

### **Computational Investigations of Furfural Valorization**

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## **Computational Investigations of Furfural Valorization**

## **Sihang Liu**

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> > PhD Thesis August 2023



## Abstract

The global crisis caused by overreliance on fossil fuels has rung the bell for finding alternatives to energy generation and chemical production. In the past decade, we have seen hopes of resolving the challenge in building a sustainable and circular biomass economy. One of the most important sectors of biomass economy is to efficiently upgrade biomass derivatives into value-added fuels and chemicals. Valorizing furfural, a platform chemical mainly derived from non-food agricultural residues, is regarded as a model process to understand biomass valorization reactions. Though great progress has been achieved in furfural valorization via both conventional thermal reactors and novel electrolyzers, there are still issues concerning elusive reaction mechanisms, poor understanding of reaction interfaces, and suboptimal reaction conditions and setups.

The Thesis begins with a study of gas-phase furfural hydrogenation towards furfuryl alcohol at metal-gas interfaces, with the target to find active and nontoxic catalysts to replace Cr-based catalysts in industry. Based on density functional theory (DFT) calculations, we show that rate-limiting steps vary on different metal surfaces, suggesting that we need to lower corresponding barriers to improve activities on different metal catalysts. Furthermore, we construct a microkinetic model to describe the activity of furfuryl alcohol production from furfural and hydrogen gas. The established activity volcano suggests that Cu-rich alloys, e.g., Cu<sub>3</sub>Ni, present enhanced activities and can become next-generation catalyst candidates for furfural hydrogenation.

To study the solvent effect on furfural hydrogenation, we then transit from the metal-gas interface to the metal-water interface. We investigate the furfural adsorption at various metal-water interfaces using *ab initio* molecular dynamics (AIMD) simulations. Different from metal-gas interfaces for our first study, aqueous phase conditions pose strong solvation penalties to furfural adsorption, which we attribute to the displacement of water interacting with the metal surface. To reduce the computational cost in simulating interfacial chemistry, we find that the OH binding energy serves as a simple descriptor to correlate with solvation energies. This helps generalize the understandings of adsorption phenomena in ultrahigh vacuum (UHV) conditions towards solvated systems. Based on the identified solvent effect, we unveil the origin of activity in aqueous phase furfural hydrogenation over strong-binding metal surfaces.

We then move on to explore the electrification of furfural hydrogenation, i.e., furfural electroreduction, using 'green' protons and electrons. We first embark on the investigation of

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furfural reduction over Cu electrodes, the most studied material for this reaction. Combining grand-canonical DFT (GC-DFT) calculations, microkinetic simulations and experiments, we unveil the possible rate-limiting steps to produce furfuryl alcohol and 2-methyl furan, lying beyond the first proton-coupled electron transfer (PCET). A general pH-potential map to boost selectivity towards more valuable 2-methyl furan product is also proposed. Furthermore, we argue that the surface hydrogenation contributes little to the overall activity on Cu terraces even under very acidic conditions.

Inspired by our experimental collaborations, we further our excursion of furfural reduction to welldefined single atom catalysts. We propose using furfural and hydrogen adsorption energies to classify the selectivity for this reaction at mild conditions. Supported molecular single atom catalysts generally bind furfural weakly and selectively produce the dimer product (hydrofuroin). The formation of the dimer is shown to be limited by the first protonation, while the coupling step is facile in solution. Furthermore, the metal center can be modified on the general metal-nitrogencarbon complex to achieve higher selectivity towards the monomer product (furfuryl alcohol). It is predicted that by modulating the metal center and coordination in the single atom motifs, we can further unleash the potential of those 'lonely' active sites in furfural reduction and other biomass electrovalorization reactions.

The theoretical insights obtained in the Thesis establish a better understanding of furfural (electro-)valorization reactions and provide rationale to design more active and selective catalysts with optimized reaction conditions.

## Resumé

Den globale krise, som skyldes overdreven afhængighed af fossile brændstoffer, har påbegyndt søgningen efter at finde alternativer til energigenerering og kemisk produktion. I det seneste årti har vi set håb om at løse udfordringerne med at opbygge en bæredygtig og cirkulær biomasseøkonomi. En af de vigtigste sektorer i biomasseøkonomien er at effektivt opgradere biomassederivater til værdiforøgende brændstoffer og kemikalier. Valorisering af furfural, som er et platformskemikalie, der hovedsageligt stammer fra nonfood landbrugsrester, er anset som en modelproces til at forstå biomasse-valoriseringsreaktioner. Selvom fremragende fremgang er opnået indenfor furfural-valorisering via både konventionel termisk katalyse og nye elektrolysatorer, så er der stadig problemer angående ufuldstændige reaktionsmekanismer, utilstrækkelig forståelse af reaktionsgrænseflader og suboptimale reaktionsbetingelser og opsætninger.

Denne afhandling begynder med et studie af termisk furfural-hydrogenering til furfurylalkohol ved metal-gas-grænsefladerne med formålet at finde aktive og ikke-giftige katalysatorer, som skal erstatte krom-baseret katalysatorer i industrien. Baseret på tæthedsfunktionalteori (DFT) beregninger viser vi, at de hastighedsbestemmende trin varierer på forskellige metaloverflader, hvilket tyder på, at vi har brug for lavere korresponderende barrierer for at forbedre aktiviteterne på katalysatorer. Derudover konstruerer vi en mikrokinetisk model til at beskrive produktionsaktiviteten af furfurylalkohol fra furfural og hydrogengas. Den etablerede aktivitetsvulkan antyder, at kobberrige legeringer, fx Cu<sub>3</sub>Ni, viser forøget aktiviteter i forhold til rene kobberkatalysatorer, og de kan blive optimeret yderligere som næste generations katalysatorkandidater for furfural-hydrogenering.

For at studere den afgørende opløsningseffekt i furfural-hydrogenering har vi derefter skiftet fra metal-gas-grænsefladen til metal-vand-grænsefladen. Vi udforsker furfural-adsorptionen på forskellige metal-vand-grænseflader ved anvendelse af ab initio molekylær dynamik (AIMD) simuleringer. Forskelligt fra metal-gas-grænsefladen fra vores første studie udgør vandfasebetingelser stærke opløsningsstraffe for furfural-adsorption, hvilket vi tillægger til forskydningen af vandinteraktionen med metaloverfladen. For at reducere beregningsomkostningerne ved simulering af grænsefladekemien har vi fundet ud af, at OHbindingsenergien virker som en simpel deskriptor til at korrelere opløsningsenergien. Dette

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hjælper med at generalisere forståelsen af adsorptionsfænomenet i ultrahøj vakuum (UHV) betingelser henimod opløste systemer. Baseret på de identificeret opløsningseffekter afslører vi oprindelsen af aktiviteten for furfural-hydrogenering i vandfase over stærkt bindende metaloverflader. Vi går derefter videre til at udforske elektrificeringen af furfural-hydrogenering, dvs. furfural elektronreduktion, ved brug af grønne protoner og elektroner. Vi går først i gang med undersøgelsen af furfural-reduktionen over kobber-elektroderne, hvilket er det mest undersøgte materiale for denne reaktion. Ved at kombinere grand-canonical DFT (GC-DFT) beregninger, mikrokinetiske simuleringer og eksperimenter afslører vi de mulige hastighedsbestemmende trin til fremstilling af furfurylalkohol og 2-metylfuran, hvilket ligger efter den første protonkoblede elektronoverførsel (PCET). Et generel pH-potentialekort er også forslået til at forøge selektiviteten for det mere værdifulde 2-metylfuran produkt. Desuden argumenterer vi for, at overflade-hydrogeneringen bidrager kun lidt til den fulde aktivitet på kobberterrasser selv under meget syrlige betingelser.

Inspireret af vores samarbejde med eksperimentalister tager vi videre på vores rejse med furfuralreduktion til veldefineret enkeltatom-katalysatorer. Vi forslår brug af furfural- og hydrogenadsorptionsenergier til at klassificere selektiviteten for denne reaktion ved milde betingelser. Støttede molekylære-enkeltatom-katalysatorer binder generelt furfural svagt og producerer selektivt et dimerprodukt (hydrofuroin). Dannelsen af dimer er vist til at være begrænset af den først protonisering, hvorimod koblingstrinnet i opløsning er ikke-begrænsende. Desuden kan metalcentrene modificeres på generel metal-nitrogen-karbon-komplekser for at opnå højere selektivitet for monomerproduktet (furfurylalkohol). Det forudsiges, at ved modulering af metalcenteret og koordinationen af enkeltatom-motivet kan vi yderligere frigøre potentialerne af disse 'ensomme' positioner furfural-reduktion aktive i og andre biomasseelektrovaloriseringsreaktioner.

Den teoretiske indsigt opnået gennem denne forskningsrejse etablerer en bedre forståelse af furfural-valoriseringsreaktioner og giver begrundelse for at designe flere aktive og selektive katalysatorer med optimerede reaktionsmiljøer.

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## Preface

This thesis is submitted in partial fulfillment of the PhD degree in Physics at the Technical University of Denmark (DTU). The work presented herein was performed at the Catalysis Theory Center, DTU between September 2020 and August 2023. The studies have been supervised by Thomas Bligaard, Georg Kastlunger and Karen Chan. The research received funding from Villum Fonden (no. 29450) and support from PRACE with the access to the JUWELS supercomputer in Juelich, Germany and Vega CPU in IZUM Maribor, Slovenia (project 2020235596).

Kongens Lyngby, August 31, 2023

SikangLiu

Sihang Liu

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Three years feel faster than three days. And I am not drunk at all to say this.

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## List of publications

### Paper I (Chapter 3)

Understanding activity trends in furfural hydrogenation on transition metal surfaces <u>Sihang Liu</u>, Nitish Govindarajan, Karen Chan ACS Catal. **2022**, 12, 20, 12902–12910

### Paper II (Chapter 4)

Solvation of furfural at metal-water interfaces: Implications for aqueous phase hydrogenation reactions

<u>Sihang Liu</u>, Sudarshan Vijay, Mianle Xu, Ang Cao, Hector Prats, Georg Kastlunger, Hendrik Heenen, Nitish Govindarajan

J. Chem. Phys. 2023, 159, 084702

### Paper III (Chapter 5)

### Unraveling the reaction mechanisms for furfural electroreduction on copper

<u>Sihang Liu<sup>#</sup></u>, Zamaan Mukadam<sup>#</sup>, Soren B Scott, Saurav Ch Sarma, Maria-Magdalena Titirici, Karen Chan, Nitish Govindarajan, Ifan EL Stephens, Georg Kastlunger EES. Catal. **2023**, 1, 539-551

### Paper IV (Chapter 6)

### Furfural electrovalorisation using single-atom molecular catalysts

Zamaan Mukadam<sup>#</sup>, <u>Sihang Liu<sup>#</sup></u>, Angus Pedersen, Jesús Barrio, Sarah Fearn, Saurav Ch Sarma, Maria-Magdalena Titirici, Soren B Scott, Ifan EL Stephens, Karen Chan, Stefano Mezzavilla Energy Environ. Sci. **2023**, 16, 2934-2944

### Paper V (Chapter 6)

Switching between outer- and inner-sphere biomass electrosynthesis via single atom catalysts <u>Sihang Liu</u>, Zamaan Mukadam, Angus Pedersen, Jesús Barrio, Maria-Magdalena Titirici, Ifan EL Stephens, Georg Kastlunger To be submitted.

### **Other publications:**

### Paper VI

# On the role of Zr to facilitate the synthesis of diesel and jet fuel range intermediates from biomass-derived carbonyl compounds over aluminum phosphate

Wenting Fang, <u>Sihang Liu</u>, Leonhard Schill, Mariusz Kubus, Thomas Bligaard, Anders Riisager Appl. Catal. B **2023**, 320, 121936

### Paper VII

On the role of Cu<sup>+</sup> and CuNi alloy phases in mesoporous CuNi catalyst for furfural hydrogenation

Wenting Fang<sup>#</sup>, <u>Sihang Liu</u><sup>#</sup>, Astrid Kjær Steffensen, Leonhard Schill, Georg Kastlunger, Anders Riisager

ACS Catal. 2023, 13, 8437-8444

### Paper VIII

Understanding the reaction mechanism of Kolbe electrolysis on Pt anodes <u>Sihang Liu<sup>#</sup></u>, Nitish Govindarajan<sup>#</sup>, Hector Prats, Karen Chan Chem Catal. **2022**, 2, 1100–1113

<sup>#</sup>equal contribution

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## **CHAPTER 1**

## Introduction and motivation

## 1.1 Overuse of fossil fuels and its consequences

Fossil fuels have ignited human's civilizations and boosted anthropogenic productivities since the Industrial Revolution around 1800s, in company with a booming global population. However, the alarmingly accelerating burning of fossil fuels in modern industries have dramatically increased the man-made  $CO_2$  and other greenhouse gas (GHG) emissions as shown in Figure 1.1.



Figure 1.1 The alarming increase in global anthropogenic  $CO_2$  emission due to burning fossil fuels and other industrial activities. Reprinted with permission from Ref<sup>1</sup>. Copyright 2014 IPCC.

The GHG emissions have been correlated directly to the increase in average surface temperatures in the last century, where anthropogenic driving forces play a dominant role. The global warming is becoming self-evident and less disbeliefs are laid upon the fact that overuse of fossil fuels nurtures the vicious circle. The consequences of global warming are severe and destructive: the increased likelihood of extreme and rare weather events, unbalanced ecosystems, rising sea water levels and declining glaciers. Besides, excessive burning of fossil fuels give rise to regional pollutions, which pose threats to sustainable development of the human society. As a result, it is high time that we find an alternative resource to manufacture useful chemicals and fuels, to reduce the reliance on unrenewable fossil fuels and close the carbon cycle. Rewinding to the beginning of human's civilization, our ancestors learnt to utilize non-food biomass wastes, e.g., dried grass, fallen leaves and tree branches to set fire, make simple tools and fertilize crops and livestock.

Nowadays, we need to borrow this old wisdom to go back to biomass residues, a renewable biological resource, produced in huge quantities each day from nature. Taking advantage of modern technologies, we could further upgrade the biomass resources to more than just raw fertilizers, but thousands of fine chemicals and purified biofuels, maximizing the use of this forgotten treasure.

### **1.2 Biomass-based circular carbon economy**



Figure 1.2 The biomass-based circular economy: photosynthetic atmospheric carbon sequestration, biomass valorization, energy flow and a closed carbon circulation. Reprinted from Ref<sup>2</sup>. Copyright 2021 Frontiers.

An emerging framework is to build a circular biomass economy (or bioeconomy, as illustrated in Figure 1.2) to exploit the potential of biomass feedstocks to both serve as atmospheric carbon sinks

and building blocks in modern manufacturing and energy section. On the one hand, plant growth shows a more efficient carbon capture from atmosphere (mainly via photosynthesis) compared to energy-intensive direct air capture. On the other, biomass feedstocks offer natural complex compounds which can be refined into downstream products with a much shorter path than the conventional fossil fuels-sourced pathways. The circular biomass economy can help achieve global net-zero emission targets, especially to decarbonize petrochemical industries.

### 1.3 Upgrading biomass into value-added products

To achieve a sustainable circular biomass economy, a crucial technology is to efficiently valorize biomass feedstocks into platform chemicals and their derivatives, where catalysis is central to accelerate and steer the reactions.



Figure 1.3 Upgrading biomass into value-added fuels, chemicals and materials with biomassderived chemicals being building blocks. Reprinted from Ref<sup>3</sup>. Copyright 2021 American Chemical Society.

As shown in Figure 1.3, derived from biomass residues, raw feedstocks i.e., lipids, proteins, and lignocellulose (cellulose, hemicellulose, and lignin) could be harvested via deconstructions. Among them, lignocellulose is the most abundant and cheapest biomass resource, stemming from

woods, short rotation crops and forestry, and agricultural residues, which are far from being efficiently utilized today<sup>4</sup>. This sector is mainly composed of cellulose (25–55 wt%), hemicellulose (10–50 wt%), and lignin (6–30 wt%), which are not competing with foods for humans. Those non-edible sugars (e.g., xylose) are further produced from (hemi)cellulose via hydrolysis, serving as precursors to furans and carboxylic acids. Other value-added molecules, such as oxygenated aromatics and even amino acids, are available through biomass refineries. In the meantime, biomass-derived carbohydrates could be promising biofuels or the precursors to liquid alkanes<sup>5.6</sup>, to make the fuel industry less dependent on fossil fuels. Sustainable production of fuels from biomass residues fulfills the carbon cycle of biomass growth to fix CO<sub>2</sub>, biofuel production and utilization to release CO<sub>2</sub>, especially upgraded with electrified valorization routes<sup>7</sup>, i.e., biomass electrovalorization in coupled with other electrochemical productions<sup>8</sup>.



## 1.4 Furfural: A platform bio-derived chemical

Figure 1.4 A classification of major products via furfural valorization reactions.

Selected as Top 30 value-added biomass-derived building block<sup>9</sup>, furfural is produced from renewable and non-food agricultural sources such as food crop residues and wood wastes via the dehydration of xylose. The synthesis of furfural from fossil-based raw materials (e.g., via the

catalytic oxidation of 1,3-dienes) is not economically competitive. The largest producer of furfural is China (ca. 70% global production capacity), followed by the Dominican Republic and South Africa, with a total 90% account of the global production capacity (ca. 280 kTon per year).<sup>10</sup> As an important platform chemical, furfural has been widely studied for catalytic valorization, e.g., further reduced mainly to furfuryl alcohol (FAL), 2-methylfuran (2-MF), hydrofuroin (HFN), tetrahydrofurfuryl alcohol (THFA) and 2-methyltetrahydrofuran (2-MTHF) or oxidized to furoic acid (FA), maleic acid (MA) and other chemicals or aminated to valuable amines, as summarized in Figure 1.4. Consuming 65% of the overall furfural production, FAL is the most important downstream chemical from furfural valorization, with primary applications in resin production, reactive solvents, and polymer industries. Notably, FAL is also a precursor to other furanic chemicals<sup>11</sup>.

### **1.4.1 Gas-phase hydrogenation of furfural**

The industrial gas-phase furfural hydrogenation feeds furfural into an evaporator comprising a packed column, a circulating pump, and a heater to maintain the temperature at ca. 400 K, with H<sub>2</sub> gas being introduced at the bottom of the reaction column. To ensure a facile hydrogenation process, molar ratio of H<sub>2</sub> is usually much higher than that of furfural. The gas-phase furfural hydrogenation was first reported in 1929 using Cu catalysts. Later, the use of copper chromite (CuCrO<sub>x</sub>) was patented in 1937 by Du Pont de Nemours. The industrial CuCrO<sub>x</sub> catalysts could reach a furfural conversion of ca. 20 µmol g<sup>-1</sup> s<sup>-1</sup>, with a high selectivity towards FAL above 90%. Following the development of CuCrO<sub>x</sub> catalysts, other Cu-based catalysts have been studied, including CuZn, CuNi, CuFe and CuCo on different supports<sup>12</sup>.

### **1.4.2 Renaissance of electrovalorization of furfural**

The electroreduction of furfural dates back to 1939 by Albert and Lowy<sup>13</sup>, when they managed to reduce furfural to the dimer product, i.e., HFN and minor FAL and resins in a KH<sub>2</sub>PO<sub>4</sub> electrolyte. Hindered by the low solubility of furfural in water and complex products, this electrochemical process has been overshadowed until a decade ago, when Nilges and Schröder achieved a selective reduction of furfural into the biofuel product 2-MF using a copper electrode<sup>14</sup>. Since then, copper electrodes have been placed at the center of furfural electroreduction. In parallel, the electrooxidation of furfural has also been investigated with an aim to produce value-added organic



acids, e.g., furoic acid (FA) and maleic acid (MA). A schematic depicting of furfural-fed electrolyzer is shown in Figure 1.5a.

Figure 1.5 Schematics for different types of furfural-involved two-electrode electrolyzers. a. furfural reduction + furfural oxidation; b. hydrogen evolution + furfural oxidation; c. furfural reduction + oxygen evolution.

### 1.4.3 The bright side of biomass electrovalorization

The electrochemical conversion of biomass feedstock is emerging as an attractive alternative pathway to produce value-added carbonaceous green e-chemicals<sup>15</sup>. The advantages for electrovalorization of furfural and other biomass derivatives include mild reaction conditions (usually operated at room temperature and ambient pressure), use of green proton (e.g., water) and sustainable electricity, easily tunable selectivity via potential and pH, and possible integrations with other electrochemical productions, e.g., furfural reduction coupled with H<sub>2</sub> evolution, furfural oxidation with CO<sub>2</sub> reduction and hydroxymethylfurfural (HMF) reductive amination reactions.

Compared to conventional water electrolyzers, the thermodynamic cell voltages could be reduced by over 1 V, if the sluggish OER is replaced by the oxidation of furfural<sup>16,17</sup> or other biomass derivatives, e.g., glycerol<sup>18</sup> and HMF<sup>19</sup>, as shown in Figure 1.6. In doing so, we could not only produce H<sub>2</sub> with higher energy efficiency (EE), but also harvest diverse value-added biomassderived products on the anode. Besides, the decrease in anodic potentials could slow down the degradation of catalysts and cell setups.



Figure 1.6 The comparison between biomass reduction/oxidation and conventional water electrolysis (forming  $H_2$  and  $O_2$ ).

## **1.5 Grand challenges in furfural valorizations**

### 1.5.1 Gas-phase hydrogenation of furfural

Gas-phase furfural hydrogenation is a mature industrialized process, which is a model reaction for biomass valorization and scaleup. However, this process faces challenges of toxic Cr in catalysts and its possible leakage, the instability of Cu component, and the average mass activity is compromising even at elevated temperature and pressure. Above all, the reaction mechanisms remain underexplored, and no universal understanding has been achieved, which hinders the establishment of a clear structure-activity relationship and slow down catalyst design for Cr-free and more active catalysts.

### **1.5.2 Electrovalorization of furfural**

Electrifying the process to upgrade furfural offers new opportunities to close the carbon cycle and harvest fine chemicals and fuels at the same time. Nevertheless, the electrochemical biomass conversion including furfural faces serious fundamental and technical challenges<sup>3</sup>:

- Low faradaic efficiency towards target products, e.g., value-added 2-MF and hydrofuroin, due to convoluted reaction networks, homogenous reactions, and competitions from hydrogen or oxygen evolution (HER or OER)
- Unclear reaction mechanisms complexed by the role of protons, potential and pH dependence, mass transport, solution reaction and elusive structures of electrochemical double layers i.e., EDLs
- The low solubility of furfural and early mass transport limits
- The instability of catalyst and membrane materials due to harsh operating conditions, electrode fouling and organic erosions
- The lack of overall reaction calibration and insufficient analytical characterizations of products, e.g., isomers and resins
- Insufficient socioeconomic analysis
- Electrolyzer optimization and scaleup to achieve continuous whole-cell productions
- Lack of theory to understand electrochemical processes at metal-water interfaces

## **1.6 The outline of Thesis**

In this Thesis, we systematically investigate furfural (electro-)valorizations from a mainly theoretical perspective, which can be catalogued into *thermal hydrogenation* and *electroreduction*. We are motivated by both opportunities and challenges in upgrading furfural and other biomass derivatives towards value-added chemicals and fuels to achieve the circular and green biomass economy, as demonstrated in Chapter 1. We then begin with a summary of major theories and methods applied in this Thesis to obtain the major computational results in Chapter 2.

Motivated by an industrial urgency to develop chromium-free active catalysts for furfural valorization, we first investigate the largest catalytic consumer of annual furfural production, *i.e.*, thermal hydrogenation of furfural towards furfuryl alcohol. In Chapter 3, we build a mean-field

microkinetic model (MKM) based on density functional theory (DFT) calculations to study the crucial thermal process of gas-phase furfural hydrogenation to furfuryl alcohol over various metals and alloys. The theoretical activity volcano helps to predict other active catalysts and point to the direction of using diluting alloys. In Chapter 4, to shed light on aqueous-phase furfural valorizations, we zoom into the interfaces of metal-water for furfural adsorption using *ab initio* molecular dynamics (AIMD) simulations. We find a general solvation penalty on furfural adsorption and simple descriptors could reduce the heavy computations. We finally correlate the weakened adsorption of furfural with observed activity on strong-binding metals for furfural hydrogenation in solvents.

In Chapter 5, we transit to electrocatalysis and focus on the electroreduction of furfural. The chunk of this Chapter is to study the elusive mechanism of furfural reduction on copper, the most-used electrode for this reaction. We apply grand-canonical DFT calculations to construct constant-potential electrochemical energetics for MKM. Combining theory and experiment, we unveil the possible rate-determining steps and propose a pH and potential-dependent mechanisms to produce furfuryl alcohol and 2-methryl furan via a proton-coupled electron transfer (PCET) dominated pathway. We stress that surface hydrogenation plays minor role relative to direct protonation on pristine copper surfaces.

In Chapter 6, we extend the electrode material for furfural reduction to the emerging 2D metaldoped nitrogen graphene. Based on a theory-based selectivity map, we show that the homogenous and heterogeneous productions could be tuned by modulating the doped metal atoms. Evidenced by experimental collaborations, we highlight that Cr single-atom catalysts can promote furfuryl alcohol over hydrofuroin production during furfural reduction at mild conditions due to their enhanced furfural adsorption compared to previously reported single atom catalysts.

We conclude the Thesis with a distilled overview of main takeaway messages and how theoretical perspectives could help understand biomass valorization reactions in general to design more active and selective catalysts for future applications.

## **CHAPTER 2**

## Theory and methods

In this Chapter, we briefly describe the electronic structure problem, how the raw energies are calculated using density functional theory (DFT), how the reaction transition states are obtained, how the constant-potential calculations are carried out in a grand-canonical DFT (GC-DFT) scheme for the electrochemical reactions, how the microkinetic model is developed and improved and how we simulate the molecular dynamics at interfaces.

### 2.1 Schrödinger equation

Solving the many-body problem for the electronic structure of molecules and solids has been a grand challenge in quantum mechanics. Specifically, the time-independent electronic structure problem can be written as an eigenvalue problem through the Schrödinger equation,

 $\widehat{H}\Psi = E\Psi(2.1)$ 

where  $\hat{H}$  is the Hamiltonian,  $\Psi$  is the wave function, and E is the energy.

This equation is an eigenvalue equation, where the wave function is an eigenfunction of the Hamiltonian operator with its corresponding eigenvalue E.

More generally, the  $\hat{H}$  equation 2.1 can be written as,

$$\widehat{\mathbf{H}} = \left(\underbrace{-\sum_{i} \frac{\hbar^{2}}{2m_{e}} \nabla_{i}^{2}}_{\widehat{T}_{e}} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}}_{\widehat{U}_{ee}} + \underbrace{\sum_{ij} \frac{Z_{j}e^{2}}{|\mathbf{r}_{i} - \mathbf{R}_{j}|}}_{\widehat{V}_{en}}\right) + \left(\underbrace{-\sum_{i} \frac{\hbar^{2}}{2M_{i}} \nabla_{i}^{2}}_{\widehat{T}_{n}} + \underbrace{\sum_{i \neq j} \frac{Z_{i}Z_{j}e^{2}}{|\mathbf{R}_{i} - \mathbf{R}_{j}|}}_{\widehat{V}_{nn}}\right) (2.2)$$

where  $\hat{T}_e$  and  $\hat{T}_n$ , are the kinetic energy operator for the electron and nuclei respectively,  $\hat{U}_{ee}$  the Coulomb operator for electrons,  $\hat{V}_{en}$ ,  $\hat{V}_{nn}$  the electron-nuclei and nuclei-nuclei interactions respectively, **r** and **R** are position vectors of electrons and nuclei respectively.

After applying the Born-Oppenheimer approximation<sup>20</sup>, which assumes a. the wave functions of nuclei and electrons in a system can be treated separately and b. a fixed position of the nuclei relative to much lighter and more dynamic electrons, the  $\hat{H}$  can be then simplified as the equation to describe the motion of electrons in the system  $\hat{H}_e$ ,

 $\widehat{H}_e = \widehat{T}_e + \widehat{U}_{ee} + \widehat{V}_{en} (2.3)$ 

Compared to the total  $\hat{H}$ , the electron-focused  $\hat{H}_e$  greatly reduce the complexity of the system and subsequent calculations. However, it is still extremely costly to solve the Schrödinger equation with multiple electrons due to overwhelming freedoms in motions.

### **2.2 Density functional theory (DFT)**

To further address the many-electron systems in the framework of Schrödinger equation, the position terms in 2.2 are approximated by functionals of the spatially dependent electron density, i.e., the density functional theory (DFT), with pioneering theorems and frameworks developed by Hohenberg, Kohn and Sham<sup>21,22</sup> in 1960s.

### 2.2.1 Hohenberg-Kohn (HK) theorems

Theorem 1. The ground-state electron density  $n(\mathbf{r})$  uniquely determines the external potential  $\hat{V}_{ext}$ . The Hamiltonian of a ground-state  $\Psi$  with an electron density can be written as<sup>21</sup>,

 $\widehat{\mathbf{H}} = \widehat{T}_e + \widehat{U}_{ee} + \widehat{V}_{ext} \ (2.4)$ 

where the external potential  $\hat{V}_{ext} = v(\mathbf{r})$ , which is a unique functional of  $n(\mathbf{r})$ . Theorem 2. The ground-state density minimizes the ground-state energy of the system.

Since  $\Psi$  is a functional of  $n(\mathbf{r})$ , so are  $\hat{T}_e$  and  $\hat{U}_{ee}$ , we then define,

 $F[n(r)] = (\Psi, (\hat{T}_e + \hat{U}_{ee})\Psi)$  (2.5)

where F[n] is a universal functional, consisting of both kinetic energy and Coulomb terms. For a given v(r), the energy functional

$$E_{v}[n] = F[n] + \int v(\boldsymbol{r})n(\boldsymbol{r})d\boldsymbol{r}$$
(2.6)

Obviously, if  $n(\mathbf{r})$  is the ground-state electron density,  $E_v[n]$  equals the ground-state energy E.

### 2.2.2 Kohn-Sham equations

In pursuit for the ground state energy of a system, Kohn and Sham introduced a local effective external potential ( $v_{eff}(\mathbf{r})$ , also called the Kohn-Sham (KS) potential) where the non-interacting particles (typically electrons) move<sup>22</sup>. The Kohn–Sham wavefunction is a single Slater determinant constructed from a set of orbitals that are the lowest-energy solutions to the eigenvalue question

$$\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 + v_{eff}(\boldsymbol{r})\right)\varphi_i(\boldsymbol{r}) = \varepsilon_i\varphi_i(\boldsymbol{r}) \ (2.7)$$

Where  $\varepsilon_i$  is the orbital energy of the corresponding KS orbital  $\varphi_i$ . Furthermore, the N-particle system density can be expressed as,

$$n(\mathbf{r}) = \sum_{i}^{N} |\varphi_{i}(\mathbf{r})|^{2} (2.8)$$

Then, the solution to KS equations is to find n(r) for the eigenvalue question in 2.7. In Kohn-Sham (KS) density functional theory, the total energy of a system can be written as a functional of charge density as,

$$E[n] = T_s[n] + \int d\mathbf{r} \, v_{ext}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{XC}[n] \, (2.9)$$

where  $v_{ext}$  is the external potential,  $T_s$  is the Kohn-Sham kinetic energy, which is written based on the Kohn-Sham orbitals as, Theory and methods

$$T_s[n] = \sum_{i=1}^N \int d\boldsymbol{r} \, \varphi_i^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m_e} \nabla_i^2\right) \varphi_i(\boldsymbol{r}) \, (2.10)$$

 $E_H$  is the Hartree (or Coulomb) energy which can be expressed as,

$$E_{H}[n] = \frac{e^{2}}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} (2.11)$$

 $E_{XC}$  is the exchange-correlation energy of the system.

In terms of Kohn-Sham potentials, the contributions can be summarized in the following equation as,

 $v_{eff}(\mathbf{r}) = v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) + v_{XC}(\mathbf{r})$  (2.12)

To solve the KS equations, a self-consistent loop should be applied as below:

- 1. Set an initial guess  $n_0(\mathbf{r})$ ;
- 2. Calculate  $v_{eff}(\mathbf{r})$  based on the initial guess and Eq. 2.12;
- 3. Solve the eigenvalue problem in Eq. 2.7 to get KS eigenstates  $\varphi_i(\mathbf{r})$  and eigenvalues  $\varepsilon_i$ ;
- 4. Use the obtained eigenstates in Step 3 to solve Eq. 2.8 to get resultant n(r);
- Compare n(r) with n<sub>0</sub>(r), if converged, output n(r) to get forces and eigenvalues..., if not converged, return to Step 2 using the n(r).

In practice, the exchange-correlation energy  $E_{xc}[n]$  is usually the only unknown term in KS-DFT, which lead to different approximations to determine the ground-state energy of interested systems.

### 2.2.3 Exchange-correlation (XC) functionals

As shown in last section, KS-DFT offers practical estimates to the ground-state energy and electron density for a many-body system, where useful information containing in the eigenvalues can be further derived. However, the only unknown term, i.e.,  $E_{XC}$ , requires extra density functional approximations. A hierarchy of different XC approximations is summarized and described as 'Jacob's ladder'<sup>23</sup> to describe the chemical accuracy from Earth (Hartree world) to Heaven (chemical accuracy).

A brief introduction of the 'Jacob's ladder': Rung 1 – local density approximation (LDA) functionals, which only depends on local electron density, e.g., PW92<sup>24</sup>; Rung 2 – generalized gradient approximation (GGA) functionals, which depends on local density and its gradients, e.g., PBE<sup>25</sup>; Rung 3 – meta-GGA functionals, which has an additional dependence on second gradient through kinetic energy density relative to GGA, e.g., M06-L<sup>26</sup>; Rung 4 – hybrid functionals, which include a fraction of Hartree-Fock exchange, e.g., PBE0<sup>27</sup>; Rung 5 – doubly hybrid functionals with virtual orbitals, e.g., B2PLYP<sup>28</sup>. Over the last decade, the machine learning has been adopted to advance density functional approximations to increase the chemical accuracy of DFT calculations<sup>29</sup>.

In this Thesis, we mainly applied GGA-level functionals such as RPBE<sup>30</sup> and optB88<sup>31</sup> to calculate the furfural valorization systems. For single-atom study, we used hybrid functional HSE06<sup>32</sup> for benchmarking furfural adsorption energies and density of states (DOS) of single atoms. In addition, the DFT calculations were mainly carried out using either the Vienna Ab initio Software Package (VASP)<sup>33</sup> or GPAW code<sup>34</sup> in combination with the Atomic Simulation Environment (ASE)<sup>35</sup> for model construction and manipulation, visualization, and analysis.

### 2.2.4 Dispersion correction

Conventional DFT is unable to describe long-range non-local correlations. In order to consider long-range interactions e.g., van der Waals (vdW) contributions to the energy, DFT calculations with dispersion corrections are needed to produce reasonable results. The dispersion contribution  $(E_{disp})$  is calculated via pairwise interactions at highly accurate quantum chemical levels and added to the KS-DFT energy  $(E_{KS-DFT})$  to obtain total energy  $(E_{DFT-disp})$  including local and non-local interactions as,

$$E_{DFT-disp} = E_{KS-DFT} - E_{disp} (2.13)$$

In this work, we applied the Grimme's D3 dispersion correction<sup>36</sup> to account for  $E_{disp}$ , which has been shown to correctly capture the adsorption phenomena (energy and configuration) of aromatic molecules (e.g., benzene, phenol and furfural) on metal surfaces in experiments<sup>37–40</sup>.

### 2.3 Nudged elastic band method

DFT calculations provide ground-state energies of interested systems, i.e., the catalytic interfaces consisting of catalyst surface, adsorbates, and solvents (e.g., water) in this Thesis. For a specific reaction within the harmonic transition state theory (hTST) approximation, it is crucial to find the transition state TS (saddle point) between two ground states (initial state IS and final state FS) to formulate the minimum energy path. In this Thesis, I applied the nudged elastic band (NEB) method<sup>41</sup> to find the TS and the corresponding minimum energy path in elementary reaction steps for the studied reactions (i.e., furfural hydrogenation, furfural reduction and hydrogen evolution). The reaction path between the energy minima of IS ( $R_0$ ) and FS ( $R_N$ ) is first constructed by a socalled elastic band with N + 1 images in total, i.e., [ $R_0, R_1, R_2, ..., R_N$ ]. The end points are fixed in NEB optimization, while the N – 1 intermediate images are optimized. Specifically, the total force on an image is the sum of the spring force along the local tangent and the true force perpendicular to the local tangent as,

$$\boldsymbol{F}_{i} = \boldsymbol{F}_{i}^{s}|_{\parallel} - \nabla E(\boldsymbol{R}_{i})|_{\perp} (2.14)$$

where the true force is expressed by,

$$\nabla E(\boldsymbol{R}_i)|_{\perp} = \nabla E(\boldsymbol{R}_i) - \nabla E(\boldsymbol{R}_i) \cdot \hat{\boldsymbol{\tau}}_i (2.15)$$

where *E* is the system energy and  $\hat{\tau}_i$  the normalized local tangent at image  $i (\hat{\tau}_i = \tau_i / |\tau_i|)$ . The spring force is,

$$\mathbf{F}_{i}^{s}|_{\parallel} = k(|R_{i+1} - R_{i}| - |R_{i} - R_{i-1}|) \cdot \hat{\tau}_{i} \hat{\tau}_{i} (2.16)$$

where k is the spring constant.

To reach a more rigorous convergence near saddle points, we also applied climbing image NEB (CI-NEB) method<sup>42</sup> for robust transition states searching after the image with highest energy is found with the regular NEB method as  $i_{max}$ . The force on this image is given by,

$$\begin{aligned} \boldsymbol{F}_{i_{max}} &= -\nabla E(\boldsymbol{R}_{i_{max}}) + 2\nabla E(\boldsymbol{R}_{i_{max}})|_{\parallel} \\ &= -\nabla E(\boldsymbol{R}_{i_{max}}) + 2\nabla E(\boldsymbol{R}_{i_{max}}) \cdot \hat{\boldsymbol{\tau}}_{i_{max}} \hat{\boldsymbol{\tau}}_{i_{max}} (2.17) \end{aligned}$$

Herein, the highest energy image feels no force of the springs and the component of the force along the elastic band is inverted. If the CI-NEB method converges, the climbing image will converge to the saddle point. Because all the images are simultaneously relaxed, there is no additional cost of for a climbing image.

### 2.4 Microkinetic simulation

DFT calculations along with transition state searching unveils the potential energy surface or minimum energy paths for a reaction. By coupling reaction energetics, we can picture the whole reaction energy landscapes, which further assist in constructing microkinetic model (MKM) to analyze and predict reaction rates under certain conditions<sup>43</sup>. In general, the rate of a reaction can be defined by the difference in forward rate and backward rate with respective dependence on rate constant and species activity. Assuming a surface coupling reaction,

 $A^* + B^* \leftrightarrow C^* + * (2.18)$ 

And the rate to product C can be described as,

 $rate = k_{+}\theta_{A}\theta_{B} - k_{-}\theta_{C}\theta_{*} (2.19)$ 

where  $k_+$  and  $k_-$  are rate constants for forward and backward reactions,  $\theta_A$ ,  $\theta_B$ ,  $\theta_C$  and  $\theta_*$  are the coverages of surface adsorbates A, B and C and surface vacant site \*, with a sum up to 1,

$$\sum_i \theta_i = 1 \ (2.20)$$

The rate constant can be calculated using the following Arrhenius equation as,

$$k = Ae^{\frac{-E_a}{k_B T}} (2.21)$$

where A is the pre-exponential factor (the frequency of effective collisions of reactive molecules in the chemical system),  $E_a$  is the activation energy,  $k_B$  is the Boltzmann constant (we used 8.617 eV/K in this Thesis) and T is the reaction temperature. A was approximated as  $10^{13}$  in this Thesis. In the transition state theory (TST) framework dating back to  $1935^{44}$ , the transition state and the reactants of the elementary steps are in quasi-equilibrium, thus, the  $E_a$  can be further calculated as the energy difference between transition and initial states as,

$$E_a = E_{TS} - E_{IS} (2.22)$$

and the reaction energy  $E_r$  can be expressed as,

$$E_r = E_{FS} - E_{IS} (2.23)$$

We assume that all reaction steps reach equilibrium at steady state as,

$$\frac{\partial \theta_i}{\partial t} = 0 \ (2.24)$$

where the  $\theta_i$  is the coverage of intermediate *i*.

To solve the multistep reaction microkinetic problem, we applied the CATMAP software package<sup>45</sup> to perform mean-field multidimensional root-finding iterative calculations using Newton's method to derive the desired equilibrium coverages and rates at steady states within a scheme of descriptor-based analysis. In this Thesis, we used furfural adsorption, potential and pH as descriptors for different microkinetic simulations.

To account for the adsorbate-adsorbate interactions, we include a self-consistent cross-interaction terms of different intermediates<sup>46</sup>, which are approximated by geometric mean of self-interaction terms (e.g., FCHO\*/FCHO\*, H\*/H\*) of two interacting adsorbates, e.g., FCHO\*/FCHOH\* and FCHO\*/H\* on different studied surfaces. Based on the definition in the TST framework, the TS coverages are extremely low, so we do not consider the interactions caused by TS.
#### 2.5 *ab initio* molecular dynamics (AIMD)

Reaction interfaces in heterogenous catalysis are dynamic. To capture the dynamics in catalytic systems especially with solvents like water, it is desirable to use a computational method that can sample the time-evolving geometrical configurations at finite temperatures. In this Thesis, we applied *ab initio* molecular dynamics (AIMD) simulations to understand the furfural adsorption at different metal-water interfaces to shed light on the aqueous-phase furfural (electro-)valorizations. Herein, *ab initio* molecular dynamics with Born-Oppenheimer approximation are performed, where the nuclei are treated as classical particles whose trajectories are computed by integrating Newtonian equations of motion. Assume a system consisting of N atoms with positions  $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_k, ..., \mathbf{R}_N)$ . The motion equation can be written as,

 $M_k \ddot{\boldsymbol{R}}_k = \boldsymbol{F}_k(\boldsymbol{R}) \ (2.25)$ 

$$\boldsymbol{F}_{k}(\boldsymbol{R}) = -\boldsymbol{\nabla}_{k} \boldsymbol{E}_{i}(\boldsymbol{R}) \ (2.26)$$

where the dots denote the derivative of trajectory with time and *k* is the index of the nuclei.

For MD simulations, the macroscopic properties are defined by the numerous microstates for the given thermodynamic condition, i.e., an ensemble, with some quantities conserved during the simulation. As for chemical reactions, a NVT ensemble is usually used, where the number of particles (N), the volume of the system (V) and the temperature (T) are conserved. The conservation of T is achieved via the energy exchange with a thermostat. Popular methods to conserve the system temperature in simulations include velocity rescaling, Nosé–Hoover thermostat, Berendsen thermostat, the Andersen thermostat and Langevin dynamics. In this Thesis, we used the Nosé–Hoover thermostat<sup>47,48</sup>, where a Hamiltonian with an extra degree of freedom for heat bath, *s*, is introduced as,

$$\widehat{H}(P, R, p_s, s) = \sum_i \frac{p_i^2}{2ms^2} + \frac{1}{2} \sum_{ij, i \neq j} U(\boldsymbol{r}_i - \boldsymbol{r}_i) + \frac{p_i^2}{2Q} + gkTln(s)$$
(2.27)

where P and R represent all coordinates r and p, Q is an imaginary mass, g is the number of independent momentum degrees of freedom of the system. The coordinates R, P and t in this

Hamiltonian are virtual. The ensemble average of the above Hamiltonian at g = 3N equals to the canonical ensemble average.

#### 2.6 Computational hydrogen electrode

In electrocatalysis, simulating the potential effect on reaction energetics is challenging. To avoid the explicit treatment of solvated protons and other interfacial properties, Nørskov et al. developed an elegant model called computational hydrogen electrode (CHE)<sup>49</sup>. In this model, zero voltage is defined versus the reversible hydrogen electrode (RHE), the proton-electron couple is defined as,

 $H^+ + e^- \leftrightarrow 0.5 H_2 \ (2.28)$ 

where the reaction is in equilibrium at zero voltage, at all values of pH, at all temperatures, and with H<sub>2</sub> at 101325 Pa pressure. The chemical potential of the proton-electron pair  $\Delta G$  can be described as a function of the applied potential as,

$$\mu(H^+) + \mu(e^-) \leftrightarrow 0.5\mu(H_{2(g)}) - eU(2.29)$$

where e is the elementary positive charge and U is the applied potential. Moreover, because the RHE is defined at 0 V and all pH values, a pH correction is not needed to the model. The potentials on RHE and SHE scales can be defined as,

$$U_{RHE} = -\frac{\Delta_f G(H^+ + e^-)}{F} (2.30)$$

$$U_{SHE} = -\frac{\Delta_f G(e^-)}{F} (2.31)$$

where F is the Faraday constant and the relation between those two scales can be calculated as,

$$U_{RHE} = U_{SHE} - \frac{\Delta_f G(H^+)}{F} = U_{SHE} + 0.059V \times pH \ (2.32)$$

where we assume a standard condition for the protons (in 1 M solution). This relationship is a key to understanding electrochemical reactivities correctly based on different simulative and experimental results.

In all, CHE model offers a simple but powerful way to analyze electrochemical reactions involving proton-electron coupled transfer (PCET) steps in a purely thermodynamic manner. However, the lack of treatment of solvated protons and electrochemical interfaces prevents it from offering insights into the reaction kinetics, more specifically, the activation energy of a PCET step at varied conditions (e.g., pH and applied potentials).

#### 2.7 Grand-canonical DFT calculations

In Chapter 5, we applied the Solvated Jellium Method (SJM)<sup>50</sup> implemented in the GPAW code<sup>34,51</sup> to calculate the electrochemical pathways of both furfural reduction and hydrogen evolution with H<sub>3</sub>O<sup>+</sup> as proton source in explicit solvents. SJM's implementation uses an effective potential cavity solvation model developed by Held and Walter<sup>52</sup>. The parameters for solvation in water applied in this Thesis<sup>53</sup>: strength of the repulsion at the atomic radii controlling the cavity size u0 = 0.18eV, surface tension 0.001148 Pa  $\cdot$  m, relative permittivity (dielectric constant)  $\epsilon = 78.36$ , temperature = 298.15K. The counter charge in SJM model was chosen as a 3Å thick jellium slab starting two vdW-radii of oxygen atoms above the highest water molecule in the water layer. The tolerance for the electrode potential deviation from target potential was set to 5mV in the calculation of stable reaction intermediates and 10mV in the case of transition state searches. The reported constant potential free energies  $G^{\Phi}$  ( $\Phi$  = work function) were calculated as a sum of the constant potential energies including the constant particle DFT energy  $E^{\Phi} = E^{ne} - n_e \mu_e$  at  $n_e$  excess electrons, and the electron's chemical potential  $\mu_e = -\Phi$ , the effective solvation free energy directly derived from the implicit solvation scheme inherent in SJM, and the vibrational free energy contributions (zeropoint energies, heat capacity and vibrational entropy) calculated from a constant potential vibrational analysis conducted at 298.15K. The symmetry factor  $\beta$ , describing the potentialdependent activation energies, was extrapolated from the calculations at three or four varied potentials.

In a nutshell, the major computational endeavors in this Thesis are determining the *potential energy surface* of chemical/physical reactions either to find the transition states or to probe the interfacial energy landscapes within a complex system consisting of *catalyst surface, adsorbate,* 

and *solvent (water)*. We would like to stress that with a relatively complex system, sufficient sampling is crucial. In addition to presenting the results from theoretical simulations, we will also discuss uncertainties in our calculations, which can help readers to formulate a more critical viewpoint between the simplified models in theory and the actual catalytic reactions in experiment. **Now, the adventures begin.** 

### **CHAPTER 3**

# Understanding activity trends in gas-phase furfural hydrogenation reactions

#### 3.1 Background and motivations

As described in Section 1.4.1, gas-phase catalytic hydrogenation of furfural towards furfuryl alcohol is the major user of annual furfural production globally. Production of furfuryl alcohol is a basic and central process for furfural valorization to various products, as shown in Scheme 3.1, where the hydrogenation of C=O bond in the -CHO to furfuryl alcohol is highlighted.



Scheme 3.1 The major hydrogenation reactions from furfural and furfuryl alcohol. The dotted red box highlights the furfural hydrogenation to furfuryl alcohol studied in this Chapter.

However, this process is limited by a. moderate activities even at elevated temperatures and b. the toxic Cr component in CuCrO<sub>x</sub> industrial catalysts, which might leak after long-time use in the reactor. It is high time we look for more active green catalysts with affordability and nontoxicity. A large range of transition metals besides Cr have shown activity towards furfuryl alcohol production, e.g., Au<sup>54</sup>, Cu<sup>55–59</sup>, Co<sup>60</sup>, Ir<sup>61</sup>, Ni<sup>62–64</sup>, Pd<sup>65,66</sup>, Pt<sup>67</sup>, Rh<sup>68</sup> and Ru<sup>69</sup>. Considering both abundance and catalytic performance (i.e., activity and selectivity), Cu-based catalysts display the most promising potential to substitute Cr in the furfural hydrogenation. However, Cu alone is still not satisfactorily active especially under low temperature and pressure<sup>70</sup>. As a result, a bunch of Cu-based alloy catalysts have been investigated, e.g., CuPt<sup>71</sup>, CuPd<sup>72</sup> and CuNi<sup>73</sup>, which are reported to show higher yields to furfuryl alcohol than Cu catalysts. Unfortunately, the catalyst development for furfuryl alcohol production is still in the stage of trial and error, with a universal mechanistic picture being absent.

In this Chapter, we present a thorough mechanistic study of furfural hydrogenation towards furfuryl alcohol on different metal surfaces. Using density functional theory (DFT) calculations and microkinetic simulations, we find the activity on weak-binding metals could be limited by  $H_2$  activation, while strong-binding ones are limited by desorption, leading to surface poison or other byproducts. The activity volcano shows that Cu is the most active catalyst among pristine single metals, but there is still a large improvement space around the activity peak. We then show that constructing bulk alloys and single atom alloys could further promote the activity to the peak Notably, Ni-doped Cu single atom alloy and diluting CuNi bulk alloys display potentials in meeting the requirement of high activity, low cost, and toxicity for next-generation of catalyst for furfuryl alcohol production.



Scheme 3.2 Possible reaction pathways proposed for furfural hydrogenation to furfuryl alcohol on transition metal surfaces. ads and des indicate adsorption and desorption steps respectively. Reprinted with permission from Paper I<sup>74</sup>. Copyright 2022 American Chemical Society.

The proposed reaction mechanism for furfural hydrogenation towards furfuryl alcohol is summarized in Scheme 3.2. Overall, the metal surface catalyzes both furfural hydrogenation reaction and  $H_2$  activation. The split H\* is the hydrogen source for gas-phase furfural hydrogenation reactions. The considered elementary steps for furfural hydrogenation towards furfuryl alcohol are listed below:

- $\circ$  H<sub>2</sub>(g) + 2\*  $\leftrightarrow$  2H\*
- $\circ$  FCHO(g) + \*  $\leftrightarrow$  FCHO\*
- $\circ \quad FCHO* + H^* \leftrightarrow FCHOH^*$
- $\circ \quad FCHO^* + H^* \leftrightarrow FCH_2O^*$
- $\circ \quad FCHOH^* + H^* \leftrightarrow FCH_2OH^*$
- $\circ \quad FCH_2O^* + H^* \leftrightarrow FCH_2OH^*$
- $\circ$  FCH<sub>2</sub>OH\*  $\leftrightarrow$  FCH<sub>2</sub>OH(g) + \*

where \* represents a single unoccupied active site. The reaction temperature is set as 400K and the pressures for furfural and hydrogen gas are set as 0.1 bar and 1 bar respectively. A moderately high H<sub>2</sub>/furfural pressure ratio was applied to reduce unwanted decarbonylation.

#### 3.2 Furfural hydrogenation at metal-vacuum interfaces



3.2.1 The adsorption energy and configuration of furfural

Figure 3.1 Adsorption free energies of furfural (FCHO) with flat or upright configurations on a. 111 and b. 211 metal surfaces. The representative adsorption configurations on Cu surfaces are shown as insets. Reprinted with permission from Paper I<sup>74</sup>. Copyright 2022 American Chemical Society.

We first calculated the furfural adsorption over different metal surfaces. As shown in Figure 3.1, planar configurations of furfural adsorption with both furan ring and aldehyde group interacting with the surface are more thermodynamically favored than upright ones on all considered metal surfaces. This result is in line with previous theoretical works<sup>75–78</sup>. Moreover, the stronger adsorption strength of furfural, the larger the difference in adsorption energies of two configurations. Therefore, at low coverages, flat configuration of adsorption should dominate, is in line with direct scanning tunneling microscopy observation on Pt(111)<sup>79</sup>. At higher coverages, furfural is reported to possibly take tilted or upright adsorption configurations, to reduce lateral interactions<sup>80</sup>. However, as previous temperature-programmed desorption results of furfural desorption on Pd(111)<sup>77</sup> and Pt(111)<sup>81</sup> suggest that, at reaction temperature for gas-phase furfural

hydrogenation (400-500 K), unstable adsorption states, e.g., upright one, should be unlikely to dominate based on Boltzmann distribution. Other weaker binding surfaces should show even less probability of non-planar furfural species. As a result, we assume that furfural takes planar configuration on considered surfaces in the following calculations of reaction profile.



**3.2.2** The calculated reaction mechanisms on representative metal surfaces

Figure 3.2 Representative reaction energetics. a. Free energy diagrams for furfural hydrogenation on Au(111), Cu(111) and Pt(111) surfaces via FCHOH\* (solid lines) and FCH<sub>2</sub>O\* (dotted lines) at 400 K,  $P_{FCHO} = 0.1$  bar,  $P_{H2} = 1$  bar; b. The adsorption configurations of key intermediates, and c. the transition state<sup>TS</sup> on Cu(111). Reprinted with permission from Paper I<sup>74</sup>. Copyright 2022 American Chemical Society.

Free energy reaction profiles of furfural hydrogenation towards furfuryl alcohol at 400 K on three representative surfaces, i.e., Au(111), Cu(111) and Pt(111) were presented in Figure 3.2. The corresponding stable intermediates and transition states on Cu(111) are showcased in Figure 3.2b and 3.2c. The H<sub>2</sub> dissociation is rate-determining step (RDS) on Au(111) with a high activation energy (E<sub>a</sub>) of 1.21 eV due to a quite weak binding of H\* on Au, while being facile (E<sub>a</sub> = 0.16 and 0.62 eV) on Pt(111) and Cu(111), in good agreement with previous calculations<sup>82,83</sup>.

As shown in Figure 3.2a, the hydrogenation of FCH<sub>2</sub>O\* is RDS on Cu(111) with  $E_a = 0.98 \text{ eV}$ , in line with a prior work on the same surface model<sup>84</sup>, while the hydrogenations of furfural via the FCHOH\* intermediate are facile on Pt(111) and Au(111) surfaces. Previously, Sitthisa et al. showed that the formations of FCHOH\* and FCH<sub>2</sub>O\* are both endothermic on Cu(111)<sup>85</sup>. However, we find that FCH<sub>2</sub>O\* formation is exothermic by nature and thermodynamically more favored by -0.54 eV than the formation of FCHOH\* on Cu(111). The discrepancy could be due to the flat configuration of FCH<sub>2</sub>O\* they used in their work is possibly not the most stable one, which we calculated to be less stable than the bending configuration by -0.42 eV. The respective adsorption structures are shown in Figure 3.2b: on the Cu(111) surface, the O of the -CH<sub>2</sub>O group in FCH<sub>2</sub>O\* inserts in the hollow site, while FCHOH\* binds the surface with the C of -CHOH in FCHOH\*. In addition, the hydrogenation of FCH<sub>2</sub>O\* proceeds with a 0.22 eV lower activation barrier than FCHOH\* hydrogenation on Cu(111). In contrast, the FCHOH\* intermediate is more thermodynamically favored on Au(111) and Pt(111) surfaces, while FCH<sub>2</sub>O\*, lying flatly like FCHOH\* on Pt(111) and Au(111), is less favored.

Finally, we find that the desorption of the product (FCH<sub>2</sub>OH\*) is limiting on Pt(111), due to its strong binding of furfural species. In fact, furan and other ring-opening hydrocarbons were reported to be side-products on Pt<sup>79</sup>, Ru<sup>86</sup> and Ni<sup>87</sup> catalysts at high temperatures. It is likely that the strong adsorption of furfural on these metal surfaces hinders further hydrogenation and triggers C-C bond breaking and ring-opening reactions at high temperatures.

#### 3.2.3 FCHOH\* vs FCH<sub>2</sub>O\* and scaling relations

Table 3.1	The formation	energies	(eV) of	FCHOH*	and	$FCH_2O^*$	on	different	metal	fcc(11	1) or
hcp(0001)	(Co and Ru) s	urfaces.									

Metals	FCHOH*	FCH <sub>2</sub> O*
Ag	-0.59	-0.97
Au	-0.99	-0.59
Co	-1.90	-2.31
Cu	-0.98	-1.52
Ir	-2.27	-2.26
Ni	-1.89	-2.16
Pb	-0.27	-0.94
Pd	-2.22	-1.75
Pt	-2.53	-1.94
Rh	-2.50	-2.39
Ru	-2.81	-2.95

Based on the calculated formation energies of FCHOH\* and FCH<sub>2</sub>O\* (referenced to FCHO(g) and 0.5H<sub>2</sub>(g)) in Table 3.1, we discovered the surface-dependent preference for those two key intermediates on varied metal surfaces as shown in Figure 3.3a. Generally, the oxyphilic surfaces (surfaces with a higher tendency to form metal oxides) besides Cu, e.g., Ag, Ni and Co, favor the formation of FCH<sub>2</sub>O\* over FCHOH\*. Notably, FCH<sub>2</sub>O\* on these oxyphilic surfaces takes the bending configuration with O inserting in the surface hollow site, making the further hydrogenation a potential rate determining step, while FCH<sub>2</sub>O\* usually adsorbs flatly on FCHOH\*-favored surfaces, such as Pt, Pd and Au. The different adsorption configurations of FCH<sub>2</sub>O\* should affect its further reactivity to FCH<sub>2</sub>OH\*.



Figure 3.3 a. The adsorption energies of FCHOH and FCH<sub>2</sub>O on the different metal (111) surfaces. The orange and green areas represent FCHOH-favored and FCH<sub>2</sub>O-favored regions respectively; b. Scaling relationships of adsorption energies between FCHO\* and the other stable adsorbates involved in the reaction pathway for furfural hydrogenation. Reprinted with permission from Paper I<sup>74</sup>. Copyright 2022 American Chemical Society.

The formation of C-binding or O-binding intermediates is an open question not only here for furfural hydrogenation, but also for general (de-)hydrogenation reactions involving key intermediates with different binding modes, e.g.,  $CO_{(2)}$  hydrogenation<sup>88,89</sup> and glycerol oxidation<sup>90</sup>. The favorability of either intermediate should depend on many factors, including but not limited by the identity of metal, the surface orientation, the local structure of active sites and reaction conditions. This general message could offer a new design principle to favor the desired pathway towards the target products in heterogenous catalysis. A good example is provided by Julia et al., who uses OH and CO binding energies to predict selectivity for CO hydrogenation to C<sub>1</sub> or C<sub>2</sub> products on metal surfaces<sup>91</sup>.

Furthermore, we find that the binding energies of all reaction intermediates, even H\* in furfural hydrogenation, scale with that of FCHO\*, as shown in Figure 3.3b. During furfural hydrogenation, the H<sub>2</sub> activation should be correlated with H\*, while the hydrogenation of furanic intermediates should be related to FCHO\* and H\*. As a reasonable simplification, we can use furfural binding energy as the sole descriptor to approximately predict the activity.

#### 3.3 The activity trend in gas-phase furfural hydrogenation

We first summarized and normalized the turnover frequency (TOF) for furfural hydrogenation towards furfuryl alcohol as a major product, in Figure 3.4a, under similar reaction conditions (ca. 500 K and < 10 bar) in previous reports<sup>92–95</sup>. We see a semi-volcanic trend of the activities for this reaction, using furfural adsorption energy as a descriptor. While Cu and Ni are at weak and strong-binding legs respectively, Cu-rich alloys approach the top of the volcano, in line with the well-known Sabatier principle<sup>96</sup>.



#### 3.3.1 The activity volcano from: theory and experiment

Figure 3.4 Activity volcano for furfural hydrogenation towards furfuryl alcohol. a. The adapted TOF plot from experiments for  $Cu^{97}$ ,  $Ni^{98}$ ,  $Pd^{99}$ ,  $Pt^{100}$ ,  $PdCu^{99}$ ,  $Cu_{216}Pd_1^{99}$ , and  $Cu_{20}Pt_1^{100}$ . Note that the  $\Delta E_{FCHO}$  on the x-axis corresponds to the (111) surface of the respective metal; b. The simulated TOF plot based on microkinetic simulations at 400K,  $P_{FCHO} = 1$  bar and  $P_{H2} = 1$  bar. M represents a metal surface and  $Cu_xM_{4-x}$  and  $Cu@M_1$  represent Cu-based bulk alloys and single-atom alloys with M, respectively. Representative configurations of  $Cu_xM_{4-x}$  and  $Cu@M_1$  surfaces are shown. Reprinted with permission from Paper I<sup>74</sup>. Copyright 2022 American Chemical Society.

Based on the reaction energetics on monometallic surfaces, we further developed a mean-field microkinetic model considering adsorbate-adsorbate interactions using the CatMAP code<sup>45</sup> to study the activity for furfuryl alcohol production over different metal surfaces under reaction conditions. For simplicity, the other metal surfaced were later fitted to the curve based on the calculated furfural binding energies.

Cu is predicted to be the most active catalyst for furfural hydrogenation towards furfuryl alcohol (cf. Figure 3.4b) among all the elemental transition metals considered in this work. The high TOF of Cu results from a low barrier for  $H_2$  activation (cf. Figure 3.1) and suitable adsorption strength of furfural species, which lead to a good overall activity.

Stepped surfaces promote the activity on weak-binding metals, while they reduce the activity on strong-binding metals. As can be seen in Figure 3.4b, stepped Cu(211) is predicted to have a higher activity by ca. 1 order than Cu(111) for furfural hydrogenation, indicating the introduction of under-coordinated sites on Cu surfaces might lead to increase in the activity for furfuryl alcohol production. A similar trend is observed on weak-binding surfaces including Ag and Au. In contrast to weak-binding metals, for the strong-binding metals including Ni, Co, Pd, Pt, Rh and Ru, stepped surfaces (211) are predicted to have lower activity than the (111) surfaces. We find that CuCr alloy binds furfural too strongly even with a dilute Cr component (i.e., Cu<sub>3</sub>Cr<sub>1</sub>), leading to a relatively low activity. However, it is also notable that CuCr catalysts are usually partially oxidized and restructured during furfural hydrogenation<sup>101</sup>, thus a different rate (likely to be higher) might be predicted for practical CuCrO<sub>x</sub> catalysts.

#### 3.3.2 Why Cu is good *again*?

In our microkinetic model, we have predicted Cu and Cu-rich bimetallic alloys to be the most active to furfuryl alcohol production at relevant conditions. This result reminds us of the advantage of Cu over other metals in general hydrogenation of C=O bond, e.g., CO<sub>2</sub> hydrogenation to methanol or CO<sup>102,103</sup>. To shed some light on the superiority of Cu, we carried out degree of rate control (DRC) analysis<sup>104,105</sup> to determine rate-limiting steps on different metal surfaces. DRC matrix could be described as,

$$X_{i,j} = \frac{dlog(r_i)}{d(\frac{-G_j}{k_BT})}$$

where  $X_{i,j}$  is the DRC matrix for the influence of species j on the rate to produce j,  $r_i$  is the production rate of i,  $G_j$  is the Gibbs free energy of species j,  $k_B$  is the Boltzman constant, and T is the reaction temperature. For a specific DRC  $x_{i,j}$ , the + sign indicates  $G_j$  should be lowered to increase  $r_i$ , and vice versa for -. If  $x_{i,j} \approx 0$ ,  $G_j$  does not affect  $r_i$  much.

We present the DRC analysis results in Figure 3.5 only including  $G_j$  that has large  $|x_{i,j}|$  (> 0.1) on  $r_i$ , here i is furfuryl alcohol and j is surface adsorbed species of FCHO\*, H\*, FCHOH-H<sup>TS</sup> and H-H<sup>TS</sup>, where the superscript <sup>TS</sup> represents transition states.



Figure 3.5 The DRC analysis of furfural hydrogenation on metal surfaces. a. FCHO\*, b. FCHOH-H<sup>TS</sup>, c. H\* and d. H-H<sup>TS</sup>. Black circle and blue triangle represent (111) and (211) surfaces, respectively.

We find that the adsorption strengths of FCHO\* and H\* are intrinsically wresting against each other, displaying different signs of DRC in Figure 3.5a and c. For strong-binding metals, e.g., Co, Ir, Ni, Pd, Pt, Rh, and Ru are limited by the furfural overbinding, thus a surface poisoning occurs. Meanwhile, most of the metals are limited by the H<sub>2</sub> activation. Interestingly, Cu is always at the gradient area of the DRC heatmap, with Cu(111) and Cu(211) at opposite sides. This result

indicates the rate to produce furfuryl alcohol on Cu catalyst (usually a combination of low and high-index surfaces) is not severely affected by any intermediates.



Figure 3.6 The calculated coverages of a. FCHO\* and b. H\* in monolayer (ML). Black circle and blue triangle represent (111) and (211) surfaces, respectively. Reprinted with permission from Paper I<sup>74</sup>. Copyright 2022 American Chemical Society.

The calculated coverages of FCHO\* and H\* in Figure 3.6 indicate that on Cu surfaces, there is a balance between the two starting adsorbates. Again, between Cu(111) and Cu(211), there could be a better surface balancing the intermediate coverages, which should lead to an even higher activity in principle (cf. Figure 3.5).

#### **3.3.3 Cu-rich CuNi alloys are predicted to be very active**

Based on the activity volcano, Cu-based bulk alloys (Cu<sub>x</sub>M<sub>4-x</sub>, x = 1, 2, 3) and Cu@M<sub>1</sub> singleatom alloys (SAAs) are then fitted to the volcano based on Cu(111) surfaces. There are several Cu-rich alloys show enhanced activities relative to Cu. Particularly, Cu<sub>3</sub>Ni<sub>1</sub> and Cu@Ni<sub>1</sub> surfaces as modeled in Figure 3.7 are predicted to show extremely high rate to produce furfuryl alcohol, as shown before in Figure 3.5. Different from Cu(111), furfural binds CuNi(111) surfaces with both furan ring and -CHO group, which slightly enhance its binding strength, thus lead to higher activities. In addition, Cu-rich Pt-group alloys also show better activities than pure metals, however, the cost for catalysts is elevated dramatically relative to Cu or CuNi.



Figure 3.7 The most stable furfural adsorption configurations on a.  $Cu_3Ni_1$  and b.  $Cu@Ni_1$  (111) surfaces.

The prediction that Cu-rich CuNi alloys are very active is in agreement with a recent study by Weerachawanasak et al.<sup>98</sup>, where CuNi alloys with a Cu-rich component show higher yields for furfuryl alcohol production relative to pure Cu and Ni-rich catalysts. In addition, Ni-rich catalysts are reported to display activity towards further hydrogenated products in vapor phase, e.g., tetrahydrofurfuryl alcohol (THFA)<sup>106</sup>. Therefore, diluting Ni content in Cu catalyst is crucial to obtain high selectivity and activity towards furfuryl alcohol. Considering the abundance, noble-metal-free and low toxicity of both Cu and Ni, we advocate for future research efforts to extensively study CuNi based bimetallic catalysts for furfural hydrogenation as they can help resolving some of the major issues that currently plague the industrial production of furfuryl alcohol using chromite-based catalyst materials. Our recent collaborative work with Fang et al. from DTU chemistry has shown the great potential in mesoporous CuNi catalysts to selectively produce furfuryl alcohol<sup>107</sup>.

Before closing this Chapter, we would like to notify the following limitations of the study demonstrated above. First, we focus on the furfural hydrogenation to furfuryl alcohol and ignore other products, e.g., ring-opening reaction to furan and deep hydrogenation to THFA. Second, our model surfaces are pure metals, however, certain supports are usually applied in experiments to enhance both activity and stability, as shown in previous studies<sup>54,55,108,109</sup>. Finally, we did not consider possible surface reconstruction and segregation under *operando* conditions, which might introduce discrepancies in the observed structure-activity relationships<sup>110–112</sup>.

### **3.4 Conclusions**

In this Chapter, we have performed DFT calculations and microkinetic simulations to study the activity trends in gas-phase furfural hydrogenation to furfuryl alcohol on various metal surfaces, one of the most studied catalytic processes for biomass valorization.

Here are the main take-away messages:

- The rate-determining steps vary on weak, moderate, and strong-binding surfaces.
- Cu is predicted to be the most active monometallic catalyst for this reaction.
- The stepped surfaces are more active than terrace surfaces for moderate/weak binding metals including Cu, Ag and Au, while the opposite trend is observed on the strong-binding metals including Pt, Pd, Ir, Ni, Co, Rh and Ru.
- o Cu-rich CuNi alloys are promising candidates to replace Cr-based catalysts.
- Discrepancies between model catalysts and actual reactive surfaces should be further explored.

### **CHAPTER 4**

### Probing the furfural adsorption at metal-water interfaces: Solvent effects on furfural valorization

In the last Chapter, we investigated gas-phase furfural valorization reactions at metal-vacuum interfaces using static DFT calculations. Meanwhile, the solvent-mediated furfural (electro-)valorization is also a pivotal process to upgrade furfural at catalyst-solvent interfaces, e.g., metal-water interfaces. A realistic description of the dynamic behavior of furfural adsorption at those interfaces demands a more robust model of metal surfaces, adsorbed furfural, and water molecules. In this Chapter, we applied ab initio molecular dynamics (AIMD) simulations to study the furfural adsorption at different metal-water interfaces, taking one step further to simulate aqueous-phase reactions.

#### 4.1 Why solvent matters and how?

#### 4.1.1 Liquid-phase furfural hydrogenation

In practice, both gas(vapor)-phase and liquid-phase furfural hydrogenation have been widely studied<sup>113,114</sup>. Liquid-phase hydrogenation displays several advantages: milder reaction conditions (especially a lower operating temperature compared to gas-phase hydrogenation, where vaporizing furfural needs high temperatures) and solvent-mediated activity and selectivity<sup>115,116</sup>.

Specifically, solvents such as water enable hydrogenation reactions under mild conditions on Ptgroup metals. For instance, Pt could catalyze furfural hydrogenation selectively to furfuryl alcohol at 50 °C in methanol<sup>117</sup> and 30 °C in water<sup>118</sup>, and Ru has been shown to achieve nearly 100% selectivity to furfuryl alcohol at 20 °C in aqueous phase<sup>119</sup>, while furfural decarbonylation to form CO that poisons the Pt surface dominates at low temperatures in the absence of a solvent<sup>79</sup>. In electrocatalysis, Pt and Pd electrodes have shown activity in reducing furfural in solvents towards value-added products, such furfuryl alcohol (FAL) and tetrahydrofurfuryl alcohol (THFA)<sup>14,120,121</sup>. The difference between gas-phase and liquid-phase reactivity of furfural hydrogenation on strongbinding metal surfaces relates to the special solvent effect on the furfural adsorption at interfaces. Moreover, the selectivity in furfural hydrogenation can be tuned using different types of solvents to hydrogenate either the aldehyde group or furan ring<sup>122,123</sup>, which can be simultaneously impacted by the selection of metal surfaces<sup>124</sup>. In general, the activity and selectivity for liquid-phase furfural valorization are governed by still elusive solvent effects<sup>125</sup>. One of the model system is aqueous-phase furfural hydrogenation at metal-water interfaces.

#### **4.1.2 AIMD studies to understand metal-water interfaces**

Understanding metal-water interfaces and the adsorption of interested species is the first step to resolve the mechanistic mysteries of aqueous-phase hydrogenation reactions. Theoretically, ab initio molecular dynamics (AIMD) is regarded as an effective computational tool to gain atomistic level insights on adsorption phenomena and catalysis at metal-water interfaces<sup>126–129</sup>. Before plunging in our results, we summarized some of the latest studies using AIMD simulations to probe adsorption at metal-water interfaces.

Heenen et al. studied several adsorbates (CO\*, COH\*, CHO\*, OCCHO\*, OH\* and OOH\*) on Cu, Au and Pt metal-water interfaces, and found the solvation energies to be dependent on both the identity of the adsorbate and the metal surface, as a result of which the solvation energies are non-transferable across metal surfaces, e.g., CO\* adsorption energy is barely affected by solvents on most of the metal surfaces, while OH\* adsorption shows over 0.5 eV stabilization on Au and Pt<sup>130</sup>. Yoon et al. reported the adsorption of larger molecules, i.e., phenol on metal-water interfaces to be destabilized on Pt(111) and Ni(111)<sup>131</sup>. Zare et al. developed a hybrid quantum mechanical/molecular mechanical (QM/MM) approach to find that the adsorption of large molecules, i.e., benzene and phenol, is dramatically weakened on Pt(111) and Cu(111) in aqueous phase at 298K, as a result of large endergonic cavity formation energy<sup>132</sup>. In summary, the adsorption of small molecules in aqueous phase could be either destabilized or stabilized compared to vacuum, while larger molecules tend to suffer from huge energetic penalties associated with the replacement of water molecules (cavity formation) in aqueous phase.

## 4.1.3 Previous experiments and theories to understand furfural adsorption at metal-water interfaces

Combining experimental isotherms and density functional theory (DFT) calculations, Akinola et al. find that the adsorption of large organic molecules (including furfural) is weakened on strongbinding surfaces like Pt and Rh in aqueous phase relative to ultra-high vacuum (UHV) conditions, which they attribute to the large enthalpic penalty for water displacement at metal/water interface<sup>133</sup>. The weakened adsorption under aqueous conditions could help explain the activity for the hydrogenation of these large organic molecules on such strong-binding surfaces at room temperature. Based on the solution calorimetry results<sup>134</sup> and previous thermodynamic cycle approaches, Singh and Campbell proposed a simple bond-additivity model to quantify the solvent energy penalty of aromatic molecules, which is mainly due to water desorption in the domain of adsorbed aromatics<sup>135</sup>.

#### 4.1.4 The remaining questions

The previous reports highlighted the crucial solvent effect of water on furfural adsorption on metal surfaces. However, the as-proposed methods strongly rely on indirect electrochemical measurements and isotherm adsorption experiments carried out at low temperatures<sup>133</sup>, which pose uncertainties to the estimated solvation energies. Besides, the atomic configurations of furfural adsorption at metal-water interfaces are unfortunately out of reach, which are crucial to investigate reaction mechanisms. In the prior endeavors, only Pt and Rh surfaces have been experimentally studied, where other hydrogenation-active metals, such as Au, Cu and Pd, remain untouched, due to the limitation in experiments, that request for perfect single crystals. Considering these remaining questions, we find that AIMD simulations can offer atomic-level knowledge into furfural adsorption behavior at metal-water interfaces, free of impact of surface impurities and restructuring. In addition to solvation energies, other critical physiochemical properties could be further derived from the simulations, using homebrew *AIMDprobe* toolkit developed with Python and Atomic Simulation Environment (ASE)<sup>35</sup> (cf. Section 4.6).



Scheme 4.1 A schematic of the various metal (Au, Cu, Pt, Pd and Rh (111))-water interfaces studied using AIMD simulations. a. before furfural adsorption, b. after furfural adsorption. The color code of atoms is shown as the inset on the right. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

## 4.2 The adsorption configurations of furfural at metal-water interfaces

As shown in Figure 3.1, furfural tends to adsorb on metal terraces flatly at low coverages. The metal-water interface models are shown in Scheme 4.1. After reaching the convergence criteria (an average drift in the total potential energy of < 0.05 eV/ps) in each trajectory, we first analyzed the furfural adsorption dynamics from a structural perspective, to understand the interactions between different components in the solvated systems: furfural-water, furfural-surface, and water-surface.





Figure 4.1 Snapshots of furfural adsorption at metal-water (upper panel) and metal-vaccum (lower panel) interfaces in AIMD simulations at 50 ps. Color codes: white -H, red -O, grey -C, gold -Au, brown -Cu, silver -Pt, dark blue -Pd and cyan -Rh. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

As a ring-like molecule, furfural can take various adsorption configurations on different metal surfaces (flat, tilted and upright), as shown in Chapter 3. Herein, we compared the results at metal-water and metal-vaccum interfaces in Figure 4.1. To our surprise, furfural adsorbs on the surfaces in water similarly to vaccum. Specifically, furfural does not really bind chemically on Au(111), but hanging a bit away from the surface. On Cu(111), furfural slightly binds the surface with its aldehyde group. On Pd, Pt and Rh(111), the furan ring all bonds the surface, while the aldehyde group binds Pd and Rh(111) but tilts away on Pt(111). Besides, it is notable that furfural adsorption creates a large void of water at the interfaces, indicating some previously adsorbed waters are desorbed.

## 4.2.2 The structual indicators: residence time, time-averaged center of mass (COM) and mean sphared displacement (MSD)



Figure 4.2 The cumulative residence time of furfural adsorption at metal-water interfaces. The furfural structure is numbered atomically as inset. We applied the last 10 ps of the three independent and converged trajectories for each interface system as raw statistics. The error bars were calculated using the three trajectories. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

Atomically, the surface bonding can be attributed to each atom in furfural via cumulative residence time in Figure 4.2. Furfural does not bind on Au at all, and Cu(111) binds it weakly via O atom in -CHO. The multiple signals of C atoms in furan group on Pd, Pt and Rh(111) suggest its strong interaction on those metals. We recommend a comprehensive study of atomic bonding using residence time as indicator for large biomass derivatives, which can form multiple bonds with the catalytic surface. The obtained statistics could help fast predict the possible chemical reactions at solid-liquid interfaces.

The positions of furfural at interfaces can be described by its center of mass (COM). The calculated COM summarized in Table 4.1 and Figure 4.3a shows that furfural closely binds over Rh, Pd and Pt(111), while it tilts away on Cu and Au(111). Interestingly, the COM of furfural at metal-water and metal-vacuum interfaces is similar.

Table 4.1 The calculated center of mass (COM) of furfural (Å) at different metal surfaces in water or in gas phase.

-



Figure 4.3 Statistical analysis of time-averaged a. centers of mass (COMs) for furfural at different metal-water interfaces and b. mean squared displacement (MSD) of furfural. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

Furthermore, we probed the time-averaged positioning of furfural (based on the COM) and its replacements in Figure 4.3b. The mean squared displacement (MSD) of furfural also indicates that furfural is the most mobility on Au(111) and slighly mobile on Cu(111), but it is not mobile on the strong-binding metal surface. Additionally, the overlapping of MSD at xy and xyz directions suggest the furfural only moves horizontally on all the surfaces without desorbing back into water layers.



4.2.3 Furfural does not benefit much from hydrogen bond formation

Figure 4.4 The time-averaged hydrogen bond formation between furfural and waters on different metal-water interfaces. The hydrogen bonds formed between adsorbed furfural and water were counted based on the distance and angle criteria as reported in Ref<sup>137</sup>. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

Hydrogen bond formation between adsorbates and solvents can benefit the stability of adsorption. Thus, we further studied the formation of directional hydrogen bonds between the furfural and water. As shown in Figure 4.4, less than 1 hydrogen bond is formed per adsorbed furfural with the water molecules, which is attributed to some rare formation events between the O atoms in -CHO or furan ring and H atoms in waters. This low degree of hydrogen bonding is comparable to the very weakly interacting CO\* at metal-water interfaces<sup>130</sup> and also reflects the slightly hydrophobic nature of furfural. The finding here rules out possible stabilization effects on furfural adsorption via hydrogen bond interactions under aqueous conditions.

### 4.3 Furfural adsorption strength is generally weakened at metalwater interfaces

#### 4.3.1 AIMD simulations get endothermic solvation energies for furfural

We derived the furfural adsorption energies at metal-water interfaces and extrapolated the solvation energies relative to the adsorption at corresponding metal-vacuum interfaces based on three AIMD trajectories.

The AIMD-based vacuum adsorption energy  $\Delta E_{FCHO\_vac\_AIMD}$ , aqueous-phase adsorption energy  $\Delta E_{FCHO\_aq\_AIMD}$  and the solvation energy  $\Delta E_{solv}$  against the adsorption in vacuum were calculated by Eq. 4.3 - 4.5 as:

$$\Delta E_{FCHO\_vac\_AIMD} = E_{slab\_FCHO\_vac\_AIMD} - E_{slab\_vac\_AIMD} - E_{FCHO(g)\_AIMD}$$
(4.3)

$$\Delta E_{FCHO_aq_AIMD} = E_{slab_FCHO_aq_AIMD} - E_{slab_aq_AIMD} - E_{FCHO(g)_AIMD}$$
(4.4)

$$\Delta E_{solv} = \Delta E_{FCHO \ aq \ AIMD} - \Delta E_{FCHO \ vac \ AIMD}$$

$$\tag{4.5}$$



Figure 4.5 Computed adsorption energies for furfural (a) in vacuum conditions and using different methods that account for solvent effects, and (b) the solvation energy for furfural on the studied surfaces estimated using AIMD simulations. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

As shown in Figure 4.5a, the adsorption energies of furfural at the metal-water interface estimated from AIMD simulations are weaker than the corresponding adsorption energies in vacuum, i.e, the solvation energies of furfural at the metal-water interface are endothermic as shown in Figure 4.5b.

The estimated adsorption energies from AIMD simulations for Pt and Rh(111) are in good agreement with solution calorimetry experiments<sup>133,134</sup> and a prior bond-additivity model<sup>135</sup>, suggesting the AIMD simulations are accurate qualitatively or even semi-quantitatively. The calculated solvation energies are all above 0.3 eV and could be as high as 0.88 and 0.96 eV on Pt and Rh respectively, far beyond the DFT intrinsic error ca. 0.2 eV<sup>138</sup>, which should have considerable impact on the adsorption phenomena of furfural under aqueous conditions.



#### 4.3.2 Furfural adsorption alters near-surface water structures

Figure 4.6 Water density profiles obtained from AIMD simulations of the different metal-water interfaces. a. Au, b. Cu, c. Pd, d. Pt and e. Rh(111). Each water molecule is positioned based on the coordinates of its oxygen atom. The vertical dotted lines denote the centers of mass of furfural above the surfaces, as shown in Figure 4.3a. The blue dotted lines represent experimental water density at ca. 298 K. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

We plotted the trajectory-averaged water density profiles perpendicular to the surfaces in Figure 4.6. The most important signature is the peaks of near-surface water (< 5 Å) are decreased with furfural adsorption. The water density peaks near surface due to the adsorption of water molecules and consequent local crowding. This peak then decreases after the adsorption of furfural and the water expelled is entering the bulk and gives rise to the elongated tails in water density profiles. The general moving-away of the water ensemble suggests less interaction with the metal surfaces, which could give rise to an extra energy penalty. Note that except for Au(111) in Figure 4.6a, all other metals (b-e) display a small shoulder peak of water density to the left of the major peak. The double peak originates from that the first-layer of water molecules bind the surfaces mainly with O atoms, forcing H atoms outward the surface to form the O void in the second water layer i.e., the typical bilayer structure of water on reactive metal surfaces<sup>139</sup>. No specific interaction of furfural with Au(111) suggests that its adsorption above the first water layer is entropy driven which is a typical behavior for hydrophobic adsorbates<sup>140,141</sup>.

#### 4.3.3 The origin of solvation penalty: water replacement



Figure 4.7 The site-normalized surface water coverage without (left axis) and the change with furfural adsorption (right axis). Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

Previous studies suggest the solvation penalty for ring-like organic molecules come from water replacements<sup>133</sup>. However, no direct correlations have been provided and the considered surfaces are limited. Herein, we calculated the site-normalized trajectory-averaged water coverages in Figure 4.7 at different metal surfaces. The surface water coverage  $\theta_w$  was calculated by averaging

the total number of adsorbed H<sub>2</sub>O molecules  $< \tilde{n_w} >$  during an AIMD trajectory and normalizing this value by the number of surface atoms per unit cell (16) as shown in Eqn 4.6.

$$\theta_w = \frac{\langle \widetilde{n_w} \rangle}{16} \tag{4.6}$$

and the change of surface water coverage  $\Delta \theta_w$  is calculated as Eqn 4.7 as,

$$\Delta \theta_{w} = \theta_{w, w/furfural} - \theta_{w, w/o furfural}$$
(4.7)

We find that without furfural adsorption, the averaged water coverages follow the trend Au < Cu < Pd  $\approx$  Pt  $\approx$  Rh(111), which agree qualitatively with previous AIMD study<sup>130</sup>. After furfural adsorption, all water coverages are reduced, with the replaced water coverages roughly increasing from Au to Rh(111).



Figure 4.8 The correlation between AIMD-derived furfural solvation energies at metal-water interfaces and the replaced surface water coverages (per surface site). Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

The correlation between solvation energies of furfural and replaced water coverages are shown in Figure 4.8, which suggests the more surface waters are displaced, the higher solvation penalties to furfural adsorption at the interfaces. Interestingly, even without surface water coverages, the

solvation energy is 0.27 eV/furfural, indicating there is an extra water reorganization penalty on furfural adsorption. For convenience, we combined the water reorganization and replacement as one factor, i.e., water replacement, in this Thesis, which are by nature due to waters being replaced with furfural intervention. This phenomenon is supposed to be correlated with both the types of hydrophobic adsorbates (molecular size and hydrophilicity) and surfaces.

## 4.3.4 OH binding energy is a good descriptor to predict solvation energies and circumvent expensive AIMD simulations



Figure 4.9 The scaling relationship between AIMD-derived furfural solvation energies at metalwater interfaces and calculated OH binding energies in vacuum. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

The solvation energy is crucial to correct the calculated reaction energetics under vacuum conditions, which help to extend our knowledge in gas-phase catalysis to liquid-phase reactions. Unfortunately, unlike the well-studied solvent effect in homogenous catalysis, the solvation energies of adsorbates in heterogenous catalysis are not only affected by solvents, but also the extended surfaces, which are far from being understood. The limited solvation energies are obtained via indirect experiments, semi-empirical models, and multiscale simulations. Among them, AIMD simulations could obtain relatively accurate solvation energies for adsorbates at

interfaces. However, this widely used methodology suffers from heavy computations to treat vast electronic degrees of freedom (DOF), resulting in a limited system of hundreds of atoms and picosecond timescales. To circumvent this shortcoming, it has been proposed that the identification of simple descriptors to predict critical quantities for metal-water interfaces can dramatically reduce computationally expensive simulations<sup>142</sup>. There are several examples to showcase this idea. Our colleagues Kelly et al. proposed OH binding energies to universally correlate with potentials of zero charge (PZC, a fundamental parameter in electrochemistry) on transition metal surfaces<sup>143</sup>. Besides, OH binding energies have also been used to predict the solvation energy of OH adsorption at metal-water interfaces<sup>130</sup>. Similarly, H<sub>2</sub>O binding energies have been applied to predict the Volta potential difference ( $\Delta \psi$ ) between the metal surfaces and water<sup>144</sup>.

As demonstrated in Section 4.3, the water replacement gives rise to the solvation penalty for furfural adsorption at interfaces, which relates to water (H<sub>2</sub>O) adsorption. Inspired by previous descriptors identified at similar interfaces, we find that the OH binding energies scale well with the solvation energies of furfural on the studied metal surfaces (cf. Figure 4.9). The stronger OH adsorption strength leads to more endothermic solvation energies, thus a more weakened furfural adsorption. The simple scaling relationship between furfural solvation energy and OH binding energy demonstrates the root in solvation penalties and can be applied to predict the solvation energies on other monometallic or even alloy surfaces. Thinking out loud, we expect that other simple descriptors would be discovered to resolve solvation energies for nonaqueous conditions, e.g., in common solvents such as benzene or ammonia, binding energies of CH<sub>x</sub> or NH<sub>x</sub> respectively might be more reasonable descriptors.

Before closing this section, we would like to point out a few setbacks in this work. First, we only performed AIMD simulations for the (111) facet. Thereby, solvent effect on other high-index surfaces cannot be hastily concluded here. Second, the total timescale per trajectory in our AIMD simulations is limited to ca. 50 - 80 ps. The short period of simulation could lead to an underrepresentation of actual structural minima and unexpected physical or chemical phenomena, as well described by the quote,

"It is analogous to making conclusions about how a human walks when only looking at less than one footstep"<sup>145</sup>.

However, the nanosecond-scale AIMD simulations needed for sufficient sampling of structures and chemical events at the metal-water interfaces<sup>146</sup> is currently not available. This limitation could be addressed by training machine learning (ML) based interatomic potentials to perform long time-scale molecular dynamics simulations of metal-water interfaces<sup>147–151</sup>. The discussed results are summarized in Table 4.2 as below.

Table 4.2 The summary of major results based on AIMD simulations in this work. The last 10 ps of 3 trajectories are used to analyze the cumulatively averaged properties: water coverage  $\theta_w$ , furfural adsorption energy  $\Delta E_{FCHO}$ , solvation energy of furfural  $\Delta E_{solv}$  and hydrogen bond formed between water, adsorbed furfural  $N_{HB}$ . Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

Surface	$\boldsymbol{\theta}_{w}$ (ML)	$\Delta E_{FCHO}$ (eV)	$\Delta E_{solv}$ (eV)	N <sub>HB</sub>
Au(111)	$0.039\pm0.002$	N/A	N/A	N/A
Cu(111)	$0.101\pm0.008$	N/A	N/A	N/A
Pd(111)	$0.150\pm0.005$	N/A	N/A	N/A
Pt(111)	$0.135\pm0.004$	N/A	N/A	N/A
Rh(111)	$0.167\pm0.003$	N/A	N/A	N/A
Au(111) + FCHO	$0.020\pm0.006$	$\textbf{-0.51} \pm 0.20$	$0.36\pm0.20$	$0.47\pm0.08$
Cu(111) + FCHO	$0.074\pm0.009$	$\textbf{-0.28} \pm 0.12$	$0.77\pm0.12$	$0.37\pm0.13$
Pd(111) + FCHO	$0.103\pm0.002$	$\textbf{-1.03}\pm0.17$	$0.64\pm0.17$	$0.37\pm0.07$
Pt(111) + FCHO	$0.069\pm0.003$	$\textbf{-0.92}\pm0.18$	$0.82\pm0.18$	$0.46\pm0.08$
Rh(111) + FCHO	$0.092 \pm 0.007$	$-1.01 \pm 0.20$	$0.96\pm0.09$	$0.27\pm0.06$

#### 4.4 The impact of solvation penalty on furfural hydrogenation

To showcase the influence of solvent effect on furfural valorization, we applied furfural hydrogenation towards furfuryl alcohol as an example to illustrate the solvation penalty on the reaction. The reaction mechanism can be found in Chapter 3, Figure 3.1. Given that the furan ring is not hydrogenated in the reaction, we assumed that all intermediates have the same solvation energy as furfural to simplify the study. The considered elementary steps for furfural hydrogenation towards furfuryl alcohol are the same to the reaction pathway in Chapter. Considering the aqueous-phase reaction conditions, the reaction temperature is set as 300K and the pressures for furfural (liquid) and hydrogen gas are set as 0.003 bar and 1 bar respectively.

#### 4.4.1 Solvation can change the rate-limiting step on overbinding surfaces



Figure 4.10 The calculated free energy diagram for furfural hydrogenation towards furfuryl alcohol on Pt(111) at 300 K and 1 bar: vacuum – black, aqueous - blue. Note that we applied the same solvation energy to all surface intermediates in the reaction to account for the major water replacement penalty caused by furanic species adsorption. Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

We show in Figure 4.10 that without solvation, the furfural hydrogenation towards furfuryl alcohol is limited by the desorption of product on Pt(111) surface, while the second hydrogenation displays the highest barrier under aqueous conditions. The overall upshift in reaction energetics is the result

of solvation penalty due to water replacement for all furanic intermediates, relieving the excessive strength in adsorption.

## 4.4.2 Solvation penalties increase reaction activity on strong-binding metal surfaces



Figure 4.11 The theoretical activity volcano for furfural hydrogenation to furfuryl alcohol at 300 K on different (111) metal surfaces in gas (black markers) and aqueous conditions based on solvation energies obtained from AIMD simulations of the metal-water interfaces considered in this work (cyan markers). Reprinted with permission from Paper II<sup>136</sup>. Copyright 2023 AIP Publishing.

Based on our previous microkinetic model<sup>74</sup>, we derived the activity volcano under vacuum conditions at 300 K, fitted with black dots in Figure 4.11. The plot indicates that strong binding metals, e.g., Ru, Rh, and Pt(111) display very low activity at room temperature for furfural hydrogenation due to the surface poisoning effect of furanic intermediates, e.g., FCHO\*, as suggested by near-unity simulated coverages. We find that the predicted catalytic activity for these strong binding metals significantly increase under aqueous conditions, where the furfural binding is greatly weakened due to the endothermic solvation energy (cyan markers in Figure 4.11). The weakened adsorption of furanic species prevents surface poisoning and also allows for sufficient coverage of H\* species, that results in the increased activity for hydrogenation. These results

provide insights on the importance of aqueous conditions in catalyzing furfural hydrogenation on the strong binding metals under moderately high room temperatures.

A note in passing that we used the solvation energy estimated for furfural for all reaction intermediates in the microkinetic model based on the assumption that the size of furanic species along the reaction pathway to furfuryl alcohol is unchanged and thus solvation energies of similar magnitude to \*FCHO can be used for the reaction intermediates. However, we note that solvent-mediated mechanisms such as H-shuttling<sup>152,153</sup> are not considered in the model which also contribute to other solvent effects for the reaction and thereby affect the overall activity predictions.

#### **4.5 Conclusions**

Understanding the surface-solvent interfaces could aid in optimizing reaction conditions for relevant catalytic reactions. In this chapter, we studied the furfural adsorption on different metal-water interfaces using AIMD simulations.

Here are the main take-away messages:

- Furfural adsorption is destabilized at the metal-water interfaces.
- The solvation penalty origins from water replacement, which correlates with surface water coverages.
- OH binding energy is a good descriptor to predict solvation energy for furfural without heavy computations.
- The solvation penalty activates furfural hydrogenation reaction on strong-binding metal surfaces, e.g., Pt and Rh.

#### 4.6 An open-access toolkit: AIMDprobe

The AIMD simulations produce oceans of data, which are not fully exploited. One of the obstacles is lack of systematic and standardized parser to postprocess the simulative results. This makes not only the majority of expensive simulations go unused, but also the quantitative comparison between different works very challenging. To consistently analyze the results of AIMD simulation for metal-water interfaces, we summarized the analyzing functions used in this Chapter and extended to other possible analysis, with a Python-written toolkit developed named as AIMDprobe (https://github.com/tjunewson/AIMDprobe).


Scheme 4.2 The illustration of AIMDprobe toolkit.

The workflow of AIMDprobe is shown in Scheme 4.2. The raw data comes from VASP-based AIMD simulations, the parser extracts structure and energy information from vasprun.xml or OUTCAR files and then applies either structure or energy probe (an ensemble of functions) to postprocess the data and output useful statistical results. In this Chapter, all statistical results were processed using this program. This program is under active development with an aim to unify postprocessing of numerous AIMD simulations in the field. We expect more transferable and comparable results from expensive *ab initio* calculations to be produced and analyzed and further used as valuable datasets for the broad machine learning.

## **CHAPTER 5**

## **Electroreduction of furfural on copper electrodes**

Electrifying chemical production offers a potentially sustainable route to reduce carbon footprints in the process by utilizing green electricity and protons<sup>154</sup>. In Chapter 3 and the end of Chapter 4, we demonstrated the furfural catalytic hydrogenation at elevated temperatures and pressures with  $H_2$  gas mainly from energy-intensive steam-reforming industry. Herein, we turn to furfural electroreduction at ambient conditions using protons directly from water and powered by electricity from sustainable resources. We will start from a brief recap of previous literature, followed by a discussion on why Cu is especially interesting and what challenges are overshadowing this process. Then we will illustrate how we apply theory to unveil major mechanisms of furfural reduction on a solvated model Cu(111) surface. The theoretical insights, the shortcomings of this study, and the grand challenges still facing biomass electrovalorization will also be discussed.

# 5.1 A summary of major products for furfural reduction on metal electrodes

The earliest reports on furfural reduction should date back to the early 20<sup>th</sup> century<sup>13</sup>, where the dimer product, i.e., hydrofuroin (HFN), was produced with up to 63% of yields on Pd electrodes at a total current density of 5 mA/cm<sup>2</sup>. Unfortunately, the investigations of this reaction slowed down, partly due to the complex reaction mechanisms, lack of advanced product analysis and underdeveloped electrochemical setups. Stimulated by the global eagerness to electrify chemical productions, the past decade has witnessed great progress in exploring furfural reduction in terms of electrode material design, mechanistic understanding, product sensitive analysis, and electrolyzer optimization and scale-up. A diversity of metal catalysts has been tested in lab to produce different products in furfural reduction, as summarized in Table 5.1.

Table 5.1 Major products for furfural electroreduction on metal electrodes reported in previous experiments. FAL, MF, HFN and THFA represent furfuryl alcohol, 2-methyl furan, hydrofuroin and tetrahydrofurfuryl alcohol respectively. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

Catalyst <sup>[Ref]</sup>	Potential	Total		Selecti	vity (%	)	Furfural				
	(V vs RHE)	current density (mA/cm <sup>2</sup> )	FAL	MF	HFN	THFA	Concentration (M)	Electrolyte			
A114	-	10	-	-	83	-	0.05	0.5 M H <sub>2</sub> SO <sub>4</sub> and water-acetonitrile mixture			
Ag <sup>156</sup>	-0.5	-	65	-	-	-	0.1	0.1 M sodium phosphate buffer at pH 6.8			
Au <sup>120</sup>	-	75	35	-	-	-	0.25	1 M H <sub>2</sub> SO <sub>4</sub>			
Cd13	-	10	-	-	43	-	0.005	10% KH <sub>2</sub> PO <sub>4</sub>			
Cu <sup>14</sup>	-	10	10	80	-	-	0.05	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$ and water-acetonitrile mixture			
$Hg^{13}$	-	23	-	-	27	-	0.005	10% KH <sub>2</sub> PO <sub>4</sub>			
Ni <sup>14</sup>	-	10	32	28	12	-	0.05	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$ and water-acetonitrile mixture			
Pb <sup>14</sup>	-	10	20	-	60	-	0.05	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$ and water-acetonitrile mixture			
Pd <sup>157</sup>	-0.5	-	55	-	-	-	0.1	0.1 M sodium phosphate buffer at pH 6.8			
Pd <sup>120</sup>	-	150	20	-	-	10	0.25	n-Butanol			
Pt <sup>121</sup>	-0.06	5-10	99	-	-	-	0.08	0.1 M H <sub>2</sub> SO <sub>4</sub>			
Ti <sup>158</sup>	-	50	60	-	-	-	0.1	DMF (with 0.1% water)			
$Zn^{13}$	-	10	-	-	20	-	0.005	10% KH <sub>2</sub> PO <sub>4</sub>			

Major products reported on metal electrodes																	
н					<b>P</b> . •												He
Li	Be		Fu	Irfury	alco	hol	F	Pinaco	ol pro	duct		в	С	Ν	0	F	Ne
Na	Mg		2-	Methy	yl fura	an	Т	etrahyo	drofurf	uryl al	cohol	AI	Si	Ρ	s	CI	Ar
к	Са	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
Cs	Ва	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	ті	Pb	Bi	Po	At	Rn

Figure 5.1 A summary of reported major products of aqueous-phase furfural reduction reaction on metal electrodes. Note that the ratios of colored regions in the box suggest the relative selectivity under similar reaction conditions.<sup>13,14,120,121,156,158–162</sup> Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

The major products reported in previous studies are summarized in Figure 5.1. Furfuryl alcohol (FAL) and hydrofuroin (HFN) are the most common products, while 2-methyl furan (2-MF) and tetrahydrofurfuryl alcohol (THFA) are only selectively produced on limited metals at very acidic conditions<sup>13,14,120,121,156,158–162</sup>. THFA is further produced via a deep reduction of precursor FAL on Pd-based electrodes<sup>120</sup>. The major parasitic reaction is hydrogen evolution reaction (HER). Here, we presented the most studied furfural reduction reactions with their standard equilibrium potentials (E<sup>o</sup> vs. RHE and derived from DFT-calculated Gibbs free energies) as below under acidic conditions with hydronium (H<sup>+</sup>) in electrolyte as proton donor. The reactions discussed in this Chapter are the production of FAL, 2-MF and H<sub>2</sub>.

- FCHO(1) + 2( $H^+ + e^-$ ) = FAL(1),  $E^o = 0.19 V$
- FCHO(1) + 4( $H^+$  +  $e^-$ ) = 2MF(g) + H<sub>2</sub>O(1), E<sup>o</sup> = 0.34 V
- FCHO(1) + 2( $H^+ + e^-$ ) = HFN(1),  $E^0 = 0.21$  V
- $FCH_2OH(1) + 4(H^+ + e^-) = THFA(1), E^o = 0.40 V$
- $\circ 2(H^+ + e^-) = H_2(g), E^o = 0 V$

### 5.2 Furfural reduction on Cu

#### 5.2.1 Why Cu is especially interesting?

Among all studied metal electrodes, copper is a multi-selective electrocatalyst for furfural reduction, as it is able to produce both FAL, a precursor to polymers and resin<sup>115</sup>, and 2-MF, a well-known alternative drop-in biofuel<sup>163</sup>, with nearly 100% selectivity at moderate potentials (ca. -0.6 V vs. RHE) and varied pHs.<sup>14</sup> In fact, Cu is the only metal that is highly selective towards both furfuryl alcohol and 2-methyl furan at different acidic conditions. Besides, Cu electrodes can achieve high furanic selectivity by suppressing HER at low overpotentials, which are also appealing for its broad interest in  $CO_{(2)}$  reduction<sup>164</sup>.

#### 5.2.2 Previous mechanistic understanding: experiment

Possible reaction pathways for furfural electroreduction to FAL and 2-MF on Cu have been proposed by Chadderdon et al<sup>165</sup> and Shan et al<sup>76</sup> (cf. Scheme 5.1). Furfural (FCHO\*), where \* indicates a surface adsorbed species, is first reduced to either FCHOH\* or FCH<sub>2</sub>O\*, via a proton-

coupled electron transfer (PCET) or surface hydrogenation of the oxygen or carbon species on FCHO\*, respectively. These intermediates are suggested to be further reduced to FAL or 2-MF via subsequent PCET (or surface hydrogenation) steps. Alternatively, FAL has also been proposed to be a precursor for 2-MF formation<sup>76</sup>.

Several attempts have been made to narrow down the mechanistic possibilities and identify the rate-determining step(s) (RDS) towards the products of furfural reduction on Cu electrodes<sup>14,166,167</sup>. For instance, Nilges and Schroder reported a lower overpotential for furfural reduction compared to HER on Cu electrodes under acidic conditions, indicating the activation barriers towards FAL and/or 2-MF are lower than those for H<sub>2</sub> production<sup>14</sup>. However, the actual mechanism for furfural reduction was not explored in this experimental study. More recently, May et al. measured partial current densities and the reaction order with respect to furfural for the production of FAL and 2-MF on Cu<sup>166</sup>. Using a simple microkinetic model, they proposed the surface hydrogenation of adsorbed furfural (FCHO\*) and C-O bond dissociation as the RDS towards FAL and 2-MF, respectively. Finally, Jung et al. reported that upon feeding FAL as the reactant for electroreduction on Cu, 2-MF was not detected as a product<sup>167</sup>. This observation rules out the hypothesis that FAL is a precursor to produce 2-MF.

The competition between proton coupled electron transfer (PCET), and electrochemical catalytic hydrogenation (ECH) in furfural reduction, where surface adsorbed species are hydrogenated by protons from the electrolyte (coupled to electron transfer from the electrode) or surface adsorbed hydrogen (denoted by H\*), respectively, is still in disputed. Chadderdon et al. proposed that ECH based mechanisms are the dominant reaction pathways for reduction of furfural towards FAL and 2-MF on Cu electrodes<sup>165</sup>, while outer-sphere reaction pathways dominate the hydrofuroin formation on a relatively inert Pb electrode<sup>168</sup>. As further evidence for the reaction mechanism, May et al. showed that selectivity to 2-MF could be dramatically reduced in favor of FAL with an increase in the electrolyte pH<sup>169</sup>. This conclusion was further strengthened in a recent study by Xu et al. where the authors reported close to 100% selectivity to FAL on a Cu electrode supported on N-doped porous carbon at pH =  $13.6^{170}$ . The strong pH-dependence of the product distribution suggests that the formation of at least one of the two products directly involves protons (or hydroxides) from solution rather than the ECH mechanism exclusively based on the involvement of H\*.

#### 5.2.3 Previous mechanistic understanding: theory

Computational studies are few in furfural reduction reaction. Lopez-Ruiz et al. presented rate expressions with extreme-scenario assumptions to show that both ECH/PCET based pathways could describe the activity trends for furfural reduction on Cu.<sup>171</sup> Shan et al. calculated the reaction energetics of ECH mechanisms and concluded that the first hydrogenation step and the C–O bond scission are possible rate-limiting steps for the formation of FAL and 2-MF, respectively<sup>76</sup>.

#### 5.2.4 Mechanistic disputes unclarified

We note that May and co-workers did not consider the possibility of PCET based pathways, where the adsorbed furanic intermediates are directly protonated by the solvent (i.e.,  $H_3O^+/H_2O$ ). However, previous theoretical studies have either neglected the activation energies associated with PCET based reaction steps in the furfural reduction mechanism or approximated them based on surface hydrogenation barriers that are insensitive to changes in applied potential and pH.



Scheme 5.1 Proposed reaction mechanisms for the furfural electroreduction reaction towards furfuryl alcohol (FAL) and 2-Methylfuran (2-MF) on Cu surfaces<sup>76,165</sup>. ( $H^+ + e^-$ ) and  $H^*$  denote proton coupled electron transfer (PCET) and surface hydrogenation (where  $H^*$  is produced via the Volmer reaction) mechanisms, respectively. The solid and dotted arrows indicate protonation step without and with the production of  $H_2O$ , respectively. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

The reaction energetics were computed for all electrochemical elementary steps illustrated in Scheme 5.1 on Cu(111) model under acidic conditions (i.e., where we assumed the major proton donor is H<sub>3</sub>O<sup>+</sup>). We employed a grand-canonical framework implemented in GPAW-SJM<sup>172</sup>. An ice-like water structure was used to represent the solvent structure in our model<sup>173</sup>, in order to approximate the endothermic solvent effect on the adsorption of larger molecules like furan compounds having a sizeable energetic penalty due to water displacement<sup>132,133</sup>. A slightly tilted orientation of furfural adsorption on Cu(111) was obtained shown in the inset of Figure 5.2, in line with a recent molecular dynamics study<sup>174</sup>. We applied the symmetry factor  $\beta$  obtained from GC-DFT calculations extrapolated from the calculations at three or four varied potentials to quantify the response of the electrochemical activation energies.

The grand-canonical formation energy of reaction states  $\Delta G_{s*}^{\Phi}(\Phi, pH)$  in the furfural reduction reaction could then be calculated as,

$$\Delta G_{s*}^{\Phi}(\Phi, pH) = G_{s*}^{\Phi}(\Phi) - G_{*}^{\Phi}(\Phi) - \sum_{i \in \{C, H, O\}} n_i G_i + N_H (\Phi - 4.4 \text{ eV} + 0.059 \text{pH}) (5.1)$$

where  $G_{S^*}^{\Phi}(\Phi)$ ,  $G_*^{\Phi}(\Phi)$  and  $\sum_{i \in \{C,H,O\}} n_i G_i$  represent the constant potential free energies of reaction intermediates including transition states, the bare slabs, and the gas(liquid)-phase references, i.e., furfural(l), H<sub>2</sub>(g) and H<sub>2</sub>O(l).  $N_H$  is the number of protons transferred to form the intermediate *S*\*. The term ( $\Phi - 4.4 \text{ eV}$ ) represents the potential on the SHE scale.

### 5.3 Major mechanistic findings

## **5.3.1** The thermodynamically favored formation of FCH<sub>2</sub>O\* is kinetically disfavored relative to FCHOH\*



Figure 5.2 The calculated constant-potential free energy diagrams of furfural reduction to furfuryl alcohol on solvated Cu(111): the competition of reaction thermodynamics and kinetics in the PCET steps from furfural (FCHO\*) to the adsorbates FCHOH\* and FCH<sub>2</sub>O\*. Color code in the insets: brown-Cu, dark grey-C, red-O, and light grey-H. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

As shown in Figure 5.2, the formation of FCH<sub>2</sub>O\* is associated with a higher activation barrier than the formation of FCHOH\*, even though FCH<sub>2</sub>O\* is thermodynamically favored. This finding is similar to the recent work by Gauthier et al. where the formation of COH\* was found to be thermodynamically disfavored but kinetically more favored than the formation of CHO\* at relatively high overpotentials during the electrochemical reduction of CO<sup>175</sup>. While FCHOH\* takes a flat adsorption configuration with the carbon of the active site (-CHOH) binding to the top site, FCH<sub>2</sub>O\* binds to the surface hollow site via its O in -CH<sub>2</sub>O. This O-binding configuration of FCH<sub>2</sub>O\* results in ca. 1 eV higher thermodynamic stability relative to FCHOH\*. However, the formation of FCH<sub>2</sub>O\* from FCHO\* displays a much higher electrochemical barrier of 0.78 eV compared to 0.21 eV for FCHOH\* at 0V vs RHE and pH 0, in line with the general trend of

electrochemical barriers for protonating C and O on metals reported before by Patel et al<sup>176</sup>. Furthermore, our simulations indicate that the further protonation of FCH<sub>2</sub>O\* is sterically hindered, as it requires the proton from the electrolyte to approach the surface-bound oxygen. Hence, the hydrogenation of FCH<sub>2</sub>O\* would prefer H\* on the surface as a reactant.



5.3.2 The second PCET steps are rate-limiting steps to both products

Figure 5.3 The complete free energy profiles to both products: furfuryl alcohol (FCH<sub>2</sub>OH, red) and 2-methyl furan (FCH<sub>3</sub>, black). Color code in the insets: brown-Cu, dark grey-C, red-O, and light grey-H. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

Figure 5.3 shows the free energy profiles towards FAL and 2-MF following a FCHOH\* pathway, highlighting the identified selectivity determining step (SDS). We find that the SDS displays comparable calculated barriers, able to explain Cu's activity towards both FAL and 2-MF formation in acidic media<sup>14,165</sup>. The second PCET step, i.e., the protonation of FCHOH\*, shows the highest barriers, hence functioning as both the RDS and SDS.

In order to estimate the competitive hydrogen evolution reaction on Cu(111), we also calculated the HER energetics under acidic conditions. We identify the Volmer step as the RDS in H<sub>2</sub> production on Cu(111), with a barrier of 0.81 eV at 0 V vs. RHE and pH 0, higher than the limiting barriers for furfural reduction reaction. Assuming a similar symmetry factor, the more sluggish HER activity predicts a more negative onset potential relative to FRR.





Figure 5.4 The calculated constant-potential free energy diagram for furfural reduction to FAL (in red) and 2-MF (in black) at 0 and -0.5 V vs. RHE at pH = 1. Note that only Volmer steps are electrochemical in this mechanism (dependent on potential and pH). Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

To better understand the role of surface hydrogenation in FRR, we also simulated the ECH-based mechanisms towards FAL and 2-MF. As shown in Figure 4.4, the formation of 2-MF and FAL are limited by the C-O bond breaking of FCH<sub>2</sub>O\* and FCH<sub>2</sub>O\* hydrogenation. The activation free energies have been determined as 1.02 eV and 0.99 eV, respectively, which are unlikely to respond significantly to an applied potential given that no electrons are directly involved in ECH pathways.

## 5.4 Microkinetic simulations and the comparison with experiments

On the basis of the calculated reaction energetics, we developed a mean-field microkinetic model to obtain mechanistic insights into acidic FRR on Cu(111). The model includes specified adsorbate-adsorbate interactions<sup>177</sup> for furanic species. As expected, FRR has a more positive onset potential than acidic HER alone (i.e., without furfural), as shown in Figure 5.5a, in qualitative agreement with our experimental current densities shown in Figure 5.5b.



5.4.1 The rate-determining step is unlikely to be the first PCET

Figure 5.5 Activity for furfural reduction reaction on Cu. a and b simulated and experimental total polarization curves with and without furfural; c and d simulated and experimental partial current densities (on log scale) towards FAL and 2-MF. Reaction conditions: 100mM furfural, 300K, pH = 1. Note that we fitted the first three data points of experimental partial current densities to obtain the Tafel slopes. We applied  $\pm$  0.3 eV error estimates for the barrier of selectivity(rate)-determining electrochemical FCHOH breaking C-O bond to account for the intrinsic uncertainty in DFT calculations and electrochemical interface simulations, which is represented by the orange and green shade areas in c. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

We argue that the lower onset overpotential for FRR with respect to HER rules out the dominance of an ECH mechanism. Since HER on Cu is limited by the adsorption of protons, the production of H\* via the Volmer step would not allow an earlier onset than for HER, in contradiction with both our theoretical and experimental findings. A case where an increase in FRR activity including surface hydrogenation compared to HER could only be achieved, if the presence of furfural benefits H\* adsorption on the metal surface, which we deem as unlikely, as furfural barely forms hydrogen bonds as shown in Figure 4.4.

The simulated partial current densities towards FAL and 2-MF in Figure 5.5c are comparable owing to their similar energetics (cf. Figure 5.3). This behavior is in line with our experimental activity, shown in Figure 5.5d. However, we refrain from making quantitative predictions on the selectivity of these two products, as a deviation of 0.1 eV in activation energy for the SDS already leads to > 75% change in selectivity<sup>178</sup>. Moreover, we also note that both the production of FAL and 2-MF suffer from mass transport limitations already at ca. -0.45 V vs RHE, indicating the previous experimental results obtained at similar conditions should be re-evaluated to deconvolute the intrinsic activity with mass transport of furfural, H<sub>3</sub>O<sup>+</sup>, and the products.

From our microkinetic models, we observe Tafel slopes of -40 mV/dec for both FAL and 2-MF production at low overpotentials in Figure 5.5c. This reflects our conclusion from the free energy analysis that the second PCET steps determine the intrinsic activity to FAL and 2-MF according to definition of the Tafel slope from Butler-Volmer theory as Eq. 5.2,

$$Tafel slope = -\frac{2.3k_BT}{e^{(N+\beta)}}$$
(5.2)

where *N* is the number of PCET steps before the RDS,  $\beta$  is the symmetry factor of the RDS, k<sub>B</sub> is the Boltzmann constant, *T* is the reaction temperature and *e* the elementary charge.

Experimentally, by employing a fast-stirring reactor, we were able to obtain partial current densities for the major reduction products that are not suffering from mass transport limitations at low overpotentials (cf. Figure 5.5d). The fitted Tafel slopes retrieved from the three lowest current densities are ca. 27 and 57 mV/dec for FAL and 2-MF, placing the respective RDS beyond the first protonation step. The simulated Tafel slope for HER is -120 mV/dec, corresponding to N = 0, which indicates the first PCET step, i.e., Volmer step is determining the H<sub>2</sub> formation. However,

the nonidealities in actual electrochemical reactions in convolution of elusive hydrodynamics<sup>179</sup> can render no preference for cardinal Tafel slopes (e.g., 60 and 120 mV/dec). This uncertainty constrains us to make conclusive remarks on the exact limiting steps, and we only suggests the RDS should lie beyond the first PCET step within the studied potential regions<sup>180</sup>.

## 5.4.2 Surface hydrogenation is unlikely to be the dominant mechanism for furfural reduction reaction on Cu



Figure 5.6 Theoretical results of furfural reduction reaction on Cu following an ECH-based mechanism. a. The simulated partial current densities (solid lines) assuming an ECH-based mechanism in comparison with experimental results (dots, cf. Figure 4.5d); b. The simulated coverages of the main surface adsorbates in the ECH-based mechanism. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

To better understand the role of surface hydrogenation in FRR, we also simulated the ECH-based mechanisms towards FAL and 2-MF, i.e., only considering surface hydrogenation of furfural by H\* produced from the Volmer step. As shown in Figure 5.6a, the formation of 2-MF and FAL are limited by the C-O bond breaking of FCH<sub>2</sub>O\* and FCH<sub>2</sub>O\* hydrogenation. The activation free energies have been determined as 1.02 eV and 0.99 eV, respectively, which are unlikely to respond significantly to an applied potential given that no electrons are directly involved in ECH pathways. The simulated current densities towards FAL and 2-MF, shown in Figure 5.6a, are more than 6 orders of magnitude lower than in the simulation based on the PCET mechanism (cf. Figure 5.5d) as well as our experimental results. The low activity towards FAL and 2-MF within the ECH

mechanism originate from a. *extremely low*  $H^*$  *coverage on* Cu(111) *surface* as shown in Figure 5.5b and b. *sluggish surface hydrogenation kinetics* at the electrochemical conditions.

A higher coverage of electrogenerated H\* would make ECH pathway more likely on hydrophilic surface. For instance, the surface hydrogenation might play crucial roles on Pd, Ni or Ti, where hydrides could form under reducing conditions<sup>181</sup>. Moreover, the restructuring of Cu surfaces driven by potential, adsorbates and electrolytes could create nonconventional active sites, which might lead to enhanced H\* coverages and thus a plausible surface hydrogenation pathway<sup>182,183</sup>. Unfortunately, this is beyond our investigation scope in the Thesis, but we would like to highlight the importance to probe the actual active sites under electrochemical conditions applying *Operando* characterizations<sup>184</sup> and simulations<sup>185</sup>, which should demand a joint endeavor of both theory and experiment<sup>186,187</sup>.

5.4.3 DRC analysis unveils RDS versus potentials to FAL and 2-MF



Figure 5.7 Degree of rate control (DRC) analysis of furfural electroreduction reaction on Cu. a and b are the DRC for FAL and 2-MF production respectively. Note that the number of actual reaction steps that determine the activity towards the respective products is 20. In order to increase readability, we only include the steps with DRC values > 0.1 in the plot, since the rest of the steps play a minor role in determining the overall activity. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

In order to identify the rate-controlling transition states and reaction intermediates for both FAL and 2-MF within the studied potential range, we performed a degree of rate control (DRC) analysis<sup>188</sup> as shown in Figure 5.7. DRC analysis is a powerful mathematical approach that has large (positive or negative) values for the most important transition states and intermediates in the considered reaction pathway. At low overpotentials (0 to -0.2 V vs. RHE), the production of FAL is limited by the protonation of FCHO\* to FCH<sub>2</sub>O\* (Figure 5.7a), suggesting at very low overpotentials (and activities), the FAL formation on Cu proceeds via FCH<sub>2</sub>O\* pathway. At moderate, experimentally relevant, overpotentials (-0.2 to -0.6 V vs. RHE) the mechanism towards FAL changes from going via the thermodynamically more stable  $FCH_2O^*$  to the kinetically preferred FCHOH\* (cf. Figure 5.7a). In contrast, as shown in Figure 5.7b, 2-MF is limited by the protonation of FCHOH\* to FCH\* (DRC  $\approx$  1) throughout the studied potential range. Below -0.6 V vs. RHE, the activity towards both FAL and 2-MF reduce with an increase in the adsorption strength of FCHOH\* as evidenced by a large negative DRC (inhibiting step), as the coverage of FCHOH\* increases and reaches saturation. In this situation, a further increase in the (already high) coverage of FCHOH\* reduces the coverage of all other furanic species on the surface, due to the repulsive interaction with the former. Furthermore, the saturation of FCHOH\* coverage increases the estimated Tafel slopes.



#### 5.4.4 pH and potential-dependent selectivity

Figure 5.8 Simulated selectivities of a. FAL and b. 2-MF at varing pHs and potentials. The red box indicates the most selective reaction conditions (low pHs and potentials) for 2-MF production. Reprinted with permission from Paper III<sup>155</sup>. Copyright 2023 Royal Society of Chemistry.

As shown in Figure 5.8, at low overpotentials, a decrease in both potential (more positive) and pH increases 2-MF formation faster than that of FAL, because in this potential region, FAL production is limited by 1<sup>st</sup>-PCET FCHO\* protonation to FCH<sub>2</sub>O\*, while 2-MF by 2<sup>nd</sup>-PCET FCHOH\* protonation (cf. Figure 5.3), resulting in a larger response to potential/pH for 2-MF in this region. In contrast, at moderately high potentials (< -0.6 V vs. SHE), FAL would dominate, due to its intrinsic lower barrier for the protonation of FCHOH\* to FCH<sub>2</sub>OH\* relative to FCH\* on Cu(111) surface. As a result, a low pH (< 1.5) and moderate potentials (ca. -0.5 V vs. SHE) is suggested to favor the value-added production of 2-MF as jet-fuel precursor over Cu terraces. Nevertheless, we would like to stress that our simulations is based on a low-index Cu(111) surface and engineering Cu electrodes to form high-index facets might facilitate the FCH\* formation over FCH<sub>2</sub>OH\*, which favors the 2-MF production over FAL at a wider potential/pH range. This proposal is supported by a recent work that the roughened Cu electrodes show higher selectivity to 2-MF than other single crystals<sup>189</sup>. In short, by optimizing potential and pH at reaction interfaces and refaceting Cu electrodes, we might be able to achieve a high reactivity (rate and selectivity) towards 2-MF.

## **5.5 Conclusions**

In this Chapter, we have combined grand-canonical DFT calculations with experiments to unveil the mechanisms of furfural reduction on copper, a model catalyst for this electrovalorization reaction.

Here are the main take-away messages:

- Cu could produce both FAL and 2-MF at acidic conditions, due to quantitatively similar rate-limiting steps, which lie beyond the first PCET step.
- Surface hydrogenation of furfural plays a minor role in overall activity, because of a low H\* coverage and a high limiting hydrogenation barrier on Cu.
- pH dependence simulation and experiment further support the PCET-based mechanism instead of ECH-based mechanism for furfural reduction on Cu.
- $\circ$  Moderate potentials and low pHs are suggested to boost 2-MF formation.

## 5.6 Outlook

In this Chapter, we unveil the underlying mechanisms of furfural electroreduction on copper, which has been realized at an extended scale using a (semi)batch furfural-fed electrolyzer, coupled with either conventional OER or other organic oxidation reactions, as illustrated on Scheme 4.2. Though progressive efforts being made, several major challenges remain unsolved in this field.



Scheme 5.2 The schematic of biomass electrolyzer with furfural reduction on cathodic side.

*First, the selectivity of furfural reduction is a complexity of catalysts, electrolytes, applied potentials and electrochemical setups.* A comprehensive understanding of those components is the precondition to steer the reaction to the desired products with improved activities and to design more reactive catalysts. Our work helps to build up the knowledge of intrinsic kinetics as a function of surface, explicit waters, pH and potentials. However, a more accurate description of electrochemical interfaces is still lacking, the reported experiments are not standardized for general analysis and *operando* active sites under furfural reduction conditions are still mysterious, which place uncertainties over our studies. A better description of electrochemical active sites and double layers are in urgent need to really disentangle the reaction mechanisms involving electron and proton transfers. Grand-canonical quantum mechanics (GC-QM) calculations with an explicit solvation environment offer us some hopes to resolve the issues beyond the *ex post facto* methods, e.g., computational hydrogen electrode (CHE). However, the application of GC-QM calculations is still lacking in biomass electrovalorizations, and this method is limited by poor sampling of

solvents and difficult discoveries for the most favored reaction landscapes, which shall be coupled with more advanced data science to increase the efficiencies.

Second, mass transport limitation is one of the major causes for low current densities of furfural reduction in aqueous conditions, due to furfural's low solubility in water under electrochemical conditions (8.3 g/100 mL, 0.86 mol/L at 20 °C). To circumvent this issue, we can shift to nonaqueous conditions, e.g., using alcohols as effective solvents. The idea has been well demonstrated using electrocatalytic palladium membrane reactors (ePMRs) to selectively reduce furfural into furfural alcohol (FAL) and tetrahydrofurfuryl alcohol (THFAL), which separate the H\* formation in water and furfural electrocatalytic hydrogenation in alcohols by Pd membranes<sup>120</sup>. Other methodologies to increase furfural availability near the electrode should be developed, and we might get some clues from conventional organic chemistry and organic battery systems.

*Third, the biomass electrovalorizations are complicated by parasitic solution reactions, whose mechanisms are barely studied.* Only very recently, several groups shed light on the formation of dimerization product of hydrofuroin by proposing a radical coupling pathway, with electrodes delivering electrons<sup>161,168</sup>. Homogenous reactions can also cause troubles. For example, polymerization of furfural and other intermediates lead to humin formation, which can severely reduce the reaction efficiency, and foul the electrodes and electrolytes. As a result, ways to prevent those pernicious side reactions, e.g., polymerization, need to be adopted for the future works.

Last, furfural reduction reaction can in principle be coupled with other value-added oxidation reactions, to replace sluggish OER ( $E^0 = 1.23 V vs. RHE$ ). A good example is a complete furfural electrolyzer, with furfuryl alcohol and furoic acid produced at cathode and anode, respectively. Biomass oxidation can result in complex product distributions, which could decrease the desired selectivity and make the product separation more expensive. In my PhD project, I have also studied the furfural oxidation reaction towards furoic acid and Kolbe electrolysis of acetic acid to ethane on Pt electrodes to unveil the origin of high overpotentials and possible rate-limiting steps<sup>190</sup>. These investigations informed me of how complex the oxidation reaction can be, especially with a detailed consideration of surface oxidation as well.

In a nutshell, biomass electrovalorization is a rising star to replace conventional biomass conversion processes, but many challenges remain partly solved or unsolved. Joint efforts are required on mechanism understanding, catalyst design, electrode engineering, electrolyzer optimization, economy, and scale-up.

## **CHAPTER 6**

## Furfural electroreduction on single atom catalysts

In Chapter 5, we investigated the furfural electroreduction on copper electrodes, to unveil the underlying mechanisms to produce furfuryl alcohol and 2-methyl furan. We also showed that the selectivity can be tuned via changing potential and acidic pH. Cu is a model catalyst for many reduction reactions; however, the products of furfural reduction are mainly monomers. Inspired by the advances in  $CO_{(2)}$  reduction reaction and our collaborations with labs in Imperial College London, we extended our theoretical investigation to emerging single-atom catalysts, which are shown to be selective to the dimer product hydrofuroin.

## 6.1 Why single atom catalysts?

Single-atom catalysts have aroused unprecedented interest in the energy-related electrocatalysis and electrosynthesis<sup>191,192</sup>, e.g., hydrogen evolution<sup>193</sup>, oxygen reduction<sup>194</sup>, CO<sub>2</sub> reduction<sup>195–197</sup> and rapidly developing ammonia electrosynthesis, e.g., via nitrate reduction<sup>198–200</sup> and even aqueous-phase nitrogen reduction<sup>201,202</sup>. The single-atom motifs with unique electronic structures<sup>203,204</sup> provide multi-dimensions to regulate the adsorption of crucial intermediates and consequent reactivities by tuning doped metal atoms<sup>205,206</sup>, coordination environments<sup>207–209</sup>, supports<sup>210</sup> and even long-range interactions<sup>211</sup>. However, the application of single-atom catalysts in furfural reduction or other biomass electrolysis has been rarely studied. Recently, we first reported that molecular single atom catalysts (Co/Cu-doped phthalocyanines) on carbon supports give rise to high yield and selectivity towards hydrofuroin, a very valuable precursor to drop-in jet fuels, at mild conditions (pH 10 and -0.5 V vs. RHE), resembling the selectivity on toxic Pb<sup>212</sup>. However, the limited molecular catalysts applied in the work cannot grasp the full spectrum of single-atom family. We therefore propose that the potential of single-atom can be further exploited by extending the single atom motifs to general metal-nitrogen-carbon (MNC) systems.



### 6.2 Single atom motifs in this study

Figure 6.1 Single-atom model catalysts in this Chapter. a. metal-nitrogen-carbon complexes  $(MN_xC)$ ; b. metal-doped phthalocyanines (MPc).

In addition to the molecular metal-doped phthalocyanines (MPc), metal-nitrogen-carbon complexes ( $MN_xC$ ) offer multiple dimensions to tune single atom motifs including metal centers and N/C coordination, as shown in Figure 6.1. Different from commercially available MPc,  $MN_xC$  is usually synthesized in lab from *in situ* templated doping, where the formation stability can be an issue. Therefore, we first calculated the formation energy of  $MN_xC$  motifs using the formula derived in a previous work<sup>213</sup> as,

$$\Delta E_{form} = E_{MN_xC} - E_{M-bulk} - E_{N_xC}$$
(6.1)

where  $E_{MN_xC}$ ,  $E_{M-bulk}$  and  $E_{N_xC}$  are the energies of  $MN_xC$ , metal M bulk and the defective *xN*-doped graphene. We choose several base metals (M = Cr, V, Ni, Mn, Fe and Co) for this study, which are cheap and have been synthesized before for other reactions.



#### 6.2.1 The formation stability of MN<sub>x</sub>C

Figure 6.2 The formation energy of single atom  $MN_xC$  catalysts. M = Cr, V, Ni, Mn, Fe and Co. Reprinted with permission from Paper V.

To include a wide spectrum of nitrogen-carbon based single atom catalysts, we vary the N coordination x of MN<sub>x</sub>C from 0 to 4, thus the C coordination changes from 4 to 0. For all the metals and local coordinations considered here, we did not see dramatic restructuring in the optimized structures, and all metal centers remain in the same plane of nitrogen-carbon matrix. As shown in Figure 6.2, the formation of MN<sub>x</sub>C catalysts is generally favored ( $\Delta E_{form} < 0$ ) in this work, which could be the result of N and C affinity on those metals, e.g., Co can form both carbide and nitride. Relatively, the MN<sub>0</sub>C motifs are the least stable relative to other N-coordinated systems. V-doped systems are generally less favored than others, which also explains the difficulty in synthesizing V-based MN<sub>x</sub>C catalysts in experiment, while Co, Fe, Ni, Mn and CrN<sub>x</sub>C catalysts are commonly applied in various electrochemical reactions. Herein, to further narrow down the experimental tests, we focused on Co, Fe, Ni and CrN<sub>x</sub>C systems in the following discussions. Notably, we only calculated the formation stability in this work, while the electrochemical stability is not considered, which can be also important for practical applications.



### **6.2.2** The adsorption of furfural on different types of catalysts

Figure 6.3 The stable furfural adsorption configurations on a. CoPc, b.  $CoN_4C$  and c. Co(0001). The color code is presented as inset. Reprinted with permission from Paper V.

As shown in Chapter 3 and 4, the furfural adsorption plays a critical role in determining its conversion. We then calculated the adsorption of furfural on different types of catalysts: MPc, MN<sub>x</sub>C and metal (M) slabs, considering both extended surfaces and single atom catalysts. As exemplified with Co systems in Figure 6.3, furfural takes quite different binding configurations. While both furan ring and -CHO bond with Co(0001) surface, furfural only tilts to slightly interact with Co single atom with its O in -CHO on CoPc and CoN<sub>4</sub>C, indicating a dramatic weakened furfural adsorption on those single atom motifs. Because the furan ring barely interacts with carbon skeleton in single-atom catalysts, it is unlikely to get ring-reduced products, e.g., THFA, over those catalysts even with a long batch reaction time, while furan-binding metals, such as Pd, can produce THFA or 2-methyltetrahydrofuran (2-MTHF) at very acidic conditions<sup>120,214</sup>. However, single atom catalysts are usually unstable in acid, thus we only consider mild pH conditions for the following study.



### 6.3 The selectivity in furfural reduction

Figure 6.4 The selectivity in furfural reduction over different catalysts. a. Faradaic efficiency (FE); b. carbon balance. Experimental details: 0.1 M potassium bicarbonate-carbonate buffer (pH 10) as electrolyte. Potential applied was -0.50 V vs. RHE for 1 hour for all chronoamperometry experiments. Scan rate: 50 mV s<sup>-1</sup>. The detected products were measured using high performance liquid chromatography (HPLC). Error bars created from two separate experiments. The 'other' products are unidentifiable organic humin products from polymerization. Reprinted with permission from Paper V.

Furfural reduction in neutral and alkaline conditions has been reported in experiments to mainly produce 2-electron products: FAL and dimer product HFN on metal and carbon electrodes as below,

• FCHO(1) + 2(
$$H^+ + e^-$$
) = FAL(1),  $E^\circ = 0.19 V$ 

• 
$$2FCHO(1) + 2(H^+ + e^-) = HFN(1), E^\circ = 0.21 V$$

As shown in Figure 6.4, molecular single atom catalysts (CuPc and CoPc) display over 60% FE and carbon balance selectivity towards the dimer product hydrofuroin and produce very little FAL, in the same category of carbon black and Pb. In contrast, Cu mainly produces FAL, in agreement with previous reports under similar conditions<sup>169</sup>. Moreover, single atom catalysts show a better resistance to polymerized product like humin relative to pure carbon catalyst.

## 6.3.1 A theoretical classification of experimental selectivity in furfural reduction

Summarizing the experiments above and previous reports under slightly alkaline conditions (cf. Table 5.1), we then proposed a descriptor-based selectivity map including metal surfaces, MPc and newly added MN<sub>x</sub>C as shown in Figure 6.5. Inspired by the selectivity map established for CO<sub>2</sub> reduction by Bagger et al.,<sup>215</sup> we applied furfural and hydrogen adsorption energies ( $\Delta G_{FCHO}$  and  $\Delta G_H$ ) to classify the experimental selectivity of furfural reduction at neutral or slightly alkaline conditions.



Figure 6.5 The selectivity map grouped based on calculated FCHO\* and H\* adsorption free energies. The shaded ovals are added to guide the eyes. The annotated marks in grey are single atom catalysts which are not experimentally studied in this work. The two dotted lines represent H\* adsorption and FCHO\* adsorption, respectively. Conditions: 300 K and 1 bar. Reprinted with permission from Paper V.

Notably, single atom catalysts especially with 4N coordination tend to bind less strongly than their extended surface counterparts, as a result of restricted binding site discussed in Section 6.2.3. For instance, Co(0001) surface binds furfural ca. 1 eV more strongly than CoN<sub>4</sub>C and CoPc, which differentiate the selectivity dramatically. Besides, MN<sub>4</sub>C displays similar adsorption energies to MPc systems, because of their 4N coordination to the centric metal atoms.

In general, there are three selectivity regions: 1. The strong adsorption of furfural leads to mainly hydrogen evolution on Rh and Ru surfaces (red region); 2. The moderate adsorption gives rise to FAL formation, which are represented by Cu (blue region); 3. The weak adsorption promotes the HFN production (green region). Those on the borders might produce multiple products. Notably, we only looked at neutral or slightly alkaline conditions, where most of the surfaces can be stable, so we are unable to capture the selectivity under other conditions, e.g., Cu can produce 2-MF under acidic conditions as we shown in Chapter 5. In addition, based on Chapter 4, the furfural adsorption suffers from water replacement, but we assume this effect is minor here due to its very limited water coverages on single atoms.

Specifically, we find that the  $MN_xC$  (M = Co, Fe and Ni) and Co/CuPc generally binds furfural weakly, similar to Pb, which are selective to HFN. Interestingly,  $CrN_xC$  (e.g.,  $CrN_4C$ ) shows increased furfural binding strength to be grouped near Au, Ag and Cu, which are selective to furfuryl alcohol. Before plunging into experimental validation, we would like to demonstrate why some single-atom catalysts are good at producing HFN.



6.3.2 Weak binding makes the surface dimerization facile

Figure 6.6 The relationship between activation energies for coupling of two FCHOH\* and the adsorption energies of furfural on extended metal surfaces. A showcase coupling process of FCHOH\* to hydrofuroin is shown as the inset. Reprinted with permission from Paper IV<sup>212</sup>. Copyright 2023 Royal Society of Chemistry.

To form HFN, the dimerization of two FCHOH is a key step. We first calculated the dimerization barriers on different extended surfaces i.e., Ag, Cu, Pb, Pt, Ru(111) and pristine graphene, as shown in Figure 6.6. We find that the activation energy of dimerization scales with furfural adsorption strength, that is, the stronger binding of furfural, the higher barrier for coupling reaction. Strong-binding surfaces, e.g., Pt and Ru, have high activation energies, indicating the surface dimerization is extremely hard. In contrast, the weak-binding surfaces such as Pb and single atom motifs are predicted to display very low surface coupling barriers as denoted by the blue arrow. However, we note that single atom motifs are isolated from each other, while FCHOH adsorbate is huge, indicating the surface dimerization pathway is not very likely on single atom motifs. This motivated us to explore other possibilities.



Figure 6.7 The calculated Gibbs free energies of possible radical reactions for FCHOH. Note that the solution phase reactions were simulated using Gaussian  $09^{216}$  with B3LYP functional and the 6-311++G(d,p) basis set<sup>217,218</sup>. The presence of water was modelled via the SMD variant of Polarizable Continuum Model (PCM) with the integral equation formalism variant<sup>219</sup>. Reprinted with permission from Paper IV<sup>212</sup>. Copyright 2023 Royal Society of Chemistry.

As evidenced by Anibal and Xu<sup>161</sup> and Liu et al.<sup>168</sup> combining electron paramagnetic resonance (EPR) spectroscopy and electrochemical tests, the extremely weak binding of furfural ( $\Delta G_{FCHO} \geq$  0 in Figure 6.5) on Pb electrodes opens a solution-coupling reaction pathway via desorbed ketyl radicals, i.e., FCHOH· to selectively produce HFN over alcohols. The same coupling pathway may also prevail over the weak-binding single-atom catalysts.

To better describe radical reaction pathways under aqueous conditions, we used Gaussian code with a PCM solvation model to calculate the Gibbs free energies of FCHOH radical reaction. As shown in Figure 6.7, we find only the dimerization of two FCHOH radicals to be exothermic (-1.53 eV). The extremely high and endothermic energies for FCHOH directly reacting with water suggests the radical pathway is not producing FAL, which should be a surface-catalyzed product via two consecutive PCETs, as shown on Cu in Chapter 5.

#### 6.3.3 MN<sub>x</sub>C offers possibility to tune selectivity beyond hydrofuroin

 $MN_xC$  complex offer other structural dimensions to tune the furfural adsorption strength as illustrated in Figure 6.5, where surface protonation products such as FAL can be made. Guided by the selectivity map, our collaborators applied an elegant template-based protocol well demonstrated in Ref<sup>220</sup> to successfully synthesize several MN<sub>x</sub>C complexes, where M = Co, Cr, Fe and Ni. The spectroscopies suggest an overall x  $\approx$  4 of N of our MN<sub>x</sub>C samples, thus we used MN<sub>4</sub>C as catalyst models in following studies. The as-synthesized samples were then tested for the furfural reduction under the same conditions with the selectivity shown as below in Figure 6.8.



Figure 6.8 The selectivity in furfural reduction over different  $MN_xC$  catalysts. 2,4,6-Triaminopyrimidine (TAP) is the template of nitrogen-carbon complex, and single M was introduced via a given metal chloride, e.g.,  $CrCl_2 \cdot 6H_2O$ . The samples were labelled as M@TAP (where M is Fe, Ni, Co, or Cr). Reaction conditions: 0.1 M potassium bicarbonate buffer (pH 10), catalyst loading was 0.1 mg cm<sup>-2</sup>. The scan rate for the LSVs was 50 mV s<sup>-1</sup>. Reprinted with permission from Paper V.

While Fe, Ni and Co@TAP exclusively produce HFN (FE<sub>FAL</sub> < 3 %), Cr@TAP sample produces ca. 18% FE<sub>FAL</sub>, which is in line with our predictions in Figure 6.5. This enhancement to FAL on CrN<sub>x</sub>C is possible due to the strengthened furfural adsorption on Cr single atoms, which help

prevent the intermediates from desorption to solution. However, we also notice that Cr@TAP still mainly produce HFN, and this indicates that the majority of nitrogen-carbon matrix that do not bind furfural serves as electron shuttle for the dimerization in solution. By increasing the density of Cr single atom, the relative TOF of furfuryl alcohol is expected to be increased. Notably, we expect that the selectivity towards FAL can be improved at lower overpotentials, where the outer sphere coupling reaction has not reach its redox potential.



Scheme 6.1 The proposed mechanism of furfural reduction on single atom catalysts. Remade with permission from Paper IV<sup>212</sup>. Copyright 2023 Royal Society of Chemistry.

The proposed mechanism for furfural reduction over single atom catalysts is presented as Scheme 6.1. The adsorption of furfural determines the initialization of either surface or solution reaction pathways. The solution reaction pathway on weak-binding single atom catalysts is limited by the redox step to form FCHOH radical and the following coupling is facile to produce hydrofuroin. In contrast, the surface pathway on strong-binding catalysts goes through two consecutive PCET steps to produce furfuryl alcohol around metal centers. Given the metal sites being isolated on the surface, we indicate that the surface coupling of two distant adsorbed FCHOH is unlikely. We believe that the mechanism considering both surface and solution reaction pathways could be instructive to other biomass electrovalorizations using single atom catalysts.

# 6.4 The challenges in simulating single atom catalysts for electrochemical reactions

Single atom catalysts are defined to be '*single*', meaning that all doped heteroatoms (active sites) should be perfectly isolated from each other. An advantage of single atom catalysts is their intrinsically well-defined active sites: the central metal atom and its unique local coordination environments, which offer an ideal catalyst model to investigate *structure-performance relationships*. Unfortunately, the perfection of those single sites is usually a daydream, especially when considering the actual reaction conditions in both synthesis procedures and electrochemical experiments. Herein, we highlight several grand challenges or gaps to simulate single atom catalysts for furfural reduction and other electrochemical reactions:

- The actual local coordination environment can vary for MN<sub>x</sub>C systems, though experimental characterizations can offer a rough estimation. This uncertainty should affect the selectivity of certain single atom catalysts. For instance, as shown in Figure 6.5, changing N coordination numbers (x) of MN<sub>x</sub>C can shift selectivity regions, e.g., CoN<sub>4</sub>C (HFN) and CoN<sub>1</sub>C (FAL).
- Electrochemical reaction conditions can affect or even destroy active sites. It has been shown that the CuPc is not stable during furfural reduction even at mild conditions, where Cu ion can dissolve into the solution<sup>212</sup>. Moreover, metal clusters can form under reducing potentials, and thus alter the active sites totally.
- 3. Kinetic study is missing in this part and the competition between HER and furfural reduction is not included. The unique single atom catalysts generally weakly bind H, but reducing the potential shall favor its adsorption, which is convoluted with a potential-dependent dipole-field effect on furfural adsorption strength.
- 4. The mass transfer at the electrochemical double layer with single atom catalysts is not studied, and it is likely to make great impact on HFN formation in solution.

## **6.5 Conclusions**

In this Chapter, we continued our journey in electrifying furfural valorization and exploited using single atom catalysts for furfural electroreduction at mild conditions, with a highlight on selectivity. Here are the main take-away messages:

- Single atom catalysts generally bind furfural weakly due to restricted adsorption area.
- *Furfural adsorption free energy* is a descriptor for selectivity in furfural reduction towards furfuryl alcohol or hydrofuroin.
- Hydrofuroin formation is likely to a solution reaction, with the protonation step limiting the rate.
- Single atom catalysts with enhanced furfural binding, e.g., CrN<sub>x</sub>C, can promote furfuryl alcohol production.

## **Concluding remarks**

Utilizing biomass resources to produce value-added chemicals and fuels has become an important topic across fundamental research and industrial applications to realize a sustainable biomass economy, as demonstrated in Chapter 1. In this Thesis, we focused on the catalytic conversion of furfural, a crucial platform biomass-derived chemical. We combined *ab initio* calculations with microkinetic simulations to unveil the reaction mechanisms and improve the understandings at actual reaction interfaces, to offer guidelines for catalyst design, reaction condition and reactor optimization in practice.

We started our journey from industry-related vapor-phase furfural hydrogenation towards furfuryl alcohol with a model of metal-vacuum interface. Our simulations suggest different rate-limiting steps on different metal surfaces and sketched out a simple descriptor of furfural binding energy for the hydrogenation activity. The model predicts Cu-rich CuNi alloys can be potential candidates to replace Cr-containing catalysts in industry. Based on extensive AIMD simulations at multiple metal-water interfaces, we then unveiled the origin of solvation penalty (destabilized adsorption) of furfural under aqueous conditions at metal-water interfaces. To circumvent heavy ab initio calculations, OH binding energies obtained from relatively cheap static DFT calculations were proposed to correlate with solvation energies, which could help predict the solvent effect on other surfaces of interest. Importantly, we exemplified how the solvent effect activates furfural hydrogenation over strong-binding metal surfaces (e.g., Pt and Rh).

Electrifying biomass valorization is a one-stone-two-bird process. We began this investigation with a detailed mechanistic study of furfural electroreduction on copper. Our grand-canonical calculations along with microkinetic simulations uncovered the crucial role of direct protonation for furfural reduction in mass-transport-free regions. We highlighted using the leverages of potential and pH to promote jet-fuel precursor 2-MF formation. In a close collaboration with the research groups in Imperial College London on single-atom catalysts, we found furfural binding energy as a selectivity descriptor for outer-sphere and inner-sphere products in furfural electroreduction reaction across extended surfaces and metal-doped single atom materials. This insight helped us to discover a new single-atom catalyst to boost inner-sphere furfuryl alcohol production.

In a nutshell, we demonstrated the importance of applying detailed theoretical simulations including (GC)-DFT calculations, microkinetic modeling, and *ab initio* molecular dynamics to gain insights at different *interfaces* in furfural (electro)valorization, serving as a model system for broad studies in biomass upgrading. We also highlighted the limitations of current works and gaps between theoretical understandings and practical applications.

Looking ahead, we expect all those exciting discoveries in this Thesis to clear fogs in the mechanistic pictures of furfural valorization with a deepened understanding of condition-structureperformance relationships. The insights obtained at different levels of theory should aid in catalyst design and reaction condition optimization. With a joint endeavor of theory and experiment, we are positive that an efficient circular biomass economy will be achieved.

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# **Included publications**

## Paper I (Chapter 3)

Understanding activity trends in furfural hydrogenation on transition metal surfaces <u>Sihang Liu</u>, Nitish Govindarajan, Karen Chan ACS Catal., **2022**, 12, 20, 12902–12910



# Understanding Activity Trends in Furfural Hydrogenation on Transition Metal Surfaces

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**ABSTRACT:** Furfural hydrogenation to furfuryl alcohol is an industrially significant reaction for biomass valorization. The hydrogenation process has been mainly catalyzed by chromite-based materials that are notorious for their toxicity, thereby highlighting the need to find alternate catalyst materials. In addition, there is a gap in the mechanistic understanding of furfural hydrogenation on transition metal surfaces. Herein, we combine density functional theory calculations and microkinetic modeling to study the reaction mechanism of furfural hydrogenation to furfuryl alcohol on terrace (111/0001) and stepped (211) transition metal surfaces. We find that the rate-determining steps for furfural hydrogenation depend on the identity of the metal, where the strong binding metals are limited by desorption of the product (furfuryl alcohol), while the moderate and weak binding metals are limited by steps involving surface hydrogenation or H<sub>2</sub>



activation. We show that the binding energy of furfural is a good descriptor to rationalize and predict the activity trends for the production of furfuryl alcohol. Among the metal and bulk/single atom alloy surfaces investigated in this work, we find Cu-based alloys to be the most active catalysts, with Cu-rich CuNi alloys predicted to be promising candidates for furfural hydrogenation.

**KEYWORDS:** furfural hydrogenation, density functional theory, microkinetic simulations, activity volcano, transition metals, biomass valorization

#### INTRODUCTION

Given the depletion of fossil resources and their impact on the climate, alternatives to produce chemicals and fuels are urgently needed. The catalytic conversion of biomass serves as a promising choice in this regard.<sup>1,2</sup> For example, we can decompose lignocellulose, one of the most abundant biomass resources<sup>3</sup> (>170 billion metric tons per year), via hydrolysis<sup>4</sup> into platform chemicals, such as liquid alkanes, 5-hydroxymethylfurfural (HMF), and furfural (denoted as FCHO in this work, where F represents the furan ring). Furfural is a crucial bio-based molecule, with a wide range of applications in synthesizing downstream products such as pharmaceuticals and polymers.<sup>5,6</sup> Concurrently, the majority (>60%) of furfural is used to produce furfuryl alcohol (FCH<sub>2</sub>OH) via catalytic valorization,<sup>7</sup> which is not only a key monomer for synthesizing furan resins, lysine, vitamin C, and other chemicals but also a crucial intermediate for the production of other deeply hydrogenated products such as 2-methylfuran, tetrahydrofurfural, and 2-methyltetrohydrofuran.<sup>8,9</sup> Furfuryl alcohol is one of the simplest products from furfural hydrogenation, with a relatively well-established reaction pathway,<sup>10,11</sup> and can be regarded as a model reaction to understand the valorization of furfural and other biomassderived chemicals.

Copper chromite catalysts ( $CuCrO_x$ ) are currently used in industry to catalyze furfural hydrogenation to furfuryl alcohol with high yields (>95%) due to their ability to selectively hydrogenate C=O bonds without affecting the C=C bonds.<sup>12,13</sup> However,  $CuCrO_x$  catalysts suffer from serious deactivation and can release toxic chromite over time to contaminate the product.<sup>14</sup> As a result, there is a growing interest to find more environment-friendly alternatives to replace the Cr component in CuCrO<sub>r</sub> catalysts.<sup>15</sup> A number of transition metals besides Cr have shown activity toward furfuryl alcohol production from furfural, e.g., Au,<sup>16</sup> Co,<sup>17</sup> Ir,<sup>18</sup> Ni,<sup>19-21</sup> Pd,<sup>22,23</sup> Pt,<sup>24</sup> Rh,<sup>25</sup> and Ru.<sup>26</sup> In particular, Cu has been widely investigated as a catalyst for furfural hydrogenation and exhibits high selectivity toward furfuryl alcohol.<sup>27-34</sup> In addition, Cu-based alloys, e.g., CuPt,<sup>35</sup> CuPd,<sup>36</sup> and CuNi,<sup>37</sup> have shown 1-3 orders of magnitude higher turnover frequency (TOF) toward furfuryl alcohol relative to monometallic Cu.

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Scheme 1. Possible Reaction Pathways Proposed for Furfural Hydrogenation to Furfuryl Alcohol on Transition Metal  $Surfaces^a$ 



<sup>*a*</sup>ads and des indicate adsorption and desorption steps, respectively.

Over the past decade, there have been some mechanistic studies based on density functional theory (DFT) for furfural hydrogenation on transition metal surfaces. The reaction pathway toward furfuryl alcohol (cf. Scheme 1) has been proposed to occur via the hydrogenation of FCHO\* (\* indicates the species is adsorbed on an active site) by a surface hydrogen (H\*) that is produced via the dissociation of H<sub>2</sub> gas (H<sub>2</sub> activation) to form either FCHOH\* or FCH<sub>2</sub>O\*. Further hydrogenation of FCHOH\*/FCH<sub>2</sub>O\* results in the formation of FCH<sub>2</sub>OH\*, which is desorbed to produce the product, furfuryl alcohol (FCH<sub>2</sub>OH).<sup>38,39</sup>

Several possible rate-limiting steps have been identified in the reaction pathway shown in Scheme 1 based on the metal identity. For instance, on Cu(111), the hydrogenation of FCHO\* to FCH<sub>2</sub>O\* was identified as the rate-determining step for furfuryl alcohol production,<sup>38</sup> while the formation of FCHOH\* is suggested to be the rate-limiting step on  $Pd(111)^{40}$  and  $Ni(111)^{41}$  surfaces. In contrast to refs 40 and 41, Liu et al. identified the desorption of adsorbed furfuryl alcohol to have the highest activation barriers on both Pd and Pt surfaces.<sup>42</sup> We note that the differences in these studies are likely due to the use of different adsorbate configurations, the employed XC functional with/without dispersion corrections. Therefore, the reaction mechanism for furfural hydrogenation on transition metal surfaces including the pathways for H<sub>2</sub> activation and the nature of the rate-limiting steps are currently under debate. The adsorption energy of furfural ( $\Delta E_{\rm FCHO}$ ) and metal identity-dependent adsorption configurations of furfural have been used to explain furfural hydrogenation activity on different metal surfaces,<sup>39,43</sup> indicating  $\Delta E_{\rm FCHO}$  to be the potential activity descriptor for furfural hydrogenation. As the simplest furfural conversion reaction and the starting step to other value-added products, the lack of comprehensive understanding of the reaction mechanism hinders the rational catalyst design for this process and beyond.

Herein, we present a comprehensive mechanistic study based on DFT calculations and microkinetic simulations to identify rate-limiting steps and activity trends for furfural hydrogenation toward furfuryl alcohol on transition metal and alloy surfaces. We find that the activity of the weak-binding metals (e.g., Au) to be limited by  $H_2$  activation or hydrogenation of furfural species, while strong-binding metals (e.g., Pt) are poisoned by the adsorption of furfuryl alcohol. The activity volcano indicates that Cu(211) is the most active catalyst among pure metal surfaces and the stepped surfaces of weak/moderate-binding metal surfaces are more active than terraces, while the opposite trend is observed on strongbinding metals. We show that bulk and single-atom alloys could further promote the activity for furfural hydrogenation beyond monometallic surfaces. Notably, Cu-based Ni-diluted single-atom alloys (Cu@Ni<sub>1</sub>) and bulk Cu alloys (Cu<sub>3</sub>Ni<sub>1</sub>) are identified as promising candidates that can meet the requirements of high activity, low cost, and low toxicity for the development of next-generation catalysts for furfural hydrogenation.

#### COMPUTATIONAL DETAILS

Density functional theory calculations were performed using the Vienna Ab initio Software Package (VASP)<sup>44</sup> employing the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.<sup>45</sup> Core electrons were described using projector augmented wave (PAW) potentials.<sup>46</sup> The PBE calculations were supplemented with Grimme's D3<sup>47</sup> correction to account for dispersion interactions of the furan ring with the metal surfaces. Note that PBE-D3 functional was suggested to overbind furanic molecules, but the trends are not affected on different metal surfaces.<sup>42</sup> Spin-polarized calculations were performed for Ni and Co-containing surfaces, while the remaining surfaces were simulated using non-spin-polarized calculations. The atomic simulation environment  $(ASE)^{48}$  was used to build  $4 \times 4 \times 4$  (111) or (0001) slabs and  $3 \times 4 \times 4$ (211) slabs that represent terrace and stepped surfaces, respectively. The bottom two layers of surface were fixed at their bulk interatomic distances. A dense Monkhorst-Pack<sup>49</sup> k-point mesh of  $12 \times 12 \times 12$  was used to obtain the optimized lattice constants of the metal, while k-point meshes of  $3 \times 3 \times 1$  and  $4 \times 3 \times 1$  were used to sample the reciprocal first Brillouin zone for the (111)/(0001) and (211) metal slabs, respectively. A 15 Å vacuum spacing is added in the z direction for all of the supercells. A plane-wave cutoff of 400 eV was used in the geometry optimizations. The geometry optimizations were considered converged when the maximum residual force on each atom was less than 0.02 eV/Å. The reaction barriers for furfural hydrogenation reaction on (111) surfaces were calculated using the climbing image nudged elastic band (CI-NEB)50 and optimized by dimer51 methods, with a force convergence criterion of 0.05 eV/Å on each atom. The transition states were confirmed by examining that only one large single imaginary frequency exists. The microkinetic simulations were performed using the open-source CatMAP code<sup>52</sup> based on the mean-field approach and the steady-state approximation including a self-consistent description of adsorbate-adsorbate interactions. In the microkinetic model,



**Figure 1.** Adsorption free energies of furfural (FCHO) with flat or upright configurations on (a) 111 and (b) 211 metal surfaces. Simulation conditions: 400 K,  $P_{FCHO} = 0.1$  bar. The representative adsorption configurations of FCHO on Cu surfaces are shown as insets.



**Figure 2.** (a) Free energy profiles for furfural hydrogenation on Au(111), Cu(111), and Pt(111) surfaces via FCHOH\* (solid lines) and FCH<sub>2</sub>O\* (dotted lines) at 400 K,  $P_{FCHO} = 0.1$  bar,  $P_{H_2} = 1$  bar; (b) adsorption configuration of stable intermediates; and (c) transition state structures for furfural hydrogenation on Cu(111).

the binding energies of FCHO\* and H\* ( $\Delta E_{\rm FCHO}$  and  $\Delta E_{\rm H}$ ) were used as descriptors and the calculated energetics on (111) surfaces were used as input for the scaling relations and the activity volcano shown in Figures 3b and 4b, respectively. The theoretical TOFs were then fitted by a parabolic function to build the activity volcano using the adsorption strength of furfural as the activity descriptor. The activities for bulk/single atom alloys were then predicted using the activity volcano based on their furfural binding strength. Further details of the microkinetic simulations are provided in the Supporting Information.

#### RESULTS AND DISCUSSION

The proposed reaction mechanism for furfural hydrogenation toward furfuryl alcohol is shown in Scheme 1. Overall, the bare metal surface catalyzes both furfural hydrogenation reaction and  $H_2$  activation. The adsorbed H\* is the hydrogen source for gas-phase furfural hydrogenation reactions. For all of the metals considered in this work, we have performed simulations on (111)/(0001) and (211) surfaces that are representative of the terrace and step sites, respectively.



Figure 3. (a) Adsorption energies of FCHOH and FCH<sub>2</sub>O on the different metal (111) surfaces investigated in this work. Orange and green areas represent FCHOH-favored and FCH<sub>2</sub>O-favored regions, respectively; (b) Scaling relationships of adsorption energies between FCHO and the other stable adsorbates involved in the reaction pathway for furfural hydrogenation.

As shown in Figure 1, flat adsorption configurations of furfural are more stable than upright ones on all of the studied metal surfaces (including terrace and step sites) under hydrogenation reaction conditions, in agreement with previous theoretical studies.<sup>10,39,41,53</sup> The interaction of the metal surface with both the furan ring (F) and aldehyde group (CHO) is likely the reason for the preference of flat configurations over the upright ones, with the latter only interacting with the surface via the aldehyde group. Moreover, the stronger the adsorption of furfural (i.e., more negative  $\Delta G_{\rm FCHO}$ ), the larger the difference in adsorption energies of two configurations. Our calculations suggest that at low coverages, the flat adsorption configuration of FCHO\* might dominate on the metal surfaces investigated in this work, which is in line with direct scanning tunneling microscopy studies that submonolayer of furfural adsorbs in a flat configuration on Pt(111).54

At higher coverages (ca. 0.5 ML), furfural is theoretically predicted to prefer tilted or upright configurations on Pd(111)to minimize the effects of lateral interactions.<sup>55</sup> We also find that on Cu, Pd, and Pt(111) surfaces, furfural prefers to take a flat adsorption configuration at low coverages, a tilted configuration at 0.25 ML, and an upright configuration at coverages >0.33 ML (cf. Figure S1). However, previous temperature-programmed studies of furfural desorption on  $Pd(111)^{53}$  and  $Pt(111)^{56}$  suggest that at reaction temperatures typically applied for gas-phase furfural hydrogenation (400-500 K), the less stable adsorption configurations, for example, upright, tend to desorb due to lower binding strength relative to flat configurations. Besides, the typical tilted configuration of furfural<sup>55</sup> still binds the surface with the -CHO group and only tilts the furan ring away, which is not involved in the reaction pathway for furfuryl alcohol. As a result, we assume that furfural and all of the other reaction intermediates take the flat configuration on all of the considered surfaces in the calculation of reaction energetics discussed below.

The free energy diagrams for furfural hydrogenation to furfuryl alcohol at 400 K on three representative surfaces: Au(111), Cu(111), and Pt(111) are shown in Figure 2a. The

two possible pathways toward furfuryl alcohol via FCHOH\* and FCH<sub>2</sub>O\* are shown in solid and dashed lines, respectively. Given the similarity in adsorption configurations of the reaction intermediates on different metal surfaces, we only depict adsorption configurations of the stable reaction intermediates and transition states on Cu(111) in Figure 2b, c. The configurations of all of the reaction intermediates and transition states for the other surfaces investigated in this work are provided in database link: https://github.com/ CatTheoryDTU/furfural hydrogenation.

We highlight the following observations based on the free energy diagram for furfural hydrogenation on Au, Cu, and Pt (111) surfaces shown in Figure 2a:

- (1)  $H_2$  activation is a rate-determining step (RDS) for furfural hydrogenation on Au(111) as a result of its high activation barrier (ca. 1.21 eV), while being facile on Pt(111) and Cu(111) surfaces.
- (2) The hydrogenation of  $FCH_2O^*$  with an activation barrier of 0.98 eV is the RDS on Cu(111) in line with a previous theoretical study.<sup>38</sup> In contrast, we find the hydrogenation of furfural via the FCHOH\* intermediate to be facile on Pt(111) and Au(111) surfaces. Previously, Sitthisa et al. showed that the formations of FCHOH\* and  $FCH_2O^*$  are both endothermic on Cu(111) surface.<sup>11</sup> However, we find that FCH<sub>2</sub>O\* formation is exothermic and thermodynamically more favored by ca. 0.54 eV than the formation of FCHOH\* on Cu(111) as shown in Figure 2a. The discrepancy between our observations and those by Sitthisa et al. could be due to the differences in the configuration of  $FCH_2O^*$ . We find that the adsorption energy of the "flat" configuration (cf. Figures S1 and S2) reported in their work to be less stable by ca. 0.42 eV than the "bending" configuration where the O of the  $-CH_2O$ group in  $FCH_2O^*$  inserts in the hollow site on Cu(111), as shown in Figure 2b.
- (3) Finally, we find that the desorption of the product  $(FCH_2OH^*)$  limits the hydrogenation activity on Pt(111) due to its strong binding of furfural species.



**Figure 4.** Activity volcano for furfural hydrogenation toward furfuryl alcohol. (a) Adapted activity plot from experiments for Cu,<sup>60</sup> Ni,<sup>61</sup> Pd,<sup>62</sup> Pt,<sup>63</sup> PdCu,<sup>62</sup> Cu<sub>216</sub>Pd<sub>1</sub>,<sup>62</sup> and Cu<sub>20</sub>Pt<sub>1</sub>.<sup>63</sup> Note that the  $\Delta E_{FCHO}$  on the *x*-axis corresponds to the (111) surfaces of the respective metals or alloys. (b) Simulated TOF plot based on microkinetic simulations at 400 K,  $P_{FCHO} = 0.1$  bar, and  $P_{H_2} = 1$  bar. M represents a metal surface, and Cu<sub>2</sub>M<sub>4-x</sub> and Cu@M<sub>1</sub> represent Cu-based bulk alloys and single-atom alloys with M, respectively. Representative configurations of Cu<sub>3</sub>Ni<sub>1</sub> and Cu@Ni<sub>1</sub> surfaces are shown as insets.

In fact, furan and other ring-opening hydrocarbons were reported to be side products on Pt,<sup>54</sup> Ru,<sup>57</sup> and Ni<sup>58</sup> catalysts at high temperatures. It is likely that the strong adsorption of furfural on these metal surfaces hinders further hydrogenation by reducing relative H\* coverage on the surface and triggers C–C bond breaking and ring-opening reactions at high temperatures.

We further observe a metal identity-dependent preference for the two key intermediates on (111) surfaces, i.e., FCHOH\* and  $FCH_2O^*$ , as shown in Figure 3a, with the binding energies displayed in Figure S1. Generally, FCHOH\* is more stable than FCH<sub>2</sub>O\* on Au, Pt, Pd, and Rh surfaces, where both the aldehyde group and furan ring of FCHOH\* interact with the metal surface, except for a weak-binding metal like Au where only the aldehyde group interacts with the metal surface, as shown in Figure S4. In contrast, the oxyphilic surfaces (surfaces with a higher tendency to form metal oxides), including Ag, Ni, Cu, Co, Pb, and Ru, favor the formation of FCH<sub>2</sub>O\* over FCHOH\*. Notably, the adsorption configuration of FCH<sub>2</sub>O\* on these oxyphilic surfaces with O atom buried at the hollow site, as shown in Figure S5, might hinder further hydrogenation of FCH<sub>2</sub>O\* as is observed for the Cu(111) surface (vide supra). A similar preference of adsorbates based on carbon-philic and oxygen-philic metals was reported in a recent study to govern the reaction pathway and selectivity during glycerol dehydrogenation.<sup>59</sup> We propose this phenomenon could be general in predicting favorable key intermediates for valorizing C/O-containing chemicals. Besides, we find that the binding energies of all reaction intermediates involved in furfural hydrogenation to scale well with FCHO\* (cf. Figure 3b), indicating that we could use a

single activity descriptor, that is, the adsorption strength of furfural  $\Delta E_{\rm FCHO}$ .

Based on the reaction energetics reported in Figure 2 and scaling relationships in Figure 3b, we further develop a mean-field microkinetic model including explicit adsorbate—adsorbate interactions using the CatMAP code<sup>52</sup> to study the activity for furfuryl alcohol production over different metal surfaces under a mild reaction condition, that is, 400 K,  $P_{\rm FCHO} = 0.1$  bar, and  $P_{\rm H_2} = 1$  bar.<sup>27,64</sup> The considered elementary steps and other simulation parameters are discussed in the Microkinetic Simulation section in the Supporting Information. The activity trends of both experiment and theory are shown in Figure 4a, b, respectively. Note that the experimental TOFs shown in Figure 4a are reported mainly for furfuryl alcohol production, where the contribution of side products is minor.

Cu is theoretically predicted to be the most active catalyst for furfural hydrogenation toward furfuryl alcohol (cf. Figure 4b) among all of the elemental transition metals considered in this work. The high TOF of Cu results from a moderate barrier for  $H_2$  activation (cf. Figure 2) and suitable adsorption strength of furfural species, which lead to a good overall activity.

Stepped surfaces promote the activity on weak-binding metals, while they suppress the activity on strong-binding metals. As can be seen in Figure 4b, Cu(211) is predicted to have a higher activity by ca. 1 order of magnitude than Cu(111), indicating that the introduction of undercoordinated sites on Cu surfaces might lead to increase in the activity for furfuryl alcohol production. A similar trend is observed on weak-binding surfaces including Ag and Au with the stepped

(211) surfaces predicted to have higher activity than (111) surfaces. On the strong-binding leg of the activity volcano plot in Figure 4b, Pd(111) is predicted to be the most active monometallic surface, followed by Co(0001) and Ni(111). In contrast to weak-binding metals, for the strong-binding metals, stepped surfaces (211) are predicted to have lower activity than the (111) surfaces. As shown in Figure 1, stepped surfaces exhibit stronger binding of furfural (i.e., more negative  $\Delta G_{\rm FCHO}$ ) especially for strong-binding metals compared to their (111) counterparts, while the H\* adsorption is a lot less sensitive to the facet identity (cf. Figure S6). As a result, the H\* coverages on strong-binding stepped surfaces are reduced as shown in Figure S6, while the FCHO\* coverages only increase moderately due to large adsorbate-adsorbate interactions. Consequently, the second-order dependence of hydrogenation activity on H\* coverage and first-order dependence on FCHO\* coverage lead to an overall decreased activity toward furfuryl alcohol formation on the strongbinding surfaces (i.e., Pt, Pd, Ir, Ni, Co, Rh, and Ru).

The simulated activity volcano (for monometallic surfaces) in Figure 4b suggests that there remains space for improvement in activity, which can also be seen in the experimental TOF data that was obtained at similar reaction conditions in Figure 4a.<sup>62</sup> To identify catalyst materials that might be closer to the top of the activity volcano in Figure 4b, we studied bulk alloys and single-atom alloys (SAAs) by combining one metal on the weak-binding leg, i.e., Cu and one metal on the strongbinding leg, for example, Pt, Pd, and Ni. For the convenience of direct synthesis in experiments, we only considered alloy candidates that have been reported in previous experimental studies of C=O hydrogenation reactions performed under similar reaction conditions (temperature and pressure).<sup>65–69</sup> We find that CuCr alloy binds furfural too strongly even with a dilute Cr component (i.e.,  $Cu_3Cr_1$ ), leading to a relatively low activity. Note that the CuCr might be oxidized during the reaction; therefore, the theoretical CuCr alloy model here might not be the actual active surfaces. Several Cu-based alloys that were investigated are predicted to have high activity (close to the top of the activity volcano) as can be seen in the inset in Figure 4b. CuPd, CuPt, CuCo, and CuNi bulk alloys and Ir-, Rh-, Ni-, Pd-, and Pt-doped Cu single atom alloys show improved activity for furfural hydrogenation compared to their parent metals. This observation is qualitatively in agreement with the experimental observations in Figure 4a: Cu<sub>216</sub>Pd<sub>1</sub> single atom alloy in ref 62 shows over two orders of magnitude higher TOF toward furfuryl alcohol than Cu and Pd with an Al<sub>2</sub>O<sub>3</sub> support; dilute CuPt alloys in ref 63 are measured to have more than one order of magnitude higher TOF compared to monometallic Cu and Pt. Furthermore, the most active catalysts should lie between Cu and Pd based on Figure 4a, b. However, we note that a major drawback of these alloy candidates is the use of expensive noble metals (Pt, Pd).

Interestingly, Cu-rich Cu<sub>3</sub>Ni<sub>1</sub> and Cu@Ni<sub>1</sub> surfaces are predicted to have high activity for the production of furfuryl alcohol, while CuNi alloys with high Ni content including Cu<sub>2</sub>Ni<sub>2</sub> and Cu<sub>1</sub>Ni<sub>3</sub> are predicted to have low activity (cf. Figure 4b) due to the overbinding of furfural on the Ni-rich active sites. The prediction that Cu-rich CuNi alloys have high activity for furfural hydrogenation is in agreement with a recent study by Weerachawanasak et al. where CuNi alloys with a Cu-rich component were reported to show higher yields for furfuryl alcohol production relative to pure Cu- and Ni-rich catalysts.<sup>61</sup> In addition, Ni-rich catalysts are reported to display

activity toward further hydrogenated products in the vapor phase, for example, tetrahydrofurfuryl alcohol (THFA).<sup>70</sup> Therefore, diluting Ni content in Cu catalyst is crucial to obtain both high selectivity and activity toward furfuryl alcohol. Considering the abundance, noble-metal-free, and low toxicity of both copper and nickel, we advocate for future research efforts to extensively study CuNi-based bimetallic catalysts for furfural hydrogenation as they can help resolving some of the major issues that currently plague the industrial production of furfuryl alcohol using chromite-based catalyst materials.

Before closing the discussion, we highlight the following limitations of our study. First, we focused on the simplest furfural valorization reaction involving the conversion of furfural to furfuryl alcohol and ignored possible side reactions, for example, ring-opening and further hydrogenation, which might selectively occur under harsher reaction conditions (i.e., higher temperature and pressure or in the presence of specific solvents).<sup>15</sup> As a result, our work does not provide insights into the selectivity of furfural hydrogenation but only indicates the activity trends of furfural hydrogenation on metal surfaces. Second, our model does not explicitly consider the effects of the oxide support typically used in experiments, which could potentially impact the reactivity of furfural hydrogenation reactions as shown in previous studies.<sup>16,27,64,71</sup> Finally, we did not consider possible surface reconstruction, segregation, and oxidation under operando conditions, which might contribute to discrepancies in the observed structure-activity relationships.<sup>72</sup>

#### CONCLUSIONS

To summarize, we have performed DFT calculations and microkinetic modeling to study the activity trends in furfural hydrogenation to furfuryl alcohol on transition metal surfaces. The rate-determining steps were identified to be H<sub>2</sub> activation, surface hydrogenation of FCHOH\*/FCH2O\*, and furfural desorption on weak-, moderate-, and strong-binding surfaces as represented by Au(111), Cu(111), and Pt(111) surfaces, respectively. We show that the furfural adsorption energy can serve as an effective activity descriptor for furfural hydrogenation, where the moderate binding strength of furfural leads to maximal predicted activity. The microkinetic simulations show that stepped (211) surfaces are more active than terrace (111) surfaces for moderate-/weak-binding metals including Cu, Ag, and Au, while the opposite trend is observed on the strong-binding metals including Pt, Pd, Ir, Ni, Co, Rh, and Ru. These observations highlight facet-dependent catalyst design principles. We further predict several Cu-based alloys to display high activity toward furfuryl alcohol production beyond monometallic candidates. In particular, we find that CuNi alloys with dilute Ni component are promising candidates to replace Cr-containing catalysts currently employed in the industrial hydrogenation of furfural to furfuryl alcohol. The observed activity trends highlight the importance of metal identity, facet, and alloying in furfural hydrogenation reaction. We anticipate that the mechanistic insights obtained in this work could aid in the rational design of catalysts for furfural hydrogenation and related biomass valorization processes.

### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c03822.

Further details on the computational methods and microkinetic simulations; FCHOH/FCH<sub>2</sub>O binding energies; effect of the surface coverage; scaling relations; stable adsorption configurations; and simulated coverages (PDF)

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S.L., N.G., and K.C. conceptualized; S.L., N.G., and K.C. contributed methodology; S.L. contributed software; S.L. and N.G. contributed investigation; K.C. contributed resources; S.L. contributed in data curation; S.L. and N.G. contributed in writing original draft; S.L., N.G., and K.C. contributed in writing review and editing; S.L. contributed in visualization; K.C. and N.G. contributed in supervision; K.C. contributed in project administration; and K.C. contributed in funding acquisition.

#### Notes

The authors declare no competing financial interest.

The atomic coordinates of the reaction intermediates on different metal surfaces investigated in this work, the input files for the microkinetic simulations, and the scripts used to reproduce the figures in the manuscript are available at the following weblink: https://github.com/CatTheoryDTU/furfural\_hydrogenation.

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## Paper II (Chapter 4)

Solvation of furfural at metal-water interfaces: Implications for aqueous phase hydrogenation reactions

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# Solvation of furfural at metal-water interfaces: Implications for aqueous phase hydrogenation reactions

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#### ARTICLE

# Solvation of furfural at metal-water interfaces: Implications for aqueous phase hydrogenation reactions

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#### ABSTRACT

Metal-water interfaces are central to understanding aqueous-phase heterogeneous catalytic processes. However, the explicit modeling of the interface is still challenging as it necessitates extensive sampling of the interfaces' degrees of freedom. Herein, we use *ab initio* molecular dynamics (AIMD) simulations to study the adsorption of furfural, a platform biomass chemical on several catalytically relevant metal-water interfaces (Pt, Rh, Pd, Cu, and Au) at low coverages. We find that furfural adsorption is destabilized on all the metal-water interfaces compared to the metal-gas interfaces considered in this work. This destabilization is a result of the energetic penalty associated with the displacement of water molecules near the surface upon adsorption of furfural, further evidenced by a linear correlation between solvation energy and the change in surface water coverage. To predict solvation energies without the need for computationally expensive AIMD simulations, we demonstrate OH binding energy as a good descriptor to estimate the solvation energies of furfural. Using microkinetic modeling, we further explain the origin of the activity for furfural hydrogenation on intrinsically strong-binding metals under aqueous conditions, i.e., the endothermic solvation energies for furfural adsorption prevent surface poisoning. Our work sheds light on the development of active aqueous-phase catalytic systems via rationally tuning the solvation energies of reaction intermediates.

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#### INTRODUCTION

Adsorption of molecules at solid–gas and solid–liquid interfaces is the heart of heterogeneous catalysis.<sup>1</sup> Adsorption energy scaling relationships have widely been used to understand the trends in catalytic activity and selectivity, providing valuable insights for mechanistic studies and catalyst design.<sup>2–7</sup> Although great progress has been made to understand the adsorption phenomena of various adsorbate species at solid–gas interfaces, the adsorption of species in the presence of solvents, e.g., water, is less studied. This knowledge gap exists although the solvent has been shown to play a significant role in governing the reactivity of heterogeneous catalysts at the solid–liquid interface.<sup>8,9</sup> The inadequate understanding of solvent effects on the adsorption of reaction intermediates hinders the transferability of acquired knowledge of a vast majority of catalytic reactions in the gas phase to their liquid-phase counterparts.

Furfural (FCHO, where F denotes the furan ring and CHO denotes the aldehyde group) is an important platform molecule derived from lignocellulose, with widespread application in polymer

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and biofuel synthesis.<sup>10,11</sup> Annually, more than 60% of produced furfural is used to produce furfuryl alcohol (FCH2OH), a key monomer to synthesize furan resins, via catalytic hydrogenation.<sup>12</sup> Both heterogeneous gas(vapor)- and liquid-phase furfural hydrogenation have widely been studied,<sup>13,14</sup> with the latter having the advantages of operating under relatively milder conditions and having a higher yield<sup>15,16</sup> with a tunable selectivity toward the desired products.<sup>17</sup> In particular, solvents, such as water, enable hydrogenation reactions on Pt-group metals even at room temperature. For instance, Pt could catalyze furfural hydrogenation selectively to furfuryl alcohol at 323 K in methanol<sup>18</sup> and 303 K in aqueous phase.<sup>19</sup> Ru has even been shown to achieve nearly 100% selectivity to furfuryl alcohol at 293 K in aqueous phase.<sup>20</sup> In contrast, the hydrogenation reaction at a solid-gas interface necessitates high temperatures on a Pt surface.<sup>21</sup> The origin of the increased activity and selectivity in aqueous phase has been attributed to different solvent effects,<sup>22</sup> including the solvent acting as a co-catalyst<sup>23</sup> or a promoter,<sup>24</sup> the opening of new reaction channels in the presence of the solvent,<sup>25</sup> and the solvent acting as a reactant,<sup>26</sup> e.g., as a proton donor.<sup>27</sup> The deviating strands in reasoning emphasize the need for the atomistic level understanding of the interaction of biomass-derived molecules, such as furfural, on metal-water interfaces.

In heterogeneous furfural hydrogenation at a solid-water interface, FCHO interacts not only with the catalyst surface but also with the surrounding water molecules, which can affect its adsorption properties and the catalytic activity. For instance, combining experimental isotherms and density functional theory (DFT) calculations, Akinola et al. revealed that the adsorption of large organic molecules (including FCHO) is weakened on strong-binding surfaces, such as Pt and Rh, in aqueous phase compared to ultrahigh vacuum (UHV) conditions. This weakening is attributed to the large enthalpic penalty associated with water displacement at the metal-water interface upon the adsorption of large organic molecules.<sup>28</sup> The weakened adsorption under aqueous conditions can also help explain the origin of the activity (at room temperature) for the hydrogenation of these large organic molecules on such strong-binding surfaces. Based on the solution calorimetry results<sup>25</sup> and previous thermodynamic cycle approaches,<sup>30</sup> Singh and Campbell proposed a simple bond-additivity model to quantify the energetic penalty for the adsorption of (flat) aromatic molecules on metal surfaces, which has mainly been attributed to water displacement during the adsorption of these large aromatic molecules.<sup>31</sup> However, the as-proposed methods strongly rely on indirect electrochemical measurements and isotherm adsorption models, which might suffer from uncertainties in the estimated results.

Ab initio molecular dynamics (AIMD) provides direct atomistic level insights into the adsorption phenomena and catalysis at metal-water interfaces.<sup>32–38</sup> For instance, Heenen *et al.* studied the adsorption of several common adsorbates (CO<sup>\*</sup>, CHO<sup>\*</sup>, COH<sup>\*</sup>, OCCHO<sup>\*</sup>, OH<sup>\*</sup>, and OOH<sup>\*</sup>) on Cu, Au, and Pt metal-water interfaces and found the solvation energies to be dependent on both the identity of the adsorbate and the metal surface. As a result, the estimated solvation energies for the adsorbates are non-transferable across metal surfaces, e.g., CO<sup>\*</sup> adsorption energy is barely affected by the presence of water on most of the metal (111) surfaces but slightly weakened on (211) surfaces,<sup>39</sup> while OH adsorption shows over 0.5 eV stabilization in aqueous phase (compared to vacuum) on Au(111) and Pt(111).<sup>40</sup> In contrast, Yoon *et al.* reported the adsorption of phenol on metal-water interfaces to be consistently destabilized on Pt(111) and Ni(111).<sup>41</sup> Zare et al. developed a hybrid quantum mechanical/molecular mechanical (QM/MM) approach to find that the adsorption of large molecules, i.e., benzene and phenol, is dramatically weakened on Pt(111) and Cu(111) in aqueous phase at 298 K, as a result of large endergonic cavity formation energy.<sup>42</sup> A recent work by Yao et al. has demonstrated the adsorption of furfural at the Cu(111)-water interface, which displays a tendency to adsorb rather than desorb into water at 443 K.43 However, most of the previous studies on biomass related processes focus on a limited number of (metal) catalysts (usually only one), making it hard to obtain generalizable conclusions. In summary, the adsorption of small molecules in aqueous phase could be either destabilized or stabilized compared to vacuum/gas conditions, while larger molecules tend to suffer from huge energetic penalties associated with the replacement of water molecules (cavity formation) in aqueous phase.

Herein, we systematically study the adsorption of furfural based on AIMD simulations at 300 K for five metal-water interfaces, i.e., Au(111), Cu(111), Pd(111), Pt(111), and Rh(111) (cf. Scheme 1), which have extensively been investigated for furfural valorization.<sup>13,26</sup> The computed furfural adsorption on these surfaces is consistently destabilized under aqueous conditions compared to vacuum conditions, i.e., the solvation energies ( $\Delta E_{sol}$ ) of furfural are positive in all cases. Our AIMD results show good agreement with previous solution calorimetry<sup>28,44</sup> and thermodynamic cycle models.<sup>31</sup> The structural analyses of the metal-water interfaces from AIMD simulations suggest that the positive solvation energies are due to the energetic penalty associated with the displacement of surface adsorbed water molecules due to furfural adsorption, evidenced by a strong correlation between the solvation energy and surface water replacement. Importantly, we find the hydroxyl (OH) binding energy to be a descriptor for the solvation energy of furfural at metal-water interfaces, which bypasses the need for expensive AIMD simulations to obtain solvation energies. In addition, we discuss the differences in the origin of the endothermic solvation energies for furfural at metal-water interfaces between



**SCHEME 1.** A schematic of the various metal [Au, Cu, Pt, Pd, and Rh(111)]–water interface models studied using AIMD simulations. (a) Without furfural adsorption and (b) with furfural adsorption. The color coding for the atoms is shown on the right.

the bond-additivity model and the AIMD simulations. Based on a simple microkinetic model developed in our previous study,<sup>14</sup> we show that the endothermic solvation energies promote the furfural hydrogenation reaction toward furfuryl alcohol on strong-binding metals. This study generalizes the solvent effects on furfural adsorption across different metal surfaces via simple scaling relations and provides a rationale for screening both catalysts and solvents to promote the catalytic activity of furfural hydrogenation and other biomass valorization reactions.

#### COMPUTATIONAL METHODS

#### **DFT calculations**

The Vienna *Ab initio* Simulation Package (VASP)<sup>45</sup> was used in this work to perform DFT and AIMD simulations using the revised Perdew–Burke–Ernzerhof (RPBE)<sup>46</sup> exchange–correlation (XC) functional complemented with the D3 dispersion correction<sup>47,48</sup> that has previously been used in the simulations of metal–water interfaces.<sup>49</sup> A plane-wave cutoff of 400 eV and a Gaussian smearing of width 0.2 eV were used in all the simulations. The electronic structure was relaxed until all forces converged to less than 0.05 eV/Å for geometry optimizations.

The metal surfaces were modeled as  $4 \times 4 \times 4$  Au, Cu, Pd, Pt, and Rh fcc(111) slabs, which are commonly used as catalysts in thermal furfural hydrogenation.<sup>13</sup> The top two layers of the metal surfaces were relaxed, while the bottom two were fixed to their bulk structures, with optimized lattice constants of 4.17, 3.58, 3.92, 3.94, and 3.80 Å, respectively. A  $3 \times 3 \times 1$  k-point mesh was applied on all surfaces. As for furfural adsorption, one furfural molecule in the unit cell with 16 surface metal atoms was used in the simulations. Both upright and flat adsorption configurations of furfural were considered in vacuum calculations, with the flat configuration being much more stable than the upright configuration, in line with a previous report.<sup>14</sup> We investigated the dependence of furfural adsorption energies on surface size at the metal-vacuum interface as shown in Fig. S1 and found out that the  $4 \times 4$  slab model is representative of furfural adsorption in the low coverage regime. Since we find furfural in this study to be only weakly solvated and to, thus, have a negligible solvation shell, we expect this size dependency to hold in an aqueous environment. The static binding energy of furfural in vacuum is obtained using Eq. (1),

$$\Delta E_{FCHO} = E_{slab} F_{CHO} - E_{slab} - E_{FCHO(g)}.$$
 (1)

An OH molecule on the top site of all metal surfaces is simulated to obtain the static vacuum OH binding energies using Eq. (2),

$$\Delta E_{\rm OH} = E_{slab}_{\rm OH} - E_{slab} - (E_{\rm H_2O(g)} - 0.5E_{\rm H_2(g)}), \qquad (2)$$

where the gas-phase energies of the reference gases, such as FCHO(g),  $H_2O(g)$ , and  $H_2(g)$ , are calculated using static DFT calculations.

#### **AIMD** simulations

AIMD simulations were performed with a 0.5 fs time step employing a Nosé thermostat set at 300 K. Forty water molecules were included in the metal–water interfaces for the fcc(111) surfaces, corresponding to roughly five layers of the aqueous solvent.

$$\Delta E_{\text{FCHO}\_vac\_AIMD} = E_{slab\_FCHO\_vac\_AIMD} - E_{slab\_vac\_AIMD} - E_{FCHO(g)\_AIMD}, \qquad (3)$$

$$\Delta E_{\text{FCHO}\_aq\_AIMD} = E_{slab\_\text{FCHO}\_aq\_AIMD} - E_{slab\_aq\_AIMD}$$

$$-E_{FCHO(g)\_AIMD},$$
(4)

$$\Delta E_{solv} = \Delta E_{\text{FCHO}\_aq\_AIMD} - \Delta E_{\text{FCHO}\_vac\_AIMD}, \tag{5}$$

where  $E_{FCHO(g)\_AIMD}$  is the gas energy of a furfural molecule derived from AIMD simulations at 300 K with a 3/2 k<sub>B</sub>T correction, because the center of mass (COM) motions are not included in the gasphase AIMD simulations.<sup>50,51</sup> Three independent trajectories were simulated out for each aqueous system with randomly generated starting configurations of the solvent water molecules. To determine the uncertainty in the measured quantities, we report the standard deviation  $\sigma$  as error bars obtained from the trials as  $\frac{\sigma}{\sqrt{n}}$ , where n = 3. Each AIMD trajectory was run for 50-70 ps after a pre-equilibration period of ~5 ps. We ensured that the individual trajectories are converged, showing an average drift in the total energy of <0.05 eV/ps after equilibration, as shown in Fig. S2. The last 10 ps of three parallel converged trajectories of each system was used as statistics to probe the converged energetics and structural properties. The z-axis distribution of water molecules was estimated using either the O or the H atoms of H<sub>2</sub>O. As shown in Fig. S3, on the studied metal surfaces, our simulation configurations reproduce the physical interfaces where the water in the region of 5-10 Å reaches the density of liquid water,<sup>52,53</sup> denoted by the blue dashed lines. The residence time of furfural chemisorption is analyzed via a "surface metal atom-furfural atom" pair count based on a cutoff criterion shown in Table S1 and explained, in more detail, in the supplementary material.

The water molecule is considered to be adsorbed on the surface if it is closer than 2.55 Å to a surface metal atom as suggested by Heenen *et al.* based on analyzing the radial distribution functions of the metal–water interface.<sup>40</sup> To account for the different covalent radii of metal atoms, we re-estimated the chemisorbed water based on  $r_{\text{H2O},Metal}$  (the atomic distance between surface metal atoms and O in H<sub>2</sub>O) in reference to Cu(111)  $r_{\text{H2O},\text{Cu}} = 2.55$  Å calculated from metal–water radial distribution functions (RDFs),<sup>40</sup>

$$r_{\rm H_2O,Metal} = 2.55 \text{\AA} \times \frac{r_{cov,metal} + r_{cov,O}}{r_{cov,\rm Cu} + r_{cov,O}},$$
(6)

with the covalent radii  $r_{cov} = 0.66$ , 1.32, 1.36, 1.39, 1.36, and 1.42 Å for O, Cu, Au, Pd, Pt, and Rh, respectively, derived from Ref. 54.

The surface water coverage  $\theta_w$  was calculated by averaging the total number of adsorbed H<sub>2</sub>O molecules  $\langle \tilde{n_w} \rangle$  during an AIMD trajectory and normalizing this value by the number of surface atoms per unit cell (16) as shown in Eq. (7),

$$\theta_w = \frac{\langle n_w \rangle}{16}.\tag{7}$$

The hydrogen bonds formed between the adsorbed furfural and water were explicitly counted by the distance and angle criteria for the bonding of O/H in furfural and H/O in  $H_2O$  as reported in Ref. 55. The major post-processing results are summarized in Table S2 of the supplementary material. The analysis functions and methodologies to obtain all energetic and structural results from the AIMD simulations are available in the AIMDprobe package: https://github.com/tjunewson/AIMDprobe.

#### **RESULTS AND DISCUSSION**

# Adsorption of furfural results in the decreased surface coverage of water at the metal-water interface

Furfural demonstrates different adsorption behaviors at the studied metal–water interfaces. In general, furfural binds flatly to all metal surfaces occupying ~5 metal atoms as displayed in Fig. S4 and does not desorb into the water bulk within the timescales of the AIMD simulations [cf. time resolution of center of mass (COM) in Fig. S5]. A detailed analysis points to the distinct differences in the adsorption configurations of furfural, which indicate an increasing binding strength following the trend Au < Cu < Pd  $\approx$  Pt  $\approx$  Rh. In a first instance, this is evident by the adsorption height (in the z direction) to the respective metal surfaces described by the distance between the COM of furfural and the metal surface as shown in Table S2.

The COM-surface distance, denoted by the vertical dotted lines in Fig. 1, shows that the furfural is located within the first water layer for the strong-binding metals, such as Pd, Pt, and Rh, and resides slightly above the first water layer [the peaks shown in Figs. 1(a) and 1(b) for Au and Cu, respectively]. These adsorption heights are accompanied by a complete immobility for Pd, Pt, and Rh and moderate and high lateral mobilities for Cu and Au, respectively [cf. furfural's mean square displacement (MSD) in Fig. S6]. Using the metal atom residence time distribution shown in Fig. S7, we can finally conclude that the furfural directly chemisorbs on Pd, Pt, and Rh, through the C atoms in the furan ring, while the -CHO group is pointing to the water on Pd and Pt and binding to Rh via its O. In comparison, a weak physisorption is found for Cu, which is evident through a sole interaction of the -CHO group's O atom resulting in a tilted adsorption geometry. No specific interaction of furfural with Au is found, indicating that its adsorption above the first water layer is entropy driven, which is a typical behavior for hydrophobic adsorbates.5

Interestingly, we find these adsorption geometries of lowcoverage furfural at the metal–water interfaces to resemble those at metal–gas interfaces (Fig. S4, upper and lower panels) and those in previous studies,  $^{58-62}$  i.e., a flatly adsorbed orientation on Pt-group metals, a flat (weakly interacting) orientation on Au, and a slightly tilted orientation on Cu. We further show in Table S3 that the calculated centers of mass (COM) of furfural at the metal–water interfaces are very close to those at metal–vacuum interfaces. These results



FIG. 1. Water density profiles obtained from the AIMD simulations of the different metal–water interfaces. (a) Au(111), (b) Cu(111), (c) Pd(111), (d) Pt(111), and (e) Rh(111); (f) the site-normalized surface water coverage without furfural adsorption (left axis) and the change with furfural adsorption (right axis). Note that water molecules are located based on the position of the oxygen atom. The vertical dotted lines in (a)–(e) highlight the centers of mass of furfural. The blue dashed lines denote the experimental density of bulk water at room temperature.

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suggest that solvent water might not affect the adsorption geometries of hydrophobic adsorbates on metal surfaces.

The averaged distribution of water molecules before and after furfural adsorption shows notable water replacement, especially near the surface (<5 Å) [cf. Figs. 1(a)–1(e)]. The density of water is the highest near the metal–water interface due to the adsorption of water molecules on the surface and consequent local crowding. The liquid–vapor interfaces on Cu are the highest (~15 Å) among the studied surfaces as shown in Fig. 1(b) due to its smallest lattice constant among the studied metals. Note that except for the Au surface, shown in Fig. 1(a), all metal surfaces display a small shoulder peak to the left of the major peak, which originates from the fact that the first layer of water molecules binds to the surfaces mainly via the O atoms. This adsorption results in H atoms pointing outward the surface to form an O-void in the second water layer, i.e., the typical bilayer structure of water on reactive metal surfaces.<sup>63</sup>

As shown in Fig. 1(f), we find that from Au to Rh, the sitenormalized surface water coverages ( $\theta_w$ ) generally increase, in line with a previous report.<sup>40</sup> We note that the calculated water coverage on Pt(111) shows good quantitative agreement with previous AIMD studies (with different surface sizes) performed using the RPBE-D3 functional (cf. Table S4). Calculations by Le *et al.* predict slightly higher water coverages,<sup>64,65</sup> which is likely due to the stronger binding of water by the PBE-D3 functional.<sup>66</sup> More importantly, the replaced water coverages upon furfural adsorption  $\Delta\theta_w$  also increase from Au to Rh. Assuming that a furfural molecule occupies the same number of surface sites (~5)<sup>31</sup> on different metal surfaces at low coverages, we expect that the replaced water coverages should be dependent on the binding strength of water or correlated binding properties, such as the OH binding energy,<sup>2</sup> on the respective metal surfaces. We will return to this point later in this paper.

We further studied the formation of directional hydrogen bonds between the adsorbate (furfural) and solvent water, which could stabilize the adsorption.<sup>67</sup> The cumulative averages of calculated hydrogen bonds formation between furfural and water are summarized in Table S1 (the bond formation criteria are detailed in the section titled COMPUTATIONAL METHODS). We find that <1 hydrogen bond is formed per adsorbed furfural molecule with the solvent water molecules. This low degree of hydrogen bonding is comparable to the very weakly interacting CO<sup>\*</sup> at the metal–water interfaces<sup>40</sup> and rules out the possible stabilization effects on furfural adsorption via hydrogen bond interactions at the metal–water interface.

# Furfural adsorption is destabilized under aqueous conditions on metal surfaces

As shown in Fig. 2(a), the aqueous-phase adsorption energies of furfural at the metal-water interfaces estimated from the AIMD simulations are all weaker than the corresponding adsorption energies in vacuum, i.e., the solvation energies of furfural on the metal surfaces are endothermic as can be seen in Fig. 2(b). Notably, the estimated adsorption energies from the AIMD simulations for Pt and Rh are in good agreement with the solution calorimetry experiments<sup>28,29</sup> and the bond-additivity model.<sup>31</sup> The calculated solvation energies for the studied metal-water interfaces are all above +0.4 eV and reach up to +1 eV on Pt and Rh, far beyond the DFT intrinsic error of ~0.2 eV on calculated adsorption



FIG. 2. Determined adsorption energies for furfural (a) in vacuum, AIMD simulations, experiments,<sup>28</sup> and the bond-additivity model;<sup>28</sup> (b) the solvation energy for furfural on the studied surfaces estimated using the AIMD simulations. The standard deviations are obtained from three independent simulation trajectories for each of the studied metal–water interfaces.

energies,<sup>68</sup> which should have a considerable impact on the adsorption phenomena and catalytic processes related to furfural under aqueous conditions. Furthermore, we find that the bond-additivity model<sup>31</sup> and AIMD simulations in this work estimate similar solvation energies of furfural on the Pt(111) surface of ~0.72 and 0.82 eV, respectively [cf. Fig. 2(a)]. However, we note that there are important differences in their origin as discussed in Fig. S8 in the supplementary material.



FIG. 3. Correlation between the AIMD-derived furfural solvation energies at the metal-water interfaces and the replaced surface water coverages (per surface site).

To shed light on the origin of the endothermic solvation energies, we further plot the solvation energies of furfural adsorption against the replaced surface water coverages as shown in Fig. 3. We find that the solvation penalty linearly increases with increasing number of replaced water molecules per site. This universal correlation strongly suggests that the destabilization of furfural adsorption at metal–water interfaces should be a result of the energetic penalty associated with the displacement of water molecules near the surface due to the introduction of a large molecule, such as furfural. We note in passing that the intercept of the linear relationship in Fig. 3 is positive (+0.27 eV), indicating an intrinsic destabilization of furfural adsorption at the metal–water interface even in the absence of competitive water adsorption.

# OH binding energy is a good descriptor to predict solvation energies and circumvent expensive AIMD simulations

The identification of simple descriptors to predict critical quantities for metal–water interfaces can be very useful for the rational design of new catalysts without the need for computationally expensive simulations.<sup>4</sup> For instance, Kelly *et al.* proposed OH binding energies to universally correlate with both potentials of zero charge and site-normalized water coverages on a number of transition metal surfaces.<sup>69</sup> In addition, the OH binding energies have been applied to predict the solvation energy of OH adsorption in aqueous phase.<sup>40</sup> Similarly, H<sub>2</sub>O binding energies have been shown to predict the Volta potential difference between the surface of metal and water.<sup>70</sup>

Inspired by the aforementioned studies on identifying simple descriptors, we find that the OH binding energies scale well with the solvation energies of furfural on the studied metal surfaces (cf. Fig. 4). A stronger binding of OH gives rise to more endothermic solvation energies, i.e., weaker binding of furfural. The linear correlation between the OH binding energy and furfural solvation energy in aqueous phase can be used to obtain a reasonable estimate of the solvation energies on different metal surfaces, hence allowing the estimation of aqueous-phase adsorption energies of furfural on metal surfaces without the need for expensive AIMD simulations. We expect that this simple descriptor can be used to estimate the energetic penalty associated with water replacement for other hydrophobic species, e.g., furan and benzene, but with different scaling relations due to differences in the nature of the metal-adsorbate interaction. In contrast to hydrophobic molecules, glycerol and other biomass derivatives with one or more -OH groups can form complicated hydrogen bond networks with protic solvents, such as water. This necessitates a more robust sampling of possible adsorption configurations for such molecules at metal-solvent interfaces. Therefore, more complicated relationships might be required to account for stabilizing effects, e.g., a separate term/descriptor to account for the energetics of hydrogen bond formation to predict the solvation energies of biomass related species containing -OH groups [e.g., glycerol and 5-hydroxymethylfurfural (HMF)] in polar, protic solvents.

Before closing this section, we would like to highlight a few shortcomings of this work. First, the AIMD simulations were only performed for the (111) surfaces of the metals considered in this study. Thereby, the trends in solvation energies on other high-index surfaces might be different to the ones observed in this work. Second, the timescales accessible by AIMD simulations are limited because of the expensive energy and force estimates needed for each timestep. The nanosecond timescales that might be needed for sufficient sampling of metal-water interfaces<sup>71</sup> are currently out of reach for AIMD simulations. This could be resolved in future studies by employing machine learning based interatomic potentials to perform long timescale molecular dynamics simulations of metal-water interfaces.<sup>71-74</sup> However, the reasonable agreement of our determined solvation energies on Pd and Pt with experimentally determined values gives us confidence in the validity of the results.



FIG. 4. Scaling relationship between the AIMD-derived furfural solvation energies at the metal–water interfaces and the calculated OH binding energies in vacuum.



FIG. 5. Theoretical activity volcano for furfural hydrogenation to furfuryl alcohol at 300 K on different (111) metal surfaces under gas (black markers) and aqueous conditions based on solvation energies obtained from the AIMD simulations of the metal–water interfaces considered in this work (cyan markers).

#### Endothermic solvation energies activate furfural hydrogenation on strong-binding metals by preventing surface poisoning

To demonstrate the implications of the differences in the adsorption energies of furfural under gas- and aqueous-phase conditions, we studied the hydrogenation of furfural toward furfuryl alcohol, a central reaction for furfural valorization.<sup>13,75</sup> Pt(111) was used as an example to highlight the effect of the solvation energy corrections to the reaction energetics containing furanic species. As shown in Fig. S9, the reaction energy for furfural adsorption on Pt(111) is significantly weakened in the aqueous phase. We then performed microkinetic simulations for furfural hydrogenation to construct the activity volcano for several (111) transition metal surfaces (cf. Fig. 5). We note that the solvation energy estimated for furfural was used for all reaction intermediates in the microkinetic simulations based on the assumption of the similar size and hydrophilicity of furanic species along the reaction pathway to furfuryl alcohol (only the aldehyde group is hydrogenated). The activity volcano under gas-phase conditions (black markers in Fig. 5) indicates that strong-binding metals, e.g., Ru, Rh, and Pt, display very low activity at room temperature for furfural hydrogenation due to the surface poisoning of furanic intermediates, e.g., FCHO\*, as shown by the simulated coverages (cf. Fig. S10). We find that the predicted catalytic activity for these strong-binding metals significantly increases if we consider the hydrogenation under aqueous conditions, where the furfural binding is greatly weakened due to the endothermic solvation energy (cyan markers in Fig. 5). In contrast, the weaker-binding metals, e.g., Au and Cu, suffer from the destabilization effect from solvation, which results in lower activities toward furfural hydrogenation. An important observation is the change in the most active metals predicted by the activity volcano under vacuum (coinage metals) and aqueous conditions (Pt-group metals).

The weakened adsorption of furanic species for the metals in the strong-binding leg of the volcano prevents surface poisoning and allows for sufficient coverage of H species, as shown in Fig. S10, which results in the increased activity for aqueous-phase hydrogenation. These results provide insights into the importance of aqueous conditions in catalyzing furfural hydrogenation on strong-binding metals at room temperatures and why Pt-group metals display activity in the electroreduction of furfural and other furanic reactants under aqueous conditions.<sup>76</sup> However, solventmediated mechanisms, such as H-shuttling,<sup>25,43</sup> possible hydrogen bond stabilization for other reaction intermediates, and high-index facets, have not been considered in the model. We postulate that the neglected stabilizing effects from both hydrogen bond formation and water-aided hydrogenation pathways on other reaction intermediates than furfural are likely to have lower energetic contributions relative to the solvation penalties resulting from water replacement, and their impact is, thus, minor. This assumption is particularly valid on stronger binding metals (Pd, Pt, and Rh). For the moderate and weak binding metals (Cu and Au), these stabilizing effects might play a bigger role in the overall aqueous-phase hydrogenation activity and compensate for the overall energetic penalty of solvation, which may, therefore, be overestimated in our study.

#### CONCLUSION

Understanding the adsorption phenomena at the metal-water interfaces aids in the optimization of reaction conditions for important aqueous-phase catalytic transformations. In this work, we studied the adsorption of furfural in aqueous phase, a platform biomass derivative, on several transition metal-water interfaces using AIMD simulations. Our work estimates large endothermic solvation energies associated with furfural adsorption on metal-water interfaces, which we attribute to the replacement of surface adsorbed water molecules in the presence of furfural. The linear correlation between the solvation energies and replaced water coverages further confirms the origin of the endothermic solvation energies. To circumvent the need for expensive AIMD simulations of metal-water interfaces, we propose the OH adsorption energy of the transition metal to be a good descriptor to estimate the solvation energies of furfural. We further bridge the understanding of furfural hydrogenation between gas and aqueous conditions via a simple microkinetic model, which can help explain the origin of the activity of aqueousphase furfural hydrogenation on Pt-group metals under mild conditions.

#### SUPPLEMENTARY MATERIAL

See the supplementary material for the convergence and major results of AIMD simulations, details of the microkinetic model, the coverage-dependent furfural adsorption energy, the snapshots of furfural adsorption configurations, the time-averaged center of mass (COM) and mean squared displacement (MSD) of furfural, the cumulative residence time of furfural, the comparison between a previous bond-additivity model and AIMD simulations, and the simulated and fitted coverages in microkinetic modeling.

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#### AUTHOR DECLARATIONS

#### **Conflict of Interest**

The authors have no conflicts to disclose.

#### **Author Contributions**

Sihang Liu: Conceptualization (equal); Data curation (equal); Formal analysis (lead); Investigation (lead); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (lead). Sudarshan Vijay: Investigation (supporting); Writing – review & editing (supporting). Mianle Xu: Investigation (supporting); Writing – review & editing (supporting). Ang Cao: Writing – review & editing (supporting). Hector Prats: Formal analysis (supporting); Investigation (supporting); Writing – review & editing (supporting). Georg Kastlunger: Investigation (supporting); Supervision (supporting); Writing – review & editing (supporting). Hendrik H. Heenen: Supervision (supporting); Writing – review & editing (supporting). Nitish Govindarajan: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Project administration (lead); Resources (equal); Supervision (lead); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

The raw data and scripts needed to reproduce the figures in the manuscript are openly available in the CatTheory GitHub repository at https://github.com/CatTheoryDTU/furfural\_solvation\_AIMD.

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## Paper III (Chapter 5)

### Unraveling the reaction mechanisms for furfural electroreduction on copper

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#### Broader context

The electro-valorization of biomass-derived chemicals has the potential to enable the sustainable production of value-added chemicals and biofuels using green electricity and an abundant source of protons. One of the most studied processes in this regard is the electroreduction of furfural, a lignin-derived platform chemical. Copper electrodes have been used to electrocatalytically reduce furfural to both furfuryl alcohol and 2-methyl furan, key precursors of polymers and drop-in jet-fuels, respectively. However, the underlying reaction mechanism remains elusive. As furfural-fed electrolyzers are being developed, optimized, and scaled up, the question arises as to whether and how we can more effectively leverage potential, pH and other electrochemical parameters to upgrade furfural into target products, especially for the production of highly profitable biofuels. An efficient advance of this scope urges us to solve the fundamental mechanistic puzzles within furfural electroreduction.

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# Unraveling the reaction mechanisms for furfural electroreduction on copper†

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Electrochemical routes for the valorization of biomass-derived feedstock molecules offer sustainable pathways to produce chemicals and fuels. However, the underlying reaction mechanisms for their electrochemical conversion remain elusive. In particular, the exact role of proton-electron coupled transfer and electrocatalytic hydrogenation in the reaction mechanisms for biomass electroreduction are disputed. In this work, we study the reaction mechanism underlying the electroreduction of furfural, an important biomass-derived platform chemical, combining grand-canonical (constant-potential) density functional theory-based microkinetic simulations and pH dependent experiments on Cu under acidic conditions. Our simulations indicate the second PCET step in the reaction pathway to be the rate- and selectivity-determining step for the production of the two main products of furfural electroreduction on Cu, i.e., furfuryl alcohol and 2-methyl furan, at moderate overpotentials. We further identify the source of Cu's ability to produce both products with comparable activity in their nearly equal activation energies. Furthermore, our microkinetic simulations suggest that surface hydrogenation steps play a minor role in determining the overall activity of furfural electroreduction compared to PCET steps due to the low steady-state hydrogen coverage predicted under reaction conditions, the high activation barriers for surface hydrogenation and the observed pH dependence of the reaction. As a theoretical guideline, low pH (<1.5) and moderate potential (ca. -0.5 V vs. SHE) conditions are suggested for selective 2-MF production.

## 1 Introduction

The electrochemical conversion of biomass-derived feedstocks towards value-added chemicals offers a sustainable route to decarbonizing the chemical industry.<sup>1,2</sup> Furfural (FCHO, F represents the furan ring and CHO the aldehyde group) is one of the most abundant biomass-derived platform chemicals with an annual production capacity of more than 2 million tons.<sup>3</sup> It serves as a critical feedstock towards the production of downstream chemicals and fuels such as furfuryl alcohol (FAL), 2-methylfuran (2-MF), tetrahydrofurfuryl alcohol, hydrofuroin

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and other furanic derivatives.<sup>3,4</sup> The electrochemical furfural reduction reaction has several advantages over thermal hydrogenation including tunable selectivity *via* applied potential or current, mild reaction conditions, the possibility of coupling to intermittent sources of renewable electricity (green electrons), and the use of water as the hydrogen source. All these aspects can dramatically reduce the carbon footprint of biomass conversion processes. Therefore, electrochemical routes for the reduction of furfural have received increased attention in recent years, although earliest attempts date back to the late 19th century.<sup>5</sup>

The past decade has witnessed great progress in exploring furfural reduction over different metal electrodes, and the major products reported in previous studies are summarized in Fig. 1. Furfuryl alcohol and hydrofuroin are the most common products, while 2-methyl furan and tetrahydrofurfuryl alcohol are only selectively produced on limited metals at very acidic conditions.<sup>5-14</sup> In particular, copper shows potential as a

multi-selective electrocatalyst for furfural reduction, as it is able to produce both FAL, a precursor to polymers and resin,<sup>15</sup> and 2-MF, a well-known alternative drop-in biofuel,<sup>16</sup> with nearly 100% selectivity at moderate potentials (*ca.* -0.6 V vs. RHE).<sup>14</sup> Possible reaction pathways for furfural electroreduction to FAL and 2-MF on Cu have been proposed by Chadderdon *et al.*<sup>17</sup> and Shan *et al.*<sup>18</sup> (*cf.* Scheme 1). Furfural (FCHO\*), where \* indicates a surface adsorbed species, is first reduced to either FCHOH\* or FCH<sub>2</sub>O\*, *via* a proton-coupled electron transfer (PCET) or surface hydrogenation of the oxygen or carbon species on FCHO\*, respectively. These intermediates are suggested to be further reduced to FAL or 2-MF *via* subsequent PCET (or surface hydrogenation) steps. Alternatively, FAL has also been proposed to be a precursor for 2-MF formation.<sup>18</sup>

Several attempts have been made to narrow down the mechanistic possibilities and identify the rate-determining step(s) (RDS) towards the products of furfural reduction on Cu electrodes.<sup>14,19,20</sup> For instance, Nilges and Schroder<sup>14</sup> reported



**Fig. 1** A summary of reported major products of aqueous-phase furfural reduction reaction on metal electrodes at moderate potentials. Note that the ratios of colored regions in the box suggest the relative selectivity under similar reaction conditions and the minor products are omitted. Cu is the only metal that is highly selective towards both furfuryl alcohol and 2-methyl furan at different acidic conditions.<sup>5–14</sup> The details for reported experiments are summarized in Table S1 (ESI<sup>+</sup>).



Scheme 1 Proposed reaction mechanisms for the furfural electroreduction reaction towards furfuryl alcohol (FAL) and 2-methylfuran (2-MF) on Cu surfaces.<sup>17,18</sup> ( $H^+ + e^-$ ) and  $H^*$  denote proton-coupled electron transfer (PCET) and surface hydrogenation (where  $H^*$  is produced *via* the Volmer reaction), respectively. The solid or dashed arrows represent elementary reduction step without or with H<sub>2</sub>O production.

a lower overpotential for furfural reduction compared to HER on Cu electrodes under acidic conditions, indicating the activation barriers towards FAL and/or 2-MF are lower than those for H<sub>2</sub> production. However, the actual mechanism for furfural reduction was not explored in this experimental study. More recently, May et al.<sup>19</sup> measured partial current densities and the reaction order with respect to furfural for the production of FAL and 2-MF on Cu. Using a simple microkinetic model, they proposed the surface hydrogenation of adsorbed furfural (FCHO\*) and C-O bond dissociation as the RDS towards FAL and 2-MF, respectively. We note that May and co-workers did not consider the possibility of PCET based pathways, where the adsorbed furanic intermediates are directly protonated by the solvent (*i.e.*,  $H_3O^+/H_2O$ ). Finally, Jung *et al.* reported that upon feeding FAL as the reactant for electroreduction on Cu, 2-MF was not detected as a product.<sup>20</sup> This observation rules out the hypothesis that FAL is a precursor to produce 2-MF.

The competition between proton coupled electron transfer (PCET), and electrochemical catalytic hydrogenation (ECH) in furfural reduction, where surface adsorbed species are hydrogenated by protons from the electrolyte (coupled to electron transfer from the electrode) or surface adsorbed hydrogen (denoted by H\*), respectively, is still in disputed. Chadderdon et al.<sup>17</sup> and Liu et al.<sup>21</sup> proposed that ECH-based mechanisms are dominant in furfural reduction towards FAL and 2-MF on Cu electrodes, while an outer-sphere reaction pathway might dominate hydrofuroin production. The researchers used selfassembled monolayers of thiols with varying carbon-chain lengths to coat the Cu or Pb surfaces to reduce surface adsorption. They attributed the resulting decrease in the production of 2-MF (more drastically) and FAL to the reduction in surface hydrogen coverages, leading to a proposed ECH mechanism on Cu. However, the surface poisoning experiments could only confirm the limiting steps for production of 2-MF and FAL are inner-sphere reactions, but do not rule out the pathway via direct protonation to adsorbed furanic intermediates (an Eley-Rideal pathway), which was not explicitly discussed in the mechanisms proposed on Cu electrodes.<sup>17</sup> In addition, their measured kinetic isotope effects lead to the conclusion that furfural reduction on Cu proceeds via an ECH mechanism due to a similar KIE behavior to HER. However, inner sphere PCET steps onto furfural adsorbed on the electrode would also lead to a KIE comparable to HER. Thus, we argue that neither surface poisoning or KIE experiments allows us to distinguish between a surface hydrogenation and PCET-based mechanisms. As further evidence for the reaction mechanism, May et al. showed that selectivity to 2-MF could be dramatically reduced in favor of FAL with an increase in the electrolyte pH.<sup>22</sup> This conclusion was further strengthened in a recent study by Xu et al. where the authors reported close to 100% selectivity to FAL on a Cu electrode supported on N-doped porous carbon at pH =  $13.6.^{23}$  The strong pH-dependence of the product distribution suggests that the formation of at least one of the two products directly involves protons (or hydroxides) from solution rather than the ECH mechanism exclusively based on the involvement of H\*.

Computational studies are few in furfural reduction reaction. Lopez-Ruiz *et al.* presented rate expressions with extreme-scenario assumptions to show that both ECH/PCET based pathways could describe the activity trends for furfural reduction on Cu.<sup>24</sup> Shan *et al.* calculated the reaction energetics of ECH mechanisms and concluded that the first hydrogenation step and the C–O bond scission are possible rate-limiting steps for the formation of FAL and 2-MF, respectively.<sup>18</sup> However, previous theoretical studies have either neglected the activation energies associated with PCET based reaction steps in the furfural reduction mechanism or approximated them based on surface hydrogenation barriers that are insensitive to changes in applied potential and pH.

Herein, we combine constant-potential DFT based microkinetic simulations, including both the PCET and ECH pathways, and pH dependent experiments under acidic conditions to study furfural reduction on Cu. The calculated reaction energetics show that although FCH<sub>2</sub>O\* is thermodynamically favored over FCHOH\*, its formation is kinetically hindered on Cu(111) at relevant potentials. The microkinetic simulations including a degree of rate control analysis indicate that the second PCET step, i.e., the protonation of C vs. O in FCHOH\* is the rate- and selectivity determining steps at moderate overpotentials towards FAL and 2-MF, respectively. Furthermore, we find that the ECH pathway plays a minor role in furfural reduction due to a combination of the low coverage of H\* predicted on Cu terrace sites and the high activation energies associated with the surface hydrogenation steps. We provide further evidence to our mechanistic conclusions by evaluating the potential and pH dependence (vs. the reversible hydrogen electrode) of both FAL and 2-MF production, which strongly suggests the involvement of a later PCET step in the RDS for furfural reduction on Cu electrodes. Guidelines for selective 2-MF production are proposed. The mechanistic insights obtained herein shed light on the competing reaction pathways in furfural reduction and provide a framework to understand reaction mechanisms in electrochemical biomass valorization, as well as multi-step electrochemical reactions in general.

## 2 Results and discussion

# 2.1 The formation of FCHOH\* is kinetically favored relative to the more thermodynamically stable $FCH_2O^*$

The reaction energetics (*i.e.* thermodynamics and activation barriers) were computed using DFT for all (electro-)chemical elementary steps illustrated in Scheme 1 and eqn (1) and (2) on Cu(111) under very acidic conditions (*i.e.* where we assume the major proton donor is  $H_3O^+$ ), employing a grand-canonical framework.<sup>25</sup> An ice-like water structure was used to represent the solvent structure in our model,<sup>26</sup> in order to approximate the endothermic solvent effect on the adsorption of larger molecules like furan compounds having a sizeable energetic penalty due to water displacement.<sup>27,28</sup> A slightly tilted orientation of furfural adsorption on Cu(111) was obtained shown in the inset of Fig. 2(a), in line with a recent molecular


**Fig. 2** The calculated constant-potential free energy diagrams of furfural reduction on Cu(111) surface. (a) The competition of reaction thermodynamics and kinetics in the PCET steps from furfural (FCHO\*) to the adsorbates FCHOH\* and FCH<sub>2</sub>O\*; (b) the complete free energy profiles to both products: furfuryl alcohol (FCH<sub>2</sub>OH, red) and 2-methyl furane (FCH<sub>3</sub>, black). Color code in the insets: brown-Cu, dark grey-C, red-O, and light grey-H.

dynamics study.<sup>29</sup> The applied computational model is shown in Fig. S1 (ESI<sup>†</sup>). We applied the symmetry factor  $\beta$  obtained from grand-canonical (GC) constant-potential calculations to quantify the response of the determined electrochemical activation energies to potential, as summarized in Table S2 (ESI<sup>†</sup>), as described in ref. 30. Note that (1) we do not include the analysis of dimer products in our study, because they are minor outer-sphere products on copper under acidic conditions;<sup>17,21</sup> (2) cation effects are not considered in this work, as the experiments were carried out in HClO<sub>4</sub> solutions free of metal cations. However, we note that investigating the effects of cation/anion identity (and microenvironment effects in general) on furfural electroreduction would be an interesting future direction.

$$FCHO(l) + 2(H^{+} + e^{-}) \leftrightarrow FCH_2OH(l)$$
(1)

$$FCHO(l) + 4(H^+ + e^-) \leftrightarrow FCH_3(g) + H_2O(l)$$
(2)

We find that the formation of FCH<sub>2</sub>O\* is associated with a higher activation barrier than the formation of FCHOH\* (cf. Fig. 2(a)), even though  $FCH_2O^*$  is thermodynamically more stable than FCHOH\*. FCHOH\* prefers to adsorb in a configuration with the -CHOH group binding at an atop site, while the -CH<sub>2</sub>O moiety in \*FCH<sub>2</sub>O binds to a hollow site, resulting in ca. 1 eV higher thermodynamic stability relative to FCHOH\* (cf. inset, Fig. 2(a)). However, we find the activation barrier for the formation of FCH<sub>2</sub>O\* via a PCET step using H<sub>3</sub>O<sup>+</sup> as the proton source to be substantially higher than the corresponding PCET barrier for the formation of FCHOH\* (0.90 eV vs. 0.48 eV at 0 V vs. RHE, pH 1 and 0.66 eV vs. 0.20 eV at -0.5 V vs. RHE, pH 1) in line with the general trend of electrochemical barriers for protonating C and O on metals reported by Patel et al.<sup>31</sup> Furthermore, our simulations indicate that the further protonation of FCH2O\* is sterically hindered, as it requires the proton from the electrolyte to approach the surface-bound oxygen on the hollow site. Hence, the hydrogenation of FCH2O\*

would prefer  $H^*$  on the surface as a reactant (*i.e.*, following the ECH pathway), which is shown to be kinetically hindered in the following section.

Fig. 2(b) shows the free energy profiles towards FAL and 2-MF, highlighting the identified selectivity determining step (SDS) which is the protonation of FCHOH\* to FCH<sub>2</sub>OH\* (FAL pathway) or to FCH\* (2-MF pathway). We note that the second PCET step, *i.e.*, the protonation of FCHOH\*, is also predicted to have the highest barrier along the reaction pathway at both potentials, hence functioning as both the RDS and SDS. We find that the SDS towards FCH<sub>2</sub>OH\* and FCH\* displays comparable activation barriers which is in agreement with their comparable activity on Cu towards both FAL and 2-MF in acidic media.<sup>14,17</sup> In addition, we calculated FCH<sub>2</sub>OH\* to FCH<sub>2</sub>\* to have a formidably high activation energy of 1.46 eV, which defies the production of 2-MF from adsorbed FAL *via* a PCET pathway.

In order to study the competing hydrogen evolution reaction on Cu(111), we also explicitly calculated the HER energetics under acidic conditions using GC-DFT (*cf.* Fig. S2, ESI $\dagger$ ). We identify the Volmer step as the RDS in H<sub>2</sub> production on Cu(111), with a barrier of *ca.* 1 eV at 0 V  $\nu$ s. RHE and pH 1, higher than the activation energies of the limiting PCET steps involved in furfural reduction under the same conditions.

# 2.2 The dominance of furfural reduction at low overpotentials compared to HER strongly indicates the dominance of PCET based pathways

On the basis of the calculated reaction energetics, we developed a mean-field microkinetic model to obtain mechanistic insights into acidic furfural reduction on Cu(111). As expected from the discussion in the previous section, cathodic current at potentials more negative than -0.5 V vs. RHE on Cu electrode is predicted to dramatically increase when there is furfural in the electrolyte, as shown in Fig. 3(a). This observation is attributed to much higher rates of furfural reduction than hydrogen evolution (cf. Fig. S3, ESI<sup>+</sup>) and is in in qualitative agreement with the experimental current densities obtained under similar conditions (*i.e.*, pH = 1), shown in Fig. 3(b). Notably, the simulated coverage map in Fig. S4 (ESI<sup>+</sup>) shows that the intermediate FCHOH\* and FCH2O\* already reach moderate coverages at quite low current densities, rationalizing a facile adsorption and first protonation step. This agrees with the finding that the furfural reduction intermediates have readily



**Fig. 3** Activity for furfural reduction reaction on Cu. (a and b) Simulated and experimental total polarization curves with furfural reduction (in black) and without furfural (HER, in red); (c) and (d) simulated and experimental partial current densities (on log scale) towards furfuryl alcohol (FAL) and 2-methyl furan (2-MF). Simulated reaction conditions: 100 mM furfural, 300 K, pH = 1. We applied  $\pm$ 0.2 eV error estimates for the barrier of selectivity (rate)-determining step for 2-MF formation *i.e.*, FCHOH\*  $\rightarrow$  FCH\* to account for the intrinsic uncertainty in DFT calculations<sup>34</sup> and electrochemical interface simulations, which is represented by the orange and green shade areas in (c). Reaction conditions: 0.1 M HClO<sub>4</sub> electrolyte (pH 1), 8 mM furfural, constant potential was applied for three hours. Error bars were produced using the results of two separate experiments, where each point warranted a fresh experiment. All experimental potentials were reported with iR corrections. No repeats were performed for -0.60 and -0.65 V vs. RHE as mass transport limitations were already reached at these potentials.

been seen before the detection of any products by Li and Kornienko using the *operando* Raman spectroscopy.<sup>32</sup>

We argue that the lower onset overpotential for furfural reduction with respect to HER is already a strong indication for the dominance of a PCET based mechanism. Since HER on Cu is limited by the adsorption of hydrogen,<sup>33</sup> and H\* is also needed for an ECH mechanism in furfural reduction, it is hard to see how furfural reduction could proceed at a higher rate than HER, as we observe, if it proceeded *via* an ECH mechanism. The only scenario where an increase in furfural reduction activity involving surface hydrogenation compared to HER could be achieved would involve improved of H\* adsorption in the presence of furfural intermediates, which we deem as unlikely.

The simulated partial current densities towards FAL and 2-MF in Fig. 3(c) are comparable owing to their similar SDS energetics (*cf.* Fig. 2(b)), in agreement with Cu's ability to produce both products in experiments. The green shaded area for 2-MF activity in Fig. 3(c), showing the spread in simulated current density upon including a 0.2 eV uncertainty in the activation energy, indicates the selectivity towards 2-MF could be enhanced by stabilizing the transition state for protonating FCHOH\* to FCH\*. We refrain from making any quantitative predictions on the selectivity of these two products, as a deviation of 0.1 eV in activation energy for the SDS already leads to >75% change in selectivity.<sup>35,36</sup>

The simulated current densities qualitatively agree with our experimental activities, shown in Fig. 3(d). We note that both the production of FAL and 2-MF suffer from mass transport limitations already at *ca.* -0.45 V *vs.* RHE indicating the previous experimental results obtained at similar conditions should be re-evaluated to deconvolute the intrinsic activity with mass transport of furfural,  $H_3O^+$ , and the products. By employing a fast-stirring reactor, we were able to obtain partial current densities for the major reduction products that are likely free from mass transport limitations at low overpotentials (*cf.* Fig. 3(d)). However, we recommend a more accurate product detection methodology should be developed and applied to report mass-transport-limitation-free activities for the facile biomass electrovalorization.

## 2.3 The rate-determining step lies beyond the first PCET for furfural reduction

From our microkinetic models, we predict Tafel slopes of 35 and 37 mV dec<sup>-1</sup> for FAL and 2-MF production at low overpotentials (*cf.* Fig. 3(c)). This reflects our conclusion from the free energy analysis that the second PCET steps determine the intrinsic activity to FAL and 2-MF according to definition of the Tafel slope from Butler–Volmer theory,

Tafel slope = 
$$-\frac{2.3k_{\rm B}T}{e(N+\beta)}$$
 (3)

where *N* is the number of PCET steps before the RDS,  $\beta$  is the symmetry factor of the RDS,  $k_{\rm B}$  is the Boltzmann constant, *T* is the reaction temperature and *e* the elementary charge.

The fitted Tafel slopes retrieved from the three lowest current densities are *ca.* 57 and 65 mV  $dec^{-1}$  for FAL and 2-MF, placing the respective RDS beyond the first protonation step in line with theory. If the first protonation were the RDS, we would expect initial Tafel slopes on the order of ca. 120 mV dec $^{-1}$ . Given the uncertainty in conventional Tafel slope fitting of experimental current densities,<sup>37</sup> we refrain from making definite conclusions on the exact rate-determining step, but indicate that the first PCET step is unlikely to be the RDS. We also indicate the selectivity of 2-MF could benefit if the formation of FCH\* from FCHOH\* is promoted, e.g., tuning the surface orientations to have more high-index surfaces, as suggested by the previous experiments that the roughened Cu electrodes show higher selectivity to 2-MF at *ca.* -0.4 V vs. RHE.<sup>32</sup> The difference between experimental and theoretical Tafel slopes could result from a convolution of actual active surfaces under reaction conditions,<sup>38,39</sup> varying transfer coefficient values<sup>37</sup> in the electrochemical reactions and early mass transport limitations.40

In order to identify the rate-controlling transition states and reaction intermediates for both FAL and 2-MF within the studied potential range, we performed a degree of rate control (DRC) analysis<sup>41</sup> (*cf.* Fig. 4). DRC analysis is a powerful mathematical approach that has large (positive or negative) values for



Fig. 4 Degree of rate control (DRC) analysis of furfural electroreduction reaction on Cu. (a) and (b) are the DRC for FAL and 2-MF production respectively. Note that the number of actual reaction steps that determine the activity towards the respective products is 20. In order to increase readability, we only include the steps with DRC values > 0.1 in the plot, as the rest of the steps play a minor role in determining the overall activity.

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the most important transition states and intermediates in the considered reaction pathway. At low overpotentials (0 to -0.2 V vs. RHE), the production of FAL is limited by the protonation of FCHO<sup>\*</sup> to FCH<sub>2</sub>O<sup>\*</sup> (Fig. 4(a)), suggesting at very low overpotentials (and activities), the FAL formation on Cu proceeds via FCH<sub>2</sub>O\* pathway. At moderate, experimentally relevant, overpotentials (-0.2 to -0.6 V vs. RHE) the mechanism towards FAL changes from going via the thermodynamically more stable \*FCH<sub>2</sub>O to the kinetically preferred \*FCHOH (*cf.* Fig. 4(a)). In contrast, as shown in Fig. 4(b), 2-MF is limited by the protonation of FCHOH<sup>\*</sup> to FCH<sup>\*</sup> (DRC  $\approx$  1) throughout the studied potential range. Below -0.6 V vs. RHE, the activity towards both FAL and 2-MF reduce with an increase in the adsorption strength of FCHOH\* as evidenced by a large negative DRC (inhibiting step), as the coverage of \*FCHOH coverage increases and reaches saturation. In this situation, a further increase in the (already high) coverage of FCHOH reduces the coverage of all other furanic species on the surface, due to the repulsive interaction with the former. Furthermore, the saturation of the FCHOH\* coverage increases the estimated Tafel slopes (*cf.* Fig. S4, ESI<sup>†</sup>). HER is determined by Volmer reaction throughout the potential range studied in this work (*cf.* Fig. S5, ESI<sup>†</sup>).

## 2.4 Electrochemical hydrogenation is unlikely to be the dominant pathway for furfural reduction on Cu

In order to better understand the role of surface hydrogenation in furfural reduction on Cu, we also simulated the ECH-based mechanisms towards FAL and 2-MF. As shown in Fig. 4(a), the formation of 2-MF and FAL are limited by the C–O bond breaking and hydrogenation of FCH<sub>2</sub>O\* respectively. The activation free energies for these limiting steps have been determined to be 1.10 eV and 0.99 eV, respectively, which are unlikely to respond significantly to an applied potential given that no electrons are directly involved in surface hydrogenation step (*i.e.*,  $\beta \approx 0$ . The ECH pathway *via* FCHOH\* is shown in Fig. S5 (ESI†), which displays an alarmingly high activation free energy of 1.20 eV for C–O bond scission of FCHOH\* to form 2-MF.

The simulated current densities towards FAL and 2-MF for the ECH pathway, shown in Fig. 5(b), are more than 6 orders of



**Fig. 5** Theoretical results of furfural reduction reaction on Cu following an ECH-based mechanism. (a) The calculated constant-potential free energy diagram for furfural reduction to FAL (in red) and 2-MF (in black) at 0 and -0.5 V vs. RHE; (b) the simulated partial current densities (solid lines) assuming an ECH-based mechanism in comparison with experimental results (dots, *cf.* Fig. 3(d)); (c) the simulated coverages of the main surface adsorbates in the ECH-based mechanism.

magnitude lower than in the simulation based on the PCET mechanism (*cf.* Fig. 3(c)) as well as our experimental results (*cf.* Fig. 3(d)). In contrast,  $H_2$  is the dominant product throughout the potential region. The low activity towards FAL and 2-MF predicted for the ECH pathway originates from (i) extremely low  $H^*$  coverage on Cu(111) as shown in Fig. 5(c) and (ii) high activation barriers for the surface hydrogenation of the reaction intermediates under the relevant reaction conditions.

A higher coverage of electrogenerated H\* might make ECH pathway more productive, *e.g.*, on Pt and Pd electrodes. We note that Zhou *et al.* recently reported the participation of H\* in furfural reduction to 2-MF on Pd-based catalysts in acid by interpreting adsorption patterns of furfural and hydrogen from *in situ* surface enhanced Raman spectroscopy (SERS).<sup>42</sup> Thus, we note that the ECH mechanism might play an important role in materials where H\* is formed *via* underpotential deposition or metal hydrides present under reaction conditions.<sup>43</sup>

The Volmer step, which in an ECH mechanism is responsible for any observed potential and pH dependence, is not predicted the rate-limiting step in furfural reduction. Thus, the Tafel slope in an ECH mechanism would be only a consequence of the coverage build-up of either H\* or furanic intermediates with potential, which we show in Fig. 5(c). Once the coverages of the reactants at the RDS are saturated, the resulting current densities in an ECH mechanism would not exhibit any potential dependence (*i.e.*,  $\beta \approx 0$ , Tafel slope  $\approx \infty$ ).

#### 2.5 pH dependence of furfural reduction on Cu

We further studied the pH dependence of furfural reduction activity highlighting the competition between furfural reduction and HER in acidic conditions. The simulated rates of FAL and 2-MF against potential and acidic pH are shown in Fig. S7 (ESI<sup>+</sup>). At low overpotentials, a decrease in both potential (more positive) and pH increases 2-MF formation faster than that of FAL, because in this potential region, FAL production is limited by 1st-PCET FCHO\* protonation to FCH2O\*, while 2-MF by 2nd-PCET FCHOH\* protonation (cf. Fig. 4), resulting in a larger response to potential/pH for 2-MF in this region. The simulated selectivity for FAL and 2-MF is presented in Fig. S8 (ESI<sup>+</sup>). To favor value-added production of 2-MF, a low pH (<1.5) and moderate potentials (ca. -0.5 V vs. SHE) is suggested in theory, which is in line with a previous viewpoint.<sup>22</sup> The respective rate and selectivity for HER is then shown in Fig. S9 (ESI<sup>+</sup>). We find that HER could outcompete furfural reduction at both extremely low and high overpotentials, thus a moderate potential range is in need promote furfural reduction and suppress H<sub>2</sub> evolution. The results presented above provide a theoretical rationale for selective furfural reduction by leveraging both the pH and applied potential.

In experiments, varying the electrolyte pH between 0.5 and 2.0 at a fixed RHE potential (-0.5 V vs. RHE) allows us to identify the dominance of a PCET or ECH based pathway as shown in Fig. 6. Given the low electrolyte pH employed in the experiments, we can safely assume  $H_3O^+$  as the dominant proton donor. A PCET based mechanism is expected to show a reduction in activity with pH in acidic conditions,<sup>44–47</sup> while the ECH mechanism directly consuming surface adsorbed



**Fig. 6** Measured and simulated partial current densities of FAL and 2-MF at varying acidic pH at -0.5 V vs. RHE. The solid lines represent the fitted current densities from our measurement, while the dashed and dash-dotted lines are the simulated current densities for the PCET and ECH based mechanisms, respectively. Reaction conditions: HClO<sub>4</sub> electrolyte adjusted in concentration for varying pH, 8 mM furfural, potential applied was -0.50 V vs. RHE for 3 hours. Error bars were produced using the results of two separate experiments.

H\* could display complex scenarios, where pH, potential and selectivity might play different roles.

As can be seen in Fig. 6, low pH favors 2-MF over FAL. The measured partial current densities towards FAL and 2-MF show a distinct negative dependence on pH: -0.57 and -0.82 dec per pH respectively. This behavior is in qualitative agreement with our microkinetic simulations of the PCET based mechanism with negative dependences of -0.37 and -0.52 dec per pH for FAL and 2-MF respectively. Quantitative differences could originate from different symmetry factors for rate-determining steps, *i.e.*, FCHOH\* protonation (*cf.* Fig. 2).<sup>44,46</sup> The larger pH dependence of 2-MF suggests that lowering pH could enhance the selectivity to 2-MF over FAL, in line with the experiments shown in Fig. S10 (ESI†) and previous reports.<sup>22</sup>

In contrast to the observations for the PCET based pathway, the simulated current density towards FAL based on the ECH mechanism is pH independent throughout the studied pH range, while that of 2-MF is strongly pH dependent (-0.98dec per pH) as shown in Fig. 6 (ECH-theory). Nonetheless, ECH mechanism towards both products displays negligible activity that is orders of magnitude lower than simulated current densities obtained for the PCET based pathway and experiments (*cf.* Fig. 6). Therefore, in addition to the calculated energetics, the observed pH dependence on activities further strengthens our conclusion of a PCET-based mechanism to be the dominant pathway for furfural reduction on Cu electrodes.

### 3 Conclusion

In this work, we present detailed microkinetic simulations based on the constant-potential DFT energetics and pH dependent

experiments to understand the reaction mechanism of furfural electroreduction on Cu. Our simulations and experiments show that Cu can produce both FAL and 2-MF in acidic conditions, where we identified the rate-determining step to lie beyond first PCET step. We then demonstrate that a surface hydrogenationbased mechanism is unlikely to be dominant for furfural electroreduction, due to the negligible H\* coverage and high (potential-independent) surface hydrogenation barriers under mild reaction conditions. Measurements and simulations performed at varying electrolyte pH further strengthen the conclusions of a PCET-dominated mechanism. The mechanistic insights herein provide directions to tune the selectivity towards tailored products for furfural reduction, e.g., more valuable 2-MF: (a) surface modulations to display better C-O bond breaking ability help enhance the yield and (b) low pH (<1.5) in combination with moderate potentials (ca. -0.5 V vs. SHE) favors 2-MF production. Besides, our work also sheds light on the role of surface-adsorbed H\* and pH-dependent activity on Cu electrodes for multi-step electroreduction reactions.

#### 4 Methods

#### 4.1 Computational details

4.1.1 Basic DFT calculation parameters. In this work, we applied the Solvated Jellium Method (SJM)<sup>30</sup> implemented in the GPAW code<sup>48,49</sup> for all the DFT calculations to consider solvation effect. An average grid spacing of 0.18 Å and a  $4 \times 3 \times 1$ *k*-points mesh were applied for the orthogonal  $3 \times 4 \times 3$  Cu(111) slab model with an ice-like water layer. Periodic boundary conditions were applied in the directions of the surface plane *i.e.*, x and y directions and open boundary conditions in the z-direction. At least 10 Å of vacuum/implicit solvent were applied between the atoms and the boundary in the z-direction. We created a field-free zone in the solvent above the asymmetric slabs via the dipolecorrection implemented in GPAW-SJM. A Fermi smearing of 0.1 eV was used in all calculations. To better describe the interaction between metal surface and furanic molecules, we used optB88-vdW functional<sup>50</sup> to account for the critical van der Waals effect on aromatic species, which has been demonstrated to relieve over-binding of the dispersion energy by PBE-D3 functionals on Cu.<sup>51</sup>

**4.1.2 GC calculation for electrochemical barriers.** SJM implementation uses an effective potential cavity solvation model developed by Held and Walter.<sup>52</sup> The parameters for solvation in water applied in this work:<sup>44</sup> strength of the repulsion at the atomic radii controlling the cavity size  $u_0 = 0.18$  eV, surface tension 0.001148 Pa m, relative permittivity (dielectric constant)  $\varepsilon = 78.36$ , temperature = 298.15 K. The counter charge in SJM model was chosen as a 3 Å thick jellium slab starting two vdW-radii of oxygen atoms above the highest water molecule in the water layer. The tolerance for the electrode potential deviation from target potential was set to 5 mV in the calculation of stable reaction intermediates and 10 mV in the case of transition state searches. The reported constant potential free energies  $G^{\Phi}$  ( $\Phi$  = work function) were calculated

as a sum of the constant potential energies including the constant particle DFT energy  $E^{\Phi} = E^{n_e} - n_e \mu_e$  at  $n_e$  excess electrons, and the electron's chemical potential  $\mu_e = -\Phi$ , the effective solvation free energy directly derived from the implicit solvation scheme inherent in SJM, and the vibrational free energy contributions (zero-point energies, heat capacity and vibrational entropy) calculated from a constant potential vibrational analysis conducted at 298.15 K.

The Nudged elastic band (NEB) method<sup>53,54</sup> has been conducted to calculate the transition states (TS). For electrochemical reactions, we calculated the TS within the SJM scheme to sustain constant potential. Initial-state structures for a reduction step always have a  $H_3O^+$  solvated in the single water layer, where the adsorption of furanic intermediates were sampled and the structure with the lowest energy was later applied as the initial state. To align with CHE equilibrium,<sup>55</sup> which refers to a proton in bulk solution, we used the ensemble energy of the initial state of acidic NEB calculations without  $H_3O^+$  and 0.5  $H_2$  as the initial state energy in free energy diagrams. We calculated the PCET barriers at 0 V vs. SHE and pH = 1 and obtained the symmetry factor  $\beta$  by the charge transfer in GC calculations for the response of the determined electrochemical activation energies to potential. The adsorbate polarization  $(\gamma)$  is neglected due to the similar polarization of different furanic species on the surface and the negligible dipole moments of HER intermediates. As for surface hydrogenation mechanism, we only considered the Langmuir-Hinshelwood mechanism, while Eley-Rideal mechanism has been suggested unlikely on Cu electrode by May et al.<sup>19</sup>

**4.1.3 Microkinetic modeling.** The microkinetic modeling was carried out using the CatMAP code<sup>56</sup> based on the mean-field approach and the steady-state approximation including a self-consistent description of adsorbate–adsorbate interactions.<sup>57,58</sup> Lateral adsorbate–adsorbate interactions were modeled using a first-order expansion in the coverage for the differential adsorption energy:

$$E_i( heta_i) = E_i^0 + \sum_j f \varepsilon_{ij} heta_j$$

where  $E_i(\theta_i)$  is the differential adsorption energy of species i given a vector of coverages  $\theta_i$ ,  $E_i^0$  is the differential adsorption energy of species *i* in the low-coverage limit,  $\varepsilon_{ij}$  is a matrix of interaction parameters for the interaction between species *i* and *j*, *f* corresponds to a piecewise-linear function for the adsorption energy as a function of coverage. As H\* is much smaller than furanic species, we assume that H\* barely affects the strength of interactions. All the interactions given by transition states are also neglected as a result of their low coverages by definition. Besides, the furanic species are similar in size and configurations, thus we approximated the  $\varepsilon_{ii}$  among FCHO\*, FCHOH\*, FCHOH\*, FCH2O\*, FCH2OH\*, FCH\*, FCH2\* and FCH<sub>3</sub>\* with self-interaction matrix of furfural, *i.e.*,  $\varepsilon_{\text{FCHO}*,\text{FCHO}*} =$ 6.82. The cross-interaction terms of different intermediates are approximated by geometric mean of self-interaction terms of two interacting adsorbates. To efficiently achieve convergence of the microkinetic models including adsorbate-adsorbate interactions,

we ramped up the interaction strength from 0 to 1 with a step size of 0.1.

A Newton root-finding algorithm with a max iteration number of 500 was used to determine the steady-state rates and coverages. A decimal precision of 200 with a convergence tolerance value of  $10^{-50}$  were used. More details could be found in ESI.<sup>†</sup>

#### 4.2 Experimental details

**4.2.1 Electrode preparation.** Cu electrodes were prepared by cutting Cu foil (99.99%, Goodfellow) into  $1 \times 1$  cm<sup>2</sup> squares

at 1.90 and 4.20 min which accounted for the two isomers formed. For simplicity, both isomers reported are combined. 2-MF was not visible in the chromatograms hence was quantified using nuclear magnetic resonance (NMR, 400 MHz Bruker AV400) spectroscopy using dimethylsulfoxide (DMSO) as an internal standard. Faradaic efficiencies (FEs) were then calculated using the following equation, where the Faraday constant is 96 485 C mol<sup>-1</sup>. Calibrations for product analysis are shown in Fig. S11 and S12 (ESI<sup>†</sup>).

Faradaic efficiency (%) =  $\frac{\text{No.electrons transferred} \times \text{moles of product} \times \text{Faraday constant}}{\text{Total charge passed}} \times 100$ 

and using fine sandpaper on each side to remove any external impurities. The electrodes were pierced with Cu wire which acted as the connection for the working electrode. The electrodes were then submerged in ethanol and sonicated in an ice bath for 20 min, with subsequent washing with MilliQ water before use.

4.2.2 Electrochemical experiments. Electrochemical measurements were carried out in a three-electrode custom-made H-cell (Cambridge Glassware) with the anolyte and catholyte chamber separated by a Nafion 117 membrane (Fuel Cell Stores). The entire cell was boiled in ultrapure MilliQ water (18.2 MOhm) before any electrochemical experiments. The catholyte chamber was purged using Ar gas (99.998%, BOC) for 10 min before use to remove any dissolved oxygen and was not purged throughout the experiments. The working and counter electrodes were Cu foil and Au mesh respectively. We used a saturated Hg/HgSO<sub>4</sub> electrode as a reference electrode which was calibrated against the reversible hydrogen electrode (RHE), hence the relevant electrochemical data in this work is reported on the RHE scale. All recorded potentials were iR corrected. The acidic electrolytes used in this work consisted of a HClO<sub>4</sub> (suprapure, Merck) at varying concentrations depending on the experiment, in all three compartments.

4.2.3 Product analysis. Aliquots of the catholyte solution were taken after chronoamperometry experiments to quantify any furfural reduction products. FAL and hydrofuroin (minor product) were quantified by high-performance liquid chromatography (HPLC, Agilent Infinity 1260 II) using purchased standards of FAL (98%, Sigma Aldrich) and furfural (99%, Sigma Aldrich) to produce calibration curves (Fig. S10 and S11, ESI<sup>+</sup>). Hydrofuroin standards were synthesized using Mg mediated homocoupling of furfural as no commercial standards were available. The full synthesis procedure is in detailed in the ESI.<sup>†</sup> A mixture of water: acetonitrile (88.7:11.3) was used as the mobile phase at a flow rate of  $1 \text{ mL min}^{-1}$ , with the samples being fed through a Zorbax SB C-18 column (4.6  $\times$ 50 mm, 3.5 micron, Agilent Technologies). The column temperature was maintained at 35 °C throughout each measurement and the products were detected by a UV-Vis detector set at 220 nm. FAL and furfural had retention times of 1.35 and 1.62 min respectively, whereas hydrofuroin produced two peaks

## Data availability

The data that underpin the findings of this study are available within the article and its ESI.† All computational raw data are available on GitHub https://github.com/CatTheoryDTU/ furfural\_electroreduction\_copper.

### Author contributions

S. L., G. K., N. G. and K. C. conceptualized the work; S. L. and N. G. carried out constant-potential DFT simulations and S. L. performed the microkinetic simulations; Z. M. designed and carried out all the electrochemical experiments, electrode preparations and product analysis; S. Ch. S. helped produce the method for HPLC analysis with Z. M.; S. L. and Z. M. wrote the original manuscript; K. C., N. G., G. K., S. B. S., M. M. T., and I. E. L. S. contributed in supervision; K. C. contributed in funding acquisition for the computational work; all authors contributed in writing, review and editing.

## Conflicts of interest

There are no conflicts to declare.

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## Paper IV (Chapter 6)

### Furfural electrovalorisation using single-atom molecular catalysts

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#### Broader context

Furfural electrovalorisation using single-atom molecular catalysts<sup>†</sup>

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The electrochemical conversion of biomass to high-value platform chemicals as a potential means to reduce our reliance on crude oil offers environmental advantages, in comparison to thermal catalysis as it takes place at room temperature and pressure. In this study, we investigate the electrochemical reduction of a biomass-derived chemical, furfural, using Cu and Co single-atom catalysts supported on carbon electrodes via non-covalent adsorption. Under mild basic electrolyte (pH 10) we have selectively produced hydrofuroin, a valuable and promising precursor to sustainable drop-in jet fuels. Density functional theory (DFT) calculations were carried out to unveil that the weak-binding molecular catalysts could give rise to a facile reaction path towards the electrochemical production of hydrofuroin. The calculated adsorption energies of furfural and hydrogen on different types of catalysts aid in mapping the experimental selectivity for furfural electroreduction, offering a general catalyst design blueprint for this reaction. Based on theoretical calculations, we tested Co and Cu phthalocyanines (Pc) adsorbed onto multi-walled carbon nanotubes (MWCNTs) to show that these single-atom molecular catalysts can display up to 65.3% faradaic efficiency for hydrofuroin production with low amounts of hydrogen evolution in pH 10 at -0.50 V vs. RHE. The stability of CoPc and CuPc towards furfural reduction is probed by time-of-flight secondary ion mass spectrometry (ToF-SIMS), where CoPc is found to be more stable with only 16% reduction in normalised counts, compared to 67% for CuPc. Mechanistically, we suggest that the rate-determining step for hydrofuroin formation on single-atom molecular catalysts should be the first proton-coupled electron transfer prior to radical coupling, which could possibly happen in solution. Our work provides new insights into utilizing single-atom catalysts for the biomass electrovalorisation to value-added fuels and chemicals

As we move away from a fossil fuel centric society, we are striving to electrify many processes using green energy. However, direct electrification is not technical viable nor cost-effective in some verticals, such as in the commodity chemicals sector or in the aviation industry. An interesting emerging approach to produce chemicals and fuel precursors from abundant biomass feedstock is a green electrochemical synthesis under mild conditions. Furfural is an archetypal biomass-derived building block that can be upgraded to biofuels or polymers precursors. Current thermochemical methods of upgrading furfural come with notable disadvantages such as high temperature or pressure and the use of unsustainable reagents. The study of electrosynthesis processes involving furfural is in its infancy and the mechanistic aspects of the reactions are poorly understood. Herein, we describe an electrochemical route to selectively synthesize value-added hydrofuroin, a key precursor to drop-in jet fuels, from furfural under mild conditions. Insights from our work could lead to a bottom-up theory-driven approach where the properties of single atom sites could be tailored to accelerate the formation of specific products or potentially to promote stereospecific electrosynthesis routes.

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## Introduction

As the worldwide climate crisis worsens, there is an urgent need to develop strategies for renewable chemical production. Ideally, a renewable chemical source would be an abundantly available waste product.<sup>1,2</sup> Lignocellulosic biomass, such as



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cellulose/hemicellulose fits this criteria and from it, a range of valuable platform chemicals can be obtained.<sup>3</sup> Among these platform chemicals are furfural (FCHO, where F denotes a furan ring) and 5-hydroxymethyl furfural (HMF). Both of these chemicals can be upgraded into a range of higher value chemicals by reduction and/or oxidation for use in renewable polymers,<sup>4,5</sup> and biofuels.<sup>6,7</sup> For example, HMF has been identified as one of the most important chemicals for a sustainable future by the U.S. Department of Energy<sup>8</sup> as it can be oxidised into 2,5-furandicarboxylic acid,<sup>9</sup> a replacement monomer in popular renewable polymers such as polyethylene terephthalate (PET).

The upgrading of furfural and HMF has been reported using various thermochemical methods,<sup>10,11</sup> however these are associated with noticeable drawbacks. For example, the present technology for reduction of HMF and furfural uses toxic CuCr catalysts along with hydrogen gas, under high temperatures and pressures.<sup>12</sup> There are also needs for reagent heavy chromatographic methods of product separation and purification, which produces tonnes of toxic chemical waste.<sup>13</sup> Recently, a general catalyst design principle for furfural hydrogenation has been proposed and summarized to resolve the issues above.<sup>14</sup>

Electrochemical biomass conversion provides several advantages over thermochemical methods:<sup>15,16</sup> (1) they can be coupled to renewable sources of electricity such as wind and solar, (2) the product selectivity can be controlled by simply varying the applied potential, and (3) water can be used as a clean and sustainable proton source instead of hydrogen gas – the majority of which is currently produced from the steam reforming of methane.<sup>17</sup>

Herein, we focus on the electrochemical reduction of furfural, which produces useful chemicals such as furfuryl alcohol (FAL), 2-methylfuran (2-MF) and hydrofuroin (Scheme 1), as well as their fully hydrogenated derivatives. FAL can be used in the production of polymers, 2-MF as a biofuel,<sup>3-6</sup> and hydrofuroin as a precursor to drop-in jet fuel.<sup>18,19</sup> The reported metal catalysts for the electrosynthesis of hydrofuroin mainly consist of Al<sup>7</sup> and Pb.<sup>18,20</sup> However, Pb is known to be toxic and both materials have selectivity issues, producing noticeable amounts of FAL and unselective radical coupling to form useless humin products.<sup>6</sup>

'Single-atom' molecular catalysts (catalysts with a single metal atom per molecule, which is assumed to be the active site) are a promising alternative to transition metal catalysts of nearly 100% atom economy.<sup>21</sup> These catalysts provide well defined active sites, as well as alternate surface adsorption configurations between the electrode and the substrate, distinct from extended metal surfaces. In addition, these catalysts provide a high concentration of active sites with unique binding properties with furfural in comparison with pure metal surfaces. Modifications to the carbon-based frameworks can be easily achieved by adding electron donating and withdrawing groups, which in turn may alter the selectivity of the active sites towards the desired products. This is very difficult to accomplish on extended electrode surfaces. Similar effects have been demonstrated with single-atom catalysts for the CO<sub>2</sub>RR where donating and withdrawing groups had diverse effects on product selectivity.<sup>22,23</sup> Frameworks for single atom catalysts, such as phthalocyanines, are typically made from carbon and nitrogen, which are inexpensive and ubiquitous in nature. For example, cobalt phthalocyanine (CoPc) is a selective catalyst for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), which occurs at a similar reduction potential (-0.5 to -1 V vs. RHE) to furfural reduction.<sup>23</sup> In addition, Cu is a well-known catalyst for the CO<sub>2</sub>RR and is the only known monometallic species which can produce C<sub>2+</sub> products in basic electrolyte,<sup>24</sup> which leads us to hypothesize Cu and even CuPc may be able to form coupling products between two or more furfural molecules under similar conditions. Both CO<sub>2</sub> reduction and furfural reduction could involve the cleavage of a C=O bond. On this basis, we hypothesised that these molecules could also be utilised to reduce furfural into higher value chemicals.

Herein, guided by theoretical calculations, we report singleatom catalysts as highly selective for furfural electroreduction



Scheme 1 Reactions being investigated and the corresponding electrochemical reactor setup. (a) Possible products available from electrochemical furfural reduction. Values of standard reduction potentials were calculated using Nernst equations and shown beneath the arrows (see details in ESI<sup>†</sup>). (b) Schematic of three-compartment cell used for electrolysis experiments.

to hydrofuroin in mildly basic (pH 10) electrolyte. Based on DFT calculations, we map the predicted experimental selectivity for the furfural reduction reaction using the adsorption energy of furfural and hydrogen, which can predict selectivity and aid in providing a basis for future catalyst design and synthesis. Specifically, we predict weak-binding molecular single-atom catalysts, i.e., CuPc and CoPc, are selective towards hydrofuroin, which is limited by the formation of the 'FCHOH' intermediate. The following electrochemical experiments confirm the prediction from theory that CuPc and CoPc display the highest selectivities towards hydrofuroin with low amounts of the hydrogen evolution reaction (HER). Besides, both the firstorder dependence on furfural concentration and even isomer distribution suggests the limiting step is the furfural protonation to FCHOH prior to coupling reaction, which likely happens in the bulk solution.

#### **Methods**

#### **Electrode preparation**

CuPc (99%, Sigma Aldrich) and CoPc (97%, Sigma Aldrich) on multi-walled carbon nanotubes (MWCNTs, 95% Nanocyl) were produced according to the protocol reported by Zhang et al.<sup>23</sup> In brief, Co/CuPc were physisorbed onto the surface of MWCNTs (1:20 Co/CuPc to MWCNT ratio) by sonicating them in an ice bath together in N,N-dimethylformamide (DMF, 99% Sigma Aldrich) for 1 h. After a further 20 h of stirring at room temperature the suspension was filtered under vacuum and washed with copious amounts of DMF, absolute ethanol (Sigma Aldrich), MilliQ water and left to dry at 80 °C overnight. Physisorption onto carbon supports was done to increase conductivity and help the phthalocyanines better adhere to the carbon cloth. The final metal loadings reached a wt/wt% of 1.21-1.65% (Table S2, ESI<sup>†</sup>), which was confirmed using X-ray photoelectron spectroscopy (XPS). The powder was made into an ink consisting of isopropanol (Sigma Aldrich) and MilliQ water (1:5.67 ratio), Nafion<sup>™</sup> ionomer (5 wt%, Sigma Aldrich), which was sonicated for 15 min in an ice bath. The ionomer: catalyst mass ratio was 0.5:1 g respectively. The catalyst ink was dropcasted onto a  $1 \times 1$  cm<sup>2</sup> carbon cloth (Freudenberg, Fuel Cell Stores) to achieve a final loading of 0.10 mg cm $^{-2}$ . Control inks using carbon black (Vulcan XC-72, Cabot) were produced using the same ink ratios. All catalyst loadings in this work were 0.10 mg  $cm^{-2}$ .

#### **Electrochemical experiments**

Electrochemical measurements were performed using an Ivium Vertex One potentiostat. Furfural reduction experiments were carried out in a custom-made three compartment H-cell (Cambridge Glassware) setup with the chambers separated with a Nafion<sup>TM</sup> 117 membrane (Fuel Cell Stores, Scheme 1b). The catholyte was purged using Ar gas (99.998%, BOC) for 20 min before any electrochemistry to remove dissolved oxygen and was not purged for the rest of the experiment. Experiments in pH 10 electrolytes were conducted in a 0.1 M potassium

bicarbonate carbonate buffer. We neglected any local pH changes at high current density in the buffer solution. A saturated Hg/HgSO<sub>4</sub> electrode (SI Analytics) and Au mesh was used as the reference and counter electrode, respectively. The reference electrode was calibrated against the reversible hydrogen electrode (RHE) and thus all potentials are reported using the RHE scale. All glassware was boiled in MilliQ water before use. Cu and Pb foils ( $1 \times 1$  cm<sup>2</sup>, 99.99%, Goodfellow) were prepared by using fine sandpaper and sonicating them in ethanol for 10 min before use.

#### Product analysis

Liquid aliquots (0.5 mL) were taken before and after preparative electrolysis experiments and diluted twice using CH<sub>3</sub>CN for analysis using high performance liquid chromatography (HPLC) which was performed by an Agilent Infinity 1260 II HPLC system (Agilent Technologies) equipped with a UV-Vis detector set at 220 nm. The aliquots were fed through a Zorbax SB C-18 column (4.6  $\times$  50 mm, 3.5-micron, Agilent Technologies). Furfural (99% Sigma Aldrich), FAL (98% Sigma Aldrich) and hydrofuroin were quantified using HPLC by producing calibration curves (Fig. S11, ESI<sup>+</sup>). Hydrofuroin standards were synthesised as no standards were commercially available. The mobile phase was a water: CH<sub>3</sub>CN mixture (88.7:11.3) with a flow rate of 1 mL min<sup>-1</sup> and the column temperature was maintained at 35 °C. Furfural and FAL had retention times of 1.62 and 1.35 min respectively. Hydrofuroin produced two peaks due to two corresponding isomers as expected, having retention times of 1.90 and 4.20 min respectively. A similar retention time between the two isomers is also seen in previous studies using a C18 column.<sup>20</sup> Hydrogen gas was quantified using gas chromatography (GC, SRI Instruments MG#5 with a thermal conductivity detector) connected to a gas outlet on the cell. The effluent was injected into the GC after a stable chronoamperometry was reached, usually after 10 min using argon as a carrier gas. Hydrofuroin standards were synthesised using Mg mediated homo-coupling of furfural following the protocol of Zhang et al.,<sup>25</sup> and both isomers are reported as combined for simplicity. In brief, a mixture of furfural (200 mg, 1.89 mmol) and Mg turnings (1 g, 41 mmol) was stirred at room temperature overnight in 0.1 M NH<sub>4</sub>Cl (99.5%, Sigma Aldrich). The reaction mixture was quenched using 3 M HCl and then was extracted using ethyl acetate (EtOAc). The organic phase was further extracted with saturated NaCl and NaHCO3, which yielded the crude product after rotary vaporisation of the organic solvent. Column chromatography was performed using a gradient of *n*-hexane and EtOAc to yield the pure hydrofuroin confirmed using <sup>1</sup>H NMR in CDCl<sub>3</sub> (38 mg, Fig. S10, ESI<sup>†</sup>). The equations below were used to calculate product selectivity (which we labelled as carbon balance), and faradaic efficiency (FE) for detected products, where the Faraday constant is 96 485 C mol<sup>-1</sup>.

Carbon balance (%) =  $\frac{\text{moles of product formed}}{\text{moles of furfural consumed}} \times 100$ 

Faradaic efficiency (%) =  $\frac{\text{no. electrons transferred} \times \text{moles of product} \times \text{Faraday constant}}{2} \times 100$ 

#### Total charge assed

#### DFT calculations

Spin-polarized density functional theory calculations were conducted using the Vienna ab initio software package (VASP).<sup>26</sup> Core electrons were described by projector augmented wave (PAW) potentials.<sup>27</sup> Valence electrons were described by plane waves with kinetic energy up to 500 eV. To better describe the interaction of furfural molecules with surfaces, the RPBE functional<sup>28</sup> with Grimme's D3<sup>29</sup> was used for dispersioncorrected GGA-DFT<sup>30</sup> calculations, while the HSE06 functional<sup>31</sup> was used for hybrid calculations to benchmark furfural adsorption on molecular catalysts. The lattice for graphene was optimized using a  $12 \times 12 \times 1$  Monkhorst-Pack<sup>32</sup> k-point mesh, while lattices for extended metal surfaces were optimized with a  $12 \times 12 \times 12$  Monkhorst–Pack k-point mesh. All geometries were optimized until forces were less than 0.02 eV  $Å^{-1}$ . Geometries and energies for transition states of coupling reactions were obtained by using the climbing image nudged elastic band (CI-NEB]<sup>33</sup> implemented within VASP at double-sized slab surfaces. Convergence criteria for the climbing image were forces lower than 0.05 eV  $Å^{-1}$ . The solution phase reactions were simulated using Gaussian  $09^{34}$  with B3LYP functional and the 6-311++G(d,p) basis set.35,36 The presence of water was modelled via the SMD variant of Polarizable Continuum Model (PCM) with the integral equation formalism variant.37

Molecular Co/CuPc, graphene and extended metal surfaces were constructed using the atomic simulation environment.<sup>38</sup>  $4 \times 4 \times 4$  slab models *i.e.*, FCC(111) for Ag, Au, Cu, Ni, Pb, Pd, Pt and Rh and HCP(0001) for Co and Ru, were constructed, with the bottom two layers fixed as bulk structures and a 15 Å vacuum spacing at *z* direction (see Fig. S4, ESI†). A large single layer,  $8 \times 12$  graphene was used to model carbon black and CNTs, with a 15 Å vacuum in the *z* direction after a convergence test.<sup>39</sup> To simulate the non-covalently carbon-supported metal-doped phthalocyanines catalysts, we placed a Cu/CoPc molecule on the  $8 \times 12$  graphene sheet to avoid periodic interactions, denoted as "Cu/CoPc" in this work (see Fig. S5a and b, ESI†).

All computational data including optimized structures, calculated energies, trajectories in DFT calculations and Python scripts to reproduce the theoretical figures in the manuscript are available at https://github.com/CatTheoryDTU/molecular\_ catalysts\_for\_furfural\_reduction.

#### ToF-SIMS

Due to hazards of MWCNT with the high extraction field, measurements were taken for CoPc and CuPc physisorbed on carbon black by the same preparation manner. The ToF-SIMS (ION-TOF V GmbH) was operated with a Bi<sub>3</sub><sup>+</sup> primary ion gun at 25 keV and 0.5 pA beam current, with a 5  $\mu$ m spot size on a 100  $\mu$ m  $\times$  100  $\mu$ m field of view, and 256  $\times$  256 pixels rastered in sawtooth mode for 25 min (100  $\mu$ s cycle time). To reduce organic species prevalent on the sample surface prior to ToF-SIMS measurements, samples were non-interlaced sputtered

with a 10 keV  $\operatorname{Ar}_{n}^{+}$  (*n* ranged ~1600–1750 in separate measurements) cluster ion beam at  $\sim 10$  nA current until reaching a dose density of  $1 \times 10^{15}$  ion cm<sup>-2</sup>. For samples measured post-chronoamperometry, the electrochemical testing was conducted without ionomer to avoid ionomer coating the surface. which could affect ion fragment counts. Fresh and postchronoamperometry samples were pressed onto double sided tape prior to ToF-SIMS measurement. The mass resolution at CoPc m/z was >4000. Data was analysed on SurfaceLab 7. Negative spectra were calibrated to C<sub>1</sub><sup>-</sup>, O<sub>1</sub><sup>-</sup>, C<sub>2</sub><sup>-</sup>, C<sub>5</sub><sup>-</sup>, C<sub>10</sub><sup>-</sup>, CoN<sub>2</sub>C<sub>2</sub><sup>-</sup>, CoN<sub>3</sub>C<sub>2</sub><sup>-</sup>, CoN<sub>3</sub>C<sub>3</sub><sup>-</sup>, and CoN<sub>8</sub>C<sub>16</sub>H<sub>32</sub><sup>-</sup>. Positive spectra were calibrated to  $H^+$ ,  $C_1^+$ ,  $C_3H_2^+$ ,  $Cu^+$ , and  $CuN_8C_{16}H_{32}^+$ . Deviation remained <100 ppm for all assigned peaks. Normalisation of peak counts was calculated based on the total ion count across the measured spectrum (870 amu). Samples were measured in four separate locations to generate standard deviation error bars and average normalised counts.

## **Results and discussion**

#### Theoretical investigation of furfural reduction reaction

Earlier works proposed<sup>19,40</sup> that the electroreduction of furfural to hydrofuroin involves two surface-catalysed proton-coupled electron transfer (PCET) to form the precursor intermediate FCHOH and a following chemical coupling reaction:

1. 2FCHO (l) + 2\*  $\leftrightarrow$  2FCHO\*, Furfural adsorption (x2) 2. 2FCHO\* + 2(H<sup>+</sup> + e<sup>-</sup>)  $\leftrightarrow$  2FCHOH\* PCET (x2)

3. 2FCHOH\*  $\leftrightarrow$  Hydrofuroin\* + \* Coupling reaction

4. Hydrofuroin\*  $\leftrightarrow$  Hydrofuroin (l) Hydrofuroin desorption

where \* denotes an unoccupied active site.

The free energy diagram for hydrofuroin formation in Fig. 1a shows that on graphene-supported CoPc and CuPc, pristine graphene and Pb(111), the first PCET step to produce FCHOH\* intermediate from adsorbed furfural (FCHO\*) is potential-determining even at -0.50 V *vs.* RHE. The calculated limiting potentials of CoPc and CuPc are 0.25 and 0.34 V respectively, similar to 0.28 V on Pb and much lower than 0.61 V on graphene, indicating CoPc and CuPc catalysts should reach a reasonable rate (current density) for hydrofuroin formation at lower overpotentials compared to the pristine graphene. Notably, the key intermediate FCHOH\* on those surfaces is not stable and tends to desorb, suggesting a possible desorption–solution radical coupling pathway.

Previous experiments show that different major products of furfural electroreduction reaction could be produced on metal or carbon-based catalysts, which are summarized in Table S1 (ESI<sup>†</sup>). Most of the catalysts could produce FAL, which is especially selective on Pt, Pd, Ni, Cu, Au, and Ag under mild



**Fig. 1** Theoretical calculations for furfural reduction reaction. (a) Free energy diagrams for the surface-catalysed hydrofuroin formation on weakbinding surfaces at -0.50 V vs. RHE. The desorption of FCHOH is referenced to a spin polarised FCHOH• in vacuum as the grey horizontal dotted line. The inset depicts of the calculated surface process to form hydrofuroin, which might be terminated due to desorption of intermediates. The atomistic structure of applied models for extended metal surface, metal-doped phthalocyanine and graphene are shown in Fig. S4 and S5 (ESI†). (b) The reported main products on different catalysts described by adsorption free energies of furfural (FCHO) and hydrogen (H) at standard conditions. The ratio of different colours in a circle indicates the relative selectivity to different products based on the experimental reports summarized in Table S1 (ESI†). Note that the most stable low-index metal surfaces are included here to represent extended metal electrode surfaces. CoPc and CuPc are predicted to be selective to hydrofuroin and alcohol. FAL, MF, and HF are abbreviations for furfuryl alcohol, 2-methylfuran and hydrofuroin respectively. Colour codes in (a): light grey-hydrogen, dark grey-carbon, red-oxygen, blue-nitrogen and pink-cobalt.

conditions. Besides, Cu is reported to be also highly selective to 2-MF in very acidic conditions. Rh and Ru mainly catalyze  $H_2$  production in the presence of furfural in electrolytes. The coupling product, hydrofuroin, could be produced on Al, Pb and pristine carbon electrodes.

Inspired by earlier work of product classification for  $CO_2$  electroreduction,<sup>41</sup> we propose herein that adsorption energies of furfural FCHO\* and H\* could serve as a simple descriptor couple for furfural reduction reaction. In Fig. 1b, several extended metal surfaces (in circles) are mapped out according to these two adsorption energies, with colours representing different major products. Notably, the surfaces binding H\* strongly, *i.e.*, Ru and Rh, produce H<sub>2</sub>. The surfaces lying in the middle of the map are selective to FAL, with Cu as an interesting multifunctional candidate to be able to also produce 2-MF, evidenced by a surface-catalysed PCET mechanism proposed by our recent report.<sup>42</sup> Pb and carbon (using pristine graphene as surface model in calculation), which bind both furfural and H quite weakly, tend to produce hydrofuroin as a major product.

To extend the product mapping to single-atom molecular catalysts, we modelled graphene-supported Cu and Co metal phthalocyanines (Cu/CoPc), which have been investigated for other electrochemical purposes.<sup>43,44</sup> We find that the metal phthalocyanines, binding furfural as weakly as to Pb and pristine graphene, could map into the hydrofuroin-selective region in Fig. 1b. A reason for weak binding on those single atom systems is that furfural only binds to centre metal atoms, with either the furan ring or the –CHO group, while carbon support barely interacts with furfural molecules as shown in Fig. S6a and b (ESI<sup>†</sup>), due to the mismatch of size between

furfural molecule and isolated single atoms. In contrast, their metal extended surface counterparts, *e.g.*, Co(0001) and Cu(111) could interact with both parts of furfural (*cf.* Fig. S6c and d, ESI†), which lead to a much enhanced furfural binding strength. This behavior needs to be considered when applying single atom catalysts to adsorb large biomass derivatives.

Besides, the activation energies for FCHOH\* coupling to form adsorbed hydrofuroin are calculated to scale with FCHO\* binding energy in Fig. S7 (ESI<sup>+</sup>) on extended surfaces, *i.e.*, the weaker binding of furfural, the lower coupling barriers of two FCHOH\*. Furthermore, we simulated the coupling of two spinpolarised FCHOH species in vacuum, shown to be barrierless as illustrated in Fig. S8 (ESI<sup>†</sup>). To better describe radical coupling reaction in solution, we also used Gaussian to calculate the Gibbs free energies of FCHOH• radical reaction in aqueous conditions,<sup>45</sup> and we found that only the dimerisation of FCHOH<sup>•</sup> radicals is exothermic (cf. Fig. S9, ESI<sup>†</sup>). The results presented above suggest that the coupling reaction on molecular catalysts is unlikely to limit the activity of furfural reduction, which can happen in solution via an outer-sphere pathway, as suggested by Liu et al. on a similarly weak-binding Pb electrode.45

Lastly, we highlight the limitation in theory, *i.e.*, solvent effect and electrochemical kinetics were not addressed in our calculations, which might increase uncertainties in the quantitative results illustrated above. However, as suggested by Akinola *et al.*,<sup>46</sup> the solvation correction for those ring-like molecules, *e.g.*, furfural, mainly comes from solvent displacement by competitive adsorption. Given that furfural species takes similar adsorption configurations on considered surface models and the sizes of molecules are barely changed during

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reaction (only –CHO group is reduced), we assume that the solvent effect for the adsorbed species should not change our qualitative trends in reaction energetics here. A more robust description of the reaction of biomass-based chemicals in solutions could improve the accuracy of the theory, *e.g.*, using *ab initio* molecular dynamics (AIMD) simulations to obtain non-transferable solvation energies.<sup>47,48</sup>

In short, our theoretical calculations suggest that molecular single-atom catalysts fall into weak-binding regions for furfural reduction and could be selective towards hydrofuroin formation, which is possibly rate-determined by the protonation of FCHO to form FCHOH intermediate prior to a facile dimerisation possibly in solution.

#### Single-atom catalysts for furfural reduction reaction

Inspired by the DFT prediction, we explored the catalytic performance of those molecular catalysts in experiments. Fig. 2a shows linear sweep voltammograms (LSVs) of various electrode materials before and after the addition of furfural, and the corresponding product profiles (Fig. 2b and c) of Cu and Co phthalocyanines compared to a control, Pb and Cu electrodes, all in pH 10. We see that each cathode material is active towards the furfural reduction reaction including the carbon support as predicted using DFT. The entirely carbon cathode produces hydrofuroin, but with lower activity and with more unaccounted charge than the phthalocyanine containing electrodes, indicating that the metal centre is a key reaction site where the carbonyl group can ligate to, hence the increase in current observed in the constant potential experiment (Fig. 2d), average current density (Fig. 2e) as well as the overall furfural conversion after 1 hour (Fig. 2f). In Fig. 1c, we confirm that Co/CuPc should be more active (smaller overpotentials) than pristine graphene towards hydrofuroin formation. This result agrees with the trend of experimental potentials at -1 mA cm $^{-2}$ in Fig. 2a qualitatively. We also observe an onset potential  $\sim$  40 and  $\sim$  130 mV more anodic for CuPc and CoPc, compared to Pb electrodes, respectively (Fig. S19, ESI<sup>+</sup>), highlighting an important advantage of using these types of materials for furfural reduction over Pb. The quantitative activity mismatch might be due to the material gap between ideal graphene sheet modelled in theory and carbon black/nanotube samples with possible defects or slight impurities in experiment.49,50 The production of hydrofuroin over an extended period of time was monitored by conducting a longer experiment (5 h reaction time) with CoPc. As the experiment progresses, the production of hydrofuroin increases linearly, with a small rise in selectivity over time and minimal amounts of FAL being formed (Fig. S18, ESI<sup>†</sup>). A gradual decrease in current was seen over time and it is primarily attributed to furfural consumption. We also explored the furfural reduction reaction on CoPc and CuPc at varying overpotentials (Fig. S17, ESI<sup>+</sup>). From the results we see a general trend on both catalysts where more cathodic potentials lead to higher FE towards hydrofuroin, whilst decreasing the selectivity towards HER and FAL production. This is likely due to a greater rate of adsorption of furfural at more cathodic potentials, as well as to a higher rate of electron transfer between the



**Fig. 2** Furfural reduction reaction on different electrode surfaces in pH 10 potassium bicarbonate buffer. (a) Linear sweep voltammograms of different cathode materials before (dashed line) and after (solid line) the addition of 8 mM furfural. CoPc and CuPc are adsorbed onto MWCNTs. The onset potential is described as the potential at which a current density of  $-1 \text{ mA cm}^{-2}$  is reached, (b) faradaic efficiencies and (c) carbon balance of detected products measured using HPLC. Calibrations curves of standards located in ESI.† (d) Constant potential measurement of different cathode materials. (e) Average current densities and (f) furfural conversion compared to initial furfural concentration on different cathode materials. Experimental details: 0.1 M potassium bicarbonate–carbonate buffer (pH 10) as electrolyte. Potential applied was -0.50 V vs. RHE for 1 hour for all constant potential experiments. Scan rate: 50 mV s<sup>-1</sup>. Error bars created from two separate experiments. The 'other' products are unidentifiable organic humin products.

electrode and furfural molecules. The maximum estimate for the turnover frequencies (TOFs) for CoPc and CuPc during the experiment was calculated using the method of Mehmood *et al.*<sup>51</sup> Using the metal wt/wt% determined by XPS, the turnover frequencies for CoPc and CuPc were calculated to be  $0.40 \pm 0.10$  and  $0.35 \pm 0.01$  hydrofuroin site<sup>-1</sup> s<sup>-1</sup> respectively. Further details and equations used to calculate TOFs are in the ESI.†

We were unable to identify the major "other" products which we assume account for the unidentified peaks in the HPLC chromatograms. The unidentified products are most likely oligomers of furfural caused by unselective radical coupling or could also be due to ring opening reactions which are known to occur during electrochemical reactions.<sup>52</sup> This problem is not entirely surprising as a similar product distribution for purely carbon electrodes was seen during previous studies on the electrochemical reduction of HMF.<sup>40,53</sup> We find a significant difference in selectivity of reduction products on Cu foil, compared to the single-atom catalysts. On the Cu foil, furfural was reduced primarily into FAL with almost 60% FE, whereas hydrofuroin was the only major product on Pb electrodes with negligible amounts of H<sub>2</sub> as predicted by DFT.

#### Catalyst stability and characterisation

The single-atom Co/CuPc catalysts were characterized to determine their stability. Confirmed by XPS, metal catalyst loading was intentionally kept low to prevent the aggregation of macrocycles into metal clusters or even nanoparticles under reducing potentials.<sup>54</sup> Only some minor clustering of Cu in CuPc was found by scanning-transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX) in Fig. S3 (ESI†). Spectra as well as further discussions of the XPS analysis are provided in the ESI.†

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was selected to probe the stability of CoPc and CuPc and their fragments prior and post constant potential testing, with their counts normalised to the total ion count. Peak assignments in the mass spectrum of CuPc<sup>-</sup> and CoPc<sup>+</sup> are shown in Fig. S13

(ESI<sup>†</sup>). For CoPc, normalised counts of CoPc<sup>-</sup> decreased by 16% between fresh and post chronoamperometry (CA) CoPc, indicating the stability of the CoPc for furfural reduction (Fig. 3b and Fig. S13, ESI<sup>†</sup>). Other prominent fragments containing Co, N and C appearing in the negative mass spectrum show decreases <30% in normalised ion counts before and after CA (Fig. S13, ESI<sup>+</sup>). It should be noted the fragment assigned to Co<sub>2</sub>N<sub>3</sub>C<sub>3</sub> has been previously proposed to originate from µ-cyano bridged CoPc dimers.55 Meanwhile, for CuPc a 67 and 69% reduction in Cu<sup>+</sup> and CuPc<sup>+</sup> normalised counts between fresh and post CA samples are observed, respectively (Fig. 2a and Fig. S13, ESI<sup>†</sup>). This suggests CuPc is removed from the surface of the catalyst during cycling, without too much Cu aggregation after 1 h. The reduced counts of dispersed CuPc across the fresh and post CA sample is also shown by imaging from ToF-SIMS of CuPc<sup>-</sup> ions in Fig. S15 (ESI<sup>†</sup>). These results indicate CuPc is less stable than CoPc towards furfural reduction, which is in line with other studies<sup>56,57</sup> showing that Cu single-atom structures aggregate and deviate from the defined CuPc structure under sufficiently reducing conditions due to their high surface energy. This instability towards aggregation is also likely the reason for the increased amounts of FAL formed on CuPc as Cu nanoparticles yield increased amounts of FAL.<sup>58</sup> The reusability of CoPc was tested through using the same electrode in two separate furfural reduction experiments at -0.50 V vs. RHE for one hour each run. From the LSVs and constant potential measurements (Fig. S20, ESI<sup>+</sup>), there is little change in the current densities from the first and second run, suggesting that CoPc shows a minimal loss in activity over this time.

## Understanding the reaction mechanisms towards hydrofuroin formation

We find that activity of hydrofuroin production follows a firstorder dependence on initial furfural concentration on both CoPc and CuPc catalysts in Fig. 4a, indicating that the coupling step (see free energy diagram in Fig. 1a) should not be the ratedetermining step (RDS). Otherwise, the dependence would be



Fig. 3 ToF-SIMS positive spectrum results of (a) CuPc and (b) CoPc before and after constant potential measurements (1 h at -0.50 V vs. RHE in pH 10 bicarbonate). Fragment counts were normalised to the total ion count with error bars representing standard deviation calculated from four independent measurements in separate locations.



Fig. 4 Mechanistic studies of hydrofuroin production on single-atom catalysts (a) Partial current densities of hydrofuroin production on CuPc and CoPc after 1 h, at -0.50 V vs. RHE constant potential. (b) HPLC chromatogram of 5 mM hydrofuroin standard compared to a reaction mixture of 20 mM furfural in 0.1 M pH 10 potassium bicarbonate buffer after 1 h at -0.50 V vs. RHE. Average peak areas are calculated using integration values from all the initial concentration experiments.

approximately second order. Furthermore, we see in the HPLC chromatogram, a roughly equal distribution of the two isomers of hydrofuroin shown in Fig. 4b. This result further evidences a first-order reaction determining the activity, suggesting the coupling step is quite facile and might even occur in bulk solution, instead of on the electrode surface which could lead to the formation of a specific isomer. This is supported by a recent study which confirmed the presence of the furfuryl radical in solution during the catalytic cycle using electron paramagnetic spectroscopy combined with DFT, using Pb electrodes.45 Accordingly, the reaction energetics in Fig. 1b shows that the protonation of FCHO\* to FCHOH\* is the only endothermic step in hydrofuroin formation pathway and the FCHOH\* tends to desorb on the molecular single-atom catalysts. The possible following radical coupling was modelled by dimerize two isolated FCHOH radical in a large unit cell to form a hydrofuroin molecule, with a barrierless trajectory shown in Fig. S7 (ESI<sup>+</sup>). To better describe radical coupling reaction in solution, we also used Gaussian to calculate the Gibbs free energies of the FCHOH<sup>•</sup> radical reaction in aqueous conditions, and we found that only the dimerization of FCHOH<sup>•</sup> radicals is exothermic as shown in Fig. S9 (ESI<sup>+</sup>). In addition, the similar reaction energetics indicate that CoPc and CuPc should show similar activity/selectivity in the furfural reduction reaction.<sup>59</sup> In short, the experiment and theory combined show that the first PCET step to form the FCHOH intermediate determines hydrofuroin production rather than the later coupling reaction over those weak-binding molecular single-atom catalysts.

Besides, we expected based on the free energy diagram that graphene should display much less activity relative to molecular catalysts at -0.50 V vs. RHE with a more sluggish first PCET step, but the experimental activities (in terms of current densities) in Fig. 2d are not quite different among different materials. This disparity could possibly result from (i). the actual microstructures of the carbon support being different from pristine graphene applied in calculations, where minute impurities are reported to

greatly promote reaction activities;<sup>50</sup> (ii) The uncertainties in DFT calculated energies could amount up to more than 0.2 eV to address the actual electrochemical interface.<sup>60</sup> Consequently, we refrain from making conclusions about the activities among the two molecular catalysts but focus on their unified properties of weak-binding to promote hydrofuroin formation.

Although increasing initial concentrations shows a positive effect of hydrofuroin production (Fig. S16, ESI<sup>†</sup>), we also see that not all the electrons were accounted for useful products with increasing starting concentrations. We show that at higher furfural concentrations the total FE is steadily decreasing, with more unidentifiable peaks becoming apparent in HPLC chromatograms. We rationalise this phenomenon on the basis that there may be a greater likeliness for unwanted humin production as well as furfural degradation at higher concentrations.<sup>40</sup>

From the results demonstrated above, we propose a reaction mechanism (Scheme 2) for the electrochemical production of hydrofuroin from furfural on single-atom molecular catalysts. Assuming the individual phthalocyanine is a flat surface, we may expect a stereoselective synthesis as well as a second-order reaction, *i.e.*, radical coupling occurs on the surface. Thus, if the electrocatalyst can be tuned to facilitate a coupling reaction without desorption, this could open potential avenues to very powerful techniques in the form of stereoselective electrosynthesis. We see some evidence of this from the minor amounts of hydrofuroin formed on Cu electrodes. The relative area from the two hydrofuroin peaks in the chromatograms is almost a 1:3 ratio compared to almost 1:1 on the single-atom catalysts (Fig. S12, ESI†).

In a general aspect, the groupings of selectivity summarized in Fig. 1b offers us a basic template for designing molecular single-atom catalysts for selective reduction of furfural to valueadded products, achieved by tuning the binding energies between the electrode surface and the substrate. For example, we could alter the product distribution on those weak-binding molecular catalysts by changing central metal elements, introducing ligands or co-solvents to stabilize biomass molecules<sup>61</sup>



Scheme 2 Proposed mechanism of hydrofuroin production in furfural reduction on metal-doped phthalocyanine where 'M' represents a metal atom/ ion.

or modifying the local coordination environment by using metal-nitrogen–carbon complex.  $^{\rm 62}$ 

## Conclusions

In this study, we show that single atom molecular catalysts of Cu/Co doped phthalocyanines could electrochemically synthesise hydrofuroin from furfural with high selectivity in a mild pH 10 bicarbonate buffer, which is supported by the theoretical prediction of product distribution for furfural reduction reaction. Combining reaction-order experiment and DFT calculations, we unravel that the rate determining step for hydrofuroin formation is most likely to be the first PCET step, while the chemical coupling step should be quite facile on weak-binding catalysts, consistent with experimental observations. This idea could be applicable to other coupling reaction of biomass molecules. For instance, weakly binding carbon electrodes serves as an excellent catalyst for HMF electrocatalytic dimerization.<sup>40</sup>

Following this work, we outline one of the key factors for single-atom catalyst design in furfural reduction reactions is the adsorption strength of furfural on active sites. Should we find a catalyst binding furfural significantly stronger than graphene, CuPc and CoPc, we envisage that we may enable the selective production of FAL or even 2-MF under acidic conditions. The theoretical and experimental insights obtained in this work could aid in catalyst design for broad biomass electrovalorisation.

## Author contributions

Z. M. and S. L. contributed equally; Z. M. designed and carried out all the electrochemical experiments, catalyst preparations and product analysis. S. Ch. S. helped develop the method for HPLC measurements. S. L. carried out DFT studies and postprocessed computational data; S. M. designed the electrochemical cell; J. B. conducted XPS experiments and analysed the data; A. P. and S. F. designed and completed ToF-SIMS experiments; Z. M. and S. L. wrote the original manuscript; All authors contributed in writing review and editing; K. C., S. B. S, S. M., M. M. T., I. E. L. S. and I. S. contributed in supervision; K. C. contributed in funding acquisition for computation.

## Conflicts of interest

There are no conflicts to declare.

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