a FE towards NH₃ of 95.7% and a current density of 90 mA/cm² at $-0.22 \text{ V}_{\text{RHE}}$.¹⁸⁶ Higher Ni concentrations were shown to strongly bind the reaction intermediates, impairing NH₃ desorption. In a different report, a Cu₅₀Ni₅₀

alloy dispersed on Cu foam in 1.0 M KOH and 0.1 M KNO₃ displayed a FE of 95% towards NH₃ at -0.1 V_{RHE}.¹⁸⁷

As emphasised in the examples above, Cu-based catalysts tend to be highly selective towards NH₃ formation. Thus, the competition between NH₂OH desorption and its complete conversion to NH₃ presents a challenge for using Cu electrocatalysts in NH₂OH production aimed at C–N coupling. In this context, a recent study attempted to lower the selectivity of Cu for NH₃ formation by using CuS nanowires for the reduction of NO₂⁻ to NH₂OH, which would then react with cyclohexanone to yield the corresponding oxime.¹⁸⁸ The presence of sulphur was intended to weaken the electroreduction activity of Cu and prevent NH₃ production. Although NH₃ remained the dominant by-product, cyclohexanone oxime was obtained with a FE of 26% at a voltage of -0.9 V versus the Ag/AgCl reference.

Following similar principles, this chapter reports the NO₃RR activity and selectivity of Cu, Zn, and Zn_{1-x}Cu_x metal electrodes towards NH₂OH for cyclohexanone oxime synthesis.

6.1.2 Pathways for the electrochemical NO₃RR

Before discussing the cyclohexanone oxime synthesis on Cu, Zn, and Zn_{1-x}Cu_x metal electrodes pertinent to this work, it is important to review the mechanisms proposed in the literature for the electrochemical NO₃RR. As mentioned in the Introduction, a plethora of products can be obtained from this process, such as NO₂⁻/HNO₂, N₂O, NO, NH₂OH, N₂H₄, and N₂.^{189,190} The reduction of NO₃⁻ to NO₂⁻ is common to all pathways and is believed to proceed through the radical anion NO₃^{•2-}, which is characterised by a standard reduction potential of -0.89 V_{SHE} and is often regarded as the potential limiting step.^{29,190} For this reason, joint experimental and computational studies have proposed the binding energy of NO₃⁻ as a descriptor of NO₃RR activity.^{191,192}

Depending on the pH, NO₂⁻ can then either bind to or desorb from the electrode surface in its anionic or protonated form (HNO₂ has a pK_a of 3.35 in water). Upon NO₂⁻ desorption, indirect routes for NO₃⁻ reduction have been suggested. For instance, experiments conducted in a highly concentrated solution of nitric acid showed HNO₂ reacting with HNO₃ to yield water and N₂O₄, which immediately decomposed to two equivalents of NO₂.¹⁹³ Alternatively, HNO₂ can be protonated to water and NO⁺,^{193,194} which is reduced to NO on the metal electrode.¹⁹⁴ The reaction of the latter with NO₂ and water restores HNO₂ (**Figure 6.1-A**).¹⁹⁴ Furthermore, the equilibrium constant for the disproportionation of

aqueous HNO_2 into water, HNO_3 , and NO is $2.22 \times 10^{+2}$ (**Figure 6.1-B**).¹⁹⁵ NO can then be evolved or bound on the electrode for further reduction.^{195,196} If $\text{HNO}_2/\text{NO}_2^-$ is retained on the cathode, NO is formed. Again, this can either stay bound or desorb.

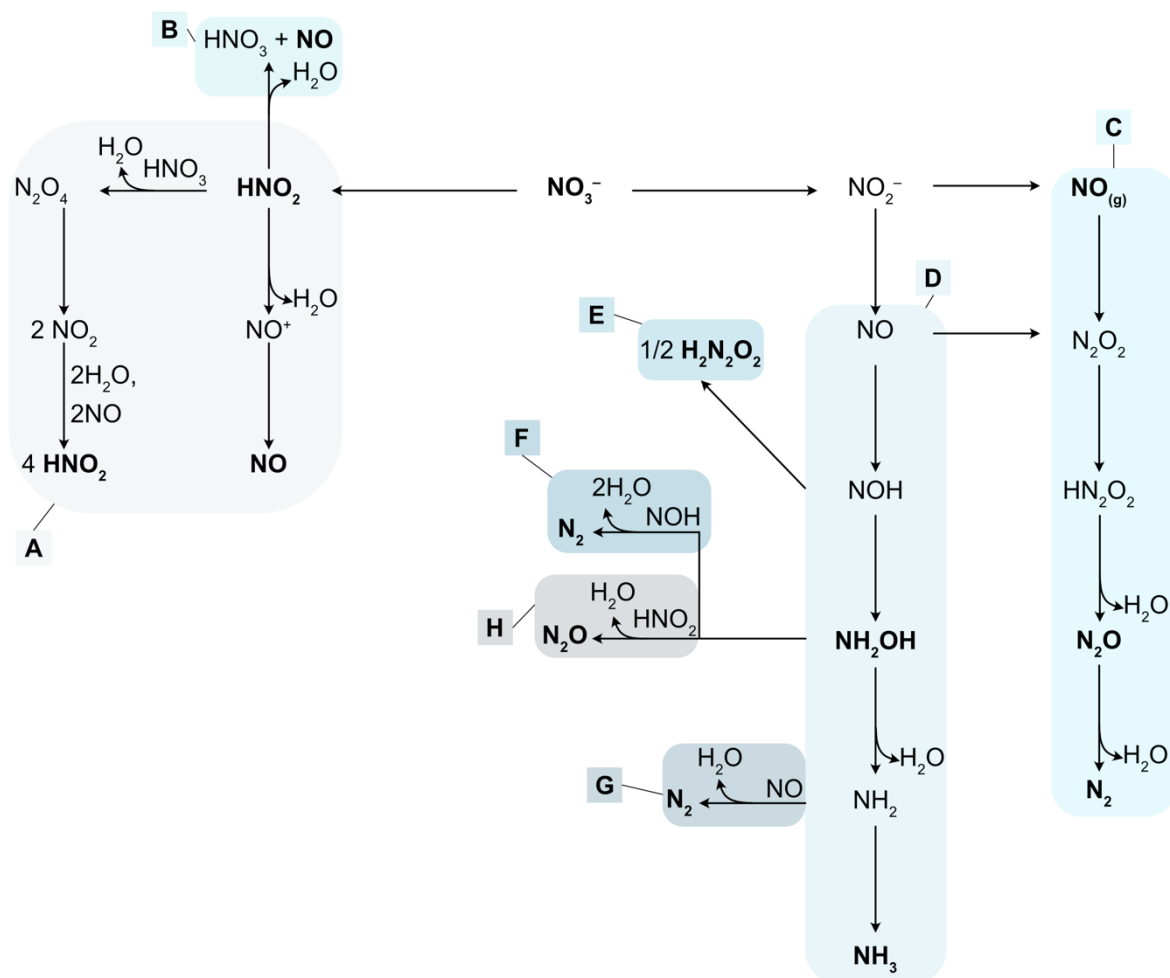


Figure 6.1 Experimentally proposed pathways for the NO_3RR to HNO_2 (A), NO (A, B, C), N_2O (C, H), N_2 (C, F, G), NH_3 (D), NH_2OH (D), and $\text{H}_2\text{N}_2\text{O}_2$ (E). Species that can be liberated into the environment as final products of the NO_3RR are indicated in bold.

Research on the NO_3RR on Ru, Rh, Ir, Pd, Pt, and Au metal electrodes demonstrated that a desorbed and a retained NO molecule coupled to N_2O_2 , which was subsequently hydrogenated to HN_2O_2 on the metal electrode and decomposed into water and N_2O .^{197,198} Because the onset potential for N_2O production was the same as that for N_2 evolution in both alkaline and acidic conditions, the authors proposed that N_2 product derived from the further reduction of N_2O (**Figure 6.1-C**).¹⁹⁷ Conversely, adsorbed NO was detected as an intermediate in NH_2OH and NH_3 production (**Figure 6.1-D**).^{199,200} Along this route, NOH can dimerise to form hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$), as illustrated in **Figure 6.1-E**.¹⁹⁶ Other by-products observed during the electroreduction of NO include N_2 and N_2O .^{201,202} Experiments conducted on a Sn electrode suggested that N_2 evolution occurs upon the reaction of NH_2OH

with NOH (**Figure 6.1-F**), as well as the coupling of NH₂ with NO (**Figure 6.1-G**).²⁰¹ The reaction of NH₂OH with HNO₂ instead led to water and N₂O (**Figure 6.1-H**).²⁰¹ Similar findings were reported for NO₂⁻ reduction on single crystal Pt(100) electrodes.²⁰²

Theoretically, the NO₃RR is usually modelled through sequential PCETs. If the hydrogenations occur at the nitrogen, NH₂OH and NH₃ are formed.^{203,200,204} If NO is instead hydrogenated at the oxygen, leading to the *N intermediate, NH₃ can be obtained through three hydrogenations and N₂ through N–N coupling. Calculation of the respective barriers on a Pt(100) surface demonstrated the formation of both products to be feasible at room temperature.²⁰⁴

6.2 Experimental results

The present chapter explores the catalytic activity and selectivity of Cu, Zn, and Zn-Cu alloy metal electrodes in the NO₃RR to NH₂OH for cyclohexanone oxime production (Eq. 6.1).

Cu, Zn, and a series of Zn_{1-x}Cu_x metal electrodes were prepared by electrodeposition from different ratios of ZnSO₄·7H₂O and CuSO₄·5H₂O on a Cu foil substrate, covered by Teflon tape, in an acid solution of 1.5 M H₂SO₄ via the dynamic hydrogen bubble template approach.²⁰⁵ This method facilitated the formation of porous surfaces through the evolution of H₂. All metal electrodes were subjected to X-ray photoelectron spectroscopy and p-XRD, which indicated partial oxidation of Cu upon exposure to the atmosphere. The elemental composition of the Zn_xCu_y metal electrodes, both in the surface and in the bulk, was characterised by energy-dispersive X-ray analysis and inductively coupled plasma optical emission spectrometry, respectively. Both techniques indicated Zn/Cu ratios corresponding to the Zn₉₃Cu₇, Zn₈₅Cu₁₅, Zn₇₄Cu₂₆, and Zn₆Cu₉₄ alloys.

The NO₃RR was conducted on the Cu, Zn, and alloy metal electrodes in an aqueous buffer of 0.5 M K₃PO₄ at pH 7.0, containing 100 mM KNO₃ and 25 mM cyclohexanone. The steady-state potential versus the RHE and the FE towards cyclohexanone oxime, NH₃, N₂, and H₂ on the different materials were measured at a constant current density of 100 mA/cm² and are reported in **Figure 6.2**. The products were characterised via ¹H-NMR, ¹³C-NMR, high-performance liquid chromatography, ion chromatography, and mass spectrometry. Cu and Zn₆Cu₉₄ mainly catalysed NH₃ formation, with a FE towards oxime below 1%. This improved to (12 ± 1)%, (27 ± 3)%, and (17 ± 3)% on Zn, Zn₉₃Cu₇ and Zn₈₅Cu₁₅, respectively. The Zn catalyst was the only one to yield a significant amount of N₂, up to

(33 ± 3)%. In terms of bias, Cu required the smallest potential (≈ -0.30 V_{RHE}) to promote the NO₃RR at a steady-state current of 100 mA/cm², while a bias of *ca.* -1.10 V_{RHE} was applied on Zn. The alloy catalysts necessitated intermediate potentials between those, ranging from approximately -0.30 to -0.80 V_{RHE} (**Figure 6.2**).

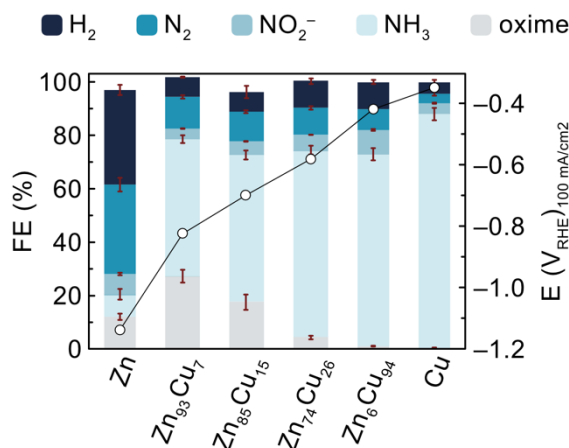


Figure 6.2 Blue bars report the FE measured towards H₂, N₂, NO₂⁻, NH₃ and cyclohexanone oxime on the Zn, Zn₉₃Cu₇, Zn₈₅Cu₁₅, Zn₇₄Cu₂₆, Zn₆Cu₉₄ and Cu metal electrodes at a steady-state current of 100 mA/cm² in an aqueous buffer of 0.5 M K₃PO₄ at pH 7.0 containing 25 mM cyclohexanone. Red lines indicate the experimental errors of the FE. The steady-state potentials versus RHE are shown as white dots.

Further studies were conducted to elucidate the reaction mechanism of NO₃RR on the aforementioned catalysts. NH₂OH was not easily detected on the cathodes due to its fast nucleophilic addition to cyclohexanone, yielding the corresponding oxime.¹⁸² Therefore, to confirm its formation, the NO₃RR was performed in the absence of the cyclohexanone reactant under the same conditions. NH₂OH was produced with a FE of $12 \pm 3\%$ and $3 \pm 1\%$ at *ca.* -1.00 and -0.80 V_{RHE} on Zn and Zn₉₃Cu₇, respectively, while it was not detected on Cu and the other alloy electrocatalysts (**Figure 6.3a**). Similarly to previous experiments, the potential required to reach a steady-state current density of 100 mA/cm² on the alloy electrodes decreased with the increase in Cu content (**Figure 6.3a**). These results suggested that Cu retained and further reduced NH₂OH to NH₃ more efficiently than Zn and the Zn₉₃Cu₇ alloy. This finding was corroborated by reducing NH₂OH to NH₃ on the catalysts, which required a potential of around -1.40 V_{RHE} on Zn and -1.20 V_{RHE} on Zn₉₃Cu₇, compared to -0.40 V_{RHE} on Cu (**Figure 6.3b**). In-situ Raman spectroscopy identified the presence of adsorbed NO₃⁻ on the Cu electrode, while the NO₃⁻ anion was detected in solution in experiments with the Zn catalyst. The bound NH₂OH intermediate was only identified on the Zn₉₃Cu₇ surface and was not observed on Zn or Cu, presumably due to fast desorption in the former and favourable reduction in the latter.

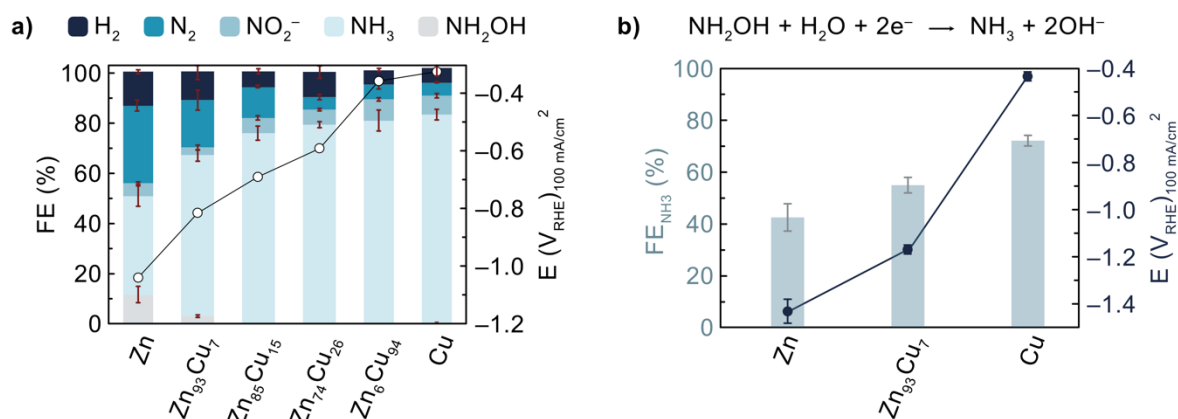


Figure 6.3 a) Blue bars report the FE towards H_2 , N_2 , NO_2^- , NH_3 and NH_2OH , obtained during the NO_3RR on the Zn, $\text{Zn}_{93}\text{Cu}_7$, $\text{Zn}_{85}\text{Cu}_{15}$, $\text{Zn}_{74}\text{Cu}_{26}$ and $\text{Zn}_6\text{Cu}_{94}$, and Cu metal electrodes in the absence of cyclohexanone, at a steady-state current of 100 mA/cm^2 in an aqueous buffer of $0.5 \text{ M K}_3\text{PO}_4$ at pH 7.0. The required steady-state potentials versus RHE are indicated as white dots. **b)** FE and potentials versus RHE required by the Zn, $\text{Zn}_{93}\text{Cu}_7$, and Cu metal electrodes for the reduction of NH_2OH to NH_3 .

Overall, experimental results indicated that NO_3^- could be successfully reduced to NH_2OH for the synthesis of cyclohexanone oxime on the Zn and $\text{Zn}_{93}\text{Cu}_7$ electrocatalysts, with the FE on Zn being impaired by the competing evolution of N_2 . The Cu-rich alloy electrodes and the pure Cu catalyst, instead, proved selective towards NH_3 formation, consistent with literature reports.¹⁸³

6.3 Computational details

Periodic DFT calculations were performed with the 6.2 revision of VASP,¹²⁶ adopting the BEEF-vdW functional.⁹⁶ Core electrons were described with projector-augmented wave pseudopotentials,¹²⁴ and valence electrons with plane waves of energy cut-off of 500 eV. The electronic occupancy in molecular species was described with a Gaussian smearing of width of 0.05 eV, while the first-order Methfessel-Paxton smearing was employed for metals with a width of 0.2 eV. The reciprocal space was sampled at the Γ -point for gas phase species, while solid state simulations were conducted with a Γ -centred grid of *ca.* 28 k -points $\times\text{\AA}$. Electronic steps were considered converged below a threshold of 10^{-6} eV.

Geometry relaxations were performed with the conjugate gradient algorithm, imposing a step size of 0.1 $\text{\AA}$ and force convergence criteria of 0.01 $\text{\AA}/\text{eV}$, without allowing the cell shape and volume to change and only relaxing the atomic positions. TS structures were optimised with the improved dimer method,¹²⁰ switching the criterion for convergence of the ionic steps to 10^{-6} eV. After optimisation, stationary points were characterised through a frequency calculation with the finite differences method and a step size of 0.02 $\text{\AA}$. Whenever

imaginary frequencies below 100 cm^{-1} were found, these were replaced with real frequencies of 12 cm^{-1} .¹⁷⁰

Gas molecules were constructed with the graphical interface of ASE,¹⁴⁴ and modelled imposing a 15 Å vacuum along all directions to avoid interactions between periodic images. To represent bulk water, a simulation cell comprising six H_2O molecules hydrogen bonded to each other was constructed in a cubic cell of 5.862 Å along the a and b axes and 5.034 Å along the c axis. This was first optimised by only allowing the atom positions to relax, and subsequently relaxing the cell shape and volume.

The bulk cell of Cu and Zn was downloaded from the Materials Project database,¹⁴⁷ selecting the one with lowest energy above hull. This was a face centred cubic cell of lattice parameter 3.577 Å for Cu (spacegroup $\text{Fm}\bar{3}\text{m}$), and an hexagonal lattice with a and b vectors of 2.614 and 4.873 Å , respectively, for Zn (spacegroup $\text{P6}_3/\text{mmc}$). The unit cell of minimum energy was then determined by enlarging and reducing the lattice parameters by 1% five times and optimising the resulting cell without allowing the volume and shape to change. The energies and volumes were then fitted to the BM equation of state,¹⁴² and the corresponding minimum was optimised by allowing the cell shape to relax but not the volume. The (111) and (101) surfaces, indicated by the experimental p-XRD spectra, were then cleaved for Cu and Zn as slabs of four layers, respectively. 15 Å of vacuum were added along the direction perpendicular to the surface, and the atoms in the two bottom layers were constrained in their bulk positions. The surface coverage analysis of the $p(1\times 2)\text{-Zn}(101)$ supercell was performed as detailed in Section 5.3.1, and the Pourbaix plot of Cu(111) is illustrated in **Figure 5.4b**.

To model the $\text{Zn}_{93}\text{Cu}_7$ electrode, it was hypothesised that the catalytic activity would be primarily affected by the surface elemental composition, rather than the bulk composition. Moreover, given the low concentration of Cu with respect to Zn, the alloy was deemed to exhibit the same crystal packing as Zn, as suggested by the experimental p-XRD data (Section 6.2). Because the interactions between Zn and Cu are more favourable than the corresponding Zn-Zn and Cu-Cu, dilute Zn-Cu alloys are known to present the least abundant element dissolved in the prevailing one.²⁰⁶ Furthermore, the presence of adsorbates has been shown to influence the identity of the species that segregates to the surface.²⁰⁶ Thus, the surface coverage of the $\text{Zn}_{93}\text{Cu}_7$ alloy at $-0.90\text{ V}_{\text{RHE}}$ was assumed from the Pourbaix diagram of Zn(101) (**Figure 6.7b**). Then, a Zn atom was substituted with Cu in a four-layered $p(1\times 2)\text{-Zn}(101)$ supercell in a step and terrace site to identify the most favourable

position of the Cu atom in the presence of the *H coverage. Such supercell dimensionality was deemed to closely reproduce the experimental ratio between the metals of 93 to 7.

A Bader charge analysis was carried out on the $p(4\times4)$ Cu(111) and $p(2\times4)$ -Zn(101) simulation cells with an adsorbed *NO₃. To this aim, the core densities and the self-consistent valence densities were computed and summed. The atomic basins were then calculated, and the net atomic charges were determined as the difference between the Bader population and the atomic valence specified in the pseudopotential.²⁰⁷

Thermodynamic corrections to the electronic energy were calculated with the thermochemistry module of ASE,¹⁴⁴ adopting the ideal gas model for gas phase molecules and the harmonic model for adsorbate species. The atoms on the surface slab were not vibrated, as outlined in Section 4.3.

6.3.1 Choice of the reference for the NO₃RR mechanism

The choice of the energy reference for the NO₃RR mechanisms is controversial. Because anions are significantly less stable in vacuum than in solution, modelling NO₃⁻ in the gas phase might provide a very unfavourable energy reference, causing its binding to be unphysically exergonic. Moreover, the NO₃RR to NH₂OH, N₂, and NH₃ involves both anionic and neutral intermediates. However, subtracting energy values pertaining to systems with different charge is not correct. Thus, the gas phase NO₃⁻ anion was ruled out as reference for the NO₃RR profile.

An attempt was made at computing the NO₃⁻ binding energy referred to HNO₃ via the thermodynamic cycle schematised in **Figure 6.4a**. This approach envisioned to sum the solvation and dissociation in solution of HNO₃ to the adsorption energy of *NO₃, modelled in a neutral cell. The energy of the proton and electron excluded from the simulation was expressed via the CHE, leading to the following equation for the Gibbs adsorption energy of the NO₃⁻ anion relative to HNO₃ in the gas phase, ΔG_3 :

$$\Delta G_3 = G_{*NO_3} - (E_* + G_{HNO_3}) + \frac{1}{2}G_{H_2} - eU_{RHE} \quad (6.2)$$

where G_{*NO_3} is the Gibbs energy of *NO₃ adsorbed on a metal slab, E_* is the electronic energy of the said metal slab, G_{HNO_3} and G_{H_2} are the Gibbs energy of gas phase HNO₃ and H₂, respectively, and U_{RHE} is the applied potential versus RHE.¹⁹²

The Bader charge analysis on $^*\text{NO}_3$ bound bidentately through two oxygen atoms on $p(4\times4)$ -Cu(111) and $p(2\times4)$ -Zn(101) supercells (**Figure 6.4b-c**), however, indicated that the slab captured a significant fraction of an electron from the metal surfaces, as reported in Table 6.1. Since the cost for the electron transfer depended on the metals, this was deemed to bias the NO_3^- binding energy calculated via the thermodynamic cycle.

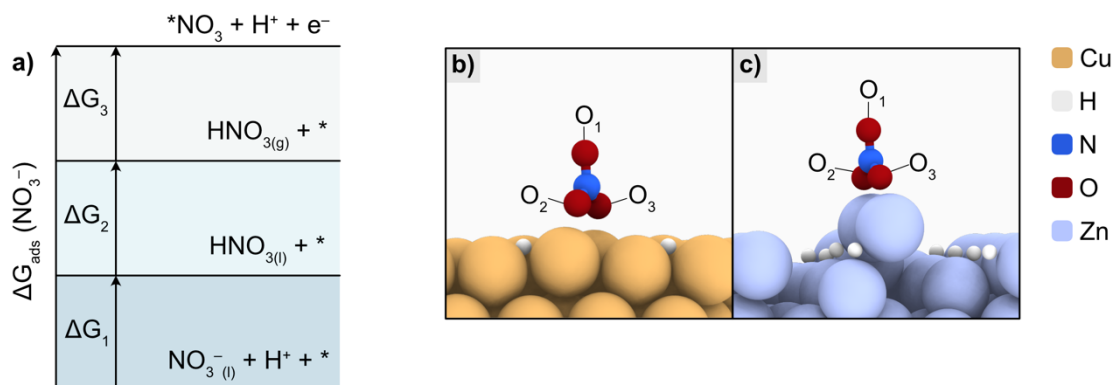


Figure 6.4 a) Thermodynamic cycle for determining NO_3^- Gibbs adsorption energy, $\Delta G_{ads}(\text{NO}_3^-)$, with respect to HNO_3 . ΔG_1 is the dissociation energy of HNO_3 in solution, ΔG_2 its solvation energy, and ΔG_3 the NO_3^- adsorption energy referred to gas phase HNO_3 (Eq. 6.2).¹⁹² Energies are not in scale. NO_3^- anion bound on a **b)** $p(4\times4)$ -Cu and **c)** $p(2\times4)$ -Zn(101) supercell, presenting the $^*\text{H}$ coverages determined in Section 6.4.2.

Table 6.1 Atomic charge (in a.u.) of the nitrogen and oxygen atoms and total charge of $^*\text{NO}_3$ adsorbed on $p(4\times4)$ -Cu(111) and $p(2\times4)$ -Zn(101) supercells presenting the $^*\text{H}$ coverages determined in Section 6.4.2.¹⁹²

	N	O ₁	O ₂	O ₃	Total
Cu(111)	0.85	-0.46	-0.56	-0.56	-0.73
Zn(101)	0.84	-0.38	-0.59	-0.59	-0.71

Nonetheless, it was noted that the reduction of NO_3^- to NO occurs before the reaction pathway branches towards NH_3 , N_2 , or NH_2OH (Section 6.1.3 and **Figure 6.5a**). Thus, adopting $^*\text{NO}$ as starting point for the mechanistic study was deemed to allow the investigation of the NO_3RR selectivity measured experimentally on the Cu, Zn, and $\text{Zn}_{93}\text{Cu}_7$ electrodes, while also involving only neutral intermediates. Gas phase NO was therefore chosen as the energy reference.

6.3.2 NO_3RR mechanism

The NO_3RR mechanism was simulated by first adsorbing NO and then assessing the energetics for the hydrogenation at the nitrogen and oxygen atom of all intermediates reported in **Figure 6.5a**. These were considered to bind as monodentate or bidentate through nitrogen and oxygen in all available adsorption sites (*i.e.* *bridge*, *hollow*, and *top*). Due to

the large number of binding modes and intermediates to be modelled on the three metals, some approximations were made based on the results of the surface coverage analysis and of the Lewis structures displayed in **Figure 6.5b**, namely:

- The adsorption through the non-hydrogenated oxygen atom of $\ast\text{NO}$, $\ast\text{NHO}$ and $\ast\text{NH}_2\text{O}$ was investigated at the sites indicated by the coverage analysis as the most favoured for $\ast\text{O}$ binding (*i.e.* *hollow* and *bridge* sites on Cu(111) and Zn(101), respectively, as reported in Tables 5.2 and 6.2).
- Because the Lewis structures of $\ast\text{NOH}$ and $\ast\text{NHOH}$ present a radical at the nitrogen, this was deemed the most favoured anchoring atom. Therefore, only the monodentate modes through nitrogen and the bidentate modes were explored.
- Since the coverage analysis of Cu(111) indicated similar $\Delta G_{\ast X}$ values for *hcp* and *fcc* sites with a slight preference for the latter ($X = \ast\text{H}/\ast\text{OH}/\ast\text{O}$, Table 5.2), and because major surface reconstruction occurred on Zn(101) upon attempting to bind any intermediate on *hollow* sites, this position was discarded from the adsorption studies.
- The sites occupied by $\ast\text{H}$ atoms from the surface coverage were deemed unavailable.
- On the $\text{Zn}_{93}\text{Cu}_7(101)$ surface, the intermediates that were most stable on Zn(101) were only modelled in their preferred binding mode. An exception was made for $\ast\text{NOH}$ due to its central role in determining the selectivity towards NH_2OH and NH_3 compared to N_2 . In this case, all the binding modes and sites were explored to ensure the determination of the most favoured $\Delta G_{\ast\text{NOH}}$.

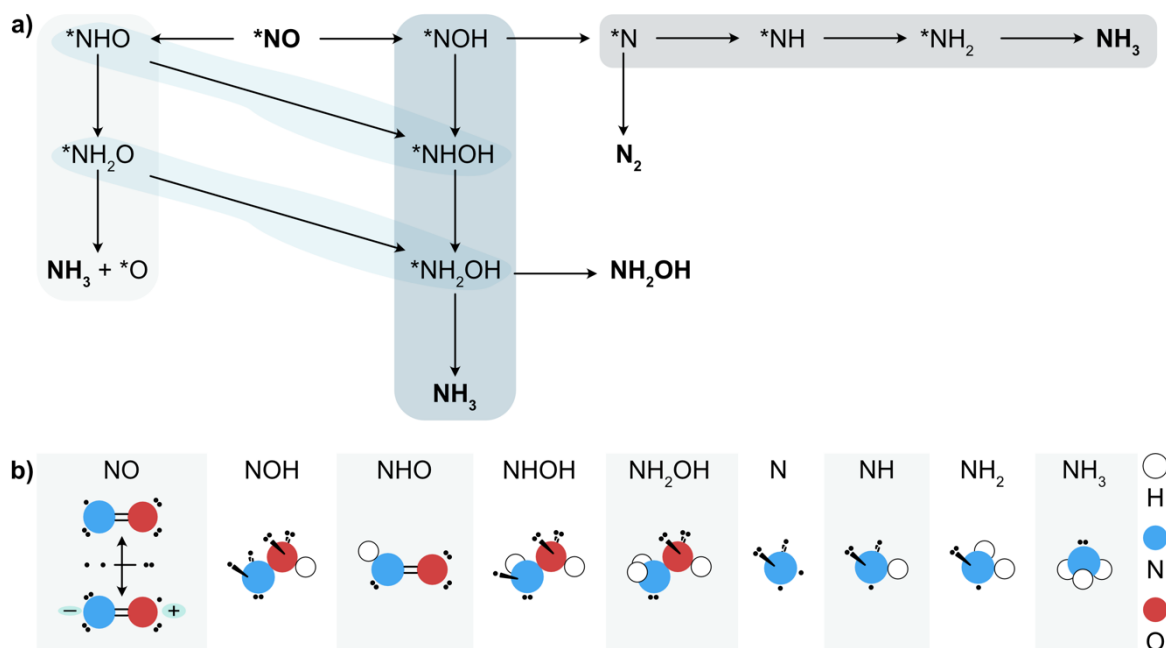


Figure 6.5 a) Schematic representation of the possible NO_3RR pathways from $\ast\text{NO}$ to NH_2OH , NH_3 and N_2 . $\ast\text{NO}$ and end-products are highlighted in bold. b) Lewis structures of the reaction intermediates in panel a).

To rationalise the competition between $^*\text{NH}_2\text{OH}$ hydrogenation to NH_3 and its desorption, it was noted that the pK_b of NH_2OH in water (*i.e.* 8.1)²⁰⁸ does not indicate its protonation to occur favourably at the experimental pH of 7. In fact, application of the Henderson-Hasselbalch equation yielded the ratio presented in Eq. 6.3:

$$\frac{[\text{NH}_2\text{OH}_2^+]}{[\text{NH}_2\text{OH}]} = 10^{(\text{pOH}-\text{pK}_b)} \simeq 8\% \quad (6.3)$$

where $[\text{NH}_2\text{OH}_2^+]$ is the concentration of the protonated NH_2OH , and $[\text{NH}_2\text{OH}]$ is the concentration of the non-protonated NH_2OH . Thus, it was deemed that the electrode was responsible for sourcing not only the electron but also the proton for the hydrogenation. For this reason, the latter was modelled sourcing a hydrogen atom from the surface coverage.

The energetics for each PCET were calculated adopting the CHE model,⁶⁵ as follows:

$$\Delta G_{*NO} = G_{*NO} - (E_* + G_{NO}) \quad (6.4)$$

$$\Delta G_{*NHO} = G_{*NHO} - \left(E_* + G_{NO} + \frac{1}{2}G_{H_2}\right) + eU_{RHE} \quad (6.5)$$

$$\Delta G_{*NOH} = G_{*NOH} - \left(E_* + G_{NO} + \frac{1}{2}G_{H_2}\right) + eU_{RHE} \quad (6.6)$$

$$\Delta G_{*N} = G_{*N} + G_{H_2O} - (E_* + G_{NO} + G_{H_2}) + 2eU_{RHE} \quad (6.7)$$

$$\Delta G_{*NH_2O} = G_{*NH_2O} - (E_* + G_{NO} + G_{H_2}) + 2eU_{RHE} \quad (6.8)$$

$$\Delta G_{*NHOH} = G_{*NHOH} - (E_* + G_{NO} + G_{H_2}) + 2eU_{RHE} \quad (6.9)$$

$$\frac{1}{2}\Delta G_{N_2} = \frac{1}{2}G_{N_2} + G_{H_2O} - (E_* + G_{NO} + G_{H_2}) + 2eU_{RHE} \quad (6.10)$$

$$\Delta G_{*NH_2OH} = G_{*NH_2OH} - \left(E_* + G_{NO} + \frac{3}{2}G_{H_2}\right) + 3eU_{RHE} \quad (6.11)$$

$$\Delta G_{NH_2OH} = G_{NH_2OH} - \left(E_* + G_{NO} + \frac{3}{2}G_{H_2}\right) + 3eU_{RHE} \quad (6.12)$$

$$\Delta G_{*NH_2} = G_{*NH_2} + G_{H_2O} - \left(E_* + G_{NO} + \frac{3}{2}G_{H_2} + G_{corr,H}\right) + 3eU_{RHE} \quad (6.13)$$

$$\Delta G_{*H} = G_{*H} + G_{H_2O} - (E_* + G_{NO} + 2G_{H_2}) + 4eU_{RHE} \quad (6.14)$$

$$\Delta G_{NH_3} = G_{NH_3} + G_{H_2O} - \left(E_* + G_{NO} + \frac{5}{2}G_{H_2}\right) + 5eU_{RHE} \quad (6.15)$$

where G_X refers to the Gibbs energy of species X and $G_{corr,H}$ is the vibrational contribution to the energy of an adsorbed $*H$ on the surface coverage. ΔG_{*H} expresses the Gibbs energy of replenishment of the hydrogen vacancy left by the hydrogenation of $*NH_2OH$ from the surface coverage. E_* is the electronic energy of the metal slab hosting the $*H$ coverage determined at reaction conditions. The kinetic barrier $\Delta G^\ddagger$ for the hydrogenation of $*NH_2OH$ to $*NH_2$ and H_2O was calculated relative to NH_2OH adsorption, which was the most exergonic step preceding $*NH_2$ formation on all investigated metals, as follows:

$$\Delta G^\ddagger = G_{TS} - \left(E_* + G_{NO} + \frac{3}{2}G_{H_2} + G_{corr,H} + \frac{1}{3}G_{H_2O-cage}\right) + 3eU_{RHE} \quad (6.16)$$

where $G_{H_2O-cage}$ is the Gibbs energy of a cage containing six H_2O molecules (Section 6.4).

6.4 Results

6.4.1 Modelling of the Zn bulk and (101) surface

To model the Zn bulk unit cell of minimum energy, a BM fitting was performed as described in Section 6.4.¹⁴² This yielded a hexagonal cell featuring a and b lattice vectors of 2.802 and 4.634 Å, respectively (**Figure 6.6a**), which compared well with the experimental values of 2.662 and 4.933 Å.²⁰⁹ The optimised Zn(101) surface presented lattice parameters of 5.415 and 2.802 Å along the a and b directions, respectively, and an angle of 105° (**Figure 6.6b**). It exhibited a surface energy of 0.048 eV/Å², calculated according to Eq. 4.1.

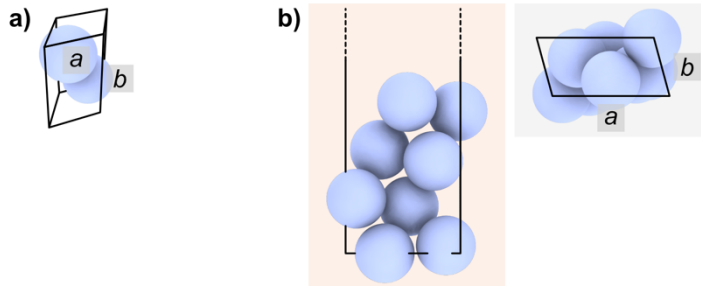


Figure 6.6 **a)** Bulk unit cell obtained for Zn through BM fitting, as described in Section 6.4. **b)** Top and side-views of the four-layered Zn(101) slab with 15 Å of vacuum along the direction perpendicular to the surface.

6.4.2 Determination of the catalysts surface state

Table 6.2 reports the binding energies at 0 V_{RHE} of a single $*H$, $*OH$ and $*O$ adsorbate on the *bridge*, *hollow*, and *top* sites of a $p(1 \times 2)$ -Zn(101) supercell, $\Delta G_{*X}(0V_{RHE})$, while the $\Delta G_{*nX}(0V_{RHE})$ values for n $*H$, $*OH$ and $*O$ species are summarised in Table 6.3. $*H$ and $*O$ adsorbates were found to preferentially bind on *hollow* sites, while $*OH$ was more stable on a *bridge* site. Therefore, these were progressively populated to identify the maximum coverage density. In the case of $*H$, the addition of the fifth adsorbate caused the surface to reconstruct. In the case of $*OH$ and $*O$, instead, only two adsorbates could be bound in the $p(1 \times 2)$ supercell before observing their migration into the sublayers.

Table 6.2 $\Delta G_{*X}(0V_{RHE})$, in eV, of a single $*H$, $*OH$ and $*O$ adsorbate on the $p(1 \times 2)$ -Zn(101) supercell in the *bridge*, *hollow*, and *top* sites. $\Delta G_{*X}(0V_{RHE})$ values were calculated according to Eq. 3.75-77. When an adsorbate diffused to a different site, this is indicated in place of $\Delta G_{*X}(0V_{RHE})$.

	$\Delta G_{*H}(0V_{RHE})$	$\Delta G_{*OH}(0V_{RHE})$	$\Delta G_{*O}(0V_{RHE})$
<i>bridge</i>	0.42	-0.12	<i>hollow</i>
<i>hollow</i>	0.35	0.02	-0.12
<i>top</i>	<i>hollow</i>	<i>bridge</i>	<i>hollow</i>

Table 6.3 $\Delta G_{*nX}(0V_{RHE})$, in eV, of n $*H$, $*OH$ and $*O$ adsorbates on the $p(1 \times 2)$ -Zn(101) supercell, calculated according to Eq. 3.75-77. The surface coverage analysis was interrupted when surface reconstruction (for $*H$) or migration of the adsorbates into the sublayers (for $*OH$ and $*O$) was observed.

n	$\Delta G_{n*H}(0V_{RHE})$	$\Delta G_{n*OH}(0V_{RHE})$	$\Delta G_{n*O}(0V_{RHE})$
1	0.35	-0.12	-0.12
2	0.83	-0.15	-0.32
3	1.29	sublayer	sublayer
4	1.81	-	-
5	reconstruction	-	-

The $\Delta G_{*nX}(0V_{RHE})$ values reported above were corrected by the applied potential on the RHE scale (Eq. 3.79-81), resulting in the plot of $\Delta G_{*nX}(U_{RHE})$ versus U_{RHE} and the corresponding Pourbaix diagram depicted in **Figure 6.7**.

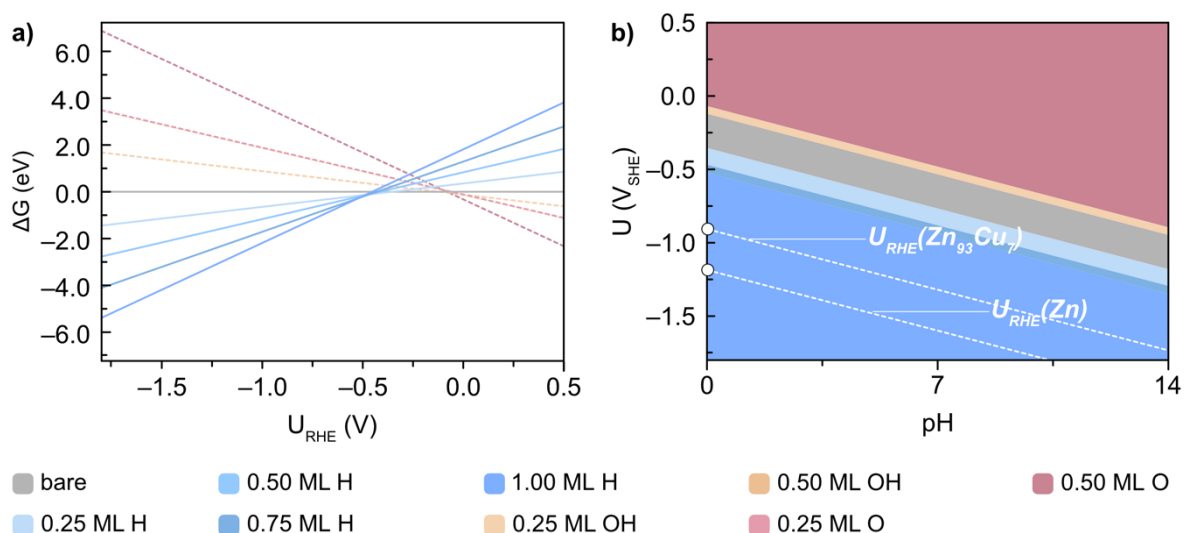


Figure 6.7 a) Plot of $\Delta G_{*nX}(U_{RHE})$ for $n *H$, $*OH$ and $*O$ as a function of the applied potential on $p(1 \times 2)$ -Zn(101). b) Pourbaix diagram showing the most stable surface state for $p(1 \times 2)$ -Zn(101) as a function of potential and pH, highlighting the values -0.90 and $-1.20 V_{RHE}$ for the $Zn_{93}Cu_7$ and Zn metal electrodes, respectively.

The Pourbaix diagrams for the $p(1 \times 2)$ -Zn(101) (**Figure 6.7b**) and $p(2 \times 2)$ -Cu(111) (**Figure 5.4b**) supercells were used to identify the most stable surface coverage under reaction conditions. More specifically, potential values of around -0.40 and $-1.20 V_{RHE}$ were adopted for the Cu(111) and Zn(101) surfaces (**Figure 6.2**). At these applied potentials, the $p(2 \times 2)$ -Cu(111) surface displayed three quarters of the *fcc* sites covered with $*H$ as illustrated in **Figure 6.8**. The $p(1 \times 2)$ -Zn(101), instead, was determined to host four adsorbed $*H$. Of these, two were retained on the *hollow* sites and two migrated to the *bridge*. To model the $Zn_{93}Cu_7(101)$ facet, a Zn atom on both a step and terrace sites in the $p(1 \times 2)$ -Zn(101) supercell featuring a full $*H$ coverage was substituted with Cu (Section 6.4). It was noted that the Zn for Cu substitution on a step site was preferred by 0.09 eV.

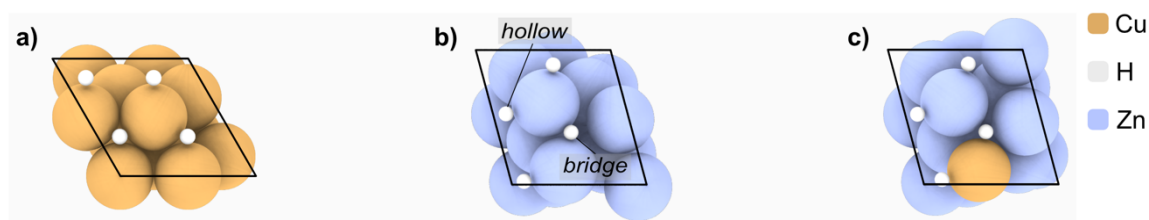


Figure 6.8 Top-views of the most stable surface coverages for the a) Cu(111), b) Zn(101), and c) $Zn_{93}Cu_7(101)$ surfaces at the applied potentials of -0.40 , -1.20 , and $-0.90 V_{RHE}$, respectively. The $*H$ atoms occupying the *bridge* and *hollow* sites on Zn(101) are also labelled.

6.4.3 Mechanism of the NO₃RR to NH₂OH and NH₃

The NO₃RR mechanism to NH₂OH and NH₃ was investigated on the Cu(111), Zn(101), and Zn₉₃Cu₇(101) slabs. The most thermodynamically favoured pathway after the adsorption of NO was the same on all surfaces, involving the hydrogenation of NO to *NHO, *NH₂O, *NH₂OH, *NH₂ and water, and NH₃. Their energetics in the preferred binding modes are illustrated in **Figure 6.9**, while Table 6.4 reports the relative energies of all the other intermediates and adsorption configurations. It was noted that the application of a more negative potential led to a more exergonic reaction pathway on the Zn catalyst, compared to Zn₉₃Cu₇ and Cu. Notably, NH₂OH desorption was only favoured on Zn₉₃Cu₇ (by -0.14 and -0.44 eV on a Zn and Cu site, respectively), slightly endergonic on pure Zn (+0.19 eV), and thermoneutral on pure Cu (by -0.03 eV). Hence, NH₂OH desorption was hypothesised to be kinetically facile on all metal electrodes. However, this observation and the exergonic formation of NH₃ on all surfaces were in contrast with the enhanced oxime production measured experimentally on Zn₉₃Cu₇ and Zn compared to Cu. Therefore, the reaction kinetics for the water-assisted hydrogenation of the *NH₂OH intermediate from the *H surface coverage were subsequently explored (Section 6.3.2). As discussed in Section 5.4.4, the absolute value of these barriers depended on the number of H₂O molecules introduced in the simulation, their spatial arrangement and the choice of water reference. Therefore, the trend between the $\Delta G^\ddagger$ values on the three catalysts was analysed, rather than their exact energy. The calculated $\Delta G^\ddagger$ were 1.11, 1.05, and 1.66 eV on the Cu(111), Zn₉₃Cu₇(101) and Zn(101) slabs, respectively (**Figure 6.9**). Based on these energy barriers, it was concluded that NH₃ formation on Zn(101) was the most impaired from the kinetic point of view when compared to Cu(111) and Zn₉₃Cu₇(101). Thus, the lower conversion of NH₃ formation on the Zn(101) electrode was attributed to the sluggish kinetics of *NH₂OH hydrogenation along with the evolution of N₂ (Sections 6.2 and 6.4.4). Furthermore, the $\Delta G^\ddagger$ calculated on both Cu(111) and Zn₉₃Cu₇(101) was also consistent with NH₃ production at room temperature. In addition, the more exergonic desorption of NH₂OH on Zn₉₃Cu₇(101) was deemed responsible for its enhanced oxime formation compared to Cu(111).

Overall, the computed kinetics and thermodynamic data for the NO₃RR of NO to NH₂OH and NH₃ were considered to be in agreement with experimental findings.

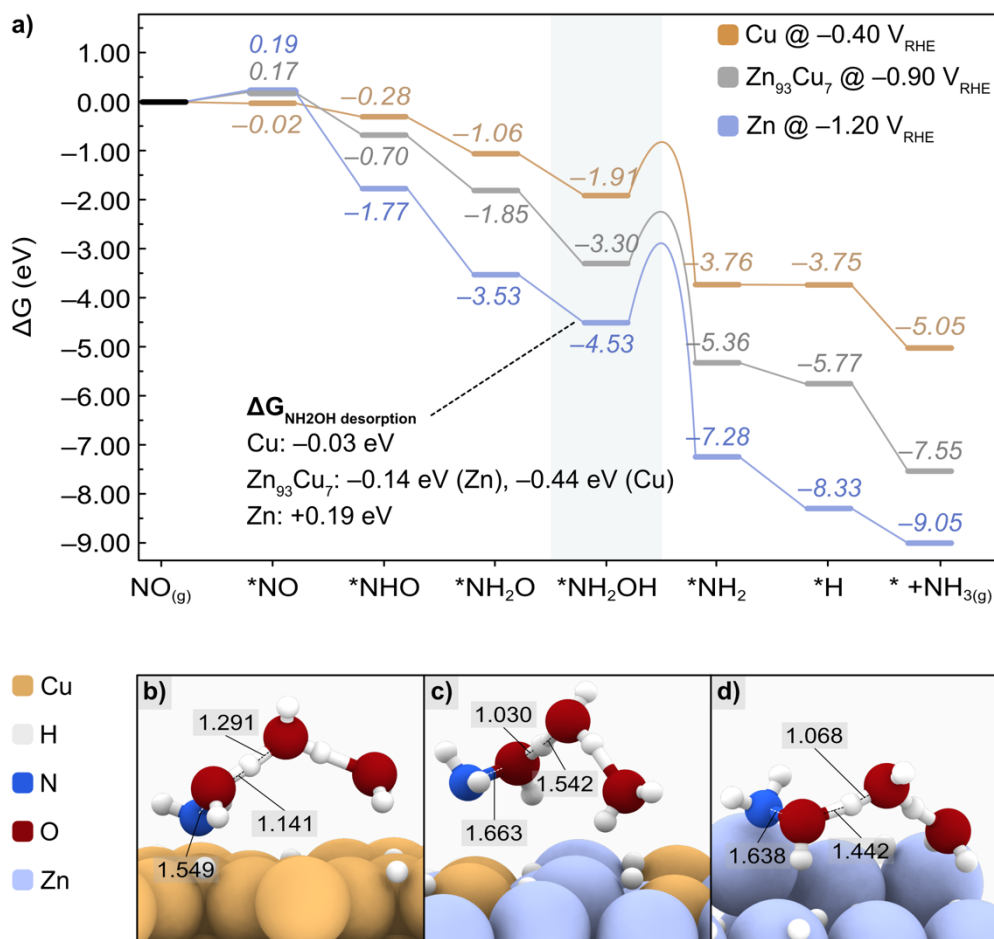


Figure 6.9 a) Gibbs energy profile for the NO₃RR of NO to NH₂OH and NH₃ calculated on $p(4\times4)$ -Cu(111), $p(2\times4)$ -Zn(101), and $p(2\times4)$ -Zn₉₃Cu₇(101) supercells at -0.40, -0.90, and -1.20 V_{RHE}, respectively. TS structures for the hydrogenation of *NH₂OH at the oxygen atom using the *H surface coverage, calculated on **b)** Cu(111) **c)** Zn(101) and **d)** Zn₉₃Cu₇(101). Relevant bond lengths are shown in Å.

Table 6.4 ΔG_{*X} values (in eV) for all intermediates and binding modes in the NO₃RR to NH₂OH and NH₃ on $p(4\times4)$ -Cu(111), $p(2\times4)$ -Zn₉₃Cu₇(111), and $p(2\times4)$ -Zn(101) at experimental potential. Binding modes expected to be unfavoured based on the Lewis structures are labelled as ‘not explored (LS)’ (Section 6.3.2). If migration to a different site, desorption, or major surface reconstruction occurred, they are indicated in place of ΔG_{*X}.

Intermediate	Mode	Cu(111)	Zn ₉₃ Cu ₇ (101)	Zn(101)
*NO	<i>N_{bridge}</i>	<i>fcc</i>	-	desorption
	<i>N_{fcc}</i>	-0.01	-	desorption
	<i>N_{top}</i>	-0.02	0.17 (Zn) ; 0.42 (Cu)	0.20
	<i>O</i>	desorption	-	desorption
	<i>bidentate</i>	<i>top</i>	-	<i>top</i>
*NHO	<i>N_{bridge}</i>	not explored (LS)	-	<i>top</i>
	<i>N_{fcc}</i>	<i>top</i>	*H	*H
	<i>N_{top}</i>	-0.28	-	-1.07
	<i>O</i>	0.18	-	reconstruction
	<i>bidentate</i>	<i>top</i>	-0.70	-1.77

*NOH	N_{bridge}	fcc	0.18	−0.95
	N_{fcc}	0.17	*H	*H
	N_{top}	0.66	0.11 (Zn)	−0.16
	O	not explored (LS)	not explored (LS)	not explored (LS)
	$bidentate$	top	desorption	−0.39
*NH₂O	N_{bridge}	not explored (LS)	-	not explored (LS)
	N_{fcc}	not explored (LS)	*H	*H
	N_{top}	bidentate	-	−2.08
	O	−0.88	-	−3.34
	$bidentate$	−1.06	−1.85	−3.53
*NHOH	N_{bridge}	−0.82	-	−3.10
	N_{fcc}	−0.43	*H	*H
	N_{top}	bidentate	-	bidentate
	O	not explored (LS)	not explored (LS)	not explored (LS)
	$bidentate$	−0.81	-	−2.78
*NH₂OH	N_{bridge}	desorption	-	desorption
	N_{fcc}	desorption	*H	*H
	N_{top}	−1.91	−3.30 (Zn); −3.00 (Cu)	−4.53
	$bidentate$	desorption	-	desorption
*NH_{2,v}	N_{bridge}	−3.76	−5.36	−7.28
	N_{fcc}	$bridge$	*H	*H
	N_{top}	$bridge$	-	−6.32
*NH₂	N_{bridge}	−3.75	−5.77 (Zn)	−8.33
	N_{fcc}	not explored (LS)	*H	*H
	N_{top}	not explored (LS)	-	not explored (LS)

6.4.4 Mechanism of the NO₃RR to N₂

The Gibbs energy profile for the NO₃RR leading to N₂ evolution was computed for the Cu(111), Zn₉₃Cu₇(101), and Zn(101) surfaces to elucidate the competition with NH₂OH and NH₃ formation. N₂ was hypothesised to form after two hydrogenations of *NO at the oxygen atom, resulting in water release, followed by N–N coupling on the surface (**Figure 6.10**).²⁰⁴ Thus, the ΔG_{*NHO} and ΔG_{*NOH} values were first compared on the metal electrodes, assuming that the *NHO intermediate would lead to NH₂OH and NH₃, while the *NOH intermediate could lead to N₂ evolution. Consistent with experimental results, ΔG_{*NOH} was found to be more thermodynamically favourable on Zn(101) than on the other electrodes. Given the high exergonicity of *NOH and *NHO formation (−0.95 and −1.77 eV, respectively) on Zn(101), it was hypothesised that *NO could be reduced to either intermediate, and their formation

would be irreversible. After the reduction of $^*\text{NOH}$ to $^*\text{N}$ on $\text{Zn}(101)$, N–N coupling was thermodynamically favourable by 1.39 eV over hydrogenation to $^*\text{NH}$, which would lead to NH_3 production. This finding was coherent with the competitive N_2 formation observed experimentally, achieving a FE of *ca.* 35% at 100 mA/cm², compared to a total of *ca.* 20% for oxime and NH_3 release (**Figure 6.2**).

On the $\text{Zn}_{93}\text{Cu}_7(101)$ and $\text{Cu}(111)$ surfaces, the $\Delta G_{^*\text{NOH}}$ values (0.11 and 0.17 eV, respectively) were consistent with a thermodynamically reversible process. Thus, the formation of $^*\text{NOH}$ on these two metals would not necessarily imply reduction to the $^*\text{N}$ intermediate. This finding was in agreement with the higher NH_2OH and NH_3 production observed experimentally on $\text{Zn}_{93}\text{Cu}_7$ and Cu compared to Zn . Specifically, they featured cumulative FEs for NH_2OH and NH_3 of 70% and 85% at 100 mA/cm², respectively, compared to 15% and 5% towards nitrogen (**Figure 6.2**). Nonetheless, the NO_3RR route proceeding through the $^*\text{NOH}$ intermediate cannot be discarded on $\text{Zn}_{93}\text{Cu}_7$ and Cu based solely on the small $\Delta G_{^*\text{NOH}}$ value. Future studies could compare the energies of $^*\text{N}$ formation and the reversible reaction to $^*\text{NO}$ on these electrodes, as well as the energy barriers for N–N coupling and $^*\text{N}$ hydrogenation to $^*\text{NH}$ and ultimately NH_3 .

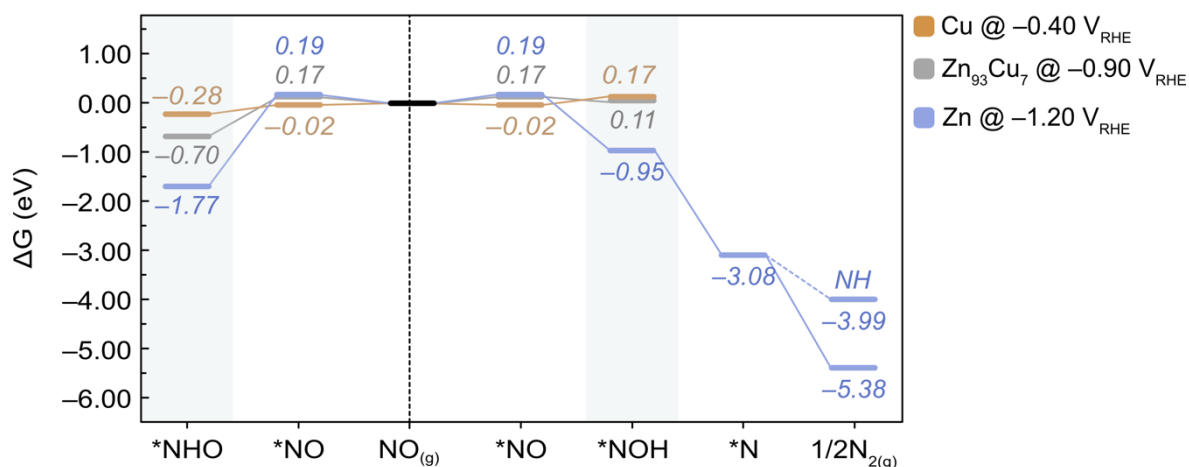


Figure 6.10 Gibbs energy profile for the competing NO_3RR pathways to $^*\text{HNO}$ and N_2 on $p(4\times 4)\text{-Cu}(111)$, $p(2\times 4)\text{-Zn}(101)$, and $p(2\times 4)\text{-Zn}_{93}\text{Cu}_7(101)$ supercells at -0.40 , -0.90 , and -1.20 V_{RHE}, respectively.

6.5 Conclusions

The NO₃RR holds significant potential for converting NO₃⁻, an ubiquitous groundwater pollutant, into chemicals such as NH₂OH. NH₂OH readily reacts with ketones, facilitating the synthesis of oximes, which are important in various industrial applications. However, the selectivity of the NO₃RR is challenged by multiple reaction pathways that can lead to a wide range of products, including NO₂⁻/HNO₂, N₂O, NO, NH₂OH, N₂H₄, and N₂.

In this study, the conversion of NO₃⁻ to NH₂OH was investigated using Zn, Cu, and Zn₉₃Cu₇ alloy electrodes, with the goal of synthesising cyclohexanone oxime through nucleophilic substitution in solution after NH₂OH desorption from the catalyst. Experimentally, the highest oxime production was achieved with a Zn₉₃Cu₇ alloy, whereas Cu predominantly yielded NH₃, and Zn produced a mixture of oxime, NH₃, and N₂, with the latter being the dominant product. The theoretical investigation of the NO₃RR mechanism indicated that NH₃ formation is thermodynamically favoured on all metal electrodes. However, on Zn, the kinetics of *NH₂OH hydrogenation to *NH₂ were found to be sluggish. Thus, NH₂OH desorption was more likely to occur at room temperature than further conversion to NH₃. On Zn₉₃Cu₇ and Cu, the $\Delta G^\ddagger$ values were consistent with *NH₂OH hydrogenation, which aligned with their higher NH₃ production. Nonetheless, the exergonic desorption of NH₂OH from the Zn₉₃Cu₇ surface was identified as a key factor for its higher oxime yield.

Regarding N₂ evolution, literature reports indicate that this process involves two consecutive hydrogenations of the *NO intermediate at the oxygen, releasing water, followed by N–N coupling. Although *NO hydrogenation at the nitrogen was preferred on all the studied surfaces, both processes were exergonic. Specifically, the formation of the *NOH intermediate was most favoured on Zn and thermodynamically reversible only on Zn₉₃Cu₇ and Cu. This finding is consistent with the higher N₂ production observed experimentally with Zn. Future studies could investigate further the kinetics of N–N coupling compared to *N hydrogenation on the three metal electrodes.

In summary, while no single descriptor fully explained the complex interplay of products for the NO₃RR on Cu, Zn, and Zn₉₃Cu₇, some key intermediates were identified as crucial for selectivity. Specifically, the NH₂OH desorption energy and the energy barrier for its hydrogenation dominated the competition between oxime and NH₃ formation, while the difference between the energies of *NOH and *NHO was suggested as a good indicator for the prevalence of N₂ evolution versus products hydrogenated at the nitrogen.

7. Conclusions and future work

The scientific community is actively working to address the climate crisis by transforming existing pollutants into valuable feedstocks and developing technologies that minimise further emissions. Heterogeneous catalysis offers several advantages in this regard, including ease of catalyst separation and recovery, reduction in chemical waste through the use of aqueous electrolytes, replacement of organometallic catalysts with solid materials, and the use of green energy sources such as sunlight and potentially renewable electricity. However, the discovery of new catalysts is hindered by the difficulty of identifying active sites on heterogeneous surfaces, which exhibit dynamic behaviour, complex chemoselectivities, and the competing HER. To overcome these challenges, experiments and theoretical studies must be combined to establish a clear link between catalyst structure and performance, paving the way for the rational design of more efficient materials.

In this thesis, three heterogeneous reactions were explored. First, the photoreduction of CO₂ to CO was investigated on ZnSe QDs functionalised with DT ligands of varying lengths, with and without the Ni(cycP) cocatalyst, in collaboration with the group of Prof. Reisner. The experimental and computational findings revealed that HER was suppressed when the DT ligands, which preferentially bind bidentately to Zn²⁺ ions, occupied these sites. Additionally, the CO₂RR was enhanced on the ZnSe | EDT system, where the ligand adopted a monodentate binding mode and formed a hydrogen bond with the activated *CO₂⁻. In contrast, the chain of HexDT and OctDT proved too long to this purpose. The addition of the Ni(cycP) cocatalyst further improved the performance of the ZnSe | DT systems, with the most endergonic intermediate, *COOH, being stabilised most effectively via a hydrogen bond with a monodentate HexDT ligand.

Overall, this study suggests that optimal ligands for photochemical CO₂RR should be hydrogen bond donors of appropriate chain length that preferentially anchor to HER active sites. Future research could focus on engineering the DT ligands to promote monodentate binding, possibly by introducing small functional groups that inhibit bidentate adsorption.

The second reaction investigated was the electroreduction of AP to APH₂ on Ag, Au, Cu, In, Ni, and Pt metal electrodes, in collaboration with the group of Prof. Reisner. Although alkaline electrolytes are known to suppress HER, they may also hinder the ability of organic substrates to hydrolyse H₂O. This study showed that, in such scenario, the cathode must dissociate H₂O and retain the reduced *H atoms, which are then transferred to the reactant in the ECH reaction. In agreement with experiments, metals with slightly endergonic (Ag,

Au) and moderately exergonic (Cu) $^*H$ binding energies displayed favourable energy profiles for AP electroreduction. However, the preferential binding of AP over H_2O on Ag and Au impaired H_2O dissociation, thus reducing the availability of surface $^*H$ atoms and lowering the ECH activity compared to Cu. Metals with strongly endergonic (In) or exergonic (Ni, Pt) $^*H$ binding instead performed poorly due to insufficient $^*H$ atoms on the cathode surface or high energy costs for yielding them to AP, respectively. In addition, the dense $^*H$ coverage of Pt and its low kinetic barrier for H–H coupling promoted HER via the Tafel mechanism.

Overall, this study complements experimental reports of the non-innocent role of electrode surface coverages, and highlights that an optimal cathode under alkaline conditions should promote H_2O hydrolysis at the working pH and retain $^*H$ atoms with moderate binding strength and coverage density. To comply with this condition, the cathode should exhibit a comparable affinity for the binding of H_2O and organic substrate, ensuring that both species can access the electrode surface. Based on these results, future studies could aim at modelling the interface between H_2O and the electrode using molecular dynamics simulations to better capture the competition between AP and H_2O adsorption under operating conditions. Additionally, expanding the metal library and substrate scope could further support the importance of moderate $^*H$ coverages in ECH reactions using alkaline electrolytes.

Finally, the electrochemical NO_3RR to cyclohexanone oxime was studied on Cu, Zn, and $Zn_{1-x}Cu_x$ metal electrodes, in collaboration with the group of Dr. Li. Cu primarily yielded NH_3 , while Zn produced a mixture of N_2 , NH_3 , and oxime (in decreasing order), and the $Zn_{93}Cu_7$ alloy generated the highest oxime yield, although NH_3 remained the dominating product. Mechanistic studies revealed that the reaction selectivity was initially determined by the hydrogenation of $^*NO$ at either the oxygen or nitrogen atom, with the former leading to N_2 (Zn) and the latter to NH_2OH and NH_3 (Cu, Zn, and $Zn_{93}Cu_7$). The balance between NH_2OH release in solution for oxime production and its further hydrogenation to NH_3 was instead found to depend on its desorption energy and reduction kinetics. Accordingly, Cu and $Zn_{93}Cu_7$ displayed a moderate kinetic barrier, allowing for NH_3 formation. On $Zn_{93}Cu_7$, however, the exergonic character of NH_2OH desorption contributed to oxime formation. In contrast, the higher energy barrier of Zn towards NH_3 production explained the presence of the oxime despite the slightly endergonic NH_2OH desorption.

In summary, this work contributes to the development of electrocatalysts for one-pot NH_2OH conversion, extending the valorisation of NO_3^- to a broader range of chemicals. Based on these findings, promising catalyst candidates should hydrogenate $^*NO$ at the nitrogen rather

than the oxygen atom, bind NH_2OH weakly, and exhibit a high kinetic barrier for its further hydrogenation.

In conclusion, this thesis demonstrates the powerful role of computational chemistry in elucidating experimental findings and providing insights for the design of more efficient cathode materials. The work presented here not only enhances our understanding of key catalytic processes, but also suggests future directions for research aimed at improving catalyst performance.

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Tuning the local chemical environment of ZnSe quantum dots with dithiols towards photocatalytic CO₂ reduction†

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Sunlight-driven CO₂ reduction to renewable fuels is a promising strategy towards a closed carbon cycle in a circular economy. For that purpose, colloidal quantum dots (QDs) have emerged as a versatile light absorber platform that offers many possibilities for surface modification strategies. Considerable attention has been focused on tailoring the local chemical environment of the catalytic site for CO₂ reduction with chemical functionalities ranging from amino acids to amines, imidazolium, pyridines, and others. Here we show that dithiols, a class of organic compounds previously unexplored in the context of CO₂ reduction, can enhance photocatalytic CO₂ reduction on ZnSe QDs. A short dithiol (1,2-ethanedithiol) activates the QD surface for CO₂ reduction accompanied by a suppression of the competing H₂ evolution reaction. In contrast, in the presence of an immobilized Ni(cyclam) co-catalyst, a longer dithiol (1,6-hexanedithiol) accelerates CO₂ reduction. ¹H-NMR spectroscopy studies of the dithiol-QD surface interactions reveal a strong affinity of the dithiols for the QD surface accompanied by a solvation sphere governed by hydrophobic interactions. Control experiments with a series of dithiol analogues (monothiol, mercaptoalcohol) render the hydrophobic chemical environment unlikely as the sole contribution of the enhancement of CO₂ reduction. Density functional theory (DFT) calculations provide a framework to rationalize the observed dithiol length dependent activity through the analysis of the non-covalent interactions between the dangling thiol moiety and the CO₂ reduction intermediates at the catalytic site. This work therefore introduces dithiol capping ligands as a straightforward means to enhance CO₂ reduction catalysis on both bare and co-catalyst modified QDs by engineering the particle's chemical environment.

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Introduction

Converting CO₂ into renewable fuels driven by solar light can contribute to alleviating the global dependence on fossil fuels.^{1,2} Colloidal quantum dots (QDs) have emerged during the last decade as light absorbers for the photocatalytic H₂ evolution reaction (HER)³ and CO₂ reduction reaction (CO₂RR).⁴ Molecular co-catalysts based on transition metal complexes are often employed in combination with colloidal QDs to facilitate the kinetically challenging multi-electron CO₂RR,^{5–7} but approaches

without an additional co-catalyst are also known and include hetero-atom doping⁸ or surface modification strategies.^{9,10} ZnSe QDs are thereby well suited because their direct band gap of 2.7 eV enables absorption of near-UV and visible light while the conduction band is located at −1.4 V (vs. NHE at pH 5.5),¹¹ which is sufficiently reductive to enable CO₂ photoreduction using molecular co-catalysts or the QD surface itself.

Approaches that go beyond the intrinsic optimization of the catalytic site and expand into the secondary coordination sphere to stabilize reaction intermediates are increasingly governing the design of CO₂ reduction electro- and photocatalysts.^{12,13} A plethora of chemical functionalities have been reported to influence the interfacial CO₂RR stretching from amino acids¹⁴ to imidazolium groups,^{15–17} amines,^{18,19} pyridines,²⁰ as well as *N*-heterocyclic carbenes²¹ and *N*-arylpyridinium salts.²² Furthermore, capping ligands with a dangling alkyl chain were employed as surface modifiers to introduce a hydrophobic environment to trap CO₂ and allow a higher substrate concentration at the catalytic site.²³ Thiols are a commonly used anchoring group amongst capping ligands

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due to the strong affinity of the thiol to soft metal surface sites and can be used to introduce a dangling chemical functionality in proximity to the colloidal nanocrystals.²⁴ Dithiols feature two thiol groups and have been explored as nanocrystal capping, multidentate anchors with a stronger affinity compared to monodentate thiols,^{25,26} cross-linking agents,²⁷ and as hole quenchers,²⁸ but they remain unexplored in the field of CO₂RR.

Inspired by our previous work^{7,17} that the surface of ZnSe QDs can be tailored towards the CO₂RR by surface-modification with an imidazolium moiety, we herein show that dithiols can influence interfacial CO₂ photoreduction facilitated by ZnSe QDs (Fig. 1). The dithiol-QD interactions are examined systematically by ¹H-NMR spectroscopy and dynamic light scattering, which reveal a solvation sphere dominated by hydrophobic interactions involving the dithiols. Under photo-reduction conditions, the presence of short dithiols promotes CO₂RR on the unfunctionalized ZnSe QDs while the presence of a long dithiol improves CO₂RR when a molecular co-catalyst is used as the main catalytic site. A systematic survey of dithiols and mercaptoalcohol/monothiol analogues shows that the second thiol moiety is essential for the observed effects. Finally, DFT calculations shed light on the length-dependent activity enhancement of the dithiols in the presence and absence of the molecular co-catalyst.

Results and discussion

Synthesis and characterization of ZnSe QDs

ZnSe QDs were prepared as reported previously⁷ by heating zinc stearate and selenium in octadecene to 300 °C followed by reactive ligand stripping²⁹ using Me₃OBF₄ to replace stearate by weakly coordinating BF₄[−] anions (ZnSe-BF₄, see Fig. S1† and ESI† for full characterization) from the surface. Transmission electron microscopy (TEM) shows highly crystalline, pseudo-spherical particles with a diameter of 4.5 ± 0.7 nm. The particles feature a strong visible-light response with a first excitonic

absorption maximum at 416 nm, determined by UV-vis spectroscopy. Powder X-ray diffraction confirms a zinc blende crystal structure accompanied by broadening due to nanostructuring.

Photocatalytic CO₂ reduction

The influence of dithiols on photocatalytic CO₂ to CO reduction was systematically studied with two well-established systems based on ZnSe-BF₄ QDs.^{7,17} More specifically, photocatalytic CO₂RR was investigated on a bare ZnSe surface with and without the presence of an immobilized molecular co-catalyst, *i.e.* phosphonic-acid functionalized Ni-cyclam Ni(cycP).³⁰ A range of alkanedithiol capping ligands with increasing length (2–8 carbons) separating the two thiol groups (1,2-ethanedithiol (EDT), 1,4-butanedithiol (BuDT), 1,6-hexanedithiol (HexDT) and 1,8-octanedithiol (OctDT)) were employed. The photocatalytic performance was investigated in an aqueous ascorbic acid (AA) solution (3 mL, 0.1 M) under a constant flow of CO₂ (4 sccm) using automated in-line gas chromatography by irradiating the samples with UV-filtered simulated solar light ($\lambda > 400$ nm, AM 1.5 G, 100 mW cm^{−2}; see ESI† for details). Unexpectedly, we find that the dithiols can activate the bare ZnSe-BF₄ for enhanced CO₂RR at conditions similar to the previously optimized system¹⁷ with a strong dependence on the dithiol length (black trace in Fig. 2 and Table S1†). After 10 h irradiation, a short dithiol (EDT, length (thiol-to-thiol) *ca.* 4.3 Å, molar ratio 100 mol_{dithiol} per mol_{QD}) enhances CO₂RR activity from 0.15 ± 0.03 μmol CO (unfunctionalized) to 0.94 ± 0.19 μmol, whereas longer dithiols (BuDT, HexDT, OctDT, length > 6.8 Å) exhibit a much less distinct effect (CO activity between 0.14 to 0.46 μmol) at a similar loading. In addition, we observe that all the dithiol ligands studied herein inhibit HER significantly without a strong dependence on the dithiol length, leading to enhanced CO-selectivities (Table S1†).

Next, we studied the influence of the same set of dithiols in the presence of the molecular co-catalyst Ni(cycP). While in this case the bare QD surface may still facilitate some CO₂RR, the 5-fold increase in CO₂ reduction activity is due to the more efficient molecular catalyst, which acts as the main site for CO₂RR. In these experiments, the dithiol loading was lowered from 100 to 50 equiv. (mol_{dithiol} per mol_{QD}) to allow sufficient space for the molecular catalyst (20 equiv. (mol_{Ni(cycP)} per mol_{QD})) and the pH was decreased to 5.5, which was found optimal for ZnSe|Ni(cycP).⁷ Interestingly, the CO₂RR performance of the hybrid QD-co-catalyst (ZnSe|Ni(cycP)) exhibits a dependence on the employed dithiol. However, unlike the system in the absence of Ni(cycP), the optimum dithiol length for the hybrid QD-co-catalyst is between four and six carbon centers (length from 6.8 Å to 9.3 Å), with a short dithiol such as EDT showing no enhancement in CO production (red trace in Fig. 2). Under optimized conditions, ZnSe|Ni(cycP)|HexDT yields 4.05 ± 0.25 μmol CO, a four-fold enhancement compared to the dithiol-free ZnSe|Ni(cycP), which produces 1.09 ± 0.18 μmol CO. Experiments also reveal that increasing the dithiol length has a nearly linear effect in suppressing HER for ZnSe|Ni(cycP) (Fig. 2A). The reason for the overall higher HER activity in the presence of Ni(cycP) is likely related to (i) the lower dithiol loading (50 equiv.

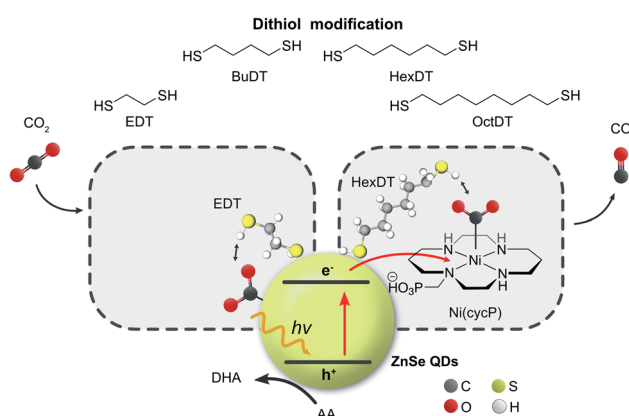


Fig. 1 Schematic representation of the photocatalyst system consisting of ligand-free ZnSe-BF₄ QDs (yellow sphere, BF₄[−] omitted for clarity) modified with dithiols of various lengths for visible light-driven CO₂ to CO reduction in either the absence or presence of a molecular co-catalyst Ni(cycP). Ascorbic acid (AA) is used as the sacrificial electron donor. DHA: dehydroascorbic acid.

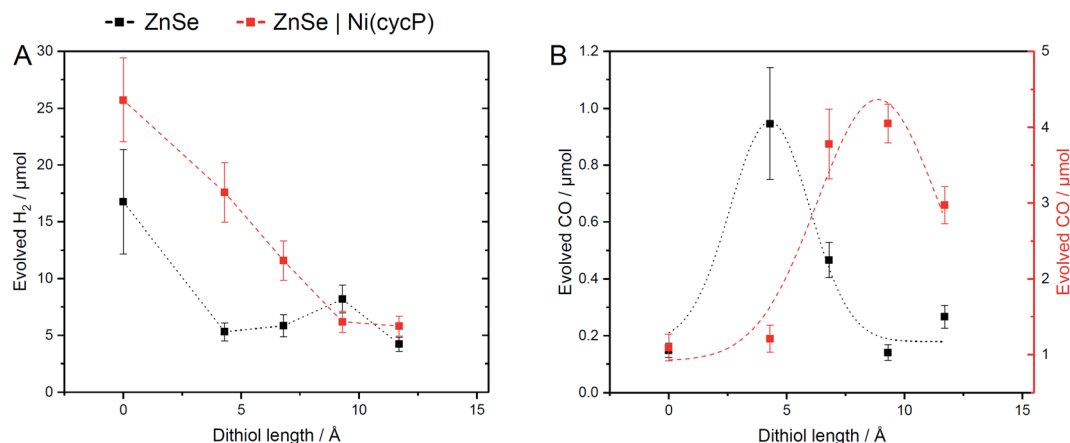


Fig. 2 Influence of dithiol ligands on photocatalytic CO₂RR using ZnSe-BF₄ QDs. The details of the structure and length of the employed dithiols are provided in Table 1 and Fig. 1. (A) Evolved H₂ and (B) evolved CO. Conditions: ZnSe|dithiol: 50 μM dithiol, pH 6.5; ZnSe|Ni(cycP)|dithiol: 25 μM dithiol, 10 μM Ni(cycP), pH 5.5. General conditions: AM 1.5 G, $\lambda > 400$ nm, 100 mW cm⁻², 10 h irradiation, 0.5 μM ZnSe-BF₄, 0.1 M AA/NaHCO₃, CO₂ constant flow (4 sccm), 25 °C. The dashed lines serve to guide the eye. The full photocatalysis dataset can be found in Fig. S2 and S3.†

vs. 100 equiv. without Ni(cycP)) and (ii) the more acidic pH of 5.5 which renders HER more feasible.

The origin of the evolved CO from CO₂ was confirmed *via* ¹³C-isotopic labelling for the best-performing cases (ZnSe|EDT and ZnSe|Ni(cycP)|HexDT), by running a photocatalytic experiment under an atmosphere of ¹³CO₂ and analyzing the head-space after reaction *via* FTIR spectroscopy. The change in reduced mass for ¹³C causes the vibration associated with CO to be shifted from 2142 cm⁻¹ (¹²CO) to 2095 cm⁻¹ (¹³CO; Fig. S4†), which confirms its assignment as ¹³CO.³¹ This observation demonstrates that all the evolved CO originates from CO₂ and no other carbon sources contribute towards the detected reaction product. Furthermore, no other gaseous or liquid products were found, and no products were evolved in the absence of electron donor, QDs or light, indicating that all components are required for photocatalytic CO₂RR (Table S2†). The control experiment of ZnSe|dithiol, in the absence of AA, which does not lead to any activity, supports that dithiols do not act as sacrificial electron donors for this particular photocatalyst, despite previous reports that have shown that thiols can act as hole quenchers for other QD-based photocatalysts.²⁸

The influence of the marginally different pH and the dithiol loadings employed for both systems (pH 6.5 for ZnSe|dithiol and pH 5.5 for ZnSe|Ni(cycP)|dithiol) was also excluded as the origin of the changes observed in product selectivity. In particular, when the pH is reversed (pH 5.5 for ZnSe|dithiol and pH 6.5 for ZnSe|Ni(cycP)|dithiol), CO production is significantly lower than at the optimal pH conditions, although trends are retained and EDT exhibits the higher activity in the absence of Ni(cycP), while HexDT in the presence of Ni(cycP) (Fig. S5 and Table S3†). When the dithiol loadings are reversed (ZnSe|dithiol at 50 equiv. mol_{dithiol} per mol_{QD}) we observe increased HER compared to the optimized conditions and CO formation still peaks with EDT, demonstrating that the changes in product selectivity are not caused by the dithiol loading (Fig. S6†). Increasing the dithiol loading to 100 equiv. in the presence of Ni(cycP) was omitted as

the ligand would presumably displace the co-catalyst on the QD surface and lead to lower CO yields, as previously observed with an amine-containing thiol capping ligand.⁷

Dithiol-QD interactions

To rationalize the influence of the dithiols on the CO₂RR, the interaction between the different dithiols and the ligand-free ZnSe-BF₄ QDs were studied in aqueous solution by liquid-phase ¹H-NMR spectroscopy. The binding of molecules onto the particle surface is reflected in significant broadening of the signals originating from protons near the nanocrystal surface due to their slow and nonuniform tumbling.^{17,32–36} These experiments involved the stepwise addition of defined quantities of dithiol (25, 50, 75, 100, and 200 equiv. (mol_{dithiol} per mol_{QD}) per injection, in acetonitrile-d₃) to a suspension of ZnSe-BF₄ QDs in D₂O, leading to the results depicted in Fig. 3. We observe that for quantities of EDT ≤ 100 equiv. per ZnSe-BF₄ QD, the signals associated to this ligand essentially vanish, which suggests a strong binding affinity of EDT to the QD surface. Only after the addition of 200 equiv. of ligand, a proton signal for bulk EDT appears, which can be assigned to its accumulation in solution. Hence, we conclude that the QD surface can accommodate at least 100 strongly interacting EDT ligands.

On the other hand, signals assigned to BuDT arise in solution from ≥50 equiv. per QD, indicating a lower loading capacity of the QD surface compared to EDT (Fig. 3A). A similar observation is found for HexDT, which may be rationalized by the longer chain length of the two ligands compared to the shorter EDT. It is notable that the ligand signals are significantly broadened in the presence of the QDs compared to a reference spectrum in D₂O (see below for interpretation). The degree of broadening increases from BuDT to HexDT indicated by the lack of fine structure of the NMR signals, which is most notable for HexDT protons from methylene groups located in the central part of the molecule, denoted as (c) in Fig. 3A.



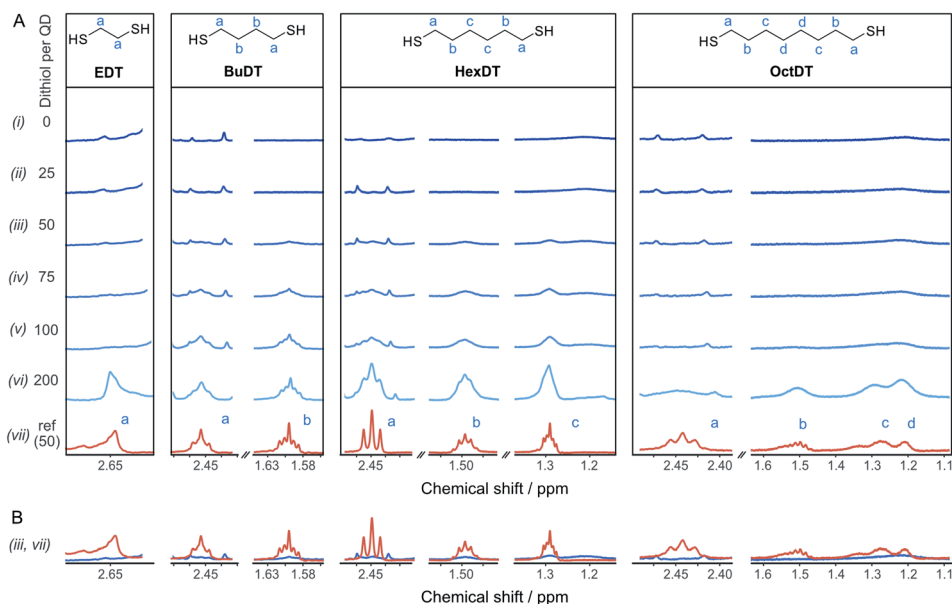


Fig. 3 Interactions of dithiols with ZnSe-QDs. (A) ¹H-NMR spectroscopy titration experiment with aliquots of dithiol (in acetonitrile-*d*₃) being added to a suspension of 2 μM ZnSe-BF₄ QDs in D₂O. Intensities are not to scale (in-between ligands) and were adjusted for optimal visibility. The spectra were referenced to the residual acetonitrile signal at 1.94 ppm. (B) Overlay of spectra (iii and vii) of the reference ligand spectrum (100 μM) in the absence (orange) and presence of ZnSe (2 μM, blue), respectively, indicating significant suppression and broadening of the ligand signals in the presence of the QD.

An overlay of the ligand signal at 100 μM (equivalent to the concentration of 50 ligands per QD) in the absence of QDs allows to assess the reduced signal intensity due to interactions of the ligands with the QDs (Fig. 3B). Proton signals assigned to an OctDT reference spectrum (in D₂O) appear at ~100 to 200 equiv. per QD. However, the signals at 1.2–1.3 ppm assigned to the central protons, denoted as (c) and (d) in Fig. 3A, appear at lower molar ratios but overlap with residual solvent signal already present in the QD solution and additionally exhibit strong broadening.

Further in-depth analysis of the ¹H-NMR spectroscopy titration experiments was performed by integrating the ligand signals (Fig. S7†). BuDT and HexDT follow a near linear increase from 25 to 200 equiv. per QD, whereas OctDT exhibits lower signal intensities overall, which vary depending on the proton signal. For this latter ligand, a very strong increase in intensity is notable from 100 to 200 equiv. per QD for the protons located at the center of the molecule (signal (d), Fig. 3A), which coincides with a substantial broadening of the signals.

The results from the NMR titration experiments suggest the existence of three QD-ligand interaction regimes. In the first regime, the ligands interact very strongly with the QD surface presumably due to covalent binding/H-bonding to the QD surface. Within this regime, the influence of the QD surface on the tumbling of the protons is so strong that the NMR signals essentially vanish.^{35,36} All dithiols tested here show this behavior for dithiol concentrations of ≤25 equiv. per QD, similarly to the previously reported ligand 3-(2-mercaptoethyl)-1-methyl-imidazolium (MEMI).¹⁷ In the second regime, the signals associated with the ligands are detectable by NMR but are broadened. This broadening indicates that the ligands are in close

vicinity of the QD surface which leads to an anisotropic chemical environment for the protons that causes the peaks to broaden – essentially caused by a superposition of many slightly shifted peaks.^{35,36} This broadening increases in the order BuDT < HexDT < OctDT with increasing dithiol hydrophobicity and length. Hence, this regime may be described as a solvation sphere in which weakly interacting ligands accumulate due to hydrophobic interactions with each other and is detectable for BuDT/HexDT/OctDT from >25 equiv. per QD. The strong broadening in the case of OctDT likely causes the overall lower signal intensities because it stretches out over a larger range of chemical shifts, preventing an accurate signal integration. In addition, the lack of well-resolved signals characteristic for ligands in solution at lower loadings (<200 equiv. per QD) may be promoted by the relatively low solubility of the dithiols in an aqueous environment, which leads to their assembly at the QD interfaces through the hydrophobic effect. Furthermore, the intensities of different protons signals of BuDT and HexDT from ≥50 equiv. per QD are nearly identical, indicating that all protons interact within the solvation sphere equally and no orientation is preferred. Finally, in the third regime, ligands accumulate in the bulk solution as evidenced by the sharp signals, which resemble the reference spectrum in the absence of QDs.

Analogues of alkanedithiols

A series of analogous ligands were studied to explore if (i) the second thiol group is a prerequisite to the enhancement effect and (ii) if this can be explained by the hydrophobic environment introduced through the dithiols. In particular, benzene-1,4-

dithiol (BenzDT, length ~ 6.4 Å) was chosen as rigid analogue to study if the flexibility of the dithiol ligand is a prerequisite for the enhanced CO activity. While BuDT has a similar length of ~ 6.8 Å and exhibits a significant impact on photocatalytic CO₂RR in the presence and absence of Ni(cycP), BenzDT suppresses HER but only marginally increases CO production, supporting that the flexibility of the dithiol is necessary for the observed enhancement effect in CO₂RR activity (Fig. 4 and Table S1†). Next, we benchmarked the dithiols against its mercaptoalcohol analogues exhibiting a comparable thiol to hydroxy length to elucidate whether the terminal hydroxy group has any effect. Indeed, ZnSe|1,2-mercaptoethanol (HO-EtSH) enhances CO formation (0.56 ± 0.06 μmol) compared to unfunctionalized ZnSe-BF₄, and approx. half activity compared to ZnSe|EDT (Fig. 4A and B), but surprisingly, HER is only marginally affected and comparable to unfunctionalized ZnSe-BF₄. A similar observation was found for ZnSe|Ni(cycP)|1,6-mercaptohexanol (HO-HexSH), which enhances CO evolution notably but does not suppress HER activity (Fig. 4C and D). In the case of monothiols (1-butanethiol (BuSH), 1-hexanethiol (HexSH)), we found that they do not affect the product selectivity compared to unfunctionalized ZnSe-BF₄ and both HER and CO reduction remain unaffected (Fig. 4).

NMR titration experiments were also extended to the selected analogues of dithiol ligands comprised of only one thiol (monothiol) as well as mercaptoalcohols. HexSH and HO-HexSH were chosen as representatives with six carbon centers and with a comparable length to HexDT. Protons assigned to HO-HexSH are detectable from ≥ 25 equiv. per QD and increase

linearly until 200 equiv. per QD (Fig. S7 and S8†). This finding suggests a weaker affinity for the QD surface compared to HexDT, presumably due to the inability to bind *via* both thiols and the increased hydrophilicity introduced through the hydroxy group. In fact, the NMR peak shape remains well-resolved, suggesting accumulation of ligands in the bulk solution (third regime). The weaker binding of HO-HexSH as compared to dithiols may explain why HER is not as sufficiently suppressed, as reported during photocatalytic CO₂RR (see above). In contrast, the monothiol equivalent, HexSH, features five distinct signals which appear to various degrees from ≥ 25 equiv. per QD (Fig. S7 and S8†). Interestingly, terminal protons in closer vicinity to the thiol group (signals denoted as (a), (b), (c) in Fig. S8†) appear later in the ¹H-NMR spectra (*i.e.*, >100 equiv.) at lower intensities compared to the protons towards the other end of the molecule (signals (d), (e), (f) in Fig. S7 and S8†). This observation confirms that the thiol indeed prefers a conformation with the thiol pointing towards the QD surface. In addition, all signals show distinct broadening similar to that observed for HexDT and OctDT, which increased in accordance with increased hydrophobic character of the dithiol ligands (Fig. 3).

The data from all described ¹H-NMR titration experiments support the following types of interactions between the studied ligands and the QD interfaces, clearly showing the differences between mono- and dithiol systems (Fig. 5 and Table 1): the overall lower dynamics of the dithiols in comparison with monothiols suggests that both dithiol -SH groups are involved in the interactions with QDs. This is corroborated by the lower

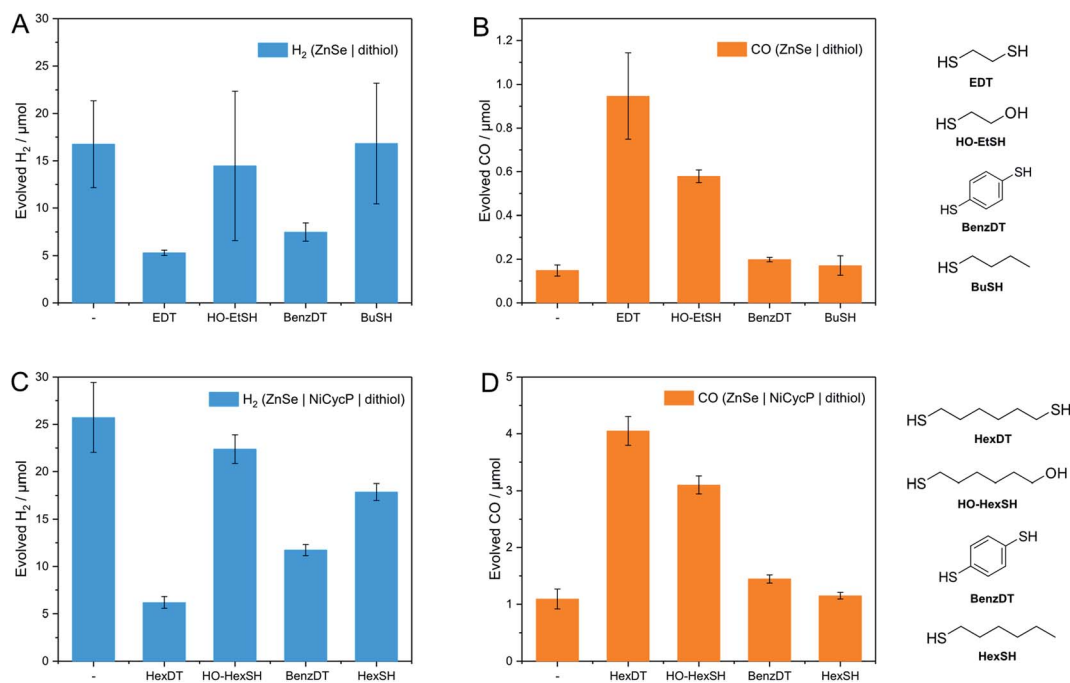


Fig. 4 Benchmarking of dithiols with analogous ligands for photocatalytic CO₂RR. (A and B) Evolved H₂ and CO in the absence of a co-catalyst: ZnSe|ligand (benchmark EDT) 50 μM ligand, pH 6.5. (C and D) Evolved H₂ and CO in the presence of a co-catalyst: ZnSe|Ni(cycP)|ligand: (benchmark HexDT) 25 μM dithiol, 10 μM Ni(cycP), pH 5.5. General conditions: AM 1.5G, $\lambda > 400$ nm, 100 mW cm⁻², 10 h irradiation, 0.5 μM ZnSe-BF₄, 0.1 M AA/NaHCO₃, CO₂ constant flow (4 sccm), 25 °C.

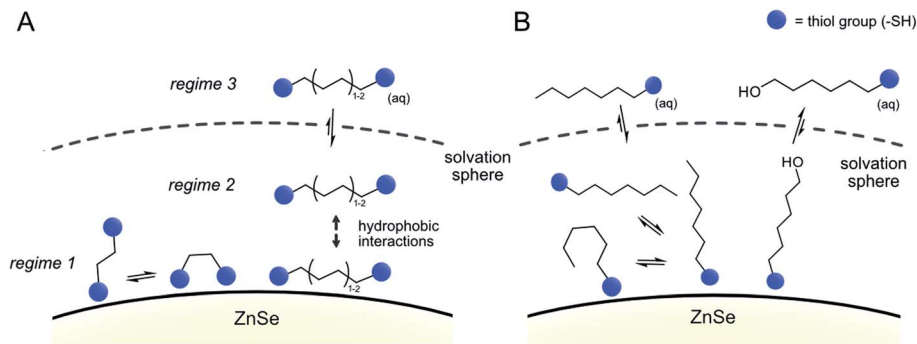


Fig. 5 Proposed binding modes of dithiol ligands on the surface of ZnSe QDs. (A) Dithiols and (B) monothiols and mercaptoalcohols.

Table 1 Summary of interactions of dithiols (and analogues) with ZnSe QDs

Ligand	Class	Length ^a /Å	No. of strongly interacting ligands
EDT	Dithiol	4.3	100
BuDT	Dithiol	6.8	25–50
HexDT	Dithiol	9.3	25–50
OctDT	Dithiol	11.7	50–100
HexSH	Monothiol	~9	25–50
HO-HexSH	Mercaptoalcohol	9.3	<25

^a Estimated by measuring the distance from the terminal thiol to the other end of the molecule in its stretched conformation.

capacity of the QD surface for the longer dithiols (BuDT, HexDT) than for the shorter EDT, suggesting that both –SH groups of the longer dithiols interact with QD surfaces and thereby occupy more space in a bidentate configuration rather than in a dangling/monodentate configuration. The bidentate binding mode of BuDT/HexDT is further supported by the observation that in the NMR titration experiments, the signals for all protons in the alkane backbone are increasing with equal intensities (Fig. S7A†). In contrast, for the monothiol (HexSH) the intensities of proton signals from terminal methylene and methyl groups increase faster in comparison with the signals from methylene groups located in the close proximity to the anchoring thiol, indicating that the monothiol binds in a preferred orientation with the terminal proton facing into the solution (Fig. S7B†). Note, these observations are indirect indications of a bidentate binding mode of dithiols but do not preclude the existence of a monodentate binding mode because NMR-spectroscopy is essentially *blind* towards the strongly interacting ligands in regime 1. Dithiols (C₄+) and monothiol HexSH bind to the QD surface strongly and after a saturation point accumulate within the solvation sphere and thereby introduce a significant degree of hydrophobicity on the QD interfaces. In addition, HO-HexSH interacts with the QD surface in a weaker manner when compared to dithiols and the terminal hydroxy group is likely to stretch into solution interacting with surrounding water molecules. This in turn limits the hydrophobic character of the solvation sphere of the QD/HO-

HexSH hybrid, lowering the number of interacting ligands, affecting both HER suppression and CO₂RR.

We next considered the possibility of dithiols to cross-link individual particles leading to larger aggregates, as reported previously.³⁷ Dynamic light scattering experiments suggest that all ligands employed here (dithiols, HexSH, HO-HexSH) facilitate some degree of agglomeration after saturation of the surface with strongly interacting ligands (>25 equiv. per QD), which is most significant for EDT (particles size ~250 nm) compared to unfunctionalized ZnSe–BF₄ (~10 nm) (Fig. S9A and B†). Nevertheless, we find that the presence of a large excess of AA already leads to much larger agglomerates of ~1600 nm regardless of any capping ligands (Fig. S9C†). Thus, the influence of the dithiol ligands is negligible compared to that of AA and we therefore believe that the different ligands do not result in performance differences based on aggregation during photocatalysis. In addition, dithiols were found to not affect the photophysics of the QDs, as confirmed by the recorded steady-state UV-vis absorption and photoluminescence (PL) spectra, which remain unchanged in the absence and presence of dithiols (Fig. S10†).

Discussion

The results from NMR titration experiments and DLS support that the effects observed during photocatalysis could stem from multiple physicochemical effects. Because the UV-vis/PL profiles remain unchanged in the presence of dithiols, effects on the QD steady-state photophysics are discarded. NMR experiments demonstrate that dithiols can introduce a hydrophobic environment (increasing with the dithiol length) which could regulate substrate access and may provide a favorable microenvironment for CO₂RR. Implications on the charge transfer dynamics cannot be excluded at this point and were observed for similar particle-ligand systems,³⁸ but should generally lead to lower electron transfer rates to acceptor molecules with longer ligands, which contrasts the photocatalytic results obtained in this work. The hydrophobic environment may explain a suppression of HER and enhanced CO₂RR due to a lower local water concentration and increased CO₂ concentration. However, this hypothesis fails to explain why no enhancement effect is observed for BuDT/HexDT on the



bare ZnSe surface, unless the effect is related to the lower capacity of the QDs for BuDT/HexDT. The local hydrophobic environment also falls short of rationalizing the lack of influence of monothiols (BuSH/HexSH), which do not enhance CO₂RR, even though they provide a hydrophobic environment. The fact that they also do not suppress HER is surprising. On the other hand, mercaptoalcohols enhance CO₂RR to a lesser extent than dithiols, but still significant compared to non-functionalized QDs. Their reduced capacity to suppress HER, however, is a further argument against hydrophobic effects as the sole explanation because the hydroxy group essentially removes hydrophobic interactions. Finally, particle agglomeration is considered an unlikely contribution to the observed trends, because even though all ligands tested form some aggregates (<250 nm) (in particular EDT), this is small in comparison to the effect of the electron donor AA, which leads to much larger aggregates of ~1600 nm.

Overall, the results point towards a more unique effect of the second thiol group in the local chemical environment of the CO₂RR site on the QD surface which influences both HER and CO₂RR. Hence, we turned to DFT simulations to explore if the dithiols may affect CO₂RR in the secondary coordination sphere of the catalytic site through non-covalent interactions (NCIs) with the reaction intermediates.

DFT calculations

Unveiling the nature of the interactions between the dithiol capping ligands and ZnSe QDs, as well as their influence on CO₂RR, is critical to drive the discovery of more efficient photocatalysts for this process. Experimental observations point towards the length and flexibility of dithiols as the main factors facilitating CO₂ activation and its subsequent reduction, either *via* a surface promoted mechanism, or a pathway enabled by the immobilized Ni(cycP) co-catalyst (see Fig. 1). Based on our recent findings on MEMI-functionalized ZnSe-QDs for CO₂RR,¹⁷ we posited that NCIs between the capping dithiol ligands and CO₂ might play a key role when non-binding thiol moieties are neighboring the second coordination sphere of the catalytic active site. In particular, we envisioned that the positive influence of the dithiols is maximized in the surface promoted mechanism when shorter ligands are used, as they can interact more strongly with the CO₂RR intermediates adsorbed on the QD surface. In contrast, longer-reaching ligands are deemed to be better suited to stabilize the CO₂RR intermediates in the co-catalyst promoted pathway, further away from the QD surface. To confirm these hypotheses, and assess the ability of dithiol ligands to suppress the competing HER, we carried out an exhaustive computational investigation by means of periodic DFT calculations using the Perdew–Burke–Ernzerhof (PBE) functional with Grimme's D3 dispersion corrections (see ESI† for details). To describe the bare ZnSe QD, we used the cubic ZnSe bulk structure shown in Fig. S11† to construct the 4-layer ZnSe(220) surface slab depicted in Fig. 6A (see Computational Methods in the ESI† for details), as this structure has been previously shown to accurately represent the morphology of the system.¹⁷

To shed light on the influence of the dithiols length on the surface promoted pathway, we performed DFT calculations on functionalized ZnSe(220) slab models using the surface concentrations observed in the NMR titration experiments for shorter (EDT) and longer (HexDT and OctDT) ligands (Table S4†). The lowest energy configuration for each of these systems corresponds to one EDT, HexDT and OctDT ligand adsorbed in a bidentate mode on the Zn sites of a ZnSe(220) surface with periodicities $p(1 \times 1)$, $p(3 \times 1)$ and $p(1 \times 3)$, respectively. Using the structures for the bare ZnSe and ZnSe|nDT (nDT = EDT, HexDT, OctDT) systems, we subsequently investigated their ability to activate CO₂ with and without a photogenerated electron, which is believed to be the first step in photocatalytic CO₂RR.³⁹ Interestingly, of all the studied systems, only ZnSe|EDT in the presence of a photogenerated electron was able to activate *CO₂ atop a surface Zn site (Fig. 6B, left), which was found to be the main active site for both CO₂RR and HER (see below). Note *CO₂ activation on the bare ZnSe-QDs surface, ZnSe|HexDT, and ZnSe|OctDT was not achieved, and resulted in CO₂ being released back into the gas-phase.

The switch from the bidentate to the monodentate binding mode is a prerequisite for CO₂ activation. This is in line with our calculations (Table S4†), which show that EDT requires the least energy for switching from a bidentate to a monodentate configuration (*i.e.* 0.15 eV compared to 0.42 and 0.17 eV for HexDT and OctDT, respectively). On the contrary, longer dithiols are, in general, more flexible and present less repulsion with the surface in a bidentate configuration, making the change to the monodentate mode more energetically demanding. We also note that all attempts to activate *CO₂ without the photogenerated electron resulted in CO₂ desorbing away from the surface. The NCI analysis between EDT and the activated *CO₂ (Fig. 6B, right) reveals that the stabilization of this intermediate is mainly governed by H-bonding between the thiol group and *CO₂ and a set of repulsive steric interactions that tie the CO₂ molecule to the surface. The exceptional ability of EDT to stabilize this first CO₂RR intermediate is in good agreement with experimental observations, which show a 6-fold (3.5-fold) increase in CO production with ZnSe|EDT compared to the bare surface and ZnSe|HexDT (ZnSe|OctDT).

To assess the influence of the dithiols length on the HER activity, we next modelled the Gibbs adsorption energy of a H atom on the surface of the functionalized QD systems as a descriptor for this process.^{40,41} Our calculations indicate that the remaining surface Zn atoms in the presence of a photogenerated electron are the main HER active sites, exhibiting nearly thermoneutral ΔG_H values of −0.28 eV, 0.26 eV and 0.06 eV on ZnSe|EDT, ZnSe|HexDT and ZnSe|OctDT, respectively. Hence, HER is predicted to occur on all the functionalized systems to a similar extent, in agreement with experiments (Fig. 2A). Note that the subtle differences observed in H₂ production with the various dithiols may be attributed to variabilities in their surface coverages and lengths. More specifically, small dithiols can cover the QD surface more efficiently – particularly EDT, whose length almost matches the interspacing between Zn atoms. On the other hand, longer dithiols such as HexDT and OctDT do not cover all the HER sites, although their accessibility is reduced with ligand



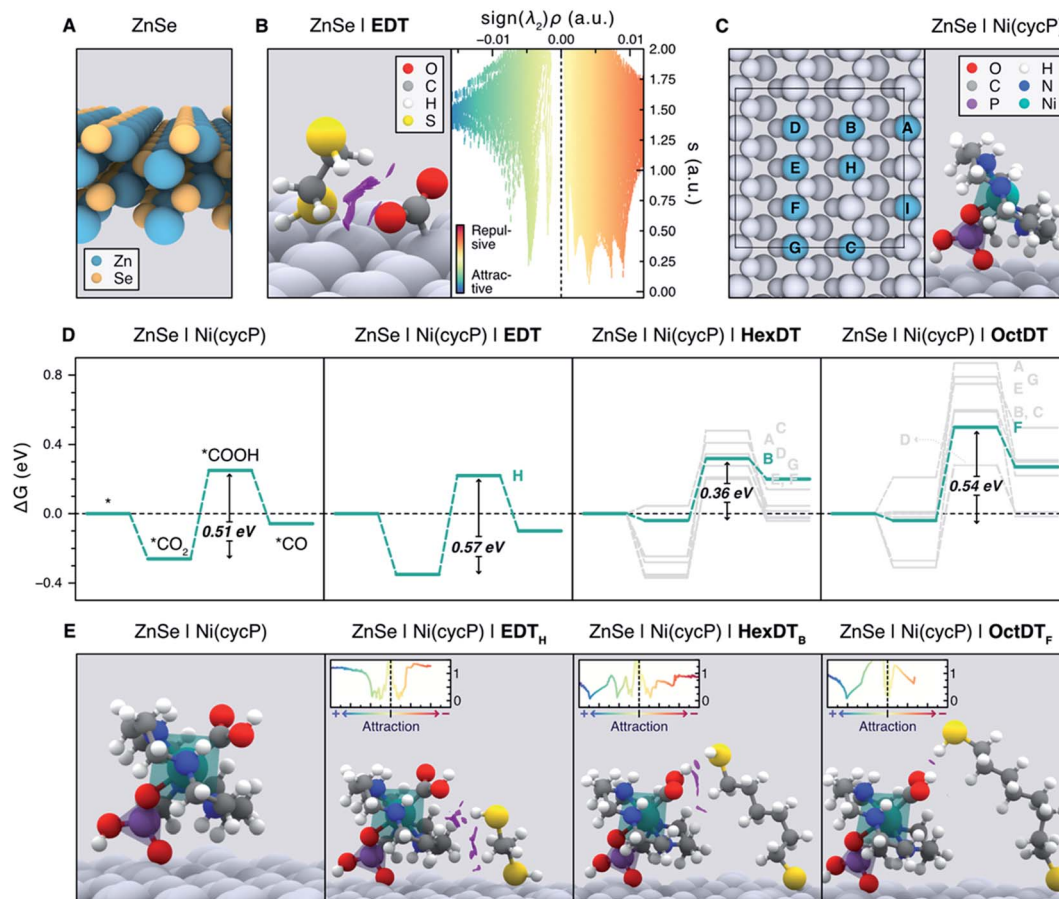


Fig. 6 (A) Side view representation of the modelled ZnSe(220) surface slab. (B) Activated ^{*}CO₂ intermediate atop a surface Zn site on ZnSe|EDT (left), displaying the non-covalent interactions (NCIs) as purple isosurfaces (isovalued = 0.4 a.u.). NCIs are represented pseudo-quantitatively on the right panel with a plot of the reduced density gradient (s) as a function of the electron density multiplied by the sign of the second eigenvalue of the Hessian matrix ($\text{sign}(\lambda_2)\rho$), which effectively displays the NCIs as distinct peaks. Colder and warmer colors depict attractive and repulsive interactions, respectively. (C) Representation of all the surface Zn sites (A–I) considered for the adsorption of Ni(cycP) and the investigated dithiols (left). Note the Ni(cycP) cocatalyst was adsorbed on the site *I* and that only the sterically accessible sites A–H were considered for ligand adsorption. The right panel depicts the side view of the ZnSe|Ni(cycP) resting state used in the mechanistic studies. (D) Gibbs energy diagrams for the CO₂RR on the bare ZnSe|Ni(cycP) and in the presence of a monodentate EDT, HexDT and OctDT ligand adsorbed on all the sterically accessible sites A–H (see labels beside the highest energy point). Gibbs energies are also provided in Table S7.† The most energetically favorable pathway for each functionalized system is highlighted in green. (E) Side view representation of the ^{*}COOH intermediate on the bare ZnSe|Ni(cycP) and the lowest-energy functionalized systems (green lines in D). NCI isosurfaces (isovalued = 0.4 a.u.) and plots (insets) are also shown. In B, C and E, surface atoms are greyed out for clarity.

length. Taken altogether, and the stronger binding of dithiols compared to H, we can rationalize the trends in HER activity observed experimentally (Fig. 2A, black trace), *i.e.* ZnSe >> ZnSe|HexDT > ZnSe|EDT $\approx$ ZnSe|OctDT.

Having elucidated the role of the dithiol ligands in the surface promoted pathway, we set out to explore their influence on the co-catalyst promoted mechanism on ZnSe|Ni(cycP) (see Fig. 1). In this case, the experimental coverage of Ni(cycP) was reproduced by modelling a *p* (3 $\times$ 2)-ZnSe(220) surface containing one co-catalyst molecule adsorbed on the surface Zn site *I* (Fig. 6C) *via* a singly deprotonated phosphonate group and two dithiol ligands, according to the experimental pH of 5.5. From this structure, all possible different configurations arising from the adsorption of two EDT, HexDT and OctDT ligands atop the remaining 8 Zn sites (sites A to H in the left panel of Fig. 6C) were considered in the presence of a photogenerated electron,

leading to a total of 1 (1), 7 (11) and 7 (6) monodentate (bidentate) configurations, respectively (see Table S5†).

The CO₂RR mechanism with a photogenerated electron was then investigated with and without the presence of capping ligands, resulting in the Gibbs energy diagrams presented in Fig. 6D. As in the surface promoted pathway, the reaction begins with the activation of CO₂, this time on the Ni center of the co-catalyst, followed by two consecutive proton-coupled electron transfer steps that yield ^{*}COOH and eventually H₂O and ^{*}CO. In the absence of dithiol ligands (ZnSe|Ni(cycP)), calculations indicate that the formation of ^{*}COOH is the only endergonic step, rendering this process as the most likely rate determining step with a Gibbs energy change of +0.51 eV. Based on this result, and the fact that CO₂ cannot be stabilized without the presence of a dithiol ligand, we conclude that ZnSe|Ni(cycP) can promote CO₂RR more efficiently, which is supported by the

7-fold increase in CO production obtained experimentally with ZnSe|Ni(cycP) compared to the bare ZnSe-QD.

When assessing the same mechanism for the different configurations with the functionalized systems, ZnSe|Ni(cycP)|nDT, we observed that the binding energies of the CO₂RR intermediates are only influenced by the presence of the mono-dentate dithiol adsorbed in the vicinity of the co-catalyst. This is because the distance between the adsorbed mono- and bidentate dithiols is *ca.* ≥ 4.0 Å (see Table S6[†]), and therefore, the presence of bidentate ligands does not affect the energetics of the reaction intermediates. Hence, we investigated the CO₂RR mechanism with only the monodentate dithiol and for those configurations wherein the non-coordinated thiol group could interact with the CO₂RR intermediates adsorbed on Ni(cycP). We note that, even though the bidentate mode is the most stable configuration for all the considered dithiols, the energy difference between this mode and the monodentate one is sufficiently small (*ca.* 0.15–0.40 eV, Table S4[†]) to consider the likely existence of a subset of monodentate ligands at room temperature. Such a subset would be difficult to detect through the NMR titration experiments conducted above. Furthermore, this monodentate configuration explains the ligand length dependence on the CO₂RR activity observed in experiments, as we describe in the following. Due to the short nature of EDT, the interaction with the coordination sphere of Ni(cycP) was only possible for the monodentate ligand on the Zn site *H* (ZnSe|Ni(cycP)|EDT_H), leading to binding energies of −0.35 eV, 0.22 eV and −0.10 eV for *CO₂, *COOH and *CO, respectively (Fig. 6D, second leftmost panel). Again, the most endergonic step was found to be the formation of *COOH with a very similar energy than that of the unfunctionalized system (0.57 vs. 0.51 eV), indicating that EDT does not influence the baseline activity of ZnSe|Ni(cycP) due to its incapacity to effectively interact with the CO₂RR intermediates in the co-catalyst promoted pathway. This was confirmed by NCI analysis, which reveals that the bulk of the interactions between EDT_H and Ni(cycP) is mainly constituted by steric effects between the hydrocarbon chain of the ligand and the base of the co-catalyst (Fig. 6E, second left panel). Therefore, the enhanced CO production observed experimentally with ZnSe|Ni(cycP)|EDT compared to ZnSe|Ni(cycP) can be attributed to the ability of EDT to favor the surface-promoted pathway, as observed in our calculations, while the decrease in HER is due to the reduced number of HER-active Zn sites available on the surface, which are covered by EDT.

For HexDT and OctDT we found a total of 7 distinct monodentate configurations that can interact with the CO₂RR intermediates on ZnSe|Ni(cycP), leading to the reaction profiles shown in the two right panels of Fig. 6D. Among these configurations, the ones exhibiting the least endergonic formation of *COOH from *CO₂ (highlighted in green) correspond to ZnSe|Ni(cycP)|HexDT_B and ZnSe|Ni(cycP)|OctDT_F, with energy changes of +0.36 and +0.54 eV, respectively. Importantly, these results indicate that HexDT has the optimal length to interact more effectively through the dangling thiol *via* H-bonding with the CO₂RR intermediates adsorbed on the co-catalyst, which reduces the energy of the most endergonic step by 0.15 eV compared to ZnSe|Ni(cycP). Indeed, NCI analysis shows that HexDT exhibits overall a set of more

favorable interactions with the *COOH intermediate compared to EDT and OctDT (Fig. 6E). We note that the latter two ligands display similar energetics than ZnSe|Ni(cycP), suggesting that EDT (OctDT) is too short (long) to efficiently interact with the CO₂RR intermediates in the co-catalyst promoted pathway.

Conclusions

In summary, we report a surface modification strategy for ZnSe QDs based on dithiols that promotes photocatalytic CO₂RR in the absence and presence of an additional molecular co-catalyst, depending on the dithiol length. The dithiol-QD interactions have been studied quantitatively using ¹H-NMR spectroscopy, allowing the determination of the number of strongly interacting ligands and revealing a solvation sphere dominated by hydrophobic interactions for the longer dithiols (C₄₊). Photocatalytic studies using ZnSe-BF₄ QDs in aqueous ascorbate solution show that EDT activates the QDs for CO₂RR accompanied by a reduction of the HER activity compared to the bare QD surface. In the presence of the molecular co-catalyst, we show that a longer dithiol such as HexDT further accelerates CO₂RR while suppressing HER. A series of control experiments employing monothiol and mercaptoalcohols render the hydrophobic effects unlikely as sole explanation of the observed changes during photocatalysis. DFT calculations provide a framework to rationalize the length dependent influence during photocatalysis, showing that EDT has the suitable length to stabilize the key *CO₂^{δ−} intermediate on the QD surface through H-bonding, promoting a surface-mediated mechanism. In contrast, the length and flexibility of HexDT allows to stabilize more efficiently the endergonic formation of *COOH on the Ni(cycP) co-catalyst. DFT calculations demonstrate that CO₂RR *via* a surface or co-catalyst-promoted pathway can be ‘switched’ on and off depending on the length of the dithiol. In addition, calculations illustrate that both CO₂RR mechanisms require the binding of the dithiol ligand in a monodentate configuration in order to stabilize the key reaction intermediates through the dangling thiol group. This explains why experiments with HO-EtSH and HO-HexSH lead to an enhanced CO₂RR activity while monothiol do not influence product selectivity as these ligands cannot stabilize the CO₂RR intermediates and do not cover efficiently the HER active sites due to their monodentate configuration. Hence, we conclude that ideal capping ligands for CO₂RR can have the ability to coordinate bidentately to the surface to block the HER active sites but should have the ability to turn monodentate to stabilize the relevant CO₂RR intermediates. In future work, we envision to expand the insights gained herein to other semiconductor systems as well as investigating polydentate ligands. Overall, this work presents dithiol capping ligands as a novel tool to manipulate photocatalytic CO₂RR and steer the product selectivity between HER and CO₂RR on colloidal nanoparticles.

Data availability

Raw data related to this article are available at <https://doi.org/10.17863/CAM.83674> (experimental data) and <https://doi.org/10.19061/iochem-bd-6-131> (computational data).



Author contributions

C. D. S., M. G.-M. and E. R. designed the project. C. D. S. prepared and characterized the ZnSe particles and conducted photocatalytic experiments. A. C. and E. M.-T. performed the DFT studies. K. S., V. B. and C. D. S. carried out NMR titration experiments. C. D. S. collected UV-vis and photoluminescence spectra. C. D. S. and K. S. performed DLS titrations. G. N. and A. J. C. prepared Ni(cyclamP). All authors analyzed the data, discussed the results and assisted with the manuscript preparation.

Conflicts of interest

The authors declare no conflict of interests.

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Review Article

The importance of surface coverages in the rational design of electrocatalysts

Anna Ciotti and Max García-Melchor



Abstract

In the last few decades, the research community has witnessed a renewed and increasing interest in electrocatalysis as a powerful tool to sustainably produce chemicals and fuels using renewable electricity. While computational studies can accelerate the discovery of more efficient and cheaper electrocatalysts, they may decelerate the process if unphysical models are used to describe chemical reactivity on the electrode surface. In this opinion piece, we highlight the importance of assessing the resting state of electrocatalysts under reaction conditions, and outline how this can be achieved through the construction of energy diagrams which portray the relative stability of surface coverages that are likely to form in aqueous electrolytes at different applied potentials and pH values. Lastly, we discuss the limitations of the current models and the prospects for further developments in the field.

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Keywords

Surface coverages, Electrocatalysis, Pourbaix diagrams, Resting state, Computational chemistry.

Introduction

During the United Nations Climate Change Conference (COP26), held in Glasgow in November 2021, nearly two hundred countries recognized the urgency to address climate change and agreed to take collective action towards the safeguarding of the environment, highlighting the importance of reducing greenhouse gas emissions [1]. At the same time, significant efforts are being deployed to decarbonize industrial processes and

develop new routes to convert pollutants into chemical fuels and feedstocks using renewable energy sources [2]. In this context, electrocatalysis is a very promising strategy as it often requires fewer synthetic steps, generates less chemical waste, and is easier to scale up compared to non-electrochemical processes [3]. Furthermore, electrocatalytic reactions can be conducted at ambient conditions, and their activity/selectivity can be optimized by tuning the applied potential, electrolyte composition, and pH.

Although remarkable progress has been made in the field of electrocatalysis in the last decades, most catalyst design approaches are still based on trial-and-error, which are very time consuming and resource intensive. Catalytic performance is also very sensitive to experimental conditions, and hence, further advances in the field may require a deeper understanding of the electrode surface (and its reactivity) under reaction conditions. This has prompted the development of advanced *in situ* and *operando* characterization techniques based on synchrotron experiments, with some successful studies recently reviewed in the literature [4,5]. Computational methods have also proven very valuable through the identification of reaction descriptors, allowing to assess catalytic performance based on the binding energies of key reaction intermediates [6–9]. Furthermore, increasing computing power has enabled high-throughput screening studies using reaction descriptors with the aim to speed up catalyst discovery [10–12]. These methods, in combination with machine learning algorithms, have boosted the rate of theoretical predictions by orders of magnitude over density functional theory (DFT) methods, enabling researchers to trawl the vast chemical space. Some successful examples of this dual approach include the prediction of promising electrocatalysts for CO₂ reduction (CO₂RR) [13,14], hydrogen evolution (HER) [15–17], and the oxygen evolution reaction (OER) [18–20].

Often times, however, theoretical predictions are not confirmed experimentally, either because of the challenging synthesis of the materials, their poor stability, or other factors not considered in the modeling (*e.g.*, surface coverages, solvent effects, competing reactions). For instance, some electrocatalysts are known to undergo reconstruction under working conditions to form the active phase [21–23] while others have their surface passivated

by ions present in the electrolyte, affecting catalytic performance [24,25]. Hence, it is important to develop catalyst design strategies whereby both the stability and the resting state of the electrode surface are considered. The latter is particularly important since reaction descriptors are typically based on binding energies calculated on bare surfaces, which may not be representative of the working electrode under experimental conditions.

In this opinion article, we review some recent examples of non-innocent surface coverages, followed by a detailed description on how to calculate binding energies of electrochemically active species. We next outline how to use these energies to assess the resting state of the electrode surface as a function of the applied voltage and pH, by using a Ni(111) surface as a case example. Finally, we discuss the advantages and limitations of such surface coverage analyses, as well as future directions in the field.

Modeling electrode surface coverages

Non-innocent role of electrode surface coverages

Chemical species present in the electrolyte can occupy active sites on the electrode surface, rendering them unavailable for catalysis. For example, in aqueous electrolytes, H, OH and O groups, as well as any other ions present in the electrolyte, can adsorb on the electrode surface blocking active sites for the binding of reagents and intermediates. This phenomenon can inhibit both the thermodynamics and kinetics of the reaction of interest, as observed for the ORR on Pt electrodes, where the rate was suppressed due to the competition for binding with the Cl^- anions present in the electrolyte [26]. Besides, surface hydrogens can undergo HER with other adsorbed H atoms (or protons from solution), compromising catalyst selectivity towards the desired product [27]. In fact, one of the major challenges in electroreductions is the suppression of HER, which typically requires less negative potentials (*i.e.* $E_{\text{H}^+/\text{H}_2}^0 = 0 \text{ V}_{\text{RHE}}$). This competition has been documented in a number of electrochemical reductions, including CO_2RR [28], nitrogen reduction (N_2RR) [29], and the hydrogenation of furfural [30]. Similarly, at positive potentials, oxo and hydroxo species in solution may compete for binding with the reagents and intermediates. Hence, by neglecting the surface coverage in theoretical studies, reaction intermediates might be predicted to bind on surface sites which are not accessible at relevant experimental conditions, leading to an inaccurate depiction of the overall mechanism as well as deceptive predictions by relying on reaction descriptors based on incorrect binding energies.

Additionally, adsorbed species can play a non-innocent role by influencing the electrochemical double-layer [31], undergoing reactions with themselves—as in the case of the HER [27] and OER [32] processes—and by

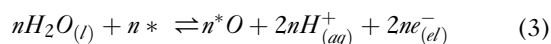
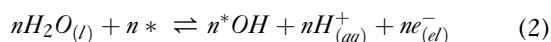
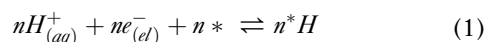
contributing to the oxidation/reduction of various substrates [33]. For example, hydrogen radicals adsorbed on ruthenium nanoclusters have been shown to be involved in the reduction of nitrate to ammonia [34], while $^*\text{OH}$ species have been deemed to promote the dehydrogenation steps in the oxidation of ethanol to acetaldehyde and acetate [35].

Finally, surface species may also affect the binding of reaction intermediates by establishing attractive/repulsive adsorbate—adsorbate interactions. For example, computational studies have shown that the presence of I^- anions on the surface of copper electrodes weaken the binding of the CO_2RR intermediates $^*\text{CO}$, $^*\text{CHO}$, and $^*\text{COH}$ [36], whereas K^+ promotes C—C coupling by stabilizing the $^*\text{CHO}$ intermediate.

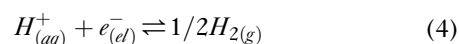
Based on the above observations, it is evident that slight changes on the electrode surface can influence the electrode—electrolyte interface, which may impact the binding of reaction intermediates and possibly lead to radically different products. This reinforces the need of determining the catalyst resting state under relevant conditions to accurately portray chemical reactivity on the electrode surface and to be able to make meaningful predictions.

Modeling binding energies of electrochemically active species

In aqueous electrolytes, the main organic species that can be adsorbed onto the electrode surface are protons, hydroxyl, and oxygen ions, according to the equations:



where, n is an integer and $*$ denotes a surface adsorption site. From Eqs. (1)–(3), the binding energies of the different adsorbates can then be derived through the computational hydrogen electrode (CHE) model, developed by Nørskov et al. [37]. This method relies on the definition of the standard hydrogen electrode (SHE), which states that a solvated proton and an electron are in chemical equilibrium with half a hydrogen molecule in the gas phase at 0 V_{RHE} :



Based on Eq. (4), the Gibbs energy of the proton and electron pair ($G_{\text{H}^+ + e^-}$) can be expressed as half of the energy of the hydrogen molecule (G_{H_2}). Hence, the

Gibbs energies of $^*\text{H}$, $^*\text{OH}$, and $^*\text{O}$ species adsorbed on the electrode surface at 0 V_{RHE} , $\Delta G_{nX,0V_{\text{RHE}}}$, can be determined as:

$$\Delta G_{nH,0V_{\text{RHE}}} = G_{nH} - (G_* + n/2G_{H_2}) \quad (5)$$

$$\Delta G_{nOH,0V_{\text{RHE}}} = G_{nOH} - (G_* + nG_{H_2O} - n/2G_{H_2}) \quad (6)$$

$$\Delta G_{nO,0V_{\text{RHE}}} = G_{nO} - (G_* + nG_{H_2O} - nG_{H_2}) \quad (7)$$

where, G_* is the Gibbs energy of the pristine electrode, G_{H_2O} is the Gibbs energy of a water molecule, and G_{ni} is the Gibbs energy of ni species (*i.e.* $^*\text{H}$, $^*\text{OH}$, $^*\text{O}$) adsorbed on the electrode.

Next, we note that applying a potential would raise the energy of the electrons by $-eV_{\text{RHE}}$ while leaving that of the hydrogen molecule and the protons unaffected. Hence, the following relation can be established from Eq. (4):

$$G_{H^+ + e^-} = 1/2G_{H_2} - eV_{\text{RHE}} \quad (8)$$

and the binding energies of the adsorbate species at a given potential ($\Delta G_{nX,RHE}$) can be formulated by combining Eqs. (5)–(7) and Eq. (8), arriving at the following expressions:

$$\Delta G_{nH,RHE} = \Delta G_{nH,0V_{\text{RHE}}} + neV_{\text{RHE}} \quad (9)$$

$$\Delta G_{nOH,RHE} = \Delta G_{nOH,0V_{\text{RHE}}} - neV_{\text{RHE}} \quad (10)$$

$$\Delta G_{nO,RHE} = \Delta G_{nO,0V_{\text{RHE}}} - 2neV_{\text{RHE}} \quad (11)$$

From Eqs. (9)–(11), it is apparent that negative (reducing) potentials will lower $\Delta G_{nH,RHE}$, whereas positive (oxidizing) potentials will lower $\Delta G_{nOH,RHE}$ and $\Delta G_{nO,RHE}$, as expected.

The effect of pH can also be accounted for by changing the reference potential from RHE to SHE, using the following relation [38].

$$G_{H^+}(pH) = G_{H^+}^0 + k_B T \ln[H_{(aq)}^+] \quad (12)$$

where $G_{H^+}^0$ is the standard Gibbs energy of a solvated proton (*i.e.* at 298 K and 1 M concentration), k_B is Boltzmann's constant, and T is the absolute temperature.

Multiplying the second term in Eq. (12) by 2.303 to convert the natural logarithm to base-10 logarithm, and using the definition of $\text{pH} = -\log[H_{(aq)}^+]$ and the temperature of 298 K, we obtain:

$$G_{H^+}(pH) = G_{H^+}^0 - 0.059pH \quad (13)$$

Using the above equation, Eqs. (9)–(11) can be reformulated against the SHE reference electrode as:

$$\Delta G_{nH,SHE} = \Delta G_{nH,0V_{\text{SHE}}} + neV_{\text{SHE}} + 0.059pH \quad (14)$$

$$\Delta G_{nOH,SHE} = \Delta G_{nOH,0V_{\text{SHE}}} - neV_{\text{SHE}} - 0.059pH \quad (15)$$

$$\Delta G_{nO,SHE} = \Delta G_{nO,0V_{\text{SHE}}} - 2neV_{\text{SHE}} - 0.118pH \quad (16)$$

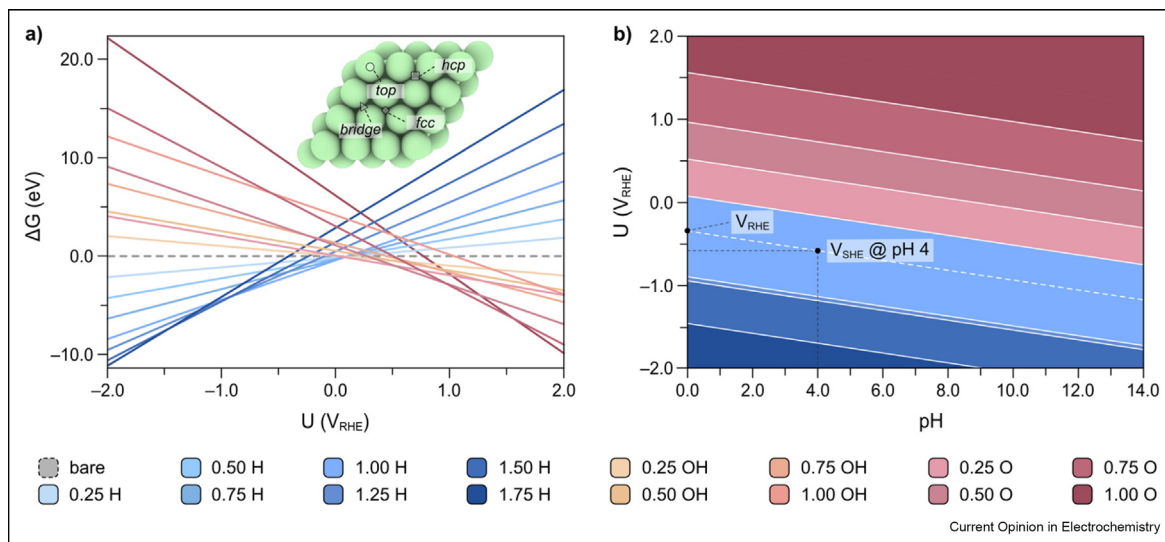
According to Eqs. (14)–(16), both $\Delta G_{nOH,SHE}$ and $\Delta G_{nO,SHE}$ are favored with increasing pH, whereas $\Delta G_{nH,SHE}$ becomes more endergonic. Hence, $^*\text{OH}$ and $^*\text{O}$ species are likely to be present on the electrode surface at high pH and positive (oxidizing) potentials, while $^*\text{H}$ coverages are favored in acidic media and at negative (reducing) potentials. This implies that a change in the reaction conditions can effectively lead to different surface coverages, which may explain the pH and potential dependence observed in many electrocatalytic processes [33,39]. There is also the possibility that the argument of ‘local pH effect’ used to rationalize reactivity trends in various electrochemical reactions [33,39–41] could be related to a change in the electrode surface coverage.

Construction of diagrams for surface coverage analysis: A case example

In this section, we outline how to construct energy diagrams to assess the resting state of the electrode surface under relevant experimental conditions, using a 4-layer Ni(111) surface reported elsewhere [42] as a case study. The modeling of surface Pourbaix diagrams within the CHE framework was first introduced by Hansen et al. by computing different coverages of H, OH, and O species [43]. This model was later on extended to Cl^- coverages to study the Deacon process on rutile oxide surfaces [44]. In this case, the thermodynamic redox potential of Cl_2 gas relative to SHE was employed to calculate the energies of the different Cl^- coverages. Building upon such methods, Groß and co-workers have made substantial contributions to the field by modelling surface Pourbaix diagrams of halides, as well as mixed coverages of halides and H atoms [45–47]. Details of the computational methods employed in the modelling of the surface coverages discussed herein can be found in the Supplementary Materials.

For the surface coverage analysis, it is always helpful to begin by determining the relative stability of a single $^*\text{H}$, $^*\text{OH}$ and $^*\text{O}$ species, $\Delta G_{X,0V_{\text{RHE}}}$, adsorbed on all the available sites of the electrode surface, in this case, the Ni(111) slab shown in the inset of Figure 1a. Next, we

Figure 1



Coverage analysis for a 4-layer Ni(111) slab with a (2×2) periodicity by considering the relative stability of different concentrations of adsorbed $^*H$, $^*OH$, and $^*O$ species. Different colors denote different surface coverages, shown at the bottom of the figure. **a)** Plot of the $\Delta G_{nX,0V_{RHE}}$ values for different surface terminations as a function of the applied potential. Inset: top view of the clean Ni(111) surface with the different adsorption sites labeled. **b)** Pourbaix diagram illustrating the most stable coverages at a given potential and pH. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

can proceed to model different surface coverages with varying concentrations of adsorbates by successively populating the available sites, from the most to the least stable, and calculate their corresponding $\Delta G_{nX,0V_{RHE}}$ values using Eqs. (5)–(7). This procedure should continue until the desorption of species or evolution of gases (*e.g.* O_2 and H_2) is observed in the simulations.

Using Eqs. (9)–(11), we can then construct the energy diagram shown in Figure 1b by plotting the $\Delta G_{nX,RHE}$ values obtained for the different coverages as a function of the applied potential. Note that each surface termination will have a different slope because of the neV_{RHE} term.

From Figure 1b, we can also observe that higher $^*H$ coverages are stabilized at more negative potentials, while denser $^*OH/^*O$ coverages are predicted at more positive potentials, as expected. In addition, we see that at each potential there is a surface termination that lies lower in energy compared to the rest, which will dominate assuming a Boltzmann distribution. It is important to note that the bare Ni surface is not predicted to be the most stable state at any potential, especially at relatively low/high potentials. This highlights the importance of conducting such surface coverage analysis before performing any modelling studies on the reactivity of electrocatalysts.

Another way to assess the resting state of the electrode surface is by plotting the coverage exhibiting the lowest

predicted value of $\Delta G_{nX,SHE}$ at each potential and pH, using Eqs. (14)–(16). This representation, known as Pourbaix diagrams, is illustrated in Figure 1b for the Ni(111) surface. From this diagram, the resting state can be assessed at any potential versus RHE or SHE, since both are related as follows [48]:

$$V_{SHE} = V_{RHE} - 0.059pH \quad (18)$$

More specifically, the y-axis in Figure 1b reports voltages against RHE (or V_{SHE} at pH 0), while values versus SHE at different pH can be read out by following the straight lines, which feature a slope of -0.059 eV per unit of pH. Importantly, these lines demarcate the stability of different surface terminations, and the points on the line are regions wherein two neighboring coverages are in equilibrium. This has important implications for the HER, for example, as the binding energy of a hydrogen atom (ΔG_H) — typically used as reaction descriptor for this process—is thermoneutral on the lines that intersect coverages which differ by one hydrogen. Hence, HER is predicted to be thermodynamically feasible at those values of pH and voltage [42].

Limitations

Surface Pourbaix diagrams can be very informative in predicting the resting state of electrocatalysts under experimental conditions and in assessing the sites available for reactivity. Nevertheless, the method outlined above presents some limitations. Firstly, the

CHE model does not account for the interactions between the adsorbates and the electrolyte, which can become particularly important when large ions are adsorbed on the electrode surface as they can be stabilized by explicit solvent molecules [49–51]. Secondly, it is possible that lines corresponding to different coverages in the $\Delta G_{nX,RHE}$ plots intersect at certain values of potential, as in the case of Ni(111) between -1.5 and $+1.5$ V_{RHE} (Figure 1a). This implies that two (or more) surface terminations are predicted to have the same stability at a given potential, and therefore, they are equally probable. Importantly, this issue can be readily identified in the $\Delta G_{nX,RHE}$ plots but not in Pourbaix diagrams, as the latter only display the coverage with the lowest predicted energy at each pH and potential. Hence, we recommend comparing both diagrams to determine whether there are any coverages which lie close in energy at the relevant experimental conditions. If so, both surfaces should be considered in subsequent reactivity studies, and their stability should be consistent with the predicted potentials required for the reaction of interest, *i.e.* *limiting potential*—defined as the potential at which all the reaction steps become thermoneutral or downhill in energy.

In addition, we note that the approach described herein does not consider coverages bearing different adsorbates, which may exist experimentally under certain reaction conditions. While this could be addressed by modelling mixed surface coverages [46], the number of combinations grows very rapidly, and hence, computational cost. In addition, the calculated energy for the mixed coverages may be more sensitive to the size of the surface slab, further increasing the complexity of the coverage analysis.

$\Delta G_{nX,RHE}$ plots and Pourbaix diagrams are also based only on reaction thermodynamics and, as such, they do not include any information about the kinetics of water hydrolysis, solvent reorganization, and diffusion of chemical species. Although this approach may provide satisfactory results when protons, hydroxyl, and oxygen ions are readily sourced by the aqueous electrolyte, it may lead to inaccurate results at very low (high) pH values, where the concentration of hydroxyl and oxygen ions (protons) is very scarce.

Lastly, adsorbate species like H might diffuse on the electrode [52], leading to an ensemble of surface configurations with regions displaying a higher/lower coverage within a very small energy range. This may result in significant differences in the binding energies of reagents and intermediates, especially if they interact strongly with the coverage, and therefore, impact the overall catalytic activity/selectivity. While the computational cost of modelling all possible configurations grows rapidly with the cell size and the presence of surface defects (*e.g.* steps, kinks, terraces),

artificial intelligence can accelerate the identification of non-equivalent surface states and their energetics [53]. These models might also enable the screening of mixed coverages, providing a more realistic picture of the chemical reactivity overall on the electrode surface [53].

Conclusions

In this opinion piece, we strongly advocate that the surface coverage of electrocatalysts under relevant experimental conditions must be assessed in all computational studies aiming at describing catalytic activity/selectivity. This is of critical importance as neglecting the coverage may lead to incorrect predictions in the adsorption sites of substrates and reaction intermediates, binding modes, and energetics. In addition, we outline the theoretical background to calculate binding energies of electrochemically active species and how to utilize these to construct energy diagrams to predict the resting state of the electrode surface at a given potential and pH. While these models have some shortcomings, they often provide a good description of the surface reactivity. Furthermore, these energy diagrams can be used to optimize the reaction conditions in order to maximize catalytic performance. Future advances in the field should focus on introducing the effect of reaction kinetics, the influence of mixed coverages, and the modeling of surface species in the presence of explicit solvent. The automation and prediction of surface coverages using more computationally efficient methods, including machine learning, is also an exciting research direction.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.coelec.2023.101402>.

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Sustainable Electrosynthesis of Cyclohexanone Oxime through Nitrate Reduction on a Zn–Cu Alloy Catalyst

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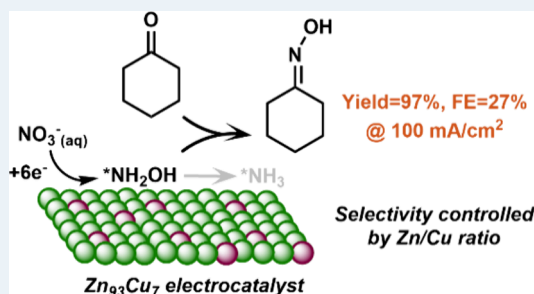
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ABSTRACT: Cyclohexanone oxime is an important precursor for Nylon-6 and is typically synthesized via the nucleophilic addition–elimination of hydroxylamine with cyclohexanone. Current technologies for hydroxylamine production are, however, not environment-friendly due to the requirement of harsh reaction conditions. Here, we report an electrochemical method for the one-pot synthesis of cyclohexanone oxime under ambient conditions with aqueous nitrate as the nitrogen source. A series of Zn–Cu alloy catalysts are developed to drive the electrochemical reduction of nitrate, where the hydroxylamine intermediate formed in the electroreduction process can undergo a chemical reaction with the cyclohexanone present in the electrolyte to produce the corresponding oxime. The best performance is achieved on a $\text{Zn}_{93}\text{Cu}_7$ electrocatalyst with a 97% yield and a 27% Faradaic efficiency for cyclohexanone oxime at 100 mA/cm^2 . By analyzing the catalytic activities/selectivities of the different Zn–Cu alloys and conducting in-depth mechanistic studies via *in situ* Raman spectroscopy and theoretical calculations, we demonstrate that the adsorption of nitrogen species plays a central role in catalytic performance. Overall, this work provides an attractive strategy to build the C–N bond in oxime and drive organic synthesis through electrochemical nitrate reduction, while highlighting the importance of controlling surface adsorption for product selectivity in electrosynthesis.



KEYWORDS: nitrate electroreduction, cyclohexanone oxime, C–N bond formation, electrosynthesis, Zn–Cu alloy catalyst, DFT calculations, reaction mechanisms

INTRODUCTION

Cyclohexanone oxime is an important feedstock in the nitrogen industry as it can undergo Beckmann rearrangement to make caprolactam, the monomeric unit of Nylon-6. With the annual global market of Nylon-6 anticipated to be as high as 8.9 million tons by 2024,¹ the production capacity of cyclohexanone oxime should also be expanded accordingly. To date, the majority of cyclohexanone oxime is produced by the nucleophilic addition–elimination reaction between cyclohexanone and hydroxylamine (NH_2OH),² which is typically generated via hydrogenation of NO_x on palladium catalysts³ or oxidation of ammonia (NH_3) by $\text{O}_2/\text{H}_2\text{O}_2$ (Figure 1a).^{4–6} However, these chemical processes generally require harsh reaction conditions (e.g., high temperatures and/or pressures, strong acidic/alkaline solutions) and therefore are challenged by a series of environmental and safety concerns. More specifically, the hydrogenation route is limited by the requirements of pressurized H_2 gas, strong acidic conditions and precious metal catalysts. Moreover, transportation and storage of concentrated NH_2OH also faces challenges, including the risk of explosion.⁷ On the other hand, NH_3 oxidation utilizes NH_2OH generated *in situ* as needed.⁴ Yet, this synthetic route still demands elevated temperatures, high

pH, and an excess of H_2O_2 as the oxidant, which also has transportation and storage issues.^{8,9} Hence, there is a strong desire for an alternative strategy to produce cyclohexanone oxime under mild conditions.

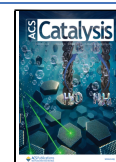
Electrosynthesis stands out as a promising synthetic strategy to enable the sustainable production of chemical feedstocks and added-value compounds by driving reactions under ambient conditions, using electrons generated from renewable electricity instead of redox reagents.^{10–14} Particularly, electrochemical nitrate reduction (NO_3R) has been demonstrated as a sustainable synthetic approach to upgrade nitrate waste into NH_3 , a very important chemical building block, thus contributing to abating the global nitrogen cycle imbalance.^{15–23} Furthermore, a series of surface-adsorbed reaction intermediates have been identified in the NO_3R to ammonia, such as $^*\text{NO}$, $^*\text{NH}_2\text{OH}$, and $^*\text{NH}_2$, which exhibit high

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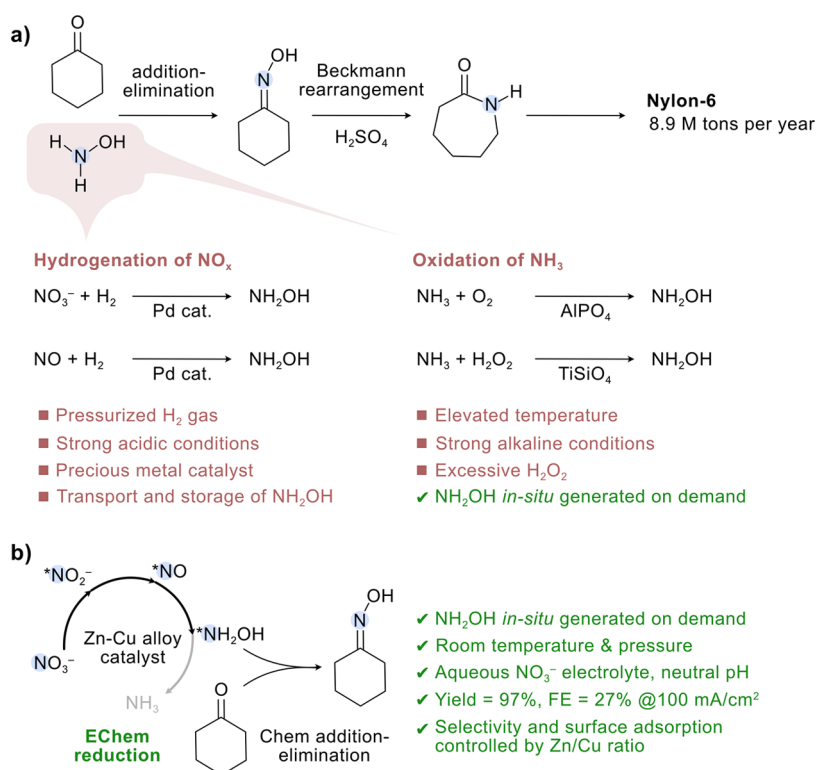


Figure 1. Developments in the synthesis of cyclohexanone oxime via thermal and electrochemical methods. (a) Current technologies to synthesize cyclohexanone oxime from cyclohexanone and hydroxylamine, wherein hydroxylamine production is limited by the harsh reaction conditions. (b) Electrosynthesis of cyclohexanone oxime via nitrate reduction under ambient conditions developed in this work. The surface-adsorbed $^*\text{NH}_2\text{OH}$ intermediate generated through the electrochemical reduction of nitrate on a Zn–Cu alloy catalyst can undergo a chemical addition–elimination reaction with the cyclohexanone present in the electrolyte to produce oxime.

nucleophilic reactivities and therefore can be coupled with chemical reactions to build C–N bonds.^{24,25} In particular, the electrochemical coreduction of CO_2 and NO_3^- has been reported as an attractive route to produce organonitrogen compounds, including urea, methylamine, and glycine.^{26–30} Recently, the Zhang and Tan groups have also shown that the $^*\text{NH}_2$ intermediate generated during NO_3R can interact with CO_2 -derived compounds (i.e., formic acid or CO) to produce formamide.^{31,32} Despite these distinctive methods, current studies on C–N bond formation via NO_3R mainly focus on coupling NO_3R intermediates with C_1 – C_2 molecules (e.g., CO_2 , CO, formic acid, oxalic acid). There are a few recent reports on electrochemical NO_3R systems, which can build C–N bonds in larger organic molecules (i.e., C_{3+} compounds), such as amino acid^{33,34} and oxime.^{35–38} However, NO_3R can generate a variety of N-containing byproducts (e.g., N_2 , NH_3 , N_2O , NO_2^-), and therefore the understanding of the intricate NO_3R reaction pathways and the controlling of N selectivity toward the desired organonitrogen products remain elusive. Furthermore, the adsorption of N species on the electrocatalyst surface, which plays a central role in tuning the product selectivity, is still largely unexplored for building C–N bonds in C_{3+} molecules.

Previous reports revealed that the surface-adsorbed $^*\text{NH}_2\text{OH}$ is a key intermediate in the NO_3R to NH_3 .^{17,18,28,39,40} Recently, the groups of Zhang, Zou, and Li have also independently reported that the $^*\text{NH}_2\text{OH}$ intermediate produced during the electrochemical reduction of $\text{NO}_3^-/\text{NO}_2^-/\text{NO}$ can undergo a C–N coupling reaction to form oxime.^{36–38} Herein, we report a two-step electro-

chemical-chemical (EChem–Chem) process for the one-pot synthesis of cyclohexanone oxime with aqueous nitrate as the N source (Figure 1b) and provide an in-depth investigation of how the product selectivity is controlled by the surface adsorption of N species. A series of Zn–Cu alloys are prepared to drive the electrochemical NO_3R step and generate $^*\text{NH}_2\text{OH}$, which can then undergo a chemical reaction with cyclohexanone in solution to produce oxime. Through a combination of experimental and computational studies, we demonstrate that the binding of the reaction intermediates on the electrocatalyst surface plays a central role in the EChem–Chem process. Particularly, we show that weak surface adsorption (e.g., on a pure Zn catalyst) can lead to high potentials for the EChem step, whereas strong adsorption (e.g., on a pure Cu catalyst) can promote this process at lower potentials but results in the complete reduction of $^*\text{NH}_2\text{OH}$ to NH_3 instead of forming oxime. Notably, we find that a Zn–Cu alloy catalyst with an optimized composition of $\text{Zn}_{93}\text{Cu}_7$ can efficiently convert aqueous NO_3^- (pH 7.0) and cyclohexanone into cyclohexanone oxime with a yield of $97 \pm 2\%$ and a Faradaic efficiency (FE) of $27 \pm 2\%$ at 100 mA/cm². The NH_2OH -mediated reaction pathway and the relationship between oxime-making activity and surface adsorption are supported by *in situ* Raman spectroscopy and theoretical calculations. Altogether, this work represents a novel strategy for the one-pot electrosynthesis of cyclohexanone oxime from aqueous NO_3^- under ambient conditions, which can upgrade NO_3^- and enable sustainable organic synthesis. This study also highlights the potential of producing value-added organonitrogen compounds via electrochemical NO_3R as well as the

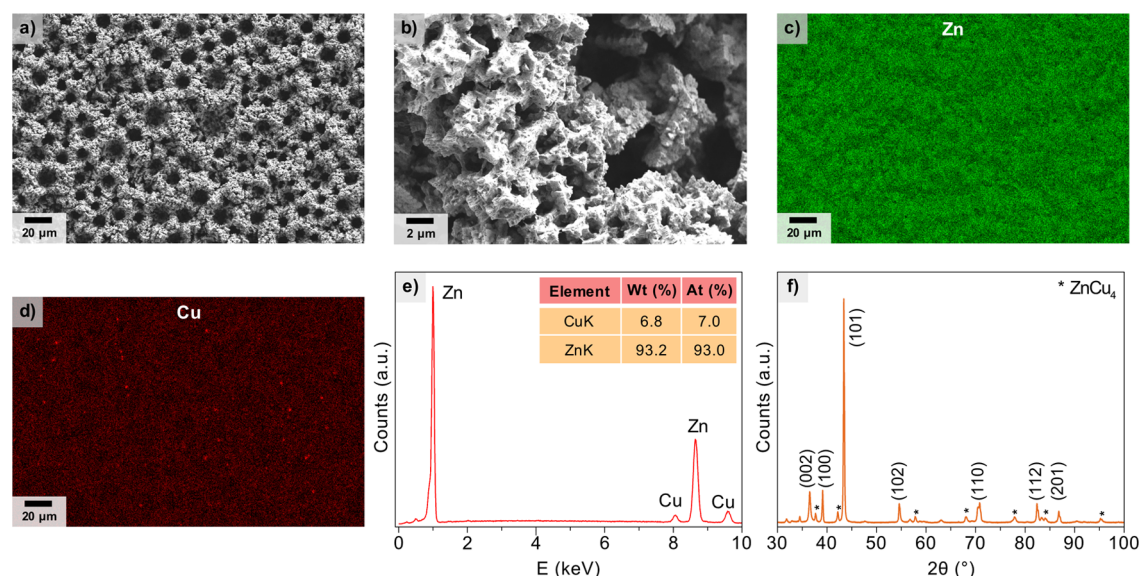


Figure 2. Structural characterization of the $\text{Zn}_{93}\text{Cu}_7$ electrocatalyst. (a, b) SEM images at different magnifications. (c) EDX mapping for Zn. (d) EDX mapping for Cu. (e) EDX quantitative elemental analysis. (f) XRD pattern. The planes in brackets are attributed to Zn (JCPDS 04–0831) and the planes with stars correspond to ZnCu_4 phase (JCPDS65–6066).

importance of controlling the binding of surface species for product selectivity in electrocatalysis.

RESULTS AND DISCUSSION

Preparation and Structural Characterization of the $\text{Zn}_{93}\text{Cu}_7$ Electrocatalyst. A $\text{Zn}_{93}\text{Cu}_7$ electrocatalyst was prepared via electrodeposition. Previous reports have demonstrated that electrodeposition of metal precursors in acid solution can generate metal films (e.g., Cu, Ag, Pd, Zn, and Sn) with highly porous surface caused by the formation of H_2 bubbles during the process, known as the dynamic hydrogen bubble template (DHBT) approach.^{41–43} Here, we utilize the DHBT method to prepare a Zn–Cu alloy catalyst, where Zn^{2+} and Cu^{2+} precursors ($\text{Zn}^{2+}/\text{Cu}^{2+}$ ratio = 60) in aqueous acidic solution were electrochemically reduced and deposited onto a Cu foil substrate to form an alloy film (see [Supporting Information](#)). Scanning electron microscopy (SEM) of the Zn–Cu alloy (Figure 2a,b) showed a uniform microporous morphology that is typically observed in metal films prepared by DHBT.

Energy-dispersive X-ray (EDX) mapping showed a homogeneous elemental distribution of Zn and Cu in the sample (Figure 2c,d), indicating the successful formation of an alloy. Furthermore, EDX quantitative analysis revealed a composition of 93 atom % and 7 atom % for Zn and Cu, respectively (Figure 2e). Inductively coupled plasma optical emission spectrometry (ICP-OES) showed a similar elemental composition for the bulk catalyst of 91% Zn and 9% Cu (Table S1). As the electrocatalytic activity and reaction pathway are mainly determined by the surface composition, instead of bulk composition, hereafter we refer to this alloy as $\text{Zn}_{93}\text{Cu}_7$. The successful formation of the alloy was also confirmed by X-ray diffraction (XRD), which mainly exhibited crystal planes of pure Zn and minor peaks of a ZnCu_4 phase (Figure 2f), with no evidence of pure Cu. Hence, the XRD results indicate that Cu was homogeneously distributed within the Zn matrix, in agreement with EDX mapping.

Electrosynthesis of Cyclohexanone Oxime by $\text{Zn}_{93}\text{Cu}_7$. The $\text{Zn}_{93}\text{Cu}_7$ alloy (surface area = 1 cm^2) was

used as working electrode to drive the electrochemical NO_3R to produce cyclohexanone oxime in 16 mL of 0.5 M aqueous potassium phosphate (KPi) buffer solution (pH 7.0) containing 100 mM KNO_3 and 25 mM cyclohexanone. Pt and Ag/AgCl electrodes were used as counter and reference electrodes, respectively, and electrochemical tests were carried out in a gastight H-type cell at constant current (chronopotentiometry). More details of the electrochemical cell setup can be found in Experimental methods and Figure S1. Electrolysis time was adjusted to keep a constant value of charges injected into the electrolyte. The potential required to achieve a certain current density was obtained from the steady-state potential of the electrolysis. A chronopotentiometry graph for electrolysis over 2.5 h at 100 mA/cm^2 can be found in Figure S2 as an example of obtaining the steady-state potential.

The liquid reaction mixture was analyzed by nuclear magnetic resonance (NMR) to identify the organic compounds present. The recorded ^1H NMR spectra before and after electrolysis, shown in Figure 3a, indicate that the cyclohexanone peaks almost disappeared after the reaction, while new peaks aligned with pure cyclohexanone oxime emerged, confirming the successful conversion of cyclohexanone into cyclohexanone oxime. The ^{13}C NMR spectrum obtained for the reaction mixture after electrolysis also supported the formation of cyclohexanone oxime (Figure 3b).

The production of cyclohexanone oxime was further confirmed by mass spectroscopy (MS, Figure S3). The reaction mixture was also analyzed by high-performance liquid chromatography (HPLC) to quantify cyclohexanone and cyclohexanone oxime (Figure S4) as well as ion chromatography (IC) to detect and quantify different nitrogen species in solution, namely, NO_3^- , NO_2^- , and NH_3 (Figure S5). In addition, the gas sample in the headspace of the H-cell was analyzed by gas chromatography (GC). Details of products characterization can be found in the [Supporting Information](#).

The FE and steady-state potential for the electrochemical NO_3R were measured at constant current densities of 5, 25, 50, 100, and 150 mA/cm^2 , the results of which are summarized in Figure 3c. At 5 mA/cm^2 , a small amount of cyclohexanone

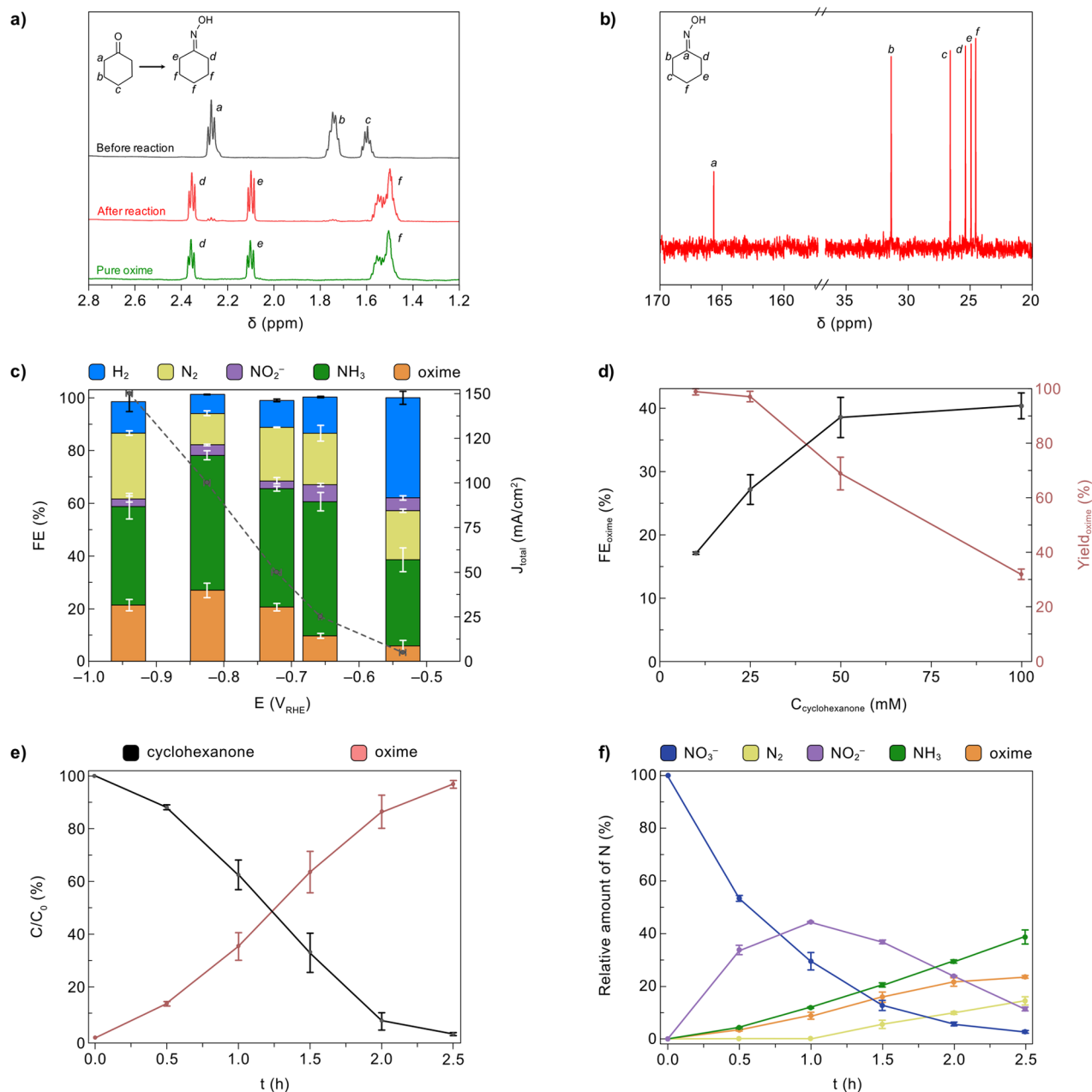


Figure 3. Electrosynthesis of cyclohexanone oxime from NO_3^- and cyclohexanone driven by a $\text{Zn}_{93}\text{Cu}_7$ -electrocatalyst. (a) ^1H NMR spectra for the reaction mixture before and after 2.5 h electrolysis, and pure cyclohexanone oxime as control. (b) ^{13}C NMR spectra for the reaction mixture after reaction. (c) FE and total current density (J_{total}) at different potentials. Potential values were obtained from the steady-state potentials for constant current electrolysis. (d) FE and yield of cyclohexanone oxime measured at 100 mA/cm^2 with different concentrations of cyclohexanone added into 100 mM KNO_3 electrolyte. (e) Conversion of cyclohexanone into cyclohexanone oxime over 2.5 h of electrolysis at 100 mA/cm^2 . (f) Relative amount of nitrogen products over 2.5 h of electrolysis at 100 mA/cm^2 . Reaction conditions: $\text{Zn}_{93}\text{Cu}_7$ cathode (surface area = 1 cm^2) immersed in 16 mL of aqueous buffer solution (0.5 M KPi, pH 7.0) containing 100 mM KNO_3 and 25 mM cyclohexanone. Error bars correspond to the standard deviation of triplicate experiments.

oxime was detected ($\text{FE} = 6 \pm 2\%$), while the major products were NH_3 and H_2 . The FE for cyclohexanone oxime increased to $27 \pm 2\%$ at 100 mA/cm^2 and -0.82 V vs reversible hydrogen electrode (V_{RHE}) and then decreased to $21 \pm 2\%$ when the current density further increased to 150 mA/cm^2 . At the different current densities investigated in this work, NH_3 was generated as the major product with FEs between 30 and 50%; other detected products included NO_2^- , N_2 , and H_2 .

The influence of different concentrations of cyclohexanone (i.e., 10, 25, 50, 100 mM; NO_3^- concentration was kept

constant at 100 mM) added to the electrolyte was investigated through 2.5 h electrolysis experiments at 100 mA/cm^2 (Figure 3d). Low concentrations of cyclohexanone (e.g., 10 mM) were found to produce cyclohexanone oxime with high yields ($99 \pm 1\%$), while the FE for cyclohexanone oxime was quite low ($17 \pm 0.3\%$). In contrast, high concentrations of cyclohexanone (e.g., 100 mM) led to high FE for cyclohexanone oxime ($40 \pm 2\%$), but the yield was lower ($32 \pm 2\%$). Therefore, a medium concentration of cyclohexanone (25 mM) was chosen to balance the yield and FE for cyclohexanone oxime.

Table 1. Control Experiments for Cyclohexanone Oxime Production

entry	cathode	C source	N source	electrolysis	cyclohexanone oxime?
1	Zn ₉₃ Cu ₇	cyclohexanone	KNO ₃	yes	yes
2	Zn ₉₃ Cu ₇	cyclohexanone	KNO ₃	no	no
3	Zn ₉₃ Cu ₇	cyclohexanone	KNO ₃	yes	no
4	Zn ₉₃ Cu ₇	cyclohexanone	KNO ₃	yes	no
5	Cu foil	cyclohexanone	KNO ₃	yes	no
6	Zn ₉₃ Cu ₇	cyclohexanone	K ¹⁵ NO ₃	yes	yes, ¹⁵ N-labeled
7	Zn ₉₃ Cu ₇	cyclohexanone	KNO ₂	yes	yes
8	Zn ₉₃ Cu ₇	cyclohexanone	NO	yes	yes
9	Zn ₉₃ Cu ₇	cyclohexanone	NH ₂ OH	yes	yes
10	Zn ₉₃ Cu ₇	cyclohexanone	NH ₃	yes	no

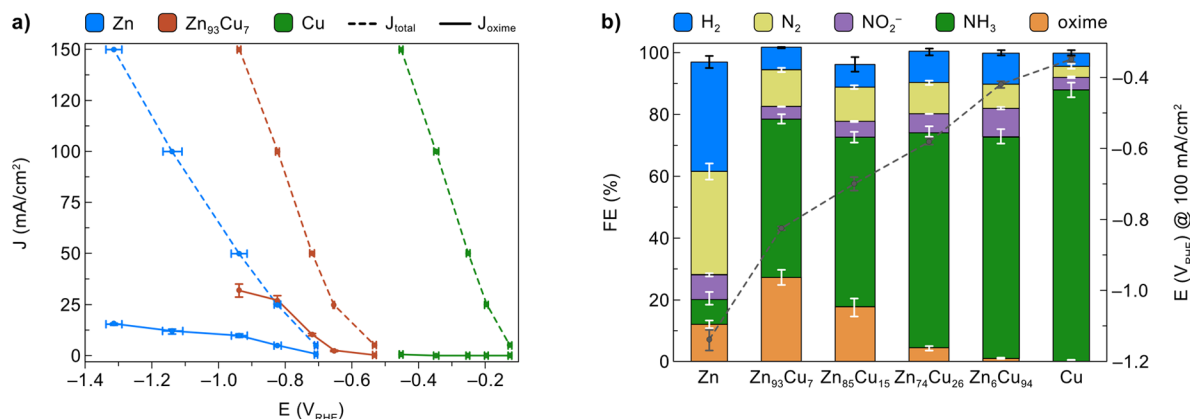


Figure 4. Production of cyclohexanone oxime from NO₃⁻ and cyclohexanone driven by different Zn/Cu electrocatalysts. (a) Total current density (J_{total}) and partial current density for cyclohexanone oxime (J_{oxime}) at different potentials for Zn, Zn₉₃Cu₇, and Cu electrocatalysts. (b) FE and potential required to achieve J_{total} at 100 mA/cm² with different Zn/Cu electrocatalysts. Reaction conditions: Zn/Cu cathode (surface area = 1 cm²) immersed in 16 mL of aqueous buffer solution (0.5 M KPi, pH 7.0) containing 100 mM KNO₃ and 25 mM cyclohexanone. Potential values were obtained from the steady-state potentials for constant current electrolysis. Error bars correspond to the standard deviation of triplicate experiments.

After optimizing the reaction conditions as 100 mA/cm² and 25 mM cyclohexanone, we next monitored the temporal changes in the concentrations of the reactants and products by analyzing reaction aliquots every 30 min over 2.5 h of electrolysis. As shown in Figure 3e, oxime was produced with $97 \pm 2\%$ yield and the ketone reactant was almost fully converted after 2.5 h (conversion $\sim 98\%$), which is consistent with the recorded ¹H NMR spectrum. These results also demonstrated a high carbon selectivity which is close to 100%, while the nitrogen selectivity was investigated by monitoring the relative amounts of all nitrogen compounds over the 2.5 h electrolysis (Figure 3f). The NO₃⁻ reactant was first converted into NO₂⁻, which achieved a maximum yield of ca. 45% after 1 h, indicating that NO₂⁻ is a reaction intermediate, in line with previous reports.^{15–20,44} After 2.5 h of electrolysis, ca. 3% NO₃⁻ and 15% NO₂⁻ remained in solution, while cyclohexanone oxime and NH₃ were the main species produced in ca. 24% and 40% yields, respectively. Under these conditions, N₂ was generated as a byproduct ($\sim 15\%$), which is consistent with previous NO₃R studies driven by Zn-rich electrocatalysts.^{45–47} Importantly, the surface structures of the Zn₉₃Cu₇ electrocatalyst remained stable after three tests of 2.5 h electrolysis (Figures S6 and S7), and the electrocatalyst could be reused to produce cyclohexanone oxime with similar FEs compared to the initial test (Figure S8).

Next, a series of control experiments were performed to confirm the C and N sources and shed light into the reaction pathway (Table 1). As expected, the reaction in the absence of

electrolysis or cyclohexanone or NO₃⁻ did not yield any oxime product (entries 2, 3 and 4). Experiments using bare Cu foil as the cathode (entry 5) were also inactive toward oxime formation, highlighting the catalytic role of the Zn₉₃Cu₇ alloy. To confirm the N source, an isotopic labeling experiment with K¹⁵NO₃ was carried out (entry 6), and the formation of ¹⁵N-labeled cyclohexanone oxime was corroborated by mass spectroscopy (Figure S9). The recorded ¹H NMR spectrum (Figure S9) also revealed the duplet splitting behavior of the ¹⁵NH₄⁺ peak generated from ¹⁵NO₃⁻ reduction, while ¹⁴NH₄⁺ produced by normal ¹⁴NO₃⁻ reduction features a triplet peak. A series of possible NO₃R intermediates, including NO₂⁻, NO, and NH₂OH, was each used as the starting N source (entries 7–9) and resulted in the formation of cyclohexanone oxime, indicating a NO₃R reaction pathway via those species that is consistent with previous studies.^{17,18,28} Finally, using NH₃ as the N source (entry 10) failed to produce any cyclohexanone oxime, further confirming that the oxime product was generated from an intermediate of NO₃R instead of the final product of NO₃R (NH₃).

Electrosynthesis of Cyclohexanone Oxime by Different Zn–Cu Alloys. Pure Zn and Cu electrocatalysts were also prepared through similar DHBT electrodeposition methods to compare their catalytic performance with that of the Zn₉₃Cu₇ alloy. The X-ray photoelectron spectroscopy (XPS) analysis revealed that the Zn/Cu catalysts were mainly in metallic phases while a small portion of metal oxide was formed due to the inevitable surface oxidation of the catalysts in the

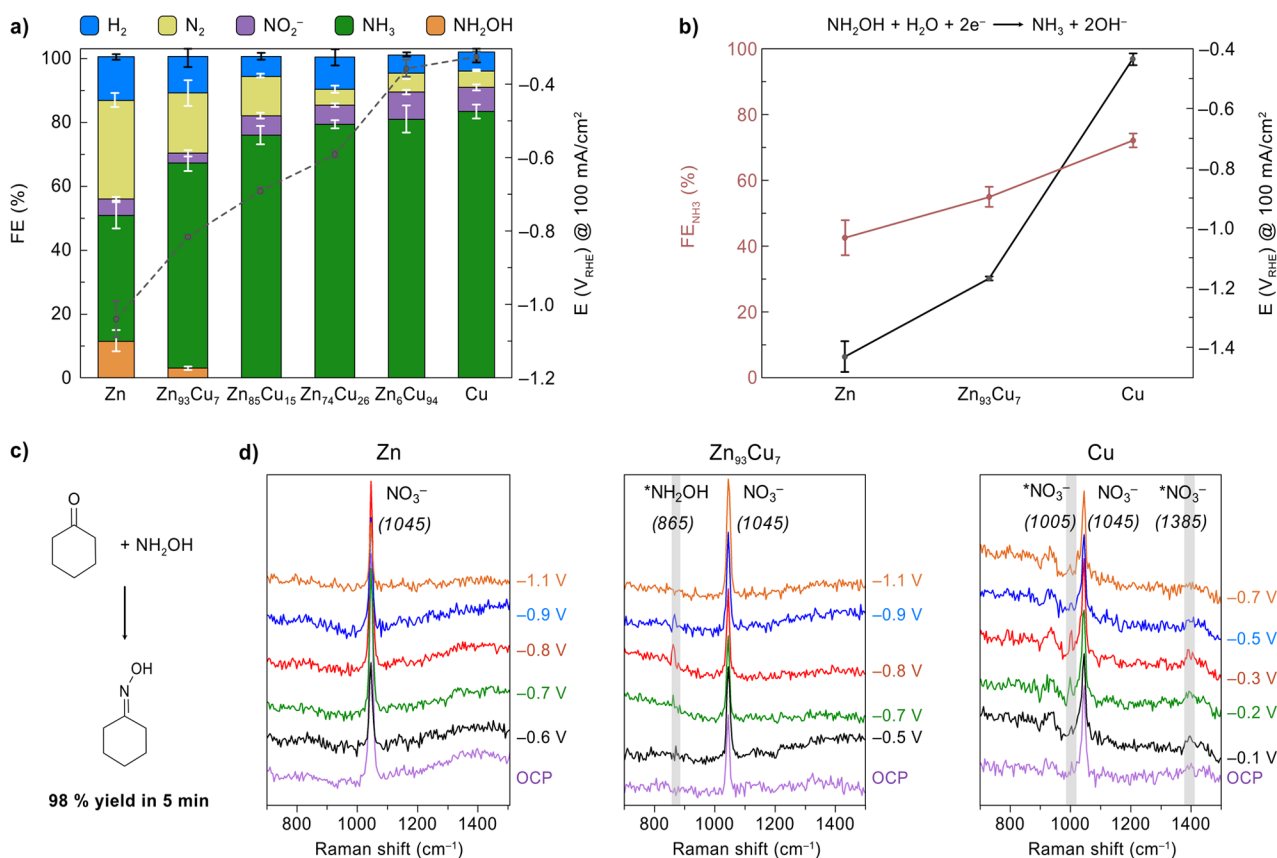


Figure 5. Mechanistic study of the NO₃R process mediated by surface-adsorbed NH₂OH. (a) Electroreduction of NO₃⁻ (without cyclohexanone) at 100 mA/cm² with different Zn–Cu alloy catalysts. (b) Electroreduction of NH₂OH to NH₃ at 100 mA/cm² for Zn, Zn₉₃Cu₇ and Cu. Reaction conditions: Zn/Cu cathode (surface area = 1 cm²) immersed in 16 mL aqueous buffer solution (0.5 M KPi, pH 7.0) containing 100 mM KNO₃ (for a) or NH₂OH (for b). Error bars correspond to the standard deviation of triplicate experiments. (c) Chemical addition–elimination reaction between cyclohexanone and NH₂OH to yield cyclohexanone oxime. Reaction conditions: 16 mL aqueous solution containing 25 mM cyclohexanone and 25 mM NH₂OH. (d) *In situ* Raman spectra for electrochemical NO₃R (without cyclohexanone) recorded at different potentials (vs RHE) on pure Zn, Zn₉₃Cu₇ alloy, and pure Cu electrocatalysts. The peak at 1045 cm⁻¹ was consistently observed for the NO₃⁻ in solution. The asterisk in the labeled species denote an adsorbed state, e.g., *NH₂OH, *NO₃⁻.

atmosphere (Figure S10). The SEM images and XRD results for pure Zn and Cu catalysts are also shown in Figures S11 and S12. As displayed in Figure 4a, pure Cu required a significantly lower potential than pure Zn to achieve the same total current density (J_{total} , top), while the Zn₉₃Cu₇ alloy showed an intermediate behavior, suggesting that the electrochemical NO₃R is more favorable on Cu. However, pure Cu could barely produce any cyclohexanone oxime, whereas pure Zn was capable of forming cyclohexanone oxime. Notably, Zn₉₃Cu₇ attained an even higher partial current density for oxime (J_{oxime} , bottom) at a significantly lower potential compared to pure Zn. For example, a J_{oxime} of 32 ± 3 mA/cm² was achieved at -0.94 V_{RHE} on Zn₉₃Cu₇, compared to 10 ± 1 mA/cm² on pure Zn.

Although pure Cu itself was deemed inactive toward cyclohexanone oxime production, the introduction of a small percentage (7%) of Cu into Zn resulted in a significantly enhanced performance. Hence, to investigate how Zn/Cu composition influences NO₃R, a series of Zn–Cu alloy catalysts were prepared by electrodeposition using precursor solutions with different Zn/Cu ratios (see Table S1 for details). The bulk composition was measured by ICP-OES analysis (Table S1). EDX analysis of the surface elemental composition (Figure S13), which is more related to the electrocatalytic activity, determined the surface composition of these samples to be Zn₉₃Cu₇, Zn₈₅Cu₁₅, Zn₇₄Cu₂₆, and

Zn₆Cu₉₄. Subsequently, the Zn–Cu alloys were tested for NO₃R at 100 mA/cm², with the measured potentials and FEs summarized in Figure 4b. As the Cu content increased, the NO₃R could be driven at lower potentials and the FE for NH₃ was significantly enhanced, consistent with previous reports that Cu is an efficient electrocatalyst for NO₃⁻ to NH₃ conversion.^{15,17,18} However, Cu-rich catalysts (i.e., Zn₆Cu₉₄ and pure Cu) resulted in low FEs for cyclohexanone oxime (<1%). The highest FE for the oxime product was achieved on Zn₉₃Cu₇ ($27 \pm 3\%$), while pure Zn and Zn₈₅Cu₁₅ produced oxime with lower FEs ($12 \pm 1\%$ and $17 \pm 3\%$, respectively). We also note that pure Zn also produced a substantial amount of N₂ (FE = $33 \pm 3\%$) and H₂ (FE = $35 \pm 2\%$) compared to the other electrocatalysts.

Based on the above experimental results and previous NO₃R studies⁴⁸ that revealed a significantly stronger adsorption of reaction intermediates on Cu compared to Zn, we posited four possible (not excluding) reasons for the different behavior observed with the Zn–Cu alloy electrocatalysts: (1) Cu has a stronger surface adsorption of NO₃⁻ than Zn and therefore facilitates the electrochemical NO₃R at lower potentials; (2) Cu favors the further electroreduction of *NH₂OH to NH₃, instead of the chemical reaction with cyclohexanone to give oxime; (3) introducing Cu into Zn creates a more porous surface morphology and thus leads to lower NO₃R potentials;

(4) pure Zn is disadvantaged by the competing NO_3R pathway toward N_2 , rather than NH_2OH or NH_3 . The difference in surface morphology for Zn, Cu, and $\text{Zn}_{93}\text{Cu}_7$ is supported by SEM images (Figure S11) and the measurements of the electrochemical active surface area (ECSA, Figure S14). Hence, we next carried out further experimental and theoretical studies to prove the other three possible reasons.

Experimental Mechanistic Studies. The detection of the NH_2OH intermediate proved very challenging in the presence of cyclohexanone because of the extremely fast nucleophilic addition of NH_2OH to the ketone. Therefore, we set out to perform electrochemical NO_3R experiments with the different Zn/Cu catalysts in the absence of cyclohexanone to confirm the formation of NH_2OH . As shown in Figure 5a, similar trends of lower potentials and higher FE toward NH_3 were observed as the Cu content increased, consistent with hypothesis 1 that Cu facilitates electrochemical NO_3R . More importantly, pure Zn and $\text{Zn}_{93}\text{Cu}_7$ were found to produce NH_2OH at 100 mA/cm^2 with FEs of $12 \pm 3\%$ and $3 \pm 1\%$, respectively (detection of NH_2OH in solution is shown in Figure S15). Pure Zn can produce more NH_2OH than $\text{Zn}_{93}\text{Cu}_7$ in the absence of cyclohexanone because the $^*\text{NH}_2\text{OH}$ produced on $\text{Zn}_{93}\text{Cu}_7$ can be further reduced to NH_3 when cyclohexanone is unavailable (see below discussion that $\text{Zn}_{93}\text{Cu}_7$ is a better NH_2OH electroreduction catalyst than pure Zn). Conversely, in the presence of cyclohexanone, $\text{Zn}_{93}\text{Cu}_7$ gave more oxime because the addition of cyclohexanone shifts the equilibrium toward cyclohexanone oxime formation, outcompeting $^*\text{NH}_2\text{OH}$ reduction. The formation of $^*\text{NH}_2\text{OH}$ and its subsequent release into the electrolyte solution were also evidenced at other current densities for $\text{Zn}_{93}\text{Cu}_7$ (Figure S16). In contrast, the other electrocatalysts with higher Cu contents did not yield any detectable amount of NH_2OH , indicating that this intermediate can be further reduced to NH_3 on Cu-rich catalysts, whereas on Zn-rich catalysts (i.e., pure Zn and $\text{Zn}_{93}\text{Cu}_7$) the $^*\text{NH}_2\text{OH}$ intermediate can desorb from the surface and accumulate in the solution to a detectable concentration.

To further understand the interaction of NH_2OH with the electrocatalyst surface, the electroreduction of NH_2OH to NH_3 was investigated on pure Zn, $\text{Zn}_{93}\text{Cu}_7$, and pure Cu (Figure 5b). Experiments with pure Cu led to a significantly higher FE for NH_3 and a lower potential compared to pure Zn and $\text{Zn}_{93}\text{Cu}_7$, demonstrating that the electroreduction of NH_2OH to NH_3 is much more favorable on the Cu surface compared to Zn. The central role of NH_2OH in the production of oxime was further confirmed by mixing cyclohexanone and NH_2OH in solution without electrolysis, which readily produced cyclohexanone oxime with 98% yield after only 5 min (Figure 5c). The fast kinetics and favorable thermodynamics of this noncatalytic addition–elimination reaction ensures effective C–N bond formation. Given that NH_2OH is the most nucleophilic species among all the proposed NO_3R intermediates and the widely known nucleophilic addition of NH_2OH to ketones,²⁸ we concluded that NH_2OH is the NO_3R intermediate that reacts with cyclohexanone to generate oxime. These results collectively support hypothesis 2 that, on Zn-rich electrocatalysts, the electrochemically generated NH_2OH tends to undergo a subsequent chemical reaction with cyclohexanone to produce oxime rather than being further reduced to NH_3 .

Further insights were obtained by analyzing the surface-adsorbed species during electrochemical NO_3R at different

potentials by *in situ* Raman spectroscopy (Figure 5d). Experiments with pure Zn showed a single Raman peak at 1045 cm^{-1} , which was attributed to the NO_3^- in solution^{49,50} (a control experiment with an aqueous KNO_3 solution in absence of electrocatalyst also showed the peak at 1045 cm^{-1}). On the other hand, for $\text{Zn}_{93}\text{Cu}_7$, a small peak at 865 cm^{-1} was observed at $-0.5\text{ V}_{\text{RHE}}$, which gradually grew as the potential increased to $-0.8\text{ V}_{\text{RHE}}$ before disappearing at $-1.1\text{ V}_{\text{RHE}}$. This peak can be attributed to the N–O stretch mode of surface-adsorbed $^*\text{NH}_2\text{OH}$ intermediate,^{49,51} providing direct experimental evidence for this species on the $\text{Zn}_{93}\text{Cu}_7$ surface. This observation also confirms hypothesis 2 that $\text{Zn}_{93}\text{Cu}_7$ can generate $^*\text{NH}_2\text{OH}$ intermediate which plays a central role in the reaction. In contrast, the pure Cu electrocatalyst exhibited two peaks at 1005 and 1385 cm^{-1} corresponding to adsorbed $^*\text{NO}_3^-$ species,^{49,50} which grew with the potential increasing to $-0.3\text{ V}_{\text{RHE}}$ and then disappeared at more negative potentials. The absence of the $^*\text{NH}_2\text{OH}$ peak on pure Cu can be explained by the favored further reduction of $^*\text{NH}_2\text{OH}$ into NH_3 on Cu. The absence of a clear Raman peak for the adsorbed $^*\text{NH}_2\text{OH}$ on pure Zn can be explained by the weak adsorption of $^*\text{NH}_2\text{OH}$ on Zn, which makes the surface-adsorbed intermediates difficult to be observed by a surface-enhanced technique. Overall, these observations on pure Cu and the absence of adsorbed species on pure Zn collectively support hypothesis 1 that Cu provides a stronger binding for NO_3^- compared to Zn, which is beneficial for electrochemical NO_3R .

Computational Mechanistic Studies. To shed further light on the different NO_3R selectivities toward NH_2OH , NH_3 , and N_2 observed with the Cu, Zn, and $\text{Zn}_{93}\text{Cu}_7$ electrocatalysts, we performed a mechanistic investigation by means of periodic density functional theory (DFT) calculations (see the Supporting Information for details). To avoid the well-documented issues associated with the modeling of charged species through the introduction of a background charge in the unit cell,^{52,53} and since the reduction from NO_3^- to nitric oxide (NO) is widely understood,^{15,37,52–54} we set the zero of energies in our calculations to be the neutral NO molecule instead of NO_3^- (see the Supporting Information for further details).

To study the NO_3R reactivity on the different electrocatalysts, we constructed Cu(111), Zn(101), and $\text{Zn}_{93}\text{Cu}_7$ (101) surface slab models (as confirmed by XRD in Figure 2f and Figure S12) followed by the assessment of their surface coverages under experimental conditions,^{55,56} as depicted in Figure S17. For Cu(111), DFT simulations predict 75% of the *fcc* sites to be covered by H atoms, while all the *bridge* positions on Zn(101) and $\text{Zn}_{93}\text{Cu}_7$ (101) are occupied by H. Taking these surface terminations as the catalyst resting state, the electroreduction of NO to N_2 , NH_2OH , and NH_3 was then explored via a series of proton-coupled electron transfer (PCET) steps, as reported elsewhere.^{17,18,28} Furthermore, at each step, the hydrogenation of both the N and O atoms was considered as well as all the possible adsorption sites for each reaction intermediate (see Tables S2 and S3).

First, the N_2 evolution reaction was investigated via the mechanism outlined below (* denotes a surface site), which involves the adsorption of NO on the electrode surface, two sequential PCETs at the O atom, and the N–N coupling followed by N_2 desorption (eqs 1–4).^{21,57}



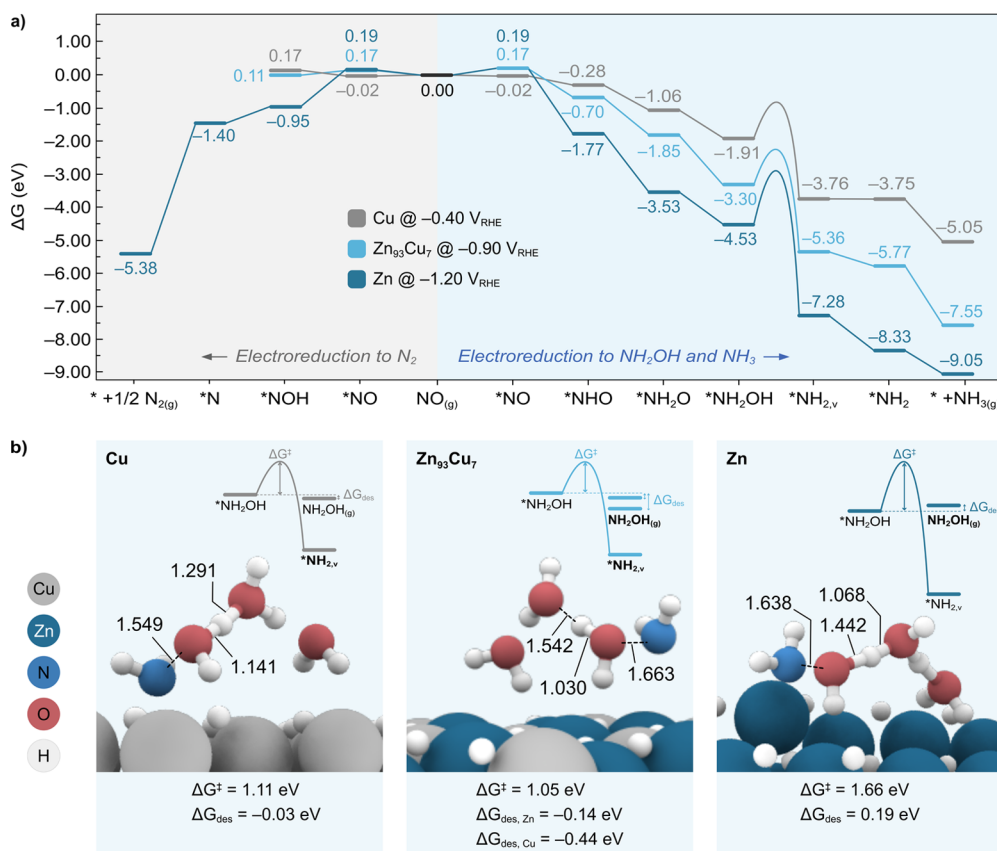


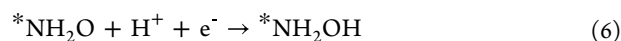
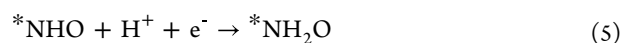
Figure 6. Computational mechanistic studies for the formation of N₂, NH₂OH, and NH₃. (a) Gibbs energy diagram for the electroreduction of NO to N₂ (left) and NO to NH₂OH and NH₃ (right) on the Cu(111), Zn₉₃Cu₇(101) and Zn(101) surfaces at the experimental applied potentials of −0.40, −0.90, and −1.20 V_{RHE}, respectively. The label *NH₂v denotes the formation of the *NH₂ intermediate from *NH₂OH by sourcing the H atom from the surface coverage, whereas the label *NH₂ indicates the same intermediate after replenishing the surface H vacancy. (b) Optimized transition state structures and associated kinetic barriers (ΔG[‡]) for the electroreduction of *NH₂OH on pure Cu (left), Zn₉₃Cu₇ (middle), and pure Zn (right). This step was modeled with two explicit water molecules to assist H transfer. Relevant bond distances are given in Å. The Gibbs energies associated to *NH₂OH desorption (ΔG_{des}) are also provided. The insets illustrate the competition between the electroreduction and desorption of *NH₂OH. The most favored species are highlighted in bold. Color code: Cu (gray), Zn (dark blue), O (red), N (blue), H (white).



The computed Gibbs energy diagrams on the different electrocatalysts are depicted in Figure 6a (left). These are reported at the experimental potentials where the same total current density of 100 mA/cm² can be achieved on the Zn, Cu, and Zn₉₃Cu₇ electrocatalysts. These diagrams revealed that the first PCET to form the intermediate *NOH (i.e., hydrogenated at the O, eq 2) is thermodynamically favorable on pure Zn (i.e., −0.95 eV), whereas this process is slightly endergonic both on pure Cu and Zn₉₃Cu₇ (i.e., +0.17 and +0.11 eV, respectively). These findings and the highly exergonic formation of N₂ predicted on Zn (i.e., −5.38 eV) are in line with the higher FE toward N₂ observed in experiments on Zn compared to Cu and Zn₉₃Cu₇ (Figure 4b). Hence, theoretical calculations support hypothesis 4 that the formation of NH₂OH (which eventually produces oxime) on pure Zn is disadvantaged by the competing NO₃R pathway toward N₂, which is marginally accessible on Cu and Zn₉₃Cu₇. These results could also explain the lower yields of oxime achieved on pure Zn relative to the Zn₉₃Cu₇ alloy (Figure 4b).

The production of NH₂OH and NH₃ relies instead on the formation of the *NHO intermediate (i.e., hydrogenated at the N), which is thermodynamically more favorable than *NOH on all the electrocatalysts investigated in this work (Figure 6a, right). Notably, while DFT calculations predict the generation of both *NOH and *NHO on Zn(101) to be essentially irreversible at room temperature due to their associated highly exergonic energies (i.e., −0.95 and −1.77 eV, respectively), for Cu and Zn₉₃Cu₇, only the formation of *NHO is thermodynamically driven (i.e., −0.28 and −0.70 eV, respectively). Hence, the relative stability between the *NHO vs *NOH intermediates and the binding strength of NH₂OH can be used as descriptors to rationalize product selectivity, as we discuss in detail below.

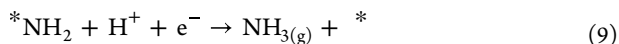
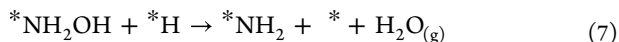
The reduction of *NHO toward *NH₂OH and NH₃ was investigated via a series of PCET steps. According to DFT calculations, the lowest energy pathway for *NH₂OH formation involves the sequential hydrogenation of the N and O atoms, as outlined in eqs 5 and 6.



As seen from Figure 6a (right), both processes are exergonic on Zn, Cu, and Zn₉₃Cu₇, supporting the formation of the

*NH₂OH intermediate on all these electrocatalysts. In particular, the trend obtained from calculations, from more to less exergonic, is Zn > Zn₉₃Cu₇ > Cu.

The subsequent electroreduction of *NH₂OH to NH₃ was then examined according to the mechanism shown in eqs 7–9.



Again, calculations predict the electroreduction of *NH₂OH to NH₃ to be thermodynamically downhill, in line with the experimental observation of NH₃ with all the studied electrocatalysts (Figures 4b and 5a). However, we note that *NH₂OH electroreduction is competing with *NH₂OH desorption from the electrode surface, which is followed by a chemical reaction with the cyclohexanone in solution to produce oxime. Therefore, to shed light on the different NH₃/oxime selectivities observed in experiments, we set out to compute both the thermodynamic driving force for *NH₂OH desorption (ΔG_{des}) and the kinetic barrier for *NH₂OH electroreduction ($\Delta G^\ddagger$), the results of which are summarized in Figure 6b. Notably, the *NH₂OH desorption is almost thermoneutral on Cu (−0.03 eV), slightly endergonic on Zn (+0.19 eV), and exergonic on the Zn₉₃Cu₇ alloy (−0.14 and −0.44 eV from Zn and Cu sites, respectively). For the modeling of the *NH₂OH electroreduction, we note that this step involves the hydrogenation of the O atom with the concomitant cleavage of the N–O bond, which can be promoted by either the aqueous electrolyte or the H surface coverage. However, given that the p*K*_b of NH₂OH in water is ca. 8.1,³⁸ it is unlikely that NH₂OH will be protonated by the aqueous electrolyte at the experimental pH 7. Hence, we focused on modeling the reaction kinetics of the *NH₂OH electroreduction by sourcing a H atom from the electrode surface.⁵⁶ Furthermore, because of the relatively large distance between the O lone pairs in *NH₂OH and the nearest surface H (ca. 3.0 Å on Cu(111) and ca. 4.2 Å on both Zn₉₃Cu₇(101) and Zn(101)), we envisioned this process to be promoted by the aqueous electrolyte. To capture this in our kinetic studies, we introduced two H₂O molecules to mediate the H transfer. This led to the following energy barriers for the different electrocatalysts: Cu (1.11 eV) ~ Zn₉₃Cu₇ (1.05 eV) < Zn (1.66 eV) (Figure 6b). With these values of $\Delta G^\ddagger$ and ΔG_{des} , we can now rationalize the NH₃/oxime selectivities on Cu, Zn₉₃Cu₇, and Zn as follows. On pure Cu, *NH₂OH electroreduction (with moderate $\Delta G^\ddagger$) is favored over *NH₂OH desorption, rendering NH₃ as the major NO₃R product. On the other hand, the high $\Delta G^\ddagger$ found for pure Zn hinders *NH₂OH electroreduction, while the slightly endergonic ΔG_{des} allows *NH₂OH desorption at room temperature, coherently with the product distribution observed experimentally (Figures 4b and 5a). Finally, on the Zn₉₃Cu₇ alloy, the moderate $\Delta G^\ddagger$ and exergonic ΔG_{des} allow both the electroreduction and desorption of *NH₂OH to occur at room temperature, in agreement with the formation of oxime and NH₃ as major products (Figures 4b).

CONCLUSIONS

In conclusion, we have prepared a Zn₉₃Cu₇ alloy that can drive the one-pot electrosynthesis of cyclohexanone oxime through

NO₃R with a yield of 97% and FE of 27% at 100 mA/cm². This electrochemical method not only enables the production of this important chemical precursor under mild conditions (room temperature, atmospheric pressure, aqueous solution, neutral pH, no toxic/expensive catalysts) compared to conventional chemical routes but also offers a promising strategy to upgrade nitrate into value-added organonitrogen compounds. In addition, this work demonstrates the central role of the *NH₂OH intermediate in this tandem EChem–Chem process, as well as the importance of controlling the surface adsorption of nitrogen species in electrosynthesis. The distinct behaviors of Zn, Cu, and ZnCu alloys observed in the experimental and theoretical studies reported in this work reveal that Cu-rich electrocatalysts can drive the NO₃R at lower overpotentials to due to their strong affinity for NO₃[−] but favor further electroreduction of *NH₂OH into NH₃. In contrast, Zn-rich electrocatalysts require higher overpotentials for NO₃R but facilitate the chemical reaction between *NH₂OH and cyclohexanone to produce oxime. Overall, this work demonstrates a novel electrochemical strategy to upgrade nitrate and drive the sustainable synthesis of cyclohexanone oxime. This study also highlights the potential and key aspects for the development of EChem–Chem tandem processes for the electrification of industrial syntheses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.3c05388>.

Experimental and computational methods, compositions of different Zn/Cu catalysts, computed ΔG_{ex} values, H-cell setup, chronopotentiometry graph, mass spec, NMR, HPLC and IC analysis of the products, SEM, EDX, ICP, ECSA, XRD, and XPS characterizations of the catalysts, reusability of the electrocatalyst, detection of NH₂OH, nitrate reduction without cyclohexanone, and computational details for the surface coverage of electrocatalysts (PDF)

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Author Contributions

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Author Contributions

J.S. and T.L. performed the electrocatalysis experiments. T.L. designed and supervised the experimental studies. A.C. performed the DFT calculations. M.G.-M. designed and supervised the computational studies. H.A. performed the SEM and EDX measurements. J.S. and H.A. performed *in situ* Raman experiments. S.R.U., A.C., T.L., and M.G.-M. cowrote the first draft. All authors contributed to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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