

Computational Studies of Pd-based Hydride Catalysts for CO₂ Reduction

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Computational Studies of Pd-based Hydride Catalysts for CO₂ Reduction

Changzhi Ai PhD Thesis, August 2023



CHANGZHI AI

Computational Studies of Pd-based Hydride Catalysts for CO₂ Reduction

PhD Thesis August 2023



Department of Energy Conversion and Storage Technical University of Denmark

Computational Studies of Pd-based Hydride Catalysts for CO₂ Reduction

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Preface

This thesis is submitted in candidacy for a Doctor of Philosophy (PhD) degree from the Technical University of Denmark (DTU). The work has been carried out between September 2020 and August 2023 at the Section for Atomic Scale Materials Modelling at the Department of Energy Conversion and Storage. These studies have been supervised by Associate Professor Heine Anton Hasen and Professor Tejs Vegge. Part of the work was carried out during a 3-month external stay at Brown University hosted by Associate Professor Andrew Peterson. Financial support was provided by the China Scholarship Council and the Villum Foundation through the research center V-Sustain (#9455).

Kongens Lyngby, August 2023 Changzhi Ai

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Abstract

Emission of the greenhouse gas carbon dioxide (CO_2) has increased rapidly with the development of industrialization in the past decades. The electrochemical CO_2 reduction reaction (CO_2RR) is considered as a promising strategy to convert CO_2 into valuable chemicals. Palladium (Pd)-based hydride catalysts hold promise for producing syngas via both CO_2RR to CO and hydrogen evolution reaction (HER) to H₂, which can be effectively synthesized into valuable chemicals. In this thesis, Pd-based hydride catalysts are systematically studied to improve the CO_2RR performance of pure Pd hydride (PdH) by doping and alloying methods with various theoretical approaches.

First, density functional theory (DFT) is used to systematically screen for stability, activity, and selectivity of transition metal dopants in PdH(111). Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re are doped into PdH surface with six different doping configurations: single, dimer, triangle, parallelogram, island, and overlayer. We find that several dopants, such as Ti and Nb, have excellent predicted catalytic activity and selectivity towards CO₂RR compared to the pure PdH.

Second, using DFT calculations in combination with active learning cluster expansion (ALCE) and Monte Carlo simulated annealing (MCSA), we identify 12 stable PdH_x(111) configurations on the DFT convex hull and investigate the binding energies of intermediates during the CO₂RR and the competing HER. Through analysis of intermediate binding energies and a microkinetic model, we identify the atomic structures of the PdH_x phase most likely to produce syngas. The high activity of the PdH_{0.6} surface can be attributed to the fact that the H segregation in the PdH_x(111) surface breaks the linear relation between HOCO^{*} and CO^{*} adsorbates.

Third, an ALCE surrogate model equipped with MCSA, CO* filter and the kinetic model are used to screen out excellent $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ catalysts with both high stablity and superior activity. Since the calculations of the convex hull are finally verified by DFT and all binding energy calculations of the limited candidates are also calculated by DFT, the calculations of all enregies are more reliable compared to those only using the surrogate model with uncertainty. Finally, the stable and active 24 candidates of $Pd_xTi_{1-x}H_y$ and 6 active candidates of $Pd_xNb_{1-x}H_y$ are found according to our approach.

Finally, a deep learning-assisted multitasking genetic algorithm is used to screen $Pd_xTi_{1-x}H_y$ surfaces containing multiple adsorbates for CO_2RR under different reaction conditions. The ensemble deep learning model can greatly speed up the structure relaxations and keep a high accuracy as well as low uncertainty of energies and forces. The multitasking genetic algorithm is used to simultaneously globally find stable surface structures at each reaction conditions. Finally, 23 stable structures are screened out under different reaction conditions. Among them, $Pd_{0.56}Ti_{0.44}H_{1.06}+25\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+50\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+25\%CO$, and $Pd_{0.88}Ti_{0.12}H_{1.06}+25\%CO$ are found to be very active for CO_2RR and suitable to generate syngas.

Resumé

Emission af drivhusgassen kuldioxid (CO₂) er steget hurtigt med udviklingen af industrialisering i de seneste årtier. Den elektrokemiske CO₂-reduktionsreaktion (CO₂RR) betragtes som en lovende strategi til at omdanne CO₂ til værdifulde kemikalier. Palladium (Pd)-baserede hydridkatalysatorer virker lovende for at producere syngas via både CO₂RR til CO og hydrogenudviklingsreaktionen (HER) til H₂, som effektivt kan syntetiseres til værdifulde kemikalier. I denne afhandling undersøges Pd-baserede hydridkatalysatorer systematisk for at forbedre CO₂RR-ydelsen af ren Pd-hydrid (PdH) ved hjælp af doping og legering, hvilket undersøges med diverse teoretiske metoder.

Først og fremmest bruges "density functional theory" (DFT) til systematisk at screene for stabilitet, aktivitet og selektivitet af overgangsmetalsdoping i PdH(111). Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W og Re dopes ind i PdHoverfladen med seks forskellige konfigurationer: enkel, dimer, trekant, parallelogram, ø og overlag. Vi finder flere dopanter, såsom Ti og Nb, der viser fremragende katalytisk aktivitet og selektivitet mot CO_2RR sammenlignet med ren PdH.

Samtidig, ved at bruge DFT-beregninger i kombination med "Active Learning Cluster Expansion" (ALCE) og Monte Carlo "Simulated Annealing" (MCSA) identificerer vi 12 stabile PdH_x(111) konfigurationer på den konvekse kurve fra DFT og undersøger bindingsenergierne af intermediater for CO₂RR samt den konkurrerende HER. Ved analyse af intermediære bindingsenergier, kombineret med en mikrokinetisk model, identificerer vi de atomare strukturer af PdH_x-fasen, der har højest sandsynlighed for at producere syngas. Den høje aktivitet af overfladen på PdH_{0.6} kan tilskrives, at hydrogensegregation på PdH_x(111) overfladen bryder den lineære relation mellem HOCO* og CO* adsorbater.

Derudover bruges en ALCE surrogatmodel udstyret med MCSA, CO*-filter og den kinetiske model til at identificere fremragende $Pd_xTi_{1-x}H_y$ og $Pd_xNb_{1-x}H_y$ katalysatorer, der både viser høj stabilitet og overlegen aktivitet. Da beregningerne af den konvekse kurve verificeres med DFT, og alle bindingsenergiberegninger for de indsnævrede kandidater også udføres med DFT, er beregningerne af alle energier mere pålidelige i forhold til kun at bruge surrogatmodellen med dens usikkerhed. Ved brug af vores tilgang finder vi 24 stabile og aktive $Pd_xTi_{1-x}H_y$ kandidater og 6 $Pd_xNb_{1-x}H_y$.

Endelig bruges en deep learning-assisteret multitaskende genetisk algoritme til at screene for $Pd_xTi_{1-x}H_y$ overflader, med flere adsorbater for CO_2RR under forskellige reaktionsbetingelser. Ensemble deep learning-modellen kan accelerere strukturrelaktionerne og opretholde høj nøjagtighed og lav usikkerhed for både energier og kræfter. Den multitaskende genetiske algoritme bruges til simultant at lede globalt efter stabile overfladestrukturer ved hver eneste reaktionstilstand. Til sidst identificeres 23 stabile strukturer ved forskellige reaktionsbetingelser. Blandt dem er: $Pd_{0.56}Ti_{0.44}H_{1.06}+25\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+50\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+25\%CO$ og $Pd_{0.88}Ti_{0.12}H_{1.06}+25\%CO$. Disse har vist sig at være meget aktive for CO_2RR og er derfor egnede til at generere syngas.

List of Publications

Paper I

Metal-doped PdH(111) catalysts for CO₂ reduction Changzhi Ai, Tejs Vegge and Heine Anton Hansen *ChemSusChem*, **2022**, 15, e202200008

Paper II

Impact of hydrogen concentration for CO_2 reduction on PdH_x : A combination study of cluster expansion and kinetics analysis Changzhi Ai, Jin Hyun Chang, Alexander Sougaard Tygesen, Tejs Vegge and

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Preprint: https://doi.org/10.26434/chemrxiv-2023-kkk48-v2

Paper III

High-throughput compositional screening of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ hydrides for CO_2 reduction Changzhi Ai, Jin Hyun Chang, Alexander Sougaard Tygesen, Tejs Vegge and Heine Anton Hansen

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Paper IV

Graph neural network-accelerated multitasking genetic algorithm for optimizing $Pd_xTi_{1-x}H_y$ surface under various CO_2 reduction reaction conditions <u>Changzhi Ai</u>, Shuang Han, Xin Yang, Tejs Vegge and Heine Anton Hansen <u>Preprint: https://doi.org/10.26434/chemrxiv-2023-0kjx4</u>

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Chapter 1 Introduction

Greenhouse gas CO₂ emissions are the primary driver of global climate change with the development of industrialization in the past decades.[1, 2] It is widely recognized that it is urgent to reduce CO₂ emissions as parties to the Paris Agreement agreed "the increase in the global average temperature to well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase to below 1.5 °C above pre-industrial levels."[3, 4] The utilization of renewable energy sources such as wind and solar energies is gradually increasing to generate electricity, and the utilization cost is decreasing. However, there are still significant challenges in storing the generated electrical energy.[5, 6] In order to overcome this challenge, the three strategies including decarbonization, carbon sequestration, and carbon recycling will play crucial roles in mitigating net CO₂ emissions.[7] The CO₂ utilization technology of the electrochemical CO₂RR is considered as a promising strategy to convert CO₂ into valuable chemicals as it is not only beneficial to carbon recycling but also conducive to increasing chemical energy storage.[8–11]



1.1 Electrochemical CO₂ reduction

Figure 1.1: Schematic diagrams of three different CO₂RR electrolyzers: (a) H-cell, (b) flow-cell, and (c) MEA-cell.[12]

Three typical electrochemical CO_2RR electrolyzers are shown in Figure 1.1. The CO_2RR process in the H-cell electrolyzer can be seen in Figure 1.1a. The anode (left) and the cathode (right) compartments are separated by an ion exchange membrane to avoid the re-oxidation of generated products over the anode. The electrode with loaded catalysts acts as the cathode or working electrode (WE), where the protons across the

membrane from the anode and CO₂ adsorbed on the electrode can generate chemical products under a given potential. This process is actually the electrochemical CO₂RR. A reference electrode (RE) close to WE is used as the potential reference to control the applied potential to WE, and a saturated calomel electrode is usually utilized. The corresponding oxygen evolution reaction (OER) happens at the anode or counter electrode (CE), where a Pt mesh or carbon electrode is usually used. Gas products can be analyzed by a gas chromatograph (GC).[13] Due to low upper current density in aqueous electrolytes and the huge Ohmic resistance caused by the large distance between anode and cathode in the H-cell, the flow-cell and membrane electrode assembly cell (MEAcell) are proposed to overcome these issues as shown in Figure 1.1b-c. Both cells use continuous gas and liquid feeds and the gas diffusion electrode (GDE), which makes the electrochemical CO₂RR directly happen in gas-liquid-solid interfaces. Compared to the flow cell, the MEA-cell does not have the liquid electrolyte layer between the cathode and membrane, and instead, it directly utilizes the thin membrane as a solid electrolyte. This can greatly reduce the low Ohmic resistance and thus improve energy efficiency for the MEA-cell. In short, the H-cell is suitable for fundamental CO₂RR studies, while the MEAcell has the potential to realize the industrialization of the electrochemical CO₂RR.[12, 14, 15]

1.2 Electrocatalysts for CO₂ reduction

Significant efforts have been made to reduce CO_2 to $C_1 - C_3$ products including formic acid (HCOOH, 2-electron product)[16, 17], carbon monoxide (CO, 2-electron product)[18–20], methane (CH₄, 8-electron product)[21–24], acetaldehyde (CH₃CHO, 10-electron product)[25], ethylene (C_2H_4 , 12-electron product)[26, 27], methylglyoxal (C₃H₄O₂, 12-electron product)[28], and ethanol (C₂H₅OH, 12-electron product)[29–31], propanol (C₃H₇OH, 18-electron product)[32]. In general, the pathways of the higher number of electron products are long, and their conversion efficiencies are usually very low. This is because a long reaction pathway makes the process complex and arduous to manipulate.[23] The conversion efficiency of CO₂RR for synthesizing multiple-electron products (C_2 and C_3), in particular, is far from the level viable for practical productions due to the consumption of a lot of electrons and protons in long pathways. [23, 33] In contrast, the Faradaic efficiencies of 2-electron products (CO or HCOO⁻) are usually higher than other products due to the short reaction pathways. Compared to liquid HCOO⁻, CO is a gas that is easier to separate, and thus, reducing CO₂ to CO appears to be more achievable. However, high overpotential is generally required due to the high stability of CO₂. Under the high overpotential, the competitive HER will also likely produce H₂. Many efforts have been made to suppress the HER, such as designing various electrocatalysts and electrodes, thus promoting high selectivity for the CO₂RR.[34] Because gas products (CO and H₂) are difficult to be separated, an alternative to finding highly selective catalysts is to tune the CO/H₂ ratio. This is because CO and H₂, as the main components of syngas, can be used as downstream reactants to synthesize many basic organic chemicals and intermediates through the Fischer-Tropsch processes.[35, 36] Therefore, it is

crucial to find efficient electrocatalysts to produce syngas with a suitable CO/H₂ ratio.

Stability, activity, and selectivity of the catalysts during the electrochemical process are usually considered.[37] Numerous previous works have been done to study metal catalysts for the CO₂RR.[22, 38] Pure transition metal catalysts are usually stable and active for CO₂RR at room temperature, but their selectivities are quite different. Pure metal catalysts can be grouped into four categories based on the selectivity: (I) Cu is classified as its own category because it is the only metal that can simultaneously reduce CO₂ to multiple hydrocarbons and multi-carbon products such as CH₄, C₂H₄ and C₃H₇OH.[11, 22, 39–43] (II) Pb, Hg, Tl, and In are most likely to produce formate (HCOO⁻) and the Faradaic efficiency of the products are over 90 %.[4] (III) Ni, Fe, Pt, and Ti produce H₂ without producing or producing only a minor amount of hydrocarbons (the Faradaic efficiency of H_2 over 90 %) via HER.[4] (IV) Au, Ag, Zn and Pd mainly reduce CO₂ to CO.[44–50] For example, Au nanoparticles formed from thick Au oxide films were reported to have high selectivity for CO₂RR to CO at 140 mV overpotential and they kept their activity for no more than 8 hours.[51] Ag nanoparticles supported on carbon have been reported to show good Faradaic efficiency of CO and low overpotential.[50] In addition, metal-nitrogen-carbon (M-N-C) electrocatalysts with high faradaic efficiencies for CO generation are also popular in the field of CO₂RR.[52–54] Among them, Fe-N-C electrocatalyst shows high selectivity and activity towards CO at low overpotentials (0.3~0.5 V). Ni-N-C electrocatalyst exhibits good selectivity and activity at higher overpotentials because it is more favorable towards HER. Co-N-C electrocatalyst has a lower selectivity for CO throughout the entire potential range [55, 56] It is worth pointing out that palladium (Pd) was reported to be a potential candidate for CO₂RR to CO.[41, 57] Moreover, Chen et al. thought the Pd catalyst was more suitable to produce syngas (CO and H_2) compared to other metals. They found that the reason why Pd showed good activity and selectivity during CO₂RR was that the Pd metal catalyst was transformed into palladium hydride (PdH). [58] The formation of PdH would significantly improve the Faradaic efficiencies of syngas products. Furthermore, the PdH(111) surface experimentally exhibited higher current density and Faradaic efficiency compared with other crystal surfaces.[58] Subsequently, in order to further improve the performance of PdH, several approaches, such as applying transition metal nitrides as promising supports and using bimetallic catalysts, have been explored in recent years.[59]

Our works are dedicated to improving CO_2RR performance of Pd hydride through doping transition metal element, tuning H concentration in PdH_x, and constructing Pd-based alloy hydrides using computational methods. They will be introduced explicitly in the following chapters.

1.3 Outline of thesis

This thesis comprises seven chapters and is structured as follows:

Chapter 1 - Introduction

The electrochemical CO₂RR technique and the experimental process are intro-

duced. Common catalysts, such as transition metals, metal-nitrogen-carbon, and Pd-based hydrides for CO_2RR are discussed in this chapter.

Chapter 2 - Theory and Methods

The computational theory and methods used in this thesis are introduced in this chapter, including density functional theory, cluster expansion, machine learning potential, local optimization, global optimization, microkinetic model, and high throughput screening workflow.

Chapter 3 - Metal-doped PdH(111)

In this chapter, doped PdH(111) is investigated by DFT for improving CO_2RR performance of pure PdH(111). Transition metal elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W and Re are doped into the PdH(111) surface in different doping configurations to explore their catalytic stability, activity, and selectivity towards CO_2RR and HER.

Chapter 4 - PdH_x(111)

The effect of hydrogen concentration in $PdH_x(111)$ on the CO₂RR is presented in this chapter. An active learning cluster expansion (ALCE) method combined with Monte Carlo simulated annealing (MCSA) is used to shed light on H concentrations of PdH_x relationship between atomic scale structure, stability, kinetic activity, and selectivity.

Chapter 5 - PdMH(111)

Based on the suggestion of doped elements in Chapter 3, the alloy hydrides of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ for CO_2RR are studied by the ALCE+MCSA method in this chapter. The promising candidates with different concentrations of Ti, Nb, and H are identified.

Chapter 6 - PdTiH(111) with Adsorbates

 $Pd_xTi_{1-x}H_y$ surfaces with multiple adsorbates for CO₂RR at various reaction conditions are explored by a graph neural learning-assisted multi-tasking genetic algorithm. All candidates at each reaction condition are screened out after the global optimization.

Chapter 7 - Conclusions and Outlook

The main conclusions in this thesis and outlook on the further improvement of our works are given in this chapter.

Chapter 2 Theory and Methods

This chapter gives introductions to various computational theory and methods. Density functional theory, cluster expansion method, machine learning potential, local optimization, global optimization, microkinetic model, and high-throughput screening workflow are introduced in detail.

2.1 Density functional theory

Matter is actually a collection of atoms. The description of the physical and chemical properties of matter is a crucial issue that plenty of scientists have been exploring. Based on quantum mechanics, density functional theory (DFT) is a remarkable approach to finding the solution that establishes a link between the properties of matter and atomic structures. Some excellent books are referenced in this section, for example, the book on electronic structures gives the basic theory and practical methods by Martin[60] and the book on electronic structure calculations for solids and molecules gives the theory and computational methods by Kohanoff.[61] The detailed introduction of DFT can be found in the books of a practical introduction of density functional theory by Sholl and Steckel[62], and a chemist's guide to density functional theory by Koch and Holthausen.[63] Here, the fundamental concepts in DFT are briefly introduced.

2.1.1 Schrödinger equation

In principle, all properties of matter can be derived by solving the time-independent, non-relativistic Schrödinger equation. The ultimate goal of most quantum chemistry methods is to solve the approximate Schrödinger equation:[63]

$$\hat{H}\Psi_i(\vec{X}_1, \vec{X}_2, ..., \vec{X}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N) = E_i \Psi_i(\vec{X}_1, \vec{X}_2, ..., \vec{X}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N)$$
(2.1)

where \hat{H} is the Hamilton operator for a system with N electrons and M nuclei. Ψ_i represents the wave function of the *i*th state of the system, which depends on $\vec{X}_1, \vec{X}_2, ..., \vec{X}_N$ and $\vec{R}_1, \vec{R}_2, ..., \vec{R}_N$ that are the coordinates of the N electrons and M nuclei, respectively. The wave function Ψ_i contains all information in the quantum system. E_i represents the numerical value of the energy of the *i*th state Ψ_i . Among them, \hat{H} operator can be expressed as the total energy:

$$\hat{H} = \hat{T}_{e} + \hat{T}_{n} + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}$$
(2.2)

where i and j run over the N electrons while A and B run over the M nuclei. The first two terms in equation 2.2 are the kinetic energies of the electrons and nuclei, respectively.

The remaining three terms are the potential of the Hamiltonian, the electrostatic attraction interaction between the electrons and the nuclei, and the Coulomb repulsion interaction between the electrons and the electrons as well as between the nuclei and the nuclei in the system, respectively. r_{iA} , r_{ij} and R_{AB} are the corresponding distances and ∇^2 is the Laplacian operator. Z_A and Z_B are the nuclear charges and M_A is the mass of A.

2.1.2 Born-Oppenheimer approximation

Considering the significant difference between the mass of electrons and nuclei, the Schrödinger equation can be further simplified. The electrons move much faster than the nuclei. Taking the extreme point of view, we can think nuclei are not moving and the electrons are moving in the field of fixed nuclei, which is the famous Born-Oppenheimer approximation.[64] Under the approximation that the positions of the nuclei are fixed in space, the kinetic energy of the nuclei is zero and the potential energy is a constant since the nucleus-nucleus repulsion does not change. Therefore, the complete Hamiltonian in Equation 2.2 can be simplified to the so-called electronic Hamiltonian¹:

$$H_{e} = T_{e} + V_{en} + V_{ee}$$

= $-\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$ (2.3)

The wave function Ψ of the system in Equation 2.1 can be splited into the electronic wave function Ψ_{e} and the nuclei wave function Ψ_{n} :

$$\Psi(\vec{X}_1, \vec{X}_2, ..., \vec{X}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N) = \Psi_e(\vec{X}_1, \vec{X}_2, ..., \vec{X}_N)\Psi_n(\vec{R}_1, \vec{R}_2, ..., \vec{R}_N)$$
(2.4)

The Schrödinger equation for the electrons can be expressed as:

$$\hat{H}_{\mathsf{e}}\Psi_{\mathsf{e}} = E_{\mathsf{e}}\Psi_{\mathsf{e}} \tag{2.5}$$

The solution of Schrödinger equation for \hat{H}_{e} includes the electronic wave function Ψ_{e} and electronic energy E_{e} . The electronic wave function Ψ_{e} is only dependent on the electron coordinates, while the nuclei coordinates do not appear in Ψ_{e} and only parametrically enter. Besides, the total energy E_{tot} of the system is the sum of electronic energy E_{e} and nucleus-nucleus repulsion potential energy \hat{V}_{nn} or E_{n} :

$$E_{\text{tot}} = E_{\text{e}} + E_{\text{n}} \tag{2.6}$$

2.1.3 Hohenberg-Kohn theorems

It should be mentioned that the wave function Ψ is not observable² and it can be represented as the form of the electron density $\rho(\vec{r})$, which is a multiple integral over all

 $^{{}^1\}hat{V}_{
m en}$ in the Hamiltonian is also termed as the external potential $V_{
m ext}$ in density functional theory.

²From now on, only the electronic Schrödinger equation is discussed and thus the subscript 'e' will be dropped.

spin coordinates of the electrons but one of the spatial variables:

$$\rho(\vec{r}) = N \int \cdots \int |\Psi(\vec{X}_1, \vec{X}_2, ..., \vec{X}_N)|^2 ds_1 d_{\vec{X}_1} \cdots d_{\vec{X}_N}$$
(2.7)

The density functional theory from wave function to electron density was introduced in 1964 when two fundamental mathematical theorems were proved by Kohn and Hohenberg.[65]

Theorem 1: For any system of interacting particles, the external potential \hat{V}_{ext} , and hence the ground-state energy from Schrödinger equation is a unique functional of the electron density $\rho(\vec{r})$.

Based on reductio ad absurdum, the first Hohenberg-Kohn theorem proves that it is impossible that two different \hat{V}_{ext} yield the same ground-state electron density. The complete ground state energy can be expressed as a functional of the ground state electron density:

$$E_{0}[\rho_{0}] = T[\rho_{0}] + E_{en}[\rho_{0}] + E_{ee}[\rho_{0}]$$

$$= \underbrace{\int \rho_{0}(\vec{r}) V_{en} d\vec{r}}_{\text{system dependent}} + \underbrace{T[\rho_{0}] + E_{ee}[\rho_{0}]}_{\text{universally valid}}$$
(2.8)

where the first term is the potential energy of nuclei-electron attraction and it depends on the actual system. $T[\rho_0]$ and $E_{ee}[\rho_0]$ are universal³ by construction and independent on the system. They can be combined into the Hohenberg-Kohn functional $F_{HF}[\rho_0]$ and the Equation 2.8 can be rewritten as:

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{\text{en}} d\vec{r} + F_{\text{HF}}[\rho_0]$$
(2.9)

Theorem 2: The total system energy gives its minimum value if the input density is the ground state density.

In other words, the total energy is the lowest energy of the system, namely ground state energy $E_0[\rho_0]$ if the electronic density is the ground state density ρ_0 , and thus the variational principle can be expressed as the following:

$$E_{0}[\rho_{0}] = \langle \Psi_{0} | \hat{H} | \Psi_{0} \rangle \leq E[\tilde{\rho}] = T[\tilde{\rho}] + \int \tilde{\rho}(\vec{r}) V_{en} d\vec{r} + E_{ee}[\tilde{\rho}] = \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$$
(2.10)

where the quantities with tilde mean any trial quantities, while the quantities with subscript zero mean the ground state.

2.1.4 Kohn-Sham equations

The Kohn–Sham approach is to replace the difficult problem of interacting many-body electrons with a set of noninteracting electrons that can be solved more easily.[66]

A rigorous many-body theory can be built by the Hohenberg-Kohn theorems using

³"universal" means the same for all electron systems, which is independent of the external potential $V_{\text{ext}(r)}$.

electron density as the fundamental quantity. The ground state energy can be shown as:

$$E_{0} = \min_{\rho \to N} \left(F[\rho] + \int \rho(\vec{r}) V_{\text{en}} d\vec{r} \right)$$
(2.11)

where $F[\rho]$ is the universal functional, which includes the kinetic energy, the classical Coulomb interaction, and the non-classical part consisting of self-interaction correction, exchange, and electron correlation effects as follows:

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + E_{ee}[\rho(\vec{r})]$$

= $T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{nonc}[\rho(\vec{r})]$ (2.12)

The idea of Kohn and Sham is to introduce the following separation for the kinetic energy:

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + E_{ee}[\rho(\vec{r})]$$

= $T_{S}[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$ (2.13)

where $T[\rho(\vec{r})]$ is split into $T_{\rm S}[\rho(\vec{r})]$ the non-interacting kinetic energy and the residual part. As Equation 2.12 does, $E_{\rm ee}[\rho(\vec{r})]$ is also split into two parts: $J[\rho(\vec{r})]$ the classical Coulomb interaction or Hartree energy and the residual part. $E_{\rm XC}[\rho(\vec{r})]$ is exchange-correlation energy and defined as the following:

$$E_{\rm XC}[\rho] = (T[\rho] - T_{\rm S}[\rho]) + (E_{\rm ee}[\rho] - J[\rho]) = T_{\rm C}[\rho] + E_{\rm nonc}$$
(2.14)

where $T_{\rm C}[\rho]$ and $E_{\rm nonc}$ are the residual part of the true kinetic energy and the true electronelectron interaction, respectively. In other words, exchange-correlation energy $E_{\rm XC}[\rho(\vec{r})]$ contains everything unknown, which means we do not know how to calculate it exactly. We finally arrive at the following equation:

$$E_{\rho(\vec{r})} = T_{\mathsf{S}}[\rho] + J[\rho] + E_{\mathsf{XC}}[\rho] + E_{\mathsf{en}}[\rho]$$

$$= T_{\mathsf{S}}[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r_{1}})\rho(\vec{r_{2}})}{r_{12}} d\vec{r_{1}} d\vec{r_{2}} + E_{\mathsf{XC}}[\rho] + \int \rho(\vec{r}) V_{\mathsf{en}} d\vec{r}$$

$$= -\frac{1}{2} \sum_{i}^{\mathsf{N}} \langle \varphi_{i} | \nabla^{2} | \varphi_{i} \rangle + \frac{1}{2} \sum_{i}^{\mathsf{N}} \sum_{j}^{\mathsf{N}} \iint |\varphi_{i}(\vec{r_{1}})|^{2} \frac{1}{r_{12}} |\varphi_{j}(\vec{r_{2}})|^{2} d\vec{r_{1}} d\vec{r_{2}} \qquad (2.15)$$

$$+ E_{\mathsf{XC}}[\rho(\vec{r})] - \sum_{i}^{\mathsf{N}} \int \sum_{A}^{\mathsf{M}} \frac{Z_{A}}{r_{1A}} |\varphi_{i}(\vec{r_{1}})|^{2} d\vec{r_{1}}$$

where the only unknown term without explicit form is E_{XC} in this equation. Similarly to the Hartree-Fock approximation[67], the variational principle is applied and the famous Kohn-Sham equation (KS equation) can be derived as follows (a detailed derivation can

be seen in the book of Parr and Yang [67]):

$$\left(-\frac{1}{2}\nabla^{2} + \left[\int \frac{\rho(\vec{r_{2}})}{r_{12}} d\vec{r_{2}} + V_{\mathsf{XC}}(\vec{r_{1}}) - \sum_{A}^{\mathsf{M}} \frac{Z_{A}}{r_{1A}}\right]\right)\varphi_{i}$$

$$= \left(-\frac{1}{2}\nabla^{2} + V_{\mathsf{eff}}(\vec{r})\right)\varphi_{i} = \varepsilon_{i}\varphi_{i}$$
(2.16)

where the terms in the square bracket can be represented as effective potential V_{eff} . The first term of the effective potential is the classical Hartree potential. The last term is external potential due to nuclei. V_{XC} defines the exchange and correlation contributions to the single electron KS equations. It can be expressed as a functional derivative of the exchange-correlation energy:

$$V_{\rm XC}(\vec{r}) = \frac{\delta E_{\rm XC}(\vec{r})}{\delta \rho(\vec{r})}$$
(2.17)

Non-interacting electrons are described by orbitals in the KS scheme. $\varphi_i(\vec{r})$ corresponds to the *i*th one-electron Kohn-Sham orbital of energy ε_i . The election density $\rho(\vec{r})$ can be given by:

$$\rho(\vec{r}) = \sum_{i}^{N} |\varphi_i(\vec{r})|^2$$
(2.18)

2.1.5 Exchange-correlation functionals

All unknown parts are collected into the exchange-correlation functional $E_{XC}(\vec{r})$ in the KS equation. The quality of the density functional method highly depends on the accuracy of the chosen exchange-correlation functional. If $E_{XC}(\vec{r})$ is exact, the KS equation would yield exact ground state energy and electron density. In fact, approximations are needed for the calculation of $E_{XC}(\vec{r})$. The two most common functionals are the local density approximation (LDA)[68] and the generalized gradient approximation (GGA)[69, 70].

The local density approximation (LDA)

The LDA is the simplest approximation proposed by Kohn and Sham in 1965. In the LDA, the key to the idea is a hypothetical uniform electron gas (UEG).[71] In this case, the electron density is considered constant at all points in space. In this system, valence electrons move on positive cores that arrive at a uniform positive background charge distribution. To do this, we assume the exchange-correlation energy is known at each observed position and from the UEG, and the energy is weighted by the probability $\rho(\vec{r})$. This approach is defined as the local density approximation (LDA). The total exchange-correlation energy $E_{\rm XC}^{\rm LDA}(\rho)$ can be given by a very simple form:

$$E_{\rm XC}^{\rm LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{\rm XC}^{\rm UEG}(\rho(\vec{r})) d\vec{r}$$
(2.19)

where $\varepsilon_{\text{XC}}^{\text{UEG}}(\rho(\vec{r}))$ is the exchange-correlation energy per particle of a UEG of density $\rho(\vec{r})$. The $\varepsilon_{\text{XC}}^{\text{UEG}}(\rho(\vec{r}))$ term can be further separated into the exchange part and the correlation part:

$$\varepsilon_{\mathsf{XC}}^{\mathsf{UEG}}(\rho(\vec{r})) = \varepsilon_{\mathsf{X}}(\rho(\vec{r})) + \varepsilon_{\mathsf{C}}(\rho(\vec{r}))$$
(2.20)

where $\varepsilon_{X}(\rho(\vec{r}))$ can be calculated from the Hartree-Fock exchange by Slater [67] and it is given by:

$$\varepsilon_{\mathbf{X}}(\rho(\vec{r})) = -\frac{3}{4} \sqrt[3]{\frac{3\rho(\vec{r})}{\pi}}$$
(2.21)

Correlation part $\varepsilon_{C}(\rho(\vec{r}))$ cannot be given by an explicit expression. However, the most accurate correlation calculations are based on the quantum Monte-Carlo simulations of the UEG In fact, the UEG model is a very good approximation for simple metals such as sodium, but it is worse for any realistic system such as complex atoms and molecules.

The generalized gradient approximation (GGA)

The LDA was the only $E_{\rm XC}$ approximation available for many years in the field of solid-state physics but not computational chemistry. This situation improved significantly until the development of the generalized gradient approximation (GGA). The functional includes not only the information about the electron density $\rho(\vec{r})$ at a specific point \vec{r} but also the information about the gradient $\nabla \rho(\vec{r})$ of the density. It can be given by:

$$E_{\mathsf{XC}}^{\mathsf{GGA}}[\rho] = \int \varepsilon_{\mathsf{XC}}^{\mathsf{GGA}}\left(\rho(\vec{r}), \nabla\rho(\vec{r})\right) d\vec{r}$$
(2.22)

Contrary to the LDA, the GGA is not uniquely defined and there are several popular GGA functionals including Perdew-Wang (PW91)[69, 72], Perdew-Burke-Enzerhof (PBE)[70], revPBE[73], RPBE[74], and Bayesian error estimation functional with van der Waals correlation (BEFF-vdW)[75]. Among them, the BEFF-vdW ensemble performs quite well for chemisorption processes.[75] Compared to the LDA, the GGA usually improves accuracy in terms of binding energy, atomic energy, bond lengths, bond angles, and so on.

Going beyond the GGA by considering second-order gradients and the non-interacting kinetic energy density, a new functional family appears, which is termed meta-generalized gradient approximation (meta-GGA)[76]. Mixing with exact exchange functional in the Hartree–Fock method leads to new hybrid functionals, such as Becke-3-parameter-Lee-Yang-Parr (B3LYP)[77] and Heyd-Scuseria-Ernzerhof (HSE06)[78].

2.1.6 Solving the Kohn–Sham equations

The Kohn-Sham equation in 2.16 is usually solved by a self-consistent field (SCF) loop as shown in Figure 2.1. More details can be seen in the chapter "Solving the Kohn–Sham equations" in the book by Martin.[60] First of all, an initial guess of electron density as the input is given and it can be used to calculate the effective potential V_{eff} given in the square bracket part in Equation 2.16. Then, the KS equation can be solved according to Equation 2.16. The new electron density as output can be generated as Equation 2.18. The self-consistency calculation would be converged if the old and new electron densities are identical under a given threshold. Otherwise, the generated electron density would enter the next cycle as the new input of the electron density until it converges.

In practice, in order to transform the partial differential equations into algebraic equations suitable for efficient implementation on a computer, solving the KS equation in Equation 2.16 typically requires the discretization of the KS orbital, which expands the KS orbital or wave function into a set of basis functions or basis sets. Common basis functions have



Figure 2.1: Flow chart of the self-consistent loop (SCF) for solving Kohn-Sham equations.

plane-wave expansion[79], LCAO (linear combination of atomic orbitals) approximations [80, 81], real-space approaches[82, 83] and so on. Among them, plane-wave is one of the most popular basis functions. A finite number of discrete grid points and symmetry can be used to reduce computational costs. Many quantities, such as total energy and density, can be obtained by integration over the grid points in the Brillouin zone. The core electrons of an atom almost have no contribution to chemical binding in solids and molecules and instead, it is mainly dominated by the valence electrons. Besides, the localized core electrons are quite computationally expensive. Hence, it is possible to approximately replace the core electrons' potentials with a pseudopotential. There are two typical pseudopotentials (USPP)[85]. A USPP-related technique projected augmented wave (PAW) method[86] is widely used due to its high accuracy and efficiency for large systems. Common DFT softwares are the Vienna Ab initio simulation package (VASP)[87, 88], GPAW[83, 89], CASTEP[90] and Quantum ESPRESSO[91] and so on.

All calculations in this thesis are carried out with spin-polarized density functional theory simulations using the VASP (version 5.4)[79, 92] and the Atomic Simulation Environment (ASE, version 3.2)[93, 94]. The effects of exchange and correlation are approximated by using the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW)[75]. The ionic cores are treated using the projector augmented wave (PAW) method[86] and the wave functions are expanded in a plane waves basis set. A cutoff energy is set as 400 eV and a Gaussian smearing of 0.05 eV is used for the electronic states. In order to remove the electrostatic dipole-dipole interaction between periodically repeated surface slabs, the dipole correction is used in the direction perpendicular to the slab for all the calculations.

2.2 Cluster expansion

DFT calculation is a phenomenally successful approach to calculate the ground state energy of a material, but it is still very expensive. It is impossible to search for the composition and concentration of material with multiple elements using only DFT due to the huge search space. In order to avoid too many expensive DFT calculations, the cluster expansion (CE) method is widely used.[95–99] CE can greatly decrease the computational cost by mapping the first principles results onto a Hamiltonian that is fast to evaluate. The main idea of the CE is to express the scalar physical quantity $q(\sigma)$ of crystal structure, which here is the electronic energy, as a function of its configuration σ that is an N-dimensional vector consisting of site variables. The configuration is decomposed into a series of clusters as shown in Figure 2.2. Each cluster (Φ) can be expressed by the associated single-site basic functions:

$$\Phi_{\mathbf{n}}(\mathbf{s}) = \prod_{i} \Theta_{n_i}(s_i)$$
(2.23)

where $\Theta_{n_i}(s_i)$ is the *n*th basic function (e.g. polynomial, trigonometric, and binary linear) for the *i*th site. Vector **n** and **s** are the order of the basis function and the site variables in the cluster, respectively. s_i is any values from $\pm m$, $(\pm m-1)$, ..., ± 1 for different atomic species M = 2*m* and varable *i* is the *i*th element in vector **s**. All symmetrically equivalent clusters are collected as the same cluster α , the average value of which is correlation function ϕ_{α} .



Figure 2.2: A cluster expansion configuration illustration of the decomposition of a bodycentered cubic lattice.[96]

The scalar physical quantity $q(\sigma)$ can be expressed as a linear expansion of cluster

functions:[95, 96]

$$q(\boldsymbol{\sigma}) = J_0 + \sum_{\alpha} m_{\alpha} J_{\alpha} \phi_{\alpha}$$

= $\sum_{\alpha} \tilde{J}_{\alpha} \phi_{\alpha}$ (2.24)

Where J_{α} denotes the effective cluster interaction (ECI) per occurrence, which must be fitted in CE. J_0 is the ECI of an empty cluster. m_{α} denotes the multiplicity factor illustrating the number of cluster α per atom. m_{α} and J_{α} are combined into the new ECI term \tilde{J}_{α} . In fact, ϕ can be calculated from the crystal structure. The equation can be simplified as follows:

$$\mathbf{q} = \mathbf{X}\boldsymbol{\omega} \tag{2.25}$$

where **q** denotes a column vector of energies here and ω is a column vector of ECI values. **X** is the correlation functions matrix where each element in row *i* and column α is given by:

$$\mathbf{X}_{i\alpha} = \phi_{\alpha}(\boldsymbol{\sigma}_i) \tag{2.26}$$

 ω can be fitted by the ordinary least squares method with regularization.[100] The ordinary least squares are used to minimize the residual sum of squared errors, which can be illustrated as:

$$\hat{\boldsymbol{\omega}} = \underset{\boldsymbol{\omega}}{\arg\min} \|\mathbf{X}\boldsymbol{\omega} - \mathbf{q}\|_2^2$$
(2.27)

where $\hat{\omega}$ is a unique solution. For regularization, l1 and l2 are the two most common schemes. Regularization can be utilized to avoid overfitting by adding a regularization term. We take the following l1 regularization as an example:

$$\arg\min_{\omega} \|\mathbf{X}\boldsymbol{\omega} - \mathbf{q}\|_{2}^{2} + \lambda \|\boldsymbol{\omega}\|_{1}$$
(2.28)

where λ is the regularization constant and $\|\omega\|_1$ is the l1-norm of the column vector ω . Furthermore, cross-validation is used to evaluate the prediction performance of the model in order to improve the model's reliability. Common CE software are the Cluster Expansion Atomic Simulation Environment package (CLEASE)[96], the alloy theoretic automated toolkit (ATAT)[101], the integrated cluster expansion toolkit (ICET)[102], the UNiversal CLuster Expansion (UNCLE)[103] and so on. All CE calculations in this thesis are performed with the CE in the CLEASE developed by Chang et. al.[96]

2.3 Machine learning potentials

The CE method has been successfully applied to predict the scalar physical quantity like energy for bulk, bare slab, or slab with one type of adsorbate system. However, the CE is very difficult to deal with the slab with multiple adsorbates due to the fixed atomic positions. Besides, it is almost impossible for the CE to predict the vector's physical quantity such as forces. In recent years, machine learning (ML) has been particularly popular to be used to construct force fields in the fields of computational material science and
computational chemistry.[104–106] It not only can tackle the more complicated structures but also can learn the vector physical quantity like forces. There are a large number of ML-based force fields that have been developed over the past decades. However, only the three most typical ML approaches are introduced here.[107, 108]

2.3.1 Kernel methods

Simple and common linear regression, such as the ordinary least squares method, has been widely used to build scaling relations as above cluster expansion model. A non-linear kernel can be utilized to augment linear regression with non-linear regression. We first simply introduce a kernel ridge regression (KRG) based on kernel methods.[109] Kernel regression can be considered as a kind of linear combination of kernel functions. Combined with the regularization, it is called the KRG and can be given by:

$$f(x) = \sum_{i=1}^{n} k(x, x_i) a_i$$

= $\mathbf{k}(x)^T \mathbf{a}$ (2.29)
= $\mathbf{k}(x)^T \mathbf{C}^{-1} \mathbf{y}$
= $\mathbf{k}(x)^T (\mathbf{K} + \lambda \mathbf{I})^{-1} \mathbf{y}$

where $k(x, x_i)$ is the kernel function that we can define as a Gaussian function. x_i is the value from the train data points $(x_i, y_i), i = 1, 2, ..., n$, while x is a variable. a_i is the parameter. The sum can be expressed as a product of vector kernel function k(x) = $(k(x, x_1), k(x, x_2), ..., k(x, x_n))$ and vector parameter a. If ignoring noise, a will reproduce all the known data points (x_i, y_i) using the model. In this case, y = Ka by introducing the $n \times n$ matrix K by $K_{ij} = k(x_i, x_j), i = 1, 2, ..., n; j = 1, 2, ..., n$ and the solution $a = K^{-1}y$. Considering the regularization, the solution would be $a = C^{-1}y$ and y is a vecter by y_i from the training data points (x_i, y_i) . C represents the regularized matrix $K + \lambda I$, where λ is the regularization and I is the identity matrix.

The results of the KRG in equation 2.29 can be actually reproduced by a Gaussian process regression (GPR) in a more general way. The GPR is a collection of all stochastic function variables f(x) indexed by a domain like space, where the variables have a Gaussian distribution and its center is the predicted average value. In the framework of the Bayesian probability theory, the GPR includes full probability distributions and thus not only can predict a property but also its uncertainties.[110] We start from Bayes' theorem and the posterior probability $\mathcal{P}(f|\boldsymbol{y}; \boldsymbol{x})$, the output probability given the train set $(\boldsymbol{x}, \boldsymbol{y})$ consisted of (x_i, y_i) , can be expressed as:

$$\mathcal{P}(f|\boldsymbol{y};\boldsymbol{x}) \propto \mathcal{P}(\boldsymbol{y}|f;\boldsymbol{x}) \mathcal{P}(f)$$
 (2.30)

where P(y|f) is the Bayesian likelihood. The prior probability P(f) is defined as a Gaussian distribution:

$$P(f(x)) = \mathcal{N}(m(x), k(x, x'))$$
 (2.31)

where the mean function is m(x). The covariance function k(x, x') is the kernel. It can be proven that the likelihood and posterior are also the Gaussian distributions. Through maximizing the posterior distribution, it can be derived the mean predicted function[111]:

$$\overline{f}(x) = m(x) + \boldsymbol{k}(x)^T \boldsymbol{C}^{-1}(\boldsymbol{y} - m(\boldsymbol{x}))$$
(2.32)

where matrix $C = K + \sigma_0^2 I$ and σ_0 is the noise value. The element of matrix K is $K_{ij} = k(x_i, x_j)$. The variance $\sigma^2(x)$ is given by:

$$\sigma^{2}(x) = k(x, x) - \boldsymbol{k}(x)^{T} \boldsymbol{C}^{-1} \boldsymbol{k}(x)$$
(2.33)

The Bayesian approach in the GPR provides an effective approach to optimize a number of hyperparameters θ , which include noise σ_0 , length scale l and prefactor k_0 in $k(x, x') = k_0 e^{\frac{-(x-x')^2}{2l^2}}$. It can be done by maximizing the marginal likelihood as follows:

$$log \mathcal{P}(\boldsymbol{y}|\boldsymbol{\theta};\boldsymbol{x}) = -\frac{1}{2}(\boldsymbol{y} - m(\boldsymbol{x}))^T \boldsymbol{C}^{-1}(\boldsymbol{y} - m(\boldsymbol{x})) - \frac{1}{2}log(det(\boldsymbol{C})) - \frac{n}{2}log(2\pi)$$
(2.34)

Considering the computational time and space complexity, the KRG and GPR are not suitable for too large train sets. The computation cost is usually $O(n^3)$ due to the need to invert the *C* matrix. The memory cost usually takes $O(n^2)$ for storing the matrix. It would be too time-consuming and expensive to calculate using the kernel methods if the train set is huge.

2.3.2 Feed-foward neural network

The biology-inspired artificial neural network has become a promising approach to constructing neural network potential due to its fast calculation speed and high accuracy. High-dimensional neural network potentials (HDNNP) were first reported by Behler and Parrinello in 2007.[112] Similar to empirical potentials construction, the total energy E of a system with N atoms can be split into a sum of atomic energy contribution E_i as:

$$E = \sum_{i}^{N} E_{i}$$
(2.35)

The Cartesian coordinates α of atom *i* are represented by R_i^{α} , which can be transformed into a series of fingerprints. They use symmetry function values G_i^{μ} as fingerprints to describe each atomic energy contribution, which can be illustrated by the energetically relevant local environment. Then the symmetry function values for atom *i* are used as input of a neural network and the output of the neural network is the predicted energy contribution of atom *i*. All predicted energy contributions of each atom can finally be combined as the final predicted energy *E*.

The architecture of the network in HDNNP is a fully connected feed-forward neural network (FFNN)[107], which consists of an input layer, hidden layers, and an output layer,

and the layers are fully connected. The equations can be given by:

$$h_{1} = \sigma(W_{1}x + b_{1}),$$

$$h_{2} = \sigma(W_{2}h_{1} + b_{2}),$$

$$\vdots$$

$$h_{L} = \sigma(W_{L}h_{L-1} + b_{L}),$$

$$y = \sigma(W_{L+1}h_{L} + b_{L+1}),$$
(2.36)

Where vector x is the input of the neural network (NNs), which is usually fingerprints of the Cartesian coordinates and it is the atom-centered symmetry functions (ACSF)[113] values in HDNNP. $W_{\rm L}$ and $b_{\rm L}$ are the weigh matrix and the bais vector in layer L. The function σ is a non-linear activation function and common activation functions have linear, sigmoid, hyperbolic, softmax, rectifier linear unit (ReLU), scaled exponential linear unit (SeLU), and sigmoid linear Unit (SiLU).[114, 115] $h_{\rm L}$ is units or nodes vector in layer L. The final result y is the output of the neural network and here is E_i . All E_i are added to obtain the total predicted energy. It should be noted that the architectures and parameters of the atomic NNs are the same for each chemical element. The process above is actually the forward propagation in FFNN. During the training, the forward propagation can yield a scalar loss through a loss function between the predicted energy and true DFT energy. In order to minimize the loss, the back-propagation algorithm[116] propagates backward the loss through the network in order to compute the gradient and adjust the model parameters (W, b). Besides, the forces can be calculated by the negative gradients of the total energy with respect to the atomic positions. Common softwares are RuNNer[117], atomistic machine-Learning package (AMP)[118], neural network potential package (n2p2)[119], PROPerty Prophet (PROPhet)[120] and so on.

The ACSF gives a series of information of radial and angular in HDNNP, which is the first fingerprint or descriptor of the neural network potentials (NNPs). Its introduction inspires lots of descriptor-base NNPs, where the descriptors are usually used as input of the FFNN. Actually, there are many other descriptors like the Coulomb matrix, Ewald sum matrix, sine matrix, many-body tensor representation (MBTR), and smooth overlap of atomic positions (SOAP).[121–125] The common feature for those environment descriptors is that they need to be predetermined and manually designed.

2.3.3 Message-passing neural networks

The above-mentioned ACSF in HDNNP needs to be chosen by an expert and the accuracy of the model is greatly dependent on the choice of the symmetry functions. Besides, it is very computationally expensive when input dimensions quickly increase. In contrast, end-to-end deep learning NNs are really popular, which directly take atomic numbers and positions as inputs to learn physical properties like energy and forces from the DFT train set.[126, 127] The graph neural network (GNN)[128] has inspired many end-to-end NNPs.[126, 127, 129–131] A structure can be decomposed into atoms and bonds, where atoms can be regarded as nodes and bonds are represented by edges in GNN. It

is worth pointing out that the global variable like the applied potential can also be added into the GNN. Through exchanging the information of nodes, edges, and global variables (optical), complex chemical properties can be learned by the ML model. This process is actually message-passing and such network is called message-passing neural networks (MPNNs)[132]. The Deep Tensor Neural Network (DTNN)[133] is a typical example, which has been refined to create SchNet[126] and PhysNet[134] and so on. There are also other well-known examples such as Nequip[135], MACE[136], and PaiNN[137].

Based on rotationally equivariant representations, PaiNN, the polarizable atom interaction neural network, is quite outstanding.[137] Scalar and vectorial representations are used in PaiNN and the vector is constrained to be equivariant to rotation by the following equation:

$$R\vec{f}(\vec{x}) = \vec{f}(R\vec{x}) \tag{2.37}$$

where R is any rotation matrix. The product of the matrix-vector is applied over the spatial dimension, which is essentially a linearity constraint for directional information given by $\frac{\vec{r}_{ij}}{\|\vec{r}_{ij}\|}$. The edge \vec{r}_{ij} is the relative position of node i and j.



Figure 2.3: The total architecture (a) of the PaiNN model and the corresponding message block (b) and update block (c).[137]

The total architecture of the PaiNN model is shown in Figure 2.3a. The inputs are the nuclear charges Z_i and positions r_i for each atom i. The nuclear charges use embeddings to generate a simple lookup table of element types and each element has a constant features dimension F. The invariant atom scalar representations \mathbf{s}_i are initialized by the embeddings (\mathbf{s}_i^0). The equivariant vector representations $\vec{\mathbf{v}}_i$ are initialized by $\vec{\mathbf{0}} \in \mathbb{R}^{F \times 3}$ ($\vec{\mathbf{v}}_i^0$). A residual structure of the interchanging message and update blocks in Figure 2.3b-c is designed. For the message block, the residuals of the scalar message function and

vector message function can be given by:

$$\Delta \mathbf{s}_{i}^{m} = (\phi_{s}(\mathbf{s}) * \mathcal{W}_{s})_{i} = \sum_{j} \phi_{s}(\mathbf{s}_{j}) \circ \mathcal{W}_{s}(\|\vec{r}_{ij}\|),$$

$$\Delta \vec{\mathbf{v}}_{i}^{m} = \sum_{j} \vec{\mathbf{v}}_{j} \circ \phi_{s}(\mathbf{s}_{j}) \circ \mathcal{W}_{vv}(\|\vec{r}_{ij}\|) + \sum_{j} \phi_{vs}(\mathbf{s}_{j}) \circ \mathcal{W}_{vs}'(\|\vec{r}_{ij}\|) \circ \frac{\vec{r}_{ij}}{\|\vec{r}_{ij}\|},$$
(2.38)

where \mathbf{s}_j and $\mathbf{\vec{v}}_j$ are scalar and vector from the information of the neighbors of atom i, respectively. Their initial values are from \mathbf{s}_i^0 and $\mathbf{\vec{v}}_i^0$, respectively. ϕ_s and \mathcal{W}_s are obtained according to Figure 2.3b. \mathcal{W}_s is the rotationally-invariant filters, which are linear combinations of radial basis functions (RBF) $\frac{\sin(\frac{n\pi}{r_{out}} \| \vec{r}_{ij} \|)}{\| \vec{r}_{ij} \|}$, $1 \le n \le 20$ and a cosine cutoff function is applied to this filters. The features of $(\phi \circ \mathcal{W})$ are split into three parts.

For the update block, the residuals of the scalar update function and vector update function can be given by:

$$\Delta \mathbf{s}_{i}^{u} = \mathbf{a}_{ss}(\mathbf{s}_{i}, \|\mathbf{V}\vec{\mathbf{v}}_{i}\|) + \mathbf{a}_{sv}(\mathbf{s}_{i}, \|\mathbf{V}\vec{\mathbf{v}}_{i}\|) \langle \mathbf{U}\vec{\mathbf{v}}_{i}, \mathbf{V}\vec{\mathbf{v}}_{i} \rangle,$$

$$\Delta \vec{\mathbf{v}}_{i}^{u} = \mathbf{a}_{vv}(\mathbf{s}_{i}, \|\mathbf{V}\vec{\mathbf{v}}_{i}\|) \mathbf{U}\vec{\mathbf{v}}_{i},$$

(2.39)

where a shared network $\mathbf{a}(\mathbf{s}_i, \|\mathbf{V}\vec{\mathbf{v}}_i\|)$ as nonlinearity is splitted into three parts \mathbf{a}_{vv} , \mathbf{a}_{sv} and \mathbf{a}_{ss} as shown in Figure 2.3c. $\|\mathbf{V}\vec{\mathbf{v}}_i\|$ is the norm of a linear combination of equivariant features and $\mathbf{U}\vec{\mathbf{v}}_i$ is also a linear combination of equivariant features $\vec{\mathbf{v}}_i$. In order to predict scalar properties like atomic energy, the atomwise readout layers are applied to the rotationally invariant representations \mathbf{s}_i . The total energy can be obtained by a sum of all atomic energies same as Equation 2.35. The calculation of the forces is negative gradients of the total energy with respect to the atomic positions as HDNNP does. The force component $F_{i,\alpha}$ acting on atom *i* with respect to coordinate $R_{i,\alpha}$, $\alpha = (x, y, z)$ can be illustrated as follows:

$$F_{i,\alpha} = -\frac{\partial E}{\partial R_{i,\alpha}} = -\sum_{j=1}^{N} \frac{\partial E_j}{\partial R_{i,\alpha}}$$
(2.40)

where N represents the number of atoms. The term $\frac{\partial E_j}{\partial R_{i,\alpha}}$ can be given by the architecture of the NNs using the chain rule.

After propagating backward a loss function to calculate the gradient of the parameters, the NNs parameters are optimized by an optimizer according to the gradients. The loss function \mathcal{L} is a combination of energy and forces loss function as follows:

$$\mathcal{L} = \frac{1 - \lambda}{N} \sum_{i=1}^{N} \left(\hat{E}_i - E_i \right)^2 + \frac{\lambda}{NM} \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{3} \left(\hat{F}_i^{jk} - F_i^{jk} \right)^2$$
(2.41)

where λ is an empirical parameter to control the balance between energy and forces loss function. N is the number of images and M is the number of atoms in a image. \hat{E}_i and E_i are the NNs and DFT energy of image i, respectively. \hat{F}_i^{jk} and F_i^{jk} are the NNs and DFT forces of atom j in the k direction. Root mean squared error (RMSE) of energy and

force between DFT and NNs predictions are calculated by:

$$E_{\text{RMSE}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(\hat{E}_{i} - E_{i}\right)^{2}}$$

$$F_{\text{RMSE}} = \sqrt{\frac{1}{3NM} \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{3} \left(\hat{F}_{i}^{jk} - F_{i}^{jk}\right)^{2}}$$
(2.42)

2.4 Local optimization

For atomic-scale DFT simulations, relaxation of atomic structure is needed to get the ground state structure. Each energy calculation may take several cpu-days and thus it is very important to have an efficient and fast optimization algorithm. Besides, parameter optimization in cluster expansion and machine learning is another key application. We already mentioned the ordinary least squares optimization in CE, but the ordinary least squares method is only suitable to solve simple optimization situations and is not scalable. Local optimizer is usually more efficient and thus used during these processes. This section mainly introduces common local optimization methods.

Local optimization is to find the local minimum, which can be expressed as $f(x^*) \leq f(x)$ for all $x \in \Omega$ close to $x^*, \Omega \subset \mathbb{R}^n$. Based on the curvature information, local optimization methods are divided into two major categories: first-order optimization algorithms and second-order optimization algorithms.[138–140]

First-order optimization algorithms are only dependent on gradient or subgradient information.[141] A common example is the gradient descent method as follows:

$$x_{i+1} = x_i - \gamma \nabla f(x_i) \tag{2.43}$$

where γ is the step size or learning rate. $\nabla f(x_i)$ is the gradient at point x_i . However, the gradient descent could be slow or even vanish when the step size is too small. It could skip the true local minimum and fail to converge or even explode the gradient when the step size is too large. Hence, there are lots of other first-order optimization algorithms proposed, such as steepest descent, stochastic gradient descent (SGD), Adam, AdaGrad, Proximal gradient descent and so on.[142–144] SGD and its variants like accelerated SGD, variance reduction SGD and stochastic coordinate descent methods are widely used to optimize the NNs parameters in machine learning. Adam and its variants are also particularly popular in machine learning because it combines the adaptive and momentum methods and is relatively stable for large data sets and high dimensional space.

Second-order optimization algorithms utilize the information from both the first-order derivative (gradient) and second-order derivative (Hessian matrix that includes the curvature information) to find the minimum.[145, 146] Compared to first-order optimization algorithms, second-order algorithms usually have much better convergence properties. Second-order algorithms usually apply a preconditioning matrix to the gradient in each

step. A typical example is Newton's method given by:

$$x_{i+1} = x_i - \gamma \boldsymbol{H}_i^{-1} \nabla f(x_i)$$

= $x_i - \gamma [\nabla^2 f(x_i)]^{-1} \nabla f(x_i)$ (2.44)

where H_i is the Hessian matrix, which is the second-order derivative of the objective function. However, it is impractical to calculate the Hessian matrix and its inverse because its size is $\mathbb{R}^{n \times n}$ and *n* could be a huge number due to the huge parameters. In order to overcome this issue, many approximations to the Hessian matrix have been made, such as quasi-Newton, Hessian-free, stochastic quasi-Newton, Gauss-Newton, and natural gradient descent methods.[147–150] Quasi-Newton methods use low-rank approximations or subsampling methods to estimate the Hessian or its inverse. Broyden-Fletcher-Goldfarb-Shanno (BFGS) is the most popular algorithm in this family, which is widely used in DFT ionic relaxation. Hessian-free methods directly avoid calculating the Hessian and its inverse and instead utilize a linear solver like conjugate gradient (CG) algorithm to get Hessian-vector products. Sometimes, CG is also considered as being between first-order and second-order algorithms, which is usually recommended to use for difficult relaxation problems in DFT calculation. In stochastic guasi-Newton methods, the limited memory version of the BFGS algorithm (LBFGS) updates the inverse of Hessian matrixes rather than the Hessian itself and is guite suitable for dealing with large-scale variables.

2.5 Global optimization

High-throughput screening of materials needs to do global optimization to search for a set of the optimal structures in a huge structure configuration space or search space. Thus, excellent global optimization algorithms are crucial in this process.

Global optimization is to find the global minimum, which can be expressed as $f(x^*) \leq f(x)$ for all $x \in \Omega$, $\Omega \subset \mathbb{R}^n$. Unlike local optimization with respect to local space, global optimization is to search for the global minimum in the entire space. Such methods are usually not based on first or second-order derivatives to determine the step direction and step width, but instead use stochastic methods, heuristics methods, and so on.[151] The typical global optimization methods have random search, Bayesian optimization, basin hopping, minima hopping, simulated annealing, and genetic algorithm (evolutionary algorithm).[152–156] Only simulated annealing and genetic algorithms are used in our works and thus introduced in detail.

2.5.1 Monte Carlo simulated annealing

Based on statistical mechanics in thermodynamics, Monte Carlo simulated annealing is a general and effective probabilistic technique for global optimization, which is analogous to the simulation of the annealing of solids.[157, 158] It has been widely applied in various fields due to its easy implementation and effectiveness. It does not require specialist knowledge about how to solve a particular issue and can be used in a variety of optimization problems without changing the basic framework.



Figure 2.4: The flow chart of Monte Carlo simulated annealing.

A typical flow chart of simulated annealing in the process of structure screening can be seen in Figure 2.4. First of all, an initial structure is randomly generated at a high temperature (initial temperature) and its energy (E_{old}) is calculated. We generate a new structure and the calculated energy is E_{new} . Then the energy difference between the old and new structures ΔE is computed. If the energy difference is less than zero, the new structure will be accepted and the old structure will be substituted by the new one. Otherwise, we accept the new structure according to the Metropolis criterion. It continuously goes to the next iteration until the number of iterations reaches. If a convergence condition is not met, the temperature gradually decreases and the number of iterations is reset. The final global minimum is found if the condition is met. In the process of lowering the annealing temperature, the result tends to be stable, but it may be a local minimum. However, there is still a probability of jumping out of the local minimum in simulated annealing and then finding the structure with the global minimum energy.[159] The key is how to determine the probability and the Metropolis criterion[160] based on Boltzmann distribution is usually used as follows:

$$\mathcal{P}_{\mathsf{acc}} = \begin{cases} 1 & \text{if } E_{\mathsf{new}} < E_{\mathsf{old}} \\ \exp\left(\frac{-(E_{\mathsf{new}} - E_{\mathsf{old}})}{k_{\mathsf{B}}T}\right) & \text{if } E_{\mathsf{new}} \ge E_{\mathsf{old}} \end{cases}$$
(2.45)

where \mathcal{P}_{acc} is the acceptance probability of changing from the old structure to the new one. Even though E_{new} is larger than E_{old} , there still exists the probability of becoming the new structure. The smaller the energy difference is, the larger the acceptance probability is. This keeps it from getting stuck in a local minimum and then can go to the global minimum.

Due to a great number of function evaluations etc., simulated annealing is really timeconsuming for larger configuration systems. A trade-off between the quality of the result and the time taken usually needs to be considered. Thus, many variants of simulated annealing have been proposed, like adaptive simulated annealing (ASA)[161], fast annealing, and very fast simulated reannealing (VFSR)[162].

2.5.2 Genetic algorithm

Genetic algorithm (GA) is a well-known metaheuristic global optimization algorithm inspired by the basic principles of biological evolution and natural selection.[163] GA is considered as a kind of more efficient method due to its dynamic operators and parallelization in huge configuration space.



Figure 2.5: The flow chart of a typical genetic algorithm.

A typical GA framework can be found in Figure 2.5. The basic elements of GA are initialization (population and fitness definition etc.), fitness calculation and evaluation, parent selection, and operators. For initialization, a bunch of parameters are set. Among them, the number of populations is a key parameter that determines the number of candidates (structures). The initial population can be random individuals or the best individuals we already know. Besides, we need to define the fitness function, such as mixing energy or surface free energy, which actually is a score for each individual and the score determines how good an individual is. Then, fitness calculation, evaluation, and update are done for the first generation. GA will go to the next generation if it does not reach convergence criteria. Otherwise, GA is terminated and gives final candidates. The selection stage decides how to select the individuals or how to choose parents. A typical method is roulette wheel selection, where every parent is represented in the wheel with a percentage based on their fitness score. The individual has a larger chance to enter the next generation if the score of an individual is higher. Operators are used to generate new individuals with different methods. Mutation, permutation, and crossover are three common operators. Taking geometry structure as an example, the mutation operator is to substitute one atom with another atom with a new element type, while the permutation operator is to swap the positions of two atoms in the structure. The Crossover operator combines one part of the first parent and another part of the second parent together to generate a new offspring structure. The operators can be randomly used multiple times. Then, the fitness functions of all offspring are calculated. The offspring are subsequently evaluated and the population is updated to go back to the convergence criteria stage. This process is repeated until it converges.

The above GA ranks the fitness functions according to their corresponding absolute value, which causes the GA to finally converge to a single global minimum. However, only an absolute global minimum value sometimes is not what we want. For example, a convex hull construction for an alloy system not only needs the global minimum composition. Instead, we have to obtain the minimum at each element concentration. In order to keep the diversity, a niche-based GA is proposed. The niche-based GA is to split the population into different unique niches, such as unique concentrations of one element in the alloy system. This method can finally generate a series of optimal values rather than only one value.

2.6 Microkinetic model

Common chemical reactions usually consist of multiple elementary reactions. In order to describe the total reaction rate, the equilibrium between elementary reactions needs to be considered. Microkinetic modeling is a great methodology to analyze the reaction mechanism. Especially, it can be used to identify critical reaction intermediates and rate-determining elementary reactions. Microkinetic modeling has been widely utilized in all kinds of common electrochemical reactions, such as CO₂RR, HER, oxygen reduction reaction (ORR), OER, and nitrogen reduction reaction (NRR).[164–166]

The reaction mechanism for CO₂ reduction to CO in this thesis is considered as follows:[167]

$$CO_2(g) + * + H^+ + e^- \longleftrightarrow HOCO*$$
 (2.46)

$$HOCO* + H^{+} + e^{-} \longleftrightarrow CO* + H_2O(I)$$
(2.47)

$$CO* \longleftrightarrow CO(g) + *$$
 (2.48)

The free energies are calculated by the computational hydrogen electrode (CHE) model[168], which provides an elegant method to avoid calculations of solvated protons. In this model, 0 V is defined based on the reversible hydrogen electrode (RHE). The reaction is defined as equilibrium at 0 V, at standard pressure:

$$H^+ + e^- \longleftrightarrow \frac{1}{2}H_2$$
 (2.49)

Therefore, the sum of the chemical potential of H^+ and e^- in equilibrium is equal to half of that of gaseous hydrogen. The free energies dependent on the applied potentials are

calculated as follows:

$$\Delta G_1 = G_{HOCO*} - G* - \mu_{CO_2(g)} - \frac{1}{2} \mu_{H_2^{\Theta}} + eU$$
 (2.50)

$$\Delta G_2 = G_{CO*} + \mu_{H_2O(I)} - G_{HOCO*} - \frac{1}{2}\mu_{H_2^{\Theta}} + eU$$
 (2.51)

$$\Delta G_3 = G_* + \mu_{CO(g)} - G_{CO_*} \tag{2.52}$$

where the applied potentials are relative to the RHE. ΔG_1 , ΔG_2 and ΔG_3 are the free energy difference of the three-step reactions for CO₂RR. G_{HOCO*}, G_{CO*} and G_{*} are the free energies of species HOCO*, CO* and surface, respectively. $\mu_{CO_2(g)}$, $\mu_{CO(g)}$, $\mu_{H_2O(l)}$ and $\mu_{H_2^{\Theta}}$ represent the chemical potentials of gaseous CO₂, gaseous CO, liquid H₂O and gaseous H₂, respectively. Moreover, experimental vapor pressures are utilized for them in this thesis. The partial pressures of H₂O and CO are 3534 Pa and 5562 Pa, respectively.[40] The partial pressure of CO₂ and H₂ are both under standard pressure 101325 Pa.[22, 40] We ignore electric field effects on adsorption energies in this thesis.

A kinetic model is utilized to study the activity for CO₂RR to CO. The net reaction rates of CO₂RR are described as[169]

$$r_1 = k_1 \theta_* p_{\text{CO}_2} - \frac{k_1}{K_1} \theta_{\text{HOCO}*}$$
(2.53)

$$r_2 = k_2 \theta_{\text{HOCO}*} - \frac{k_2}{K_2} \theta_{\text{CO}*}$$
(2.54)

$$r_3 = k_3 \theta_{\text{CO}*} - \frac{k_3}{K_3} \theta_* p_{\text{CO}}$$
(2.55)

where k_1 , k_2 , k_3 represent forward rate constants for the three steps of CO₂RR. K_1 , K_2 , K_3 are the corresponding equilibrium constants and backward rate constants can be calculated by forward rate constant over the corresponding equilibrium constants. For example, the backward rate constant is equal to k_1/K_1 . p and θ represent the partial pressure and surface coverage, respectively. For the electrochemical step 1 and step 2 with coupled electron-proton transfer, the forward rate constants are denoted as

$$k_{i=1,2} = A' \exp\left(-\frac{\beta e(U-U_i^0)}{k_{\rm B}T}\right)$$
 (2.56)

where the pre-exponential factor A' is a material independent constant. A value of $A' = 3.6 \times 10^4 \text{ s}^{-1}$ is used as in previous work.[169] k_B is the Boltzmann constant and β is a symmetry factor which is set as 0.5 here. U_i^0 is the reversible potential of reaction step *i*

$$U_i^0 = -\frac{\Delta G_i}{e} \tag{2.57}$$

where ΔG_i is the reaction free energy difference at zero voltage (vs. RHE) calculated by

DFT using the CHE model. The corresponding equilibrium constants are given by

$$K_i = \exp\left(-\frac{e(U - U_i^0)}{k_{\mathsf{B}}T}\right) \tag{2.58}$$

For the chemical step 3 with no electron or proton transfer, the rate constant is approximated as

$$k_3 = \nu \exp\left(-\frac{E_{\text{CO}*}}{k_{\text{B}}T}\right) \tag{2.59}$$

where E_{CO*} represents the binding energy of intermediate CO*. A typical pre-exponential factor ν is 10 ¹³ s⁻¹.

2.7 High-throughput screening workflow



Figure 2.6: The flow chart of a typical high-throughput screening workflow with active learning.

It is very important to have an automatic workflow in the process of high-throughput screening. On the one hand, the automatic workflow can greatly improve computational efficiency and minimize manual interference. All tasks can run sequentially and automatically according to the pre-set. In other words, subsequent tasks automatically start until previous tasks are finished and subsequent tasks can use data from previous tasks. On the other hand, it is obviously beneficial to generate reproducible results. A typical high-throughput screening workflow with active learning can be seen in Figure 2.6. First of all, an initial database is used to train a model that can be the cluster expansion model or machine learning (ensemble) model. Then the model can be utilized to do global optimiza-

tion which can be Monte Carlo simulated annealing or genetic algorithm. The generated optimal structures are calculated by DFT calculation and the DFT data can be fed to the model to do active learning until it is converged. There are several common tools used to build workflows, such as AiiDa[170], Fireworks[171], and MyQueue[172].

Chapter 3 Metal-doped PdH(111)

This chapter is based on paper I and the corresponding supporting information can be seen in Appendix A.

3.1 Introduction

Numerous previous studies have been done to study metal catalysts for the CO₂RR. Gold (Au)[45, 46], silver (Ag),[49, 50] and copper (Cu)[39] are most widely studied for the electrochemical CO₂RR and show good performance for CO production. Au nanoparticles formed from thick Au oxide films were reported to have high selectivity for CO₂RR to CO at 140 mV overpotential, keeping their activity for no more than 8 hours.[51] Kim et al. reported Ag nanoparticles supported on carbon have good Faradaic efficiency and low overpotential.[50] Raciti et al. reported that Cu nanowires produced by electrochemical reduction are highly active and selective for the CO₂RR to CO at an overpotential of 0.3 V.[39] However, Au, Ag, and Cu can not tune the desired CO/H₂ ratio with high CO₂RR catalytic activity.[58, 167] In addition, M-N-C electrocatalysts with high faradaic efficiencies for CO generation are also popular in the field of CO₂RR. Among them, Fe-N-C electrocatalyst shows high selectivity and CO formation activity at low overpotentials (0.3 to 0.5 V). Ni-N-C electrocatalyst exhibits good selectivity and activity at higher overpotentials because it is more favorable toward the HER. Co-N-C electrocatalyst has a lower selectivity for CO throughout the entire potential range.[55]

Pd was reported to be a potential candidate catalyst for CO_2RR to CO by Gao et al. in 2015.[57] Moreover, Chen et al. thought the Pd catalyst was more suitable to produce syngas (CO and H₂) compared to other metals, and that the reason why Pd showed good activity and selectivity during electrochemical CO_2RR was the Pd metal catalyst was transformed into palladium hydride. [58] The formation of PdH would significantly improve Faradaic efficiencies of production of CO and H₂. Furthermore, the PdH(111) surface experimentally exhibited higher current density and Faradaic efficiency compared with other crystal surfaces.[58] Subsequently, in order to further improve the performance of PdH, several approaches, such as applying transition metal nitrides as promising supports and using bimetallic catalysts, have been explored in recent years.[59]

In this chapter, DFT simulations are performed to study transition metal-doped PdH catalysts. Due to the difficult formation of HOCO* on pure PdH(111), we explore the possibility of lowering the HOCO* formation energy through doping transition metal elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re) into the PdH(111) surface in different configurations to systematically study their properties. First, the doping formation energies are calculated to illustrate the stability of different doped surfaces. Then, the scaling relations between reaction intermediates, free energy

diagrams, and kinetic model are carried out to explore the CO_2RR catalytic activities after doping. Finally, selectivity toward CO_2RR and HER is also studied to describe the competition between CO and H₂.

3.2 Simulation details

Bulk PdH is in the rock salt (NaCI) crystal structure and the (111) surface, which is energetically the most stable, is considered in this chapter. A 3×3 supercell model of the PdH(111) with six bilayers is built and each bilayer consists of one Pd atomic layer and one H atomic layer, where the bottom three bilayers are fixed in their bulk positions during optimization. A $3 \times 3 \times 1$ Monkhorst-pack grid[173] of k-points is applied to sample the first Brillouin zone of the PdH(111) slab. The convergence threshold of Hellman-Feynman force is set to 0.01 eV $Å^{-1}$, and the energy convergence criteria on each atom was set to 10^{-6} eV atom⁻¹. A vacuum layer of about 15 Å is adopted in the z direction to separate periodic slab images and avoid interactions between them. In order to further improve accuracy it CO₂RR free energy diagram, a +0.15 eV correction per C=O is applied for systematic overbinding corrections with the BEEF-vdW functional, +0.15 eV for HOCO* and +0.1 eV for H₂.[174, 175] For solvent stabilization correction at the water-catalyst interface, -0.25 eV for HOCO* and -0.1 eV for CO* are used in all calculations, respectively.[40] The effects of the electric field at the electrochemical interface of catalysis on the free energy of the adsorbates are ignored in this treatment. All calculation processes, data collection, and analysis are performed in a custom-built workflow and a computational database is freely available in the DTU Data Repository.[176]

The formation energies E_{form} of PdH doped with transition metals are calculated according to the following definition:

$$E_{\text{form}} = E_{\text{nM-doped}} - E_{\text{pure}} - n\mu_{\text{M}} + n\mu_{\text{Pd}}$$
(3.1)

where $E_{nM-doped}$ denotes the energy of doping the PdH(111) slab with n metal atoms, while E_{pure} is the energy of the pure undoped PdH(111) slab. μ_{M} and μ_{Pd} represent the chemical potential of the doped metal atom and Pd, respectively.

The binding energies E_{b} of different intermediates in this chapter are given by the following equation:

$$E_{b} = E_{*+\text{intermediate}} - E_{*} - E_{\text{intermediate}}$$
(3.2)

where $E_{*+\text{intermediate}}$ is the total DFT energy of slab and intermediate. E_* and $E_{\text{intermediate}}$ are the energies of clean slab and intermediate with respect to gas phase molecules, respectively.

The calculations of Gibbs free energy (G) are obtained from

$$G = E_{\mathsf{DFT}} + E_{\mathsf{ZPE}} + \int C_p \mathsf{d}T - TS$$
(3.3)

where E_{DFT} represents the DFT energy with overbinding correction and solvent stabilization correction. E_{ZPE} represents the zero-point energy of the species. C_p and S are the heat capacity and entropy, respectively, and *T* is temperature. E_{ZPE} , C_p and entropy of slabs are obtained from statistical mechanics using the harmonic approximation throughout calculations of vibrational frequencies. We assume that variations in these terms are small compared with that of binding energies and thus the energies of these terms for pure PdH(111) are applied to other surfaces as listed in Table A.9. Gas-phase species are obtained by ideal gas methods and the corresponding free energies are listed in Table A.10.



3.3 Results and discussions



Before investigating transition metal element dopants, the pure PdH(111) surface is first studied by DFT with the BEEF-vdW functional. The crystal constants of optimized bulk PdH are a=b=c=4.138 Å, which is well consistent with the experimental results 4.090 Å.[177] Figure A.1 shows the top and side view of pure PdH(111) structures. The PdH(111) slab is built by optimized bulk PdH and its lattice constants are a=b=8.778 Å and c=27.140 Å. The top and side views of pure PdH(111) with adsorbates HOCO*, CO*, H*, and OH* are shown in Figure A.2. We notice that HOCO*, CO*, and OH* tend to adsorb on the top site of PdH, while H* prefers to adsorb on the hollow site according to their binding energies in Table A.1. Figure A.3 demonstrates the CO₂RR free energy diagram of PdH(111) at 0 V (vs. RHE), at room temperature. The free energies of the HOCO*, CO*, and CO intermediates in this diagram are 0.820, 0.216, and 0.123 eV, respectively. Because the HOCO* formation step has the highest free energy, this reaction step is the potential-limiting step on pure PdH(111). This is consistent with the DFT results of 0.67 eV for the HOCO* step found by Sheng *et al.* using the PW91 functional.[58] At the same time, the HER free energy diagram of PdH(111) at 0 V (vs. RHE) is also shown in Figure A.4 and

the free energy of the Volmer step is 0.501 eV, which is lower than 0.820 eV for CO_2RR . Therefore, the CO_2RR steps are thermodynamically more difficult than the HER steps for pure PdH. Experiments by Sheng *et al.* found that the CO/H₂ ratio is always lower than 1 at different potentials and thus shows CO has a lower proportion, which has good agreement with computational results.[58]



Figure 3.2: The formation energies of doping PdH(111) with different elements in different doping configurations.

In order to improve the CO₂RR performance of PdH, the impact of doping transition metal elements into the PdH(111) surface is explored below. As displayed in Figure 3.1, we try to dope different elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W and Re into PdH(111) surface in different doping configurations which we demote as: single, dimer, triangle, parallelogram, island and overlayer, respectively. Their formation energies per dopant atom in the different doping configurations are first calculated and shown in Table A.2 and in Figure 3.2. We find, in most cases, that overlayer doping is the most unstable, while single doping is the most stable when an element is doped in different configurations. Moreover, the doping formation energies of Sc, Ti, Zn, Y, Zr, Nb, Hf, and Ta in all doping configurations are negative except for overlayer doping of Zn. This demonstrates that Sc, Ti, Zn, Y, Zr, Nb, Hf, and Ta are easier to be doped into PdH compared to other elements. We note that for the largest dopants: Sc, Zn, Y, Zr, Ag, Cd, and Hf significant destabilization of the overlayer structure compared to single dopant by more than 1 eV can be observed. This is likely caused by the increased strain with the full overlayer.

The CO₂RR free energy diagrams of doping PdH(111) with different elements in differ-



Figure 3.3: The free energy diagrams of doped PdH(111) with doping elements in different configurations.

ent configurations are calculated to explore the possibility of lowering the potential-limiting HOCO* step as displayed in Figure 3.3. The free energies are calculated using the most stable adsorption sites according to the binding energies in Table A.3-A.8 and the corresponding specific free energies are listed in Table A.11-A.16 in the Appendix A. For single atom doping of PdH(111), Fe, Zr, Nb, and Ru doping effectively decrease the free energy of the HOCO* step by -0.003, -0.06, -0.07, and -0.15 eV, respectively, compared to the pure PdH. However, the doping formation energies of Fe and Ru are positive and thus unstable. Therefore, the candidates for lowering the HOCO* step are Nb and Zr-doped PdH for doping with a single atom. For dimer doping of PdH(111), the free energies of HOCO* step of Sc, Ti, V, Cr, Mn, Fe, Y, Zr, Nb, Mo, Ru, Hf, Ta, W and Re are downhill relative to undoped PdH. Their free energy differences with respect to PdH are -0.39, -0.04, -0.01, -0.63, -0.30, -0.143, -0.88, -0.63, -0.04, -0.16, -0.19, -0.18, -0.10, -0.03, -0.01 eV, respectively. Among them, Sc, Ti, Zr, Nb, Hf, and Ta are stable according to their doping formation energies, and thus they are possible candidates for CO₂RR for this case. Doping with Y dimers is neglected due to structural distortion upon optimization. Still, for the triangle doping, Sc, Ti, V, Cr, Mn, Fe, Zr, Nb, Mo, Ru, Hf, Ta, W and Re doping leads to a free energy reduction of the potential-limiting step, and the free energy differences compared to pure PdH(111) are -0.30, -0.17, -0.34, -0.57, -0.32, -0.30, -0.50, -0.24, -0.23, -0.21, -0.42, -0.41, -0.06, and -0.27 eV, respectively. (Y doping is removed due to large structure distortion.) The ones that could be stable are still Sc, Ti, Zr, Nb, Hf, and Ta-doped PdH. Similarly, there are more doping elements that can lower the potential-limiting step: Sc, Ti, V, Cr, Mn, Fe, Co, Zr, Nb, Mo, Ru, Hf, Ta, W, and Re

in the parallelogram configuration. Their free energy differences with respect to PdH are -1.02, -0.31, -0.29, -0.41, -0.32, -0.46, -0.39, -0.42, -0.28, -0.49, -0.37, -0.57, -0.25, -0.66, and -0.66 eV, respectively. In the parallelogram configuration Zn, Y, and Cd doping are discarded due to large structural distortion. Again the most promising stable candidates are Sc, Ti, Zr, Nb, Hf, and Ta dopants. It is worth noticing that Sc doping in this case greatly decreases the HOCO* step and the line connecting HOCO* to CO* in the free energy diagram intersects with lines from other dopants. This illustrates that Sc doping clearly breaks the scaling relation between HOCO* and CO*. For the case of island doping, the free energies of Sc, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, Ru, Rh, Ta, W and Re are downhill compared with that of the undoped PdH(111), and the free energy differences are -1.002, -0.423, -0.325, -0.293, -0.747, -0.565, -0.160, -0.592, -0.864, -0.333, -0.032, -0.817, -0.466, and -0.424 eV, respectively. Y, Zn, Zr, Cd, and Hf doping are discarded due to large structure distortion in the island configuration. However, the stable dopants are Sc, Ti, Nb, and Ta in light of their negative formation energies. In the last configuration of overlayer doping, several structures are not stable after binding the reaction intermediates including Sc, Y, Zn, Zr, Cd, and Hf overlayer surfaces. This may again be related to the large size of these dopants and the corresponding lattice mismatch that can be seen in Table A.17, and thus they are removed in this case. Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, Ta, W and Re doping can effectively reduce the free energy of HOCO* step and the free energy differences are -0.232, -0.222, -0.423, -0.884, -1.971, -1.234, -0.844, -0.196, -0.329, -0.554, -0.093, -0.577, -0.611, and -0.939 eV, respectively, but only Ti, Nb, Ta and V doping are the stable ones. The candidates of different configurations for CO₂RR are finally summarized in Table 3.1. Overall, we find that Ti, Sc, Nb, Zr, Hf and Ta doping of PdH(111) are promising dopant candidates in most configurations.



Figure 3.4: Structures of intermediates (a) HOCO* (one bond), (b) CO*, (c) H* and (d) OH* on the top sites of a doped PdH(111) surface. (e) HOCO* forms two bonds with PdH(111). The blue spheres are Pd atoms, the small white spheres represent H atoms, the big grey spheres represent dopant atoms, the red spheres are O atoms, and the small grey spheres are C atoms. (f) Charge density difference figure for HOCO* with two bonds. The blue region represents charge depletion while the yellow region means charge accumulation.

Doping configurations	Possible candidates
Single	Nb, Zr
Dimer	Sc, Ti, Nb, Zr, Hf, Ta
Triangle	Sc, Ti, Nb, Zr, Hf, Ta
Parallelogram	Sc, Ti, Nb, Zr, Hf, Ta
Island	Sc, Ti, Nb, Ta
Overlayer	Ti, Nb, Ta, V

Table 3.1: Possible candidates for different PdH(111) doping configurations according to free energy diagrams.



Figure 3.5: The scaling relation of intermediates on doped PdH(111) with different elements between HOCO* and CO* in different dopant configurations. The red line is fitted to Fe, Co, Ni, Cu, Ru, Rh, and Ag-doped PdH(111) where HOCO* forms one bond to the surface. The blue line is fitted to all doped PdH(111).

The scaling relations of intermediates on doped PdH(111) with different elements in different doping configurations are further studied to understand catalytic performance. Taking the top site adsorption as an example, the structures of the surface with HOCO*, CO*, H*, and OH* are displayed in Figure 3.4a-d. The binding energies in the most stable sites are, however, applied in the following analysis with the corresponding data listed in Table A.3-A.8. Figure 3.5 shows the scaling relation between HOCO* and CO* in the six dopant configurations. We use R², a statistical measure that represents the proportion of the variance between two variables, to describe how well a linear scaling relation is fitted, and a good fit has R² close to 1. In Figure 3.5a-f, Fe, Co, Ni, Cu, Ru, Rh, and Ag doping are marked in red dots and the corresponding fitted lines are also shown in red. They

display clear linear scaling relations in all configurations with R² values 0.84, 0.88, 0.89, 0.96, 0.97 and 0.86, respectively. This is because they all form only a C-metal bond on the top of one dopant in all doping configurations according to optimized HOCO* structures as shown in Figure 3.4a. The fitted lines of the six doping cases using all doping elements are displayed by the blue lines. They show much lower R² values of 0.42, 0.36, 0.51, 0.48, 0.41, and 0.80, respectively. This is because the surfaces doped with Sc, Ti, Nb, Zr, Zn, V, Mn, Mo, Cr, Hf, Cd, W, Ta, and Re mostly tend to form two bonds to the surface consisting of a C-metal (C-M) and an O-metal (O-M) on two different metal atoms for HOCO* on the surface as displayed in Figure 3.4e. A small part of them, however, forms two bonds to the same metal atom as shown in Figure A.11. All structures are summarized in the database in the Appendix A and the corresponding formation of two bonds can be found in the database. The C-M and O-M bond lengths of HOCO* on the doped surfaces in different configurations are listed in Table A.18 and A.19, and O-M bond lengths are summarized in Figure A.15. We have chosen a surface-oxygen distance of 2.7 Å to determine whether a bond is formed between the O in HOCO and the surface because few surfaces have O-M bond lengths between 2.4 and 2.8 Å. A more detailed discussion is given in the Appendix A. For example, Figure 3.4f shows the charge density difference for HOCO* on the Ti parallelogram doped surface, which clearly demonstrates that two bonds form on the surface. The bond length of C-Ti is 2.259 Å and the bond length of O-Ti is 2.032 Å. We therefore conclude the formation of two bonds breaks the previous single C-metal scaling relations and thus reduces the R². Furthermore, the dopant structures resulting in the formation of two bonds show stronger HOCO* binding with the surface compared to their CO* binding energy, which may be the reason the free energies of the HOCO* step with the two bonds are relatively low in Figure 3.3. Figure A.12 shows the scaling relations of adsorbates HOCO* vs. OH* in different doping configurations. Similarly, for the surfaces doped with Fe, Co, Ni, Cu, Ru, Rh, and Ag, their HOCO* binding energies can be well linear with the OH* energies, and the R² values are 0.81, 0.82, 0.81, 0.63, 0.77 and 0.83 in different doping configurations, respectively. However, their scaling relations of total metal element doped surfaces have worse R² values of 0.03, 0.46, 0.62, 0.60, 0.80, and 0.50, respectively. This could also be attributed to the formation of the two bonds of HOCO* on the surfaces as we described before. The scaling relations between CO* and H* intermediates on doped PdH(111) surfaces in different doping configurations are also shown in Figure A.13. The CO* and H* intermediates display good scaling relations with R^2 values of 0.68, 0.80, 0.74, 0.66, 0.78, and 0.49. This can be attributed to the fact that only one atom in CO* and H* interacts with the surfaces.

In order to further study the kinetic activity of doped PdH(111), a kinetic model is utilized. In Figure 3.6, the activity volcano of doped PdH(111) for CO₂RR in different doping configurations is given. It is seen that the kinetic activities depend on the binding energies of both HOCO* and CO*. The partial pressure of CO₂ and CO are 101325 Pa and 5562 Pa, respectively, and the overpotential (the difference between the applied potential and the equilibrium potential calculated with the BEEF-vdw functional) is set to 0.3 V. It can be noted that Ti, Sc, Nb and Zr demonstrate excellent catalytic activities in different doping



Figure 3.6: Activity volcano plots of doped PdH(111) with different elements for CO₂RR at 0.3 V overpotential in different dopant configurations.

configurations. Among them, Sc doping with dimer, triangle, and island configurations, Zr doping with dimer, triangle, and parallelogram configurations and Hf doping with dimer, triangle, and parallelogram configuration are close to the center of the volcano and thus show good activities. However, according to binding energy in Figure A.12, OH* binding of Sc, Zr, and Hf are so strong on the PdH surface, which will cause OH* poisoning. Besides, we notice that Ti doping with parallelogram and overlayer configuration and Nb doping with overlayer configuration are also closer to the center of the volcano compared to PdH. Furthermore, the free energies of OH* are smaller than 0.3 eV and thus will not be poisoned at 0.3 V overpotential. Therefore, they are expected to have better kinetic activities than pure surface. However, we can find that the CO* binding of Ti and Nb doping is stronger than pure PdH, which limits their kinetic activities at room temperature due to slow CO desorption. In order to further improve CO* activities of noneletrochemical step, one could increase the temperature. As shown in Figure A.14, we take Ti doping in the parallelogram configuration as an example. With the temperature increasing, the partial current density of CO* would increase and 7.72 mA/cm² can be achieved at 350K. In addition, we calculate surface stability and the corresponding Pourbaix diagram[178, 179] of HOCO*, CO*, H*, OH*, metal ion dissolution, for PdH(111) surfaces including Ti doping in parallelogram and overlayer configurations, Nb doping with overlayer configurations, and pure PdH(111) as displayed in Figure A.20-A.25. The detailed methods are given in the Appendix A. It is noticed that ion dissolution is unfavorable when the potential is less than or equal to -0.304, -0.290, -0.224, and 1.017 V at pH = 0 for these four configurations, and the dissolution potential will be more negative as pH increases. This means that these three doped surfaces are stable under negative bias typically required for CO₂ reduction, but that stability might be an issue above the working potential.

Figure 3.7 illustrates the selectivity for CO₂RR and HER of doped PdH(111) in dif-



Doping elements



ferent doping configurations with the corresponding data listed in Tables A.3-A.8. We apply $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ as a descriptor to demonstrate the trend of producing CO and H₂. When the value of $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ is more negative, it indicates that there would be higher selectivity toward CO₂RR. Otherwise, the more positive value of $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ represents the higher selectivity toward HER. We find that a majority of elements doped PdH in different doping configurations will generate more H₂ than CO according to Figure 3.7. However, some overlayer dopings such as Sc, Mn, Fe, Co, Ni, and Zr prefer to generate more CO. It is worth noting that the values for Ti and Nb doping are more negative than for pure PdH(111) in most doping configurations and thus tend to produce more CO.

3.4 Conclusions

In this chapter, we utilize density functional theory calculations to study the CO₂RR and the competing HER on PdH(111). 22 transition metal elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re are doped into the PdH(111) surface with different doping configurations to explore their catalytic performance. Doping formation energies show Sc, Ti, Zn, Y, Zr, Nb, Hf, and Ta dopants are easier to dope into the surface. Free energy diagrams identify Ti, Sc, Nb, Zr, Hf, and Ta as possible doping candidates that lower the HOCO^{*} limiting step for the CO₂RR. The scaling relations of HOCO^{*} vs. CO^{*} binding energies in different doping configurations display

well-defined scaling relations for Fe, Co, Ni, Cu, Ru, Rh, and Ag doping, because HOCO* and CO* intermediates all form a single C-metal on the surfaces. However, the formation of the two bonds consisting of one C-metal and one O-metal bond breaks the scaling relation for other dopants, which is the reason why these dopants have strong HOCO* binding compared to the CO* binding. According to kinetic volcano plots, Ti doping with parallelogram and overlayer configuration and Nb doping with overlayer configuration are further found to have better kinetic activities than pure PdH(111) at a low overpotential of 0.3 V. At the same time, Ti and Nb are also possible to generate more CO compared with pure surface based on their selectivity toward the CO₂RR and HER. This chapter provides good guidance for studying Pd-base alloy hydrides.

Chapter 4 PdH_x(111)

This chapter is based on paper II and the corresponding supporting information can be seen in Appendix B.

4.1 Introduction

Metallic Pd electrocatalyst has received attention for reducing CO₂ to CO; it not only exhibits good selectivity and activity but also can split CO and H₂ simultaneously to synthesize gas with an adjustable H_2 to CO ratios.[167] Pd is usually considered as a favorable HER catalyst, but it can also produce CO at a very similar ratio to H₂.[58] Chen et al. revealed that carbon-supported palladium (Pd/C) nanoparticles can generate CO and H₂ simultaneously in an aqueous electrolyte with a tunable CO/H₂ ratio from 0.5 to 1, which is a favorable ratio range to perform Fischer-Tropsch reaction that already exists in the industrial processes.[58] Chen et al. continued to explore the influence of different facets of Pd with cubic and octahedral particles dominated by Pd(100) and Pd(111) surfaces, respectively.[167] Their results show that the octahedral Pd particles have better activity and selectivity than cubic Pd particles, and both can produce suitable CO/H_2 ratios between 1 and 2, which are desirable ratios for the Fischer-Tropsch process. It is worth noting that experiments show that a key factor of the high performance is that Pd particles are transformed into Pd hydrides.[167, 180] In fact, there could be different concentrations of H in Pd hydrides (PdH_x) controlled by the applied potential, which has an important influence on the CO_2RR performance. [180, 181] Experiments only give the relation between the applied potential and CO₂RR performance, and corresponding DFT calculations have only compared the performance of pure Pd and stoichiometric PdH. However, the best concentration of H of PdH_x surface for CO_2RR to CO is not given, and it is unclear whether there is a saturation concentration of H.

Some previous theoretical efforts have been done to study CO₂RR or HER properties of PdH_x. Chen et al. reported the free energy diagram of Pd(111) and PdH(111). They concluded that the CO* desorption from the metal Pd(111) surface could be the ratelimiting step due to strong CO* binding compared to PdH(111).[58, 167] Chorkendorff and co-workers reported hydrogen adsorption on palladium and palladium hydride at 1 bar. They showed the relation between the adsorption energy of H and surface H coverage on Pd(111) and Pd hydride slabs, and that the H binding energies became weaker as H coverage increased. They thought the adsorption and desorption of H₂ are faster on β -Pd hydride than α -Pd hydride at 1 bar.[182] Erhart et al. constructed the phase diagrams of bulk Pd hydride and Pd-Au hydride using a cluster expansion and studied their thermodynamic properties. [183]. However, these theoretical efforts have not systematically investigated the effect of H concentration on CO₂RR. This chapter uses an active learning cluster expansion (ALCE) model equipped with Monte Carlo simulated annealing to search for the stable composition of $PdH_x(111)$ surfaces. Energies calculated by DFT are used to train the ALCE model and find the ground state CE structures of each H concentration of PdH_x from the CE convex hull. Furthermore, we perform DFT relaxation to verify the CE convex hull and finally get the DFT convex hull to identify the ground state DFT candidates. Once the stable candidates are found, the CO₂RR activity and selectivity are further studied. As a result, PdH, PdH_{0.97}, and PdH_{0.60} are finally screened out to be the most active candidates and able to generate CO/H₂ with suitable ratios.

4.2 Simulation details

All spin-polarized DFT calculations are carried out to train the cluster expansion model and calculate adsorption energies using the ASE [93, 94] and the VASP with the PAW method.[86–88] The BEEF-vdW ensemble is used for exchange and correlation functional, which performs quite well for chemisorption processes. [75] The first Brillouin zone is sampled by a $3 \times 3 \times 1$ Monkhorst-pack grid[173]. 400 eV is set for cutoff energy. The dipole correction is utilized in the z direction to remove the electrostatic dipole-dipole interaction due to periodically repeated surface slabs in all calculations. The structures are relaxed until all Hellman-Feynman forces are less than 0.01 eV/Å and the energy convergence criterion is within 10^{-6} eV. More DFT calculation details can be found in the Appendix B.

Monte Carlo simulated annealing at each H concentration of PdH_x is performed in order to search for the ground state structure of each concentration, which is carried out in CLEASE. The standard Metropolis Monte Carlo at each temperature during simulated annealing is used and has the acceptance probability \mathcal{P}_{acc} as follows:[96]

$$\mathcal{P}_{\mathsf{acc}} = \min\left\{1, \ \exp\left(\frac{-(E_{\mathsf{new}} - E_{\mathsf{old}})}{k_{\mathsf{B}}T}\right)\right\}$$
(4.1)

Where E_{new} and E_{old} are the energies of new and old structures, respectively. k_B is the Boltzmann constant and T denotes temperature. The temperatures are set as 10^{10} , 10000, 6000, 4000, 2000, 1500, 1000, 800, 700, 600, 500, 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 2 and 1 K. For each temperature, 1000 Monte Carlo sweeps are applied (1 sweep includes N steps, where N is the number of atoms.)

4.3 Results and discussions

To illustrate the structures of the $PdH_x(111)$ surface, we take an H concentration of 50% as an example here and display the side and top views in Figure 4.1. The structure has four bilayers, including 16 Pd atoms and up to 16 H atoms. It can be seen that PdH_x has a Pd atom (blue spheres) framework, with the smaller H atoms (white spheres) filling octahedral sites between the larger Pd atoms. Red virtual atoms show H vacancies. The PdH_x(111) slab is cut from the optimized bulk PdH with the crystal constants a = b = c = 4.138 Å and the slab size is $4 \times 4 \times 4$ with a = b = 11.704 and c = 28.362 Å. Here, we



Figure 4.1: (a) The side view and (b) the top view of $PdH_x(111)$ surface that take H concentration of 50% as an example. The blue spheres are Pd atoms, the white spheres represent H atoms, and the red spheres are H vacancies.

ignore the crystal constants variation when the H concentrations change because they vary only in a small range, approximately 0.2 Å from 0 to 1 for H concentration, which is less than 5% of the lattice constants of PdH.[184] Besides, previous work reported the strain of PdH only has a small impact on the performance of CO_2RR and HER.[185]

There can be up to 64 H atoms in the $PdH_{x}(111)$ surface as shown in Figure 4.1. It is impossible to run DFT calculations for all the possible structures (2⁶⁴ neglecting symmetry). Instead, we utilize an ALCE surrogate method. The workflow of the ALCE for $PdH_{x}(111)$ is shown in Figure B.1. After defining the CE settings, we generate 50 random H concentration structures of PdH_x to form the initial database pool and then relax the structures to get their DFT energies, which can be used to train the CE model and get the initial ECI values. If the RMSE between DFT energies and CE energies is less than 5 meV/atom, we consider the CE model converged. Otherwise, more random structures will be generated and run by DFT, which are finally added to the database pool to verify if the CE model is converged. Once we have the converged the CE model, Monte Carlo simulated annealing (MCSA) with the CE calculator is performed to search for ground state structures for each H concentration of PdH_x , which gives 63 MCSA in total because the numbers of H range from 0 to 64 (concentration from 0 to 1) except pure slabs Pd(111) and PdH(111). The CE convex hull can be calculated according to all ground state structures at each concentration of H of PdH_x . Theoretically, the stable structures could be found from the vertices of the CE convex hull at this point. However, considering the uncertainty of the processes, the obtained ground state structures should be verified by DFT calculations. Therefore, the possible stable candidates of the CE convex hull are further collected, relaxed by DFT calculations, and finally added to the database pool to continue the next new round. At the same time, the DFT convex hull is also carried out until its convergence. The criterion of convergence is defined that the shape of the DFT convex hull will not change for three rounds. After that, the final stable candidates can be found according to converged DFT convex hull, and their CO₂RR activity and selectivity toward CO and H₂ are further studied.



Figure 4.2: (a) The linear fitting plot of CE energy and DFT energy for 50 random structures. (b) The ECI distribution was obtained from cluster expansion fitting. (c) The DFT convex hull curve of mixing energy as a function of H concentration in round 9. (d) The H concentration of each layer as a function of the total concentration of H for the structures of the DFT lowest energies in each concentration.

To study stable compositions of $PdH_x(111)$, CE calculations are performed using the CLEASE package. Figure 4.2a shows the linear fitting between CE energies (E_{CE}) and DFT energies (E_{DFT}) when we have 50 random structures in round 1. It can be seen that both 10-fold cross-validation error and RMSE are really small, 1.043 meV/atom and 0.450 meV/atom, respectively, which illustrates that the CE model is really good for the $PdH_{x}(111)$ surface. The ECI value distribution as a function of cluster diameter (1st, 2nd, 3rd, or 4th nearest neighbor) is displayed in Figure 4.2b. It can be noticed that the ECIs of 0, 1, and 2-bodies are larger, while there are more 3-body and 4-body ECI values closer to 0. To avoid overfitting, we choose to use up to 4-body interactions and neglect high terms. To get accurate stable compositions, ALCE is carried out to deal with the uncertainty of the CE. After 9 rounds, the vertices of the DFT convex hull are unchanged in the last three rounds, which means the convex hull is converged. In addition, the fitting RMSEs remain small during the 9 rounds as displayed in Figure B.4 and Figure B.5, meaning that the CE models remain good. For each round, simulated annealing at each H concentration is calculated to find ground state structures as the example round 1 in Figure B.3. As shown in Figure 4.2c, 12 stable candidates can be finally obtained and are marked by black crosses. They are Pd₆₄, Pd₆₄H₂, Pd₆₄H₄, Pd₆₄H₈, Pd₆₄H₁₀, Pd₆₄H₁₃, Pd₆₄H₃₁, Pd₆₄H₃₉, Pd₆₄H₅₃, Pd₆₄H₆₂, Pd₆₄H₆₃ and Pd₆₄H₆₄ and the corresponding H concentrations are 0,

0.0313, 0.0625, 0.1250, 0.1563, 0.2031, 0.4844, 0.6094, 0.8281, 0.9688, 0.9844 and 1, respectively. The side and the top view of optimized example structures among them can be found in Figure B.10. Figure 4.2d shows the H distributions of each layer as a function of total concentrations of H in the slabs for the slabs of the DFT lowest energies in each concentration. The first layer is first filled up with H, then the fourth and third layers are filled up, respectively. Finally, the sublayer (second layer) will be finally filled at last. Possible artifacts due to the finite thickness of the model slab should be considered. To further confirm our conclusion, the $PdH_{x}(111)$ structures with more atomic layers with one missing layer are explored as displayed in Figure B.11 and B.12 in the Appendix B. It can still be found that removing the sublayer H has the lowest energy and thus will be filled at last, independent of the slab thickness. In addition, semi-grand canonical Monte Carlo calculations are implemented to study H chemical potential, temperature, and pressure influence on H concentration as shown in Figure B.14, B.15 and B.16 and the corresponding analysis can be found in the Appendix B. Besides, all bare candidate surfaces are used to study the Pourbaix diagram and the phase transformation process from Pd to PdH under the applied potential in Figure 4.5c-d assuming the surface to be in equilibrium with protons and electrons at all potentials. The corresponding computational details can be found in the Appendix B. Figure 4.5c shows the relative free energy of surface structure as a function of potential at pH 7.3, where the H concentration increases when the larger potentials are applied. The corresponding H concentration as a function of applied potential is shown in Figure 4.5d. This displays metal Pd can be completely transformed to Pd hydride at a potential of about -0.6 V vs. RHE assuming the surface is in equilibrium with protons and electrons. However, the characterization of Pd aerogels by Schmidt and co-workers suggests H concentration is saturated around 60% already at -0.1 V,[181] which suggests the surface can be in equilibrium with H_2 gas rather than protons and electrons. In that case, the $Pd_{64}H_{39}$ surface is likely the active surface for CO production.

After identifying stable candidates on the DFT convex hull, their CO_2RR and HER performances are further studied. Figure 4.3a shows the different adsorption sites of a random structure, which are displayed in small green spheres. They are automatically found according to local similarity, which compares the similarity of local structure as displayed in Figure 4.3c. The similarity is defined by comparing the neighbor list information of each adsorbate within a 2.8 Å cutoff sphere, including numbers of neighbor atoms, neighbor element types, and distance lists between adsorbate and neighbor atoms. We consider them to be the same adsorption site if the similarity is 1; otherwise, they are different sites. Here only the top site, fcc site, and hcp site are considered, and the fcc sites very close to H atoms (less than 1 Å) are not considered because adsorbates located in these sites can easily react with the neighboring H. We do not consider bridge sites because they are unstable. All information on surface structures with adsorbates on all unique sites can be found in our database.[186] Binding energies of adsorbates of HOCO*, CO*, OH* and H* on the most stable sites of all PdH_x candidates are shown in Figure 4.3b and the corresponding data can be found in Table B.1. It can be seen that



Figure 4.3: (a) Adsorption sites schematic diagram on $PdH_x(111)$ surface. (b) Binding energies of HOCO*, CO*, OH*, and H* as a function of H concentration. (c) Cutoff sphere schematic diagram of adsorbate on $PdH_x(111)$ surface. (d) Free energy diagram of CO₂RR of candidates. The insets show HOCO* and CO* adsorption surface structures. The blue spheres are Pd atoms, the small white spheres represent H atoms, the grey spheres are C atoms, the red spheres are O atoms and the small green spheres denote adsorption sites.

the binding energies of all adsorbates gradually increase as the concentration of H goes up from 0 to 1, especially for the adsorbate CO*. The CO₂RR free energy diagram of all candidates with adsorbates on the most stable sites is displayed in Figure 4.3d, and the corresponding data can be found in Table B.2. We notice that most surfaces have very negative binding energies and thus have strong CO* binding, which results in CO* poisoning, especially for candidates with low H concentration. For example, the free energies of Pd₆₄, Pd₆₄H₂, Pd₆₄H₄, Pd₆₄H₈ and Pd₆₄H₁₀ at CO* step are -1.259, -1.196, -1.189, -1.017 and -0.938 eV, respectively. They have so strong CO* binding that CO* is very hard to release from the surface, which is the reason why CO* poisoning happens. This can also be found in Figure B.13e. On the other hand, for candidates with high H concentration, their free energies at HOCO* are very high. For example, the free energy of Pd₆₄H₆₂ at the HOCO* step is 1.121 eV, which is too weak to bind HOCO* at low overpotential. Therefore, the ideal CO₂RR candidate should have strong HOCO* binding and weak CO* binding. It is worth noting the PdH surface with full H occupation does not have

too high HOCO* free energy step (0.79 eV), and weak CO* free energy (0.22 eV) and thus no CO* poisoning. Besides, $Pd_{64}H_{63}$ has very weak CO* binding, 0.392 eV of CO* free energy, and acceptable HOCO* free energy. $Pd_{64}H_{39}$ has weak HOCO* binding free energy (0.686 eV) and acceptable CO* adsorption. Thus, $Pd_{64}H_{64}$, $Pd_{64}H_{63}$ and $Pd_{64}H_{39}$ are possible candidates of CO₂RR, which is consistent with the activity volcano in Figure 4.5a.



Figure 4.4: Scaling relations for adsorbates on $PdH_x(111)$ configurations on the convex hull.

To further understand the catalytic performance of $PdH_{x}(111)$ surfaces, the scaling relations between different adsorbates are shown in Figure 4.4 and the binding energy relations with error ellipsoids can be found in Figure B.13. The relations E_{CO*} vs. E_{HOCO*} , E_{OH*} vs. E_{HOCO*} , E_{H*} vs. E_{HOCO*} , E_{OH*} vs. E_{CO*} , E_{H*} vs. E_{CO*} and E_{H*} vs. E_{OH*} are displayed in 4.4a-f, respectively, and their R² values are given, which is a statistical measure to illustrate how well the linear scaling relations are fitted. For the ideal scaling relation, the R² value is close to 1. Otherwise, it is worse if the R² value is close to 0. We can see that their R² values are 0.72, 0.65, 0.68, 0.87, 0.77, and 0.60, respectively, which demonstrates that they have good scaling relations. However, it can also be noticed that there are some obvious outliers. For example, Pd₆₄H₃₉ in Figure 4.4f is far from the best-fit line. This might be attributed to H segregation, which breaks the scaling relation. The H concentration distribution plots of clean surfaces and surfaces with adsorbates are displayed in Figure B.8 and Figure B.9 in the Appendix B. It can be noticed that there are fewer H atoms in the 1st layer and more H atoms in the 2nd layer for OH*, while more H is in the 1st layer and less H is in the 2nd layer compared to that of the clean surface for Pd₆₄H₃₉.

A kinetic model explores the CO_2RR activity for the $PdH_x(111)$ surfaces. Figure 4.5a shows the activity volcano at -0.5 V overpotential at room temperature. The current den-



Figure 4.5: (a) Activity volcano plot of $PdH_x(111)$ candidates for CO_2RR at -0.5 V overpotential. (b) Selectivity plot toward CO and H₂. (c) Stability of ground state structures at pH 7.3. (d) The concentration of H as a function of potentials. The dashed line shows the saturation of H if the surface is in equilibrium with H₂ at 1 bar.

sity depends on both $E_{\text{HOCO}*}$ and $E_{\text{CO}*}$, which is more accurate than a single descriptor. We notice that PdH_x with low H concentration is far away from the apex of the volcano due to the strong CO binding, which means they have poor kinetic activity. The completely H-filled Pd₆₄H₆₄ is the closest to the apex, illustrating that it has the best activity. In addition, Pd₆₄H₃₉ and Pd₆₄H₆₃ also exhibit good kinetic activity for higher H concentration. Besides, according to Figure 4.4b, we can see that the OH* binding energies on Pd₆₄H₆₄, Pd₆₄H₃₉ and Pd₆₄H₆₃ are weak, so OH* will not poison them. Figure 4.5b shows the selectivity of all candidates toward CO and H₂. We compare the binding energies of the first step of the CO₂RR and the HER. If the binding energy of H* is lower than that of HOCO*, it means HER is thermodynamically preferred over CO₂RR and the catalyst tends to produce more H₂. We notice that all of the candidates tend to generate more H₂ as shown in Figure 4.5b. Besides, Pd₆₄H₆₄ is very close to the black dashed line and can produce more CO, and thus its CO/H₂ ratio is closer to components of syngas compared to other candidates.

The statistical distribution of all candidates is calculated to reveal the effect of H and Pd on binding energies. Here, the statistical data of binding energies includes all possible adsorption sites on all the candidate surfaces. Figure 4.6a-d display the frequencies of H, Pd, and the total atoms within a sphere with a 2.8 Å radius centered on the adsorbate as



Figure 4.6: Distribution of atom Pd and H of all candidates within the cutoff sphere as a function of HOCO*, CO*, OH*, and H* binding energies. The yellow curves are fitted Gaussian distribution of H.

a function of the binding energies of HOCO*, CO*, H* and OH*, respectively. In addition, Figure 4.6a-b indicate the most favorable binding energy for HOCO* and CO* marked in blue, respectively. We see the tendency that the binding energies for all adsorbates are weaker when there are H atoms within the cutoff sphere of adsorbates. The fitted Gaussian distributions of H are also shown in the yellow curves in Figure 4.6. Their positions at the center of the peak are 0.60, -0.15, 0.44, and 1.52 eV, respectively, which are relatively weak in their corresponding binding energy distributions. Therefore, it can be concluded that H atoms weaken the binding energies of all adsorbates on PdH_x surface. To further verify the conclusion, the partial density of states (PDOS) of the d-band is calculated. Figure B.17 shows the PDOS of the bare surfaces of all candidates, and the corresponding d-band centers are given. It can be seen that d-band centers gradually decrease as H concentrations increase. The linear fit between d-band centers and H concentrations is also shown in Figure B.18. The R-squared value is used to describe the degree of their linear relation. The linear relation will be stronger if the R-squared value is closer to 1. The R-squared value is 0.87 in Figure B.18 and thus they have a strong linear relation. The lower d-band center means weaker binding energy.[187] We further calculate d-band centers for surfaces with HOCO* and CO* to support this. Figure B.19 and Figure B.22 show the PDOS and d-band center for all candidate surfaces with HOCO* and CO*, respectively. Their corresponding linear fits between H concentrations and d-band centers

and between adsorbate binding energies and d-band centers for all surfaces with adsorbates are shown in Figure B.20 and Figure B.22, respectively. It can be noticed that there are still very good scaling relations between H concentration and d-band centers for surfaces with adsorbates. Their binding energies have a good linear relation with d-band centers. This can be further concluded that increased H concentration can weaken the binding energy.

4.4 Conclusions

In this chapter, the impact of H concentration on $PdH_{x}(111)$ surfaces on the CO₂RR and the HER has been studied using theoretical methods. Active learning cluster expansion equipped with Monte Carlo simulated annealing has been implemented to find stable $PdH_{x}(111)$ surface candidates. We have obtained 12 stable candidates from converged DFT convex hull, which are Pd₆₄, Pd₆₄H₂, Pd₆₄H₄, Pd₆₄H₈, Pd₆₄H₁₀, Pd₆₄H₁₃, Pd₆₄H₃₁, $Pd_{64}H_{39}$, $Pd_{64}H_{53}$, $Pd_{64}H_{62}$, $Pd_{64}H_{63}$ and $Pd_{64}H_{64}$. We have carried out a method to find adsorption sites and then calculate the binding energies automatically. Their free energies are further calculated, illustrating the $PdH_x(111)$ surfaces with low H concentration have CO* poisoning. The scaling relations between different adsorbates show there are still good linear relations, but the segregation of H may have an influence on their scaling relations. According to the activity volcano, Pd₆₄H₆₄, Pd₆₄H₆₃ and Pd₆₄H₃₉ corresponding H concentrations of 1, 0.97, and 0.60 respectively, show high current densities at an overpotential of 0.5 V. The Pd₆₄H₃₉ surface is stable when the surface is in equilibrium with H₂ gas, and the H concentration matches well with the experimentally determined 60% H concentration of Pd hydride.[181] Due to the existence of the competitive reactions between CO₂RR and HER, the selectivity plot toward CO and H₂ is calculated and illustrates these three candidates have better CO production compared to others, especially for Pd₆₄H₆₄. The statistical distribution of Pd and H atoms in all candidates reveals that H atoms can weaken the binding energies of all adsorbates, which may provide good guidance to tune the binding energy.

Chapter 5 PdMH(111)

This chapter is based on paper III and the corresponding supporting information can be seen in Appendix C.

5.1 Introduction

Although the Faradaic efficiency for CO formation on Pd is lower than that on Au, Ag, and Zn, Pd can simultaneously generate H_2 at a similar Faradaic efficiency due to the competitive HER. The generated CO and H₂ are the main components of syngas, which can be directly used to synthesize valuable chemical products via the Fischer-Tropsch processes.[4] Several works report that Pd-based catalysts can also produce syngas through electrochemical CO₂RR. Sheng et al. report that carbon-supported Pd/C can simultaneously generate syngas with a CO to H_2 ratio between 0.5 and 1.[58] The current density can reach $0.6 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ at $-0.7 \,\mathrm{V}$ overpotential vs. reversible hydrogen electrode (RHE). In this electrochemical process, metal Pd nanoparticles are transformed into Pd hydride as observed by in-situ X-ray absorption spectroscopy and in-situ X-ray diffraction. Density functional theory (DFT) calculations showed that PdH weakens the binding energies of both CO* and H*.[58] Zhu et al.[167] illustrated that different facets of Pd nanoparticles have an influence on their performance in CO_2RR to syngas; for example, Pd(111) surface has a higher activity of CO₂RR and better CO selectivity than the Pd(100) surface. The CO partial current density of PdH(111) in their work can reach $17 \,\text{mA}\,\text{cm}^{-2}$ at $-0.7 \,\text{V}$ overpotential vs. RHE, while that of PdH(100) is around 3 mA cm^{-2} , which is greater than that of commercial Pd catalysts. DFT calculations explain that forming PdH(111) makes CO* desorption no longer difficult and thus improves the activity of CO₂RR.[167]

Liu et al.[188] reported that Pd-modified niobium nitride (Pd/NbN) can produce a much higher partial current density of syngas and larger CO Faradaic efficiency than Pd-modified vanadium nitride (Pd/VN) catalyst and commercial Pd/C catalyst. Among them, the CO partial current density of Pd/NbH is the highest at around 0.7 mA cm^{-2} at -0.7 V vs. RHE. In-situ X-ray diffraction illustrated the formation of PdH in Pd/NbN, which weakens *CO desorption and enhances the CO₂ conversion to syngas.[188] Lee et al.[59] reported the use of Pd-based bimetallic hydrides for producing syngas using the electrochemical CO₂RR approach. The second metal, such as Co, Ni, Cu, Ag, and Pt, was chosen to form alloys with precious metal Pd nanoparticles, and concentrations of the second metals were fixed at 25 % in their work. After applying potentials, the CoPd, NiPd, CuPd, AgPd, and PtPd alloys were transformed to (CoPd)H, (NiPd)H, (CuPd)H, (AgPd)H, and (PtPd)H, respectively, and their potentials of alloy hydrides formation were -0.322, -0.352, -0.434, -0.544 and -0.544 V vs. RHE, respectively. (AgPd)H, (CuPd)H, (NiPd)H, and (CoPd)H show higher CO partial current density than that of PdH. According to their
CO/H₂ ratio, (CuPd)H and (NiPd)H are more suitable to produce syngas with the ratio range between 1 and 2.[59] Our previous study[189] using DFT suggested that among the transition metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re doped into PdH(111) at different doping configurations, Ti and Nb doping yielded a higher performance of CO₂RR than undoped PdH(111). Furthermore, their generated CO and H₂ are suitable for generating syngas.[189] This gives clear guidance to further study of Ti- and Nb-Pd alloy hydrides.

In this chapter, Pd-based alloy hydrides $Pd_xM_{1-x}H_y$ (PdMH)¹ are studied to explore higher performance catalysts. Our previous work on doped-PdH showed that doping Ti and Nb into PdH can improve the CO₂RR activity, suggesting that the Pd alloy hydrides with better performance are likely to be found in the $Pd_xTi_{1-x}H_v$ and $Pd_xNb_{1-x}H_v$ phase space. However, the complex nature of the compositional and structural phase space that includes different compositions of alloy hydrides, different concentrations of the metal element and H of alloy hydrides, different adsorption sites, and different adsorbates, makes it intractable to screen out the stable and active $Pd_xM_{1-x}H_y$ catalysts DFT calculations. Herein, an ALCE surrogate model equipped with MCSA, a CO* filter, and a kinetic model are used to identify promising $Pd_xTi_{1-x}H_v$ and $Pd_xNb_{1-x}H_v$ catalysts with high stability and superior activity. Finally, 24 stable and active candidates of $Pd_xTi_{1-x}H_y$ and 6 active candidates of $Pd_xNb_{1-x}H_y$ are found via our approach. Among them, the Pd_{0.23}Ti_{0.77}H, Pd_{0.19}Ti_{0.81}H_{0.94} and Pd_{0.17}Nb_{0.83}H_{0.25} display superior current densities of approximately 5.1, 5.1 and 4.6 μ A cm⁻² at -0.5 V overpotential, respectively, which are significantly higher than that of PdH at $3.7 \,\mu\text{A cm}^{-2}$. The free energy diagram shows that their HOCO* binding is not too weak, while their CO* binding is not too strong, resulting in enhanced activities. The statistical analysis shows that the binding energies are mainly contributed by the elements Ti/Nb and H. Hence, three candidates, Pd_{0.23}Ti_{0.77}H, $Pd_{0.19}Ti_{0.81}H_{0.94}$, and $Pd_{0.17}Nb_{0.83}H_{0.25}$, are recommended in this chapter.

5.2 Simulation details

All DFT calculations are performed using the ASE [93, 94] with the VASP with the PAW method.[86, 87, 92] The exchange and correlation functional used in this chapter is the BEEF-vdW ensemble.[75] The cutoff energy is set to 400 eV and the electronic smearing width is 0.05 eV. A Monkhorst-Pack grid of $3 \times 3 \times 1$ is used to sample the first Brillouin zone.[173] The electronic relaxation is set to stop when the energy difference between two steps is smaller than 10^{-6} eV . The ionic relaxation will converge when all the forces' norms are less than 0.01 eV Å^{-1} . The Pd_xM_{1-x}H_y (111) surface is utilized because the PdH(111) surface is the most stable in experiments (M is the metal element Ti or Nb).[167] To remove the electrostatic dipole-dipole interaction in the *z* direction due to periodic boundary conditions, a vacuum layer of approximately 15 Å is added, and the dipole correction is applied along the *z* direction. A 4×4 surface supercell cell of the Pd_xM_{1-x}H_y (111) is utilized. Four atomic bilayers are used, each consisting of one Pd or

¹For simplicity, it is sometimes abbreviated as PdMH, where M means metal elements (only Ti and Nb in this chapter).

M atomic layer (M is Ti or Nb element) and one H or X atomic layer (X denotes H vacancy). We fix the bottom two bilayers in their bulk positions when relaxing the slab.

The Cluster Expansion in the Atomic Simulation Environment software package, namely CLEASE,[96] is used to implement CE calculations of the surface. The initial slabs and corresponding relaxed energies are used to train the CE model, which can quickly predict the energies of the given new structures and thus greatly reduce the computational cost. Up to 4-body clusters are included in this chapter, with the cutoff radii of 6.0, 5.0, 4.0 Å for 2-body, 3-body, and 4-body clusters, respectively. MCSA is carried out to find the ground-state structure at each concentration. 65×65 MCSAs are implemented in parallel for each active learning iteration (65 H concentrations and 65 metal (Ti or Nb) concentrations in this chapter). Each MCSA uses standard Metropolis Monte Carlo at decreasing temperatures of 10^{10} , 10000, 6000, 4000, 2000, 1500, 1000, 800, 700, 600, 500, 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 2, and 1 K. 1000 Monte Carlo sweeps are set at each temperature and each sweep has N attempted swaps (N is the number of atoms in the cell).

The binding energies, E_b , of adsorbates are calculated as:

$$E_b = E_{*+ads} - E_* - E_{ads},$$
 (5.1)

where E_{*+ads} is the DFT energy of the surface with an adsorbate. E_* is the DFT energy of the clean surface, and E_{ads} is the DFT energy of the adsorbate. The adsorbates include HOCO^{*}, CO^{*}, OH^{*}, and H^{*}. The binding energy calculations of HOCO^{*}, OH^{*}, and H^{*} are referenced to CO₂, H₂, and H₂O gas molecules, respectively, while that of CO^{*} is referenced to CO gas molecule. The stabilization energy and zero point energy are considered when the OH^{*} binding energy is calculated. The stabilization calculation details can be seen in Figure C.19 and the corresponding description in Appendix C.

The mixing energy, E_{Mixing} , is calculated to obtain the convex hull of $Pd_xM_{1-x}H_y$ according to:

$$E_{Mixing} = E_{\mathsf{Pd}_{\mathsf{x}}\mathsf{M}_{1-\mathsf{x}}\mathsf{H}_{\mathsf{y}}} - x\mu_{\mathsf{Pd}(\mathsf{bulk})} - (1-x)\mu_{\mathsf{M}(\mathsf{bulk})} - y\frac{1}{2}\mu_{\mathsf{H}_{2}(\mathsf{g})}$$
(5.2)

where $E_{Pd_xM_{1-x}H_y}$ is the DFT energy of $Pd_xM_{1-x}H_y$, where x is the concentration of element Pd and y is the concentration of element H. $\mu_{Pd(bulk)}$ and $\mu_{M(bulk)}$ denote the chemical potentials of bulk Pd and bulk metal M, respectively. $\mu_{H_2(g)}$ is the chemical potential of H₂ gas at 1 bar.

The Gibbs free energy (G) is calculated from:

$$G = E_{\mathsf{DFT}} + E_{\mathsf{ZPE}} + \int C_p \mathsf{d}T - TS$$
(5.3)

where E_{DFT} , E_{ZPE} , C_p , and S are the DFT energy, the zero point energy, the heat capacity, and entropy, respectively. The free energy calculations of gas-phase species utilize the ideal gas approximation. The harmonic approximation is used to calculate the free energy of the slabs with adsorbate. The free energy calculations of HOCO^{*}, CO^{*}, OH^{*}, and H^{*} are references to CO₂ gas, H₂ gas, and liquid H₂O. A +0.15 eV correction per C=O, +0.15 eV correction for HOCO* and +0.1 eV correction for H₂ are used for systematic overbinding corrections with the BEEF-vdw functional in all calculations.[174, 189] The free energy calculations of the molecules and various adsorbates can be found in Table A.9 and Table A.10, which are the same as in our previous work.[189] To avoid calculations of solvated protons, the computational hydrogen electrode (CHE) model is used in this chapter.[168]

5.3 Results and discussions



Figure 5.1: The workflow of the processes of the screening stable and active candidates of $Pd_xM_{1-x}H_y$ for CO_2RR . The top and side views of an example structure are given for the first 4 stages. The top views of HOCO* and CO* of an example candidate for the last stage. The blue spheres are Pd atoms, and the big grey spheres are metal M atoms (e.g., Ti). The white spheres are H atoms. The small grey spheres in adsorbates are C atoms, and the red spheres are O atoms.

The workflow for the screening of stable and active candidates of $Pd_xM_{1-x}H_y$ for the CO_2RR can be divided into the following five stages. The first stage shows the search space of the slabs of each $Pd_xM_{1-x}H_y$. For the $4 \times 4 \times 4$ bare slabs, there are 64 metal sites, which can be occupied by either Pd or the metal M, and 64 hydrogen sites which can be occupied by H or be vacant. Thus, the search space (including symmetrically identical slabs) is $2^{64} \times 2^{64} \approx 3.4 \times 10^{38}$, which is intractable to run DFT calculation for all slabs. To handle the huge search space, the ALCE model equipped with MCSA in parallel is utilized to obtain the ground-state slabs at each concentration. The specific implementation of the ALCE+MCSA can be seen in Figure C.1. The ALCE can obtain the accurate surrogate model to speed up the CE energy prediction of the new given slabs, while MCSA is used to obtain the ground-state structures at each concentration quickly. During this stage (the second stage), 100~200 stable bare slabs are found according to the DFT convex hull, which is a huge reduction of search space from the original 3.4×10^{38} possible configurations. Since there are several unique adsorption sites for each stable bare surface, a local similarity comparison method is implemented to find unique sites.[190] After finding

the unique adsorption sites, CO* adsorbate is added to the bare slabs, and its binding energies are calculated using DFT. During this stage (the third stage), 600~900 unique slabs with CO* are found. The kinetic model in the fourth stage can be built to find the active range of CO* binding energies, reducing the number of possibly active slabs down to 200~300. Because the number of slabs is limited at this point, the binding energies of HOCO*, OH*, and H* adsorbates can now be calculated via DFT. In the last stage, the final candidates can be found through the kinetic model dependent on the binding energies of CO* and HOCO* at the most stable adsorption sites. Finally, less than 30 stable and active candidates of $Pd_xM_{1-x}H_y$ are found. All structures for the final candidates with adsorbates can be found in our database.[191]



Figure 5.2: The 10-fold CV or RMSE as a function of ALCE iterations for $Pd_xTi_{1-x}H_y$ (a) and $Pd_xNb_{1-x}H_y$ (b). The linear fitting plots of CE energy and DFT energy of ALCE iteration 12 for (c) $Pd_xTi_{1-x}H_y$ and (d) $Pd_xNb_{1-x}H_y$.

To quickly and accurately obtain the energies of slabs, a good surrogate model is very important. Here, The ALCE method is carried out to train the CE model. The CE candidates are extracted from the CE convex hull and calculated by DFT and then added to the train set of the CE. We re-train the CE model with the new train set and then get new CE candidates from the new CE convex hull. During this process, we focus on the DFT convex hull of each iteration rather than the CE convex hull, which means the CE convex hull will be confirmed by DFT, and thus, the DFT convex hull is more reliable. This differs from other approaches that directly use the convex hull predicted from the surrogate

model. As are shown in Figure 5.2a and Figure 5.2b, both $Pd_xTi_{1-x}H_v$ and $Pd_xNb_{1-x}H_v$ have 12 ALCE iterations. The green curves are 10-fold cross-validation (CV) errors that we mainly focus on. The initial 10-fold CV error of $Pd_xTi_{1-x}H_v$ is 10.276 meV/atom as shown in Figure C.2, which is a large error because only 50 random structures are in the initial train set. During the process of ALCE, the new structures of 50, 50, 200, 406, 500, 528, 382, 339, 320, 312, and 279 are added into the train set from iteration 2 to iteration 12, respectively. Their fitting plots can be found in Figure C.3, Figure C.4 and Figure C.5. The 10-fold CV is gradually decreased and finally maintains stable at around 2.0 meV/atom as seen in Figure 5.2c. A similar case is observed for $Pd_xNb_{1-x}H_y$ in Figure 5.2b. Its initial 10-fold CV error is as large as 10.276 meV/atom as shown in Figure C.20. Then, we add the new structures of 488, 499, 546, 575, 444, 437, 373, 272, 321, 342, and 352 into the train set from iteration 2 to iteration 12, respectively. The 10-fold CV error drops rapidly since iteration 2 and then remains stable at about 3.2 meV/atom, where the fitting plots can be seen in Figure C.21, Figure C.22, Figure C.23, and Figure 5.2d. Besides, the orange curves in Figure 5.2a and Figure 5.2b are the RMSEs of only train sets (without test sets) for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$. They are very small at first and then gradually go up to stable values, and finally, the RMSEs are close to their 10-fold CV errors. This could be because the overfitting is very large at first and gradually decreases as more structures are added to the train set.



Figure 5.3: The CE convex hull plots of ALCE iteration 12 for (a) $Pd_xTi_{1-x}H_y$ and (b) $Pd_xNb_{1-x}H_y$. The DFT convex hull plots of ALCE iteration 12 for (c) $Pd_xTi_{1-x}H_y$ and (d) $Pd_xNb_{1-x}H_y$.

To identify stable compositions of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, their CE and DFT

convex hull plots are calculated. Before obtaining the CE convex hull, the most stable slabs at each unique H and Pd concentration are first calculated by MCSA. Since there are 65×65 unique concentrations, MCSAs at each concentration are implemented to get 65×65 stable slabs, which can be used to calculate CE convex hull. The points on the vertices of the CE convex hull are likely to be stable compositions considering the uncertainty of the CE model. The possible stable candidates from the CE convex hull need to be verified by the DFT convex hull. To better understand the shape of the convex hull for $Pd_xTi_{1-x}H_v$ and $Pd_xNb_{1-x}H_v$, their 3D CE convex hulls in iteration 12 are displayed in the Figure C.13 and Figure C.31. However, in order to clearly see the specific concentrations of the convex hull, the 2D convex hulls are used in the following. Figure 5.3a and Figure 5.3b show the CE convex hull plots of the ALCE final iteration 12 for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, respectively. The CE convex hull of iteration 1-11 of $Pd_xTi_{1-x}H_y$ can be found in Figure C.10, Figure C.11 and Figure C.12, while that of $Pd_xNb_{1-x}H_y$ can be found in Figure C.28, Figure C.29 and Figure C.30. We notice that the CE convex hull of the last iteration is guite different from the initial one, but that of the last several iterations are very similar. This is because the CE model in the beginning is not good enough, and the overfitting is very large. However, the CE model is eventually improved and there is almost no overfitting in the end. It is worth pointing out that this situation is more obvious for the DFT convex hull. Figure 5.3c and Figure 5.3d display the DFT convex hull plots of the ALCE in iteration 12 for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, respectively. The previous iterations 1-11 of the DFT convex hull of $Pd_xTi_{1-x}H_y$ are shown in Figure C.6, Figure C.7 and Figure C.8, while that of the DFT convex hull for $Pd_xNb_{1-x}H_y$ are shown in Figure C.24, Figure C.25 and C.26. Since there are very similar tendencies for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, we only take $Pd_xTi_{1-x}H_y$ as an example here. We can notice that the DFT convex hull shapes greatly differ in the first 5 iterations. After that, their shapes become quite similar. Especially, the DFT convex hulls for the last 3 iterations are almost identical and thus we conclude that the DFT convex hull is converged. Furthermore, the volume of the DFT convex hull is a more straightforward quantity to understand whether the convex hull is converged. As shown in Figure C.9 and C.27, we can see that the volume of the DFT convex hull is rapidly going up in the first 5 iterations and finally reaches a stable maximum in the last several iterations, which further verify the converged DFT convex hull. However, we should clarify that it is very difficult to ensure that all the global ground state structures are located for any model at 65×65 concentrations. Even though our ALCE method with MCSA makes DFT convex hull converged, there still exists the rare probability that the true global ground state structures are not found, but the number of them is so few that we do not consider them. Finally, we find 125 stable slabs for $Pd_xTi_{1-x}H_y$ and 116 stable slabs for $Pd_xNb_{1-x}H_y$, which has greatly reduce the search space.

In order to further study the CO₂RR activity of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, a kinetic model is built as illustrated in Equation 2.53, Equation 2.54 and Equation 2.55. As shown in Figure 5.4a and Figure 5.4c, the activity volcano plots of the $Pd_xTi_{1-x}H_y(111)$ and the $Pd_xNb_{1-x}H_y(111)$ depend on the binding energies of CO* and HOCO* and the color bars show the current density calculated by the kinetic model at -0.5 V overpotential. The white



Figure 5.4: Activity volcano plot of (a) the $Pd_xTi_{1-x}H_y(111)$ candidates and (b) the corresponding partial magnification of black dashed area for CO_2RR at -0.5 V overpotential. Activity volcano plot of (c) the $Pd_xNb_{1-x}H_y(111)$ candidates and (d) the corresponding partial magnification of black dashed area for CO_2RR at -0.5 V overpotential.

dots in the Figures are all candidates after screening by the CO* filter in stage 4 in Figure 5.1, and $Pd_xTi_{1-x}H_v(111)$ has 111 candidates and $Pd_xNb_{1-x}H_v(111)$ has 76 candidates. The red dot is the slab of $Pd_{64}H_{64}$, about 3.7 μ A cm⁻², used for the comparison. It can be noticed that there are lots of candidates with better CO₂RR activity than that Pd₆₄H₆₄ for the $Pd_xTi_{1-x}H_y(111)$ in Figure 5.4a and they can be seen in the black dashed rectangle. For the $Pd_xTi_{1-x}H_y(111)$, 24 active candidates can be found in detail in the partial magnification in Figure 5.4b, which can be divided into four categories. The dots marked by blue have comparable current densities $(3.7-4.2 \,\mu\text{A}\,\text{cm}^{-2})$ compared to the pure Pd₆₄H₆₄; the current densities of the dots marked by red, yellow, and black are sequentially better than that of $Pd_{64}H_{64}$. Especially, the current densities of the $Pd_{15}Ti_{49}H_{64}$ and $Pd_{12}Ti_{52}H_{60}$ can reach at about $5.1 \,\mu\text{A}\,\text{cm}^{-2}$ that is significant greater than Pd₆₄H₆₄. There is no too strong OH* binding on these active candidates as shown in Figure C.16 and thus no OH* poisoning. Besides, it can be noticed that the active candidates have a higher concentration of Ti and H. For the $Pd_xNb_{1-x}H_v(111)$, there are fewer active candidates, only 5 comparable slabs, which are shown in the partial magnification Figure 5.4d. They are $Pd_8Nb_{56}H_{27}$, $Pd_{12}Nb_{52}H_{56}$, $Pd_{15}Nb_{49}H_{29}$, $Pd_{36}Nb_{28}H_{33}$ and $Pd_{11}Nb_{53}H_{16}$, which have high Nb concentraion. Especially, the Pd₁₁Nb₅₃H₁₆ has the highest current density, $4.6 \,\mu\text{A}\,\text{cm}^{-2}$. The

OH^{*} binding on these active candidates is not too strong and thus does not poison the surfaces as shown in Figure C.34. Besides, it is worth mentioning that the candidates of the Pd alloy hydride have much better CO_2RR activity than the corresponding candidates of the doped Pd hydride in our previous work.[189]



Figure 5.5: Free energy diagram of (a) CO_2RR and (b) HER of active candidates for the $Pd_xTi_{1-x}H_y(111)$. Free energy diagram of (c) CO_2RR and (d) HER of active candidates for the $Pd_xNb_{1-x}H_y(111)$.

In order to further understand the catalytic activities of active $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ candidates, the free energy diagrams of the CO₂RR and HER are shown in Figure 5.5. The black curves in all Figures are the free energy diagram of pure $Pd_{64}H_{64}$, which is used as a reference. The CO₂RR free energy diagrams in Figure 5.5a and Figure 5.5c illustrate that the HOCO* step of $Pd_{64}H_{64}$ is the potential limiting step, which means the free energy of the HOCO* is too high and thus the HOCO* binding is too weak to form efficiently on the surface. We notice that all of the HOCO* steps of the active candidates are lower than that of $Pd_{64}H_{64}$, which results in stronger HOCO* binding on the surface and thus makes the reaction 2.46 easier. Besides, it can be noticed that the majority of active candidates have a stronger binding of CO* than $Pd_{64}H_{64}$, but the binding energy should not be too strong to avoid CO* poisoning. The CO₂RR free energy diagrams of all candidates at stage 4 in Figure 5.1 are also displayed in Figure C.14 and Figure C.32, most of them are inactive for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$. This is be-

cause either their HOCO* step is so high (the binding is too weak) that it is too difficult to produce HOCO*, or the CO* step is too low (the binding is too strong)causing CO* poisoning. For the $Pd_{15}Ti_{49}H_{64}$, $Pd_{12}Ti_{52}H_{60}$, and $Pd_{11}Nb_{53}H_{16}$ with high current densities, their HOCO* binding is not weak and the CO* binding is not strong, which is the reason why they are very active. However, the HER free energy diagrams for both $Pd_xTi_{1-x}H_v$ and $Pd_xNb_{1-x}H_y$ indicate that the candidates that are active for CO_2RR also have better HER performance than $Pd_{64}H_{64}$ as shown Figure 5.5b and Figure 5.5d. All of them have lower free energy of the Volmer step compared to the Pd₆₄H₆₄, which can improve their HER activity. The HER free energy diagrams of all candidates at stage 4 in Figure 5.1 are also given in Figure C.15 and Figure C.33. We notice that most candidates have a stronger binding of H* than Pd₆₄H₆₄ and the bindings are not strong, which leads to their high HER activity. However, the candidates with high concentrations of H and Pd have weaker binding of H* than Pd₆₄H₆₄ and thus lower HER activity, which is consistent with our previous work.[190] In addition, there are no obvious scaling relations between the binding energies of different adsorbates for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ as shown in Figure C.16 and Figure C.34, which may be attributed to the high complexity of the composition of the surfaces and the different stable adsorption sites. Figure C.18 and Figure C.36 describe the selectivity of all candidates toward CO and H₂ for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, where $\Delta G_{HOCO*} - \Delta G_{H*}$ is used as a descriptor to illustrate the tendency towards CO₂RR and HER. The more positive value of $\Delta G_{HOCO*} - \Delta G_{H*}$ tends to generate more H₂, while the more negative value will produce more CO₂. It can be seen that a majority of candidates can produce more H₂ than CO₂ and only a small part of candidates can generate more CO₂.

To further reveal the role of each element in affecting the binding energies, the statistical distributions of the binding energy of different adsorbates as a function of the frequency of appearance of each element in a local environment are displayed in Figure 5.6. The grey rectangle area is the active zone for HOCO* or CO* according to the kinetic model for CO production. Figure 5.6a and Figure 5.6b are the distributions of the binding energies of HOCO^{*} and CO^{*} for $Pd_xTi_{1-x}H_v$. Most of the HOCO^{*} binding energies are not in the active zone, and only a small part of elements Ti and H is distributed in this active zone. However, the center of the CO* binding energies is nearly in the middle of the active zone. The distributions of the OH^{*} and H^{*} binding energies for $Pd_xTi_{1-x}H_y$ are also shown in Figure C.17. It is worth pointing out that Pd is distributed in the weak binding zone of the HOCO*, CO*, and OH*, which implies that Pd may weaken their binding. This is not the case for H* distribution as the element Pd is mainly distributed in the center of the zone of the H^{*} binding energies. For the $Pd_xNb_{1-x}H_y$, the distributions of binding energies of HOCO*, CO*, OH* and H* are displayed in Figure 5.6c-d and Figure C.35a-b, respectively. Similar to the $Pd_xTi_{1-x}H_y$, most of the binding energies of the HOCO* are higher than the active zone, and only a tiny part of Ti and H is in the HOCO* active zone. The centers of the distributions for the element Pd, Nb, and H are roughly in the middle of the CO* binding. Their OH* and H* distributions are displayed in Figure C.34. The metal element Pd is obviously only in the weak binding zone of the OH* (1.0-2.0 eV), while element



Figure 5.6: Distribution of atom Pd, Ti, and H of all candidates within the cutoff sphere as a function of (a) the HOCO* and (b) the CO* binding energies. Distribution of atom Pd, Nb, and H of all candidates within the cutoff sphere as a function of (c) HOCO* and (d) CO* binding energies.

Nb is mainly in the strong binding zone of the OH*. This means element Pd may weaken the OH* binding. Pd is mainly distributed in the strong binding zone of the H*. It is worth noting that the frequency of occurrence of element Pd is very low within the local spheres for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, which is much lower than that of Ti/Nb and H. This indicates that the adsorbates binding to elements Ti/Nb and H mainly contribute to the binding energy of the candidates.

5.4 Conclusions

We have used a surrogate model ALCE+MCSA, a CO* filter, and a kinetic model to screen high-performance catalysts of alloy hydrides of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ for CO₂RR, which greatly reduces the massive search space. Due to the large complexity that includes different compositions of alloy hydrides, different concentrations of metal elements and H of alloy hydrides, different adsorption sites, and different adsorbates, it is impossible to find the stable and active catalysts only using the density functional theory calculation. We utilize the high precision and low overfitting ALCE model with RMSE of about 2 or 3 meV/atoms, and a large amount of MCSA to identify the ground state Pd alloy hydride surfaces from the convex hull. Adsorption sites and binding energies of adsorbates are also accurate as they are also calculated from DFT. Finally, 24 ac-

tive candidates of $Pd_xTi_{1-x}H_y$ and 5 active candidates of $Pd_xNb_{1-x}H_y$ are screened out according to the kinetic model. Especially, the $Pd_{15}Ti_{49}H_{64}$ ($Pd_{0.23}Ti_{0.77}H$), $Pd_{12}Ti_{52}H_{60}$ ($Pd_{0.19}Ti_{0.81}H_{0.94}$) and $Pd_{11}Nb_{53}H_{16}$ ($Pd_{0.17}Nb_{0.83}H_{0.25}$) have good stability and excellent current densities (approximate 5.1, 5.1 and 4.6 μ A cm⁻², respectively), which are greatly higher than that of $Pd_{64}H_{64}$ at 3.7 μ A cm⁻². These are because their HOCO* binding is not too weak, and CO* binding is not too strong. Consequently, three candidates $Pd_{0.23}Ti_{0.77}H$, $Pd_{0.19}Ti_{0.81}H_{0.94}$ and $Pd_{0.17}Nb_{0.83}H_{0.25}$ are recommended for further experimental investigations.

Chapter 6 PdTiH(111) with Adsorbates

This chapter is based on paper IV and the corresponding supporting information can be seen in Appendix D.

6.1 Introduction

To search for the relevant surface structures while handling the complexity, three key factors need to be considered. Firstly, a global optimization method, such as minima hopping[192], simulated annealing [190, 193], or a GA[194–197], needs to be utilized to find the global minimum of a property of interest. Secondly, surrogate models including cluster expansion[96] or machine learning potentials[112, 137] can be used to speed up the calculations. The cluster expansion model can predict the energy of a given structure with reasonable accuracy, but it is very difficult to apply for complex systems, such as a surface with multiple adsorbates potentially in contact with an explicit solvent. Recently, machine learning interatomic potentials have gained significant attention due to their computational efficiency and accuracy. They offer a promising alternative to the cluster expansion model for complex chemical systems. Broadly, machine learning potentials can be classified into three categories: kernel methods such as Gaussian approximation potentials[198, 199], descriptor-based feed-forward neural networks (such as the Behler-Parrinello neural network potential[112, 118, 119]), and deep neural networks[137, 200]. Among them, deep neural networks, particularly rotationally equivariant message-passing neural networks, have become highly popular owing to their rapid and precise predictions for directional properties, like forces and dipole moments. Notable examples of these models include Neguip[135], MACE[136], and PaiNN[137]. Last but not least, it is also crucial to determine what physical properties need to be optimized. Structural stability is usually the property that we should consider optimizing first. There are two common types of stability: thermodynamical compound stability[201] and electrochemical stability[179]. The compound stability is determined by the convex hull of formation energy or mixing energy. It means a structure is thermodynamically stable if it is in its lowest energy state, or in chemical equilibrium with its components. During electrochemical reactions, electrochemical stability is another key factor determining if the material is thermodynamically stable in an aqueous electrochemical system. The most common method is to construct a surface Pourbaix diagram, which plots surface free energy as a function of applied potential and pH value. Besides, the surface free energy can also depend on additional state variables, such as chemical potentials, temperature, pressure, etc.

Significant efforts have been made in the Pd-based hydride system to establish relationships between the structures and the electrochemical performance.[18, 58] Our previous systematic doping study builds the relationship between transition metal doping and the CO₂RR activity. 22 transition metal elements are doped into the PdH (111) surface with different doping configurations, and Ti-doped Pd hydride shows high CO₂RR and HER activity.[189] Based on this information, the Ti-Pd alloy hydride system with a higher complexity is also likely to accommodate very active candidates. Subsequently, the chemical composition of the alloy hydride $Pd_xTi_{1-x}H_y(111)$ surface is searched by ALCE+MCSA according to the compound stability.[202] Some stable $Pd_xTi_{1-x}H_y$ structures are finally found to be very active for the CO₂RR and the HER. However, the adsorbate coverage and mixtures of different adsorbate species under the electrochemical reaction conditions are ignored during this structure searching process, which is crucial in the electrochemical CO₂RR and HER.[203, 204] It is very challenging to consider the above because the search space increases drastically due to the huge complexities associated with the structure and reaction conditions. Herein, this chapter focuses on dealing with these complexities to identify relevant structures under diverse reaction conditions in a fast and accurate way.

In this chapter, we apply a graph neural network-assisted multitasking genetic algorithm to screen $Pd_xTi_{1-x}H_y^{-1}$ surface with adsorbates under different CO_2RR conditions. The complex structural configurations result in a huge search space, where a deep learning model is used to speed up the atomic-scale calculations. Structures from DFT relaxations are used to train an ensemble of PaiNN models and the trained models are utilized to optimize the new structures and calculate their energy uncertainty. The surface free energy is used to evaluate the surface stability, which is dependent on temperature, CO partial pressure, applied potential, and the chemical potential difference of Pd and Ti. Due to the complexity of the state variables above, a multitasking genetic algorithm employing the maximum gain dynamic niching (MGDN) algorithm [205] is used to search for stable $Pd_xTi_{1-x}H_y$ surface structures simultaneously under all considered reaction conditions. Finally, 23 stable surface structures with adsorbates were found to be stable under different reaction conditions. Among them, $Pd_{0.56}Ti_{0.44}H_{1.06}+25\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+50\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+25\%CO$, and $Pd_{0.88}Ti_{0.12}H_{1.06}+25\%CO$ are found to be active for the CO_2RR .

6.2 Simulation details

All DFT calculations are performed by the VASP equipped with the PAW method.[87, 92] The ASE is used as the interface to all VASP calculations in this chapter.[93, 94] The BEEF-vdW functional[75] is used. A $3 \times 3 \times 1$ Monkhorstpack grid of k-points is used, and the energy cutoff is set to 400 eV.[173] The forces and the energy convergence criterion for all structure relaxations are set as 0.01 eV/Å and 10^{-5} eV, respectively.

The surface free energy is used for constructing the fitness function F_i in the GA global optimization. F_i can be calculated as follows:[206]

$$F_i = -(\gamma - \kappa_i * \sigma_i) \tag{6.1}$$

¹For simplicity, it is sometimes abbreviated as PdTiH in this thesis.

where κ is a factor that determines the relative weight of the predicted mean and uncertainty, and 0 and 1 are used in our calculations. σ is the standard deviation of the ensemble energies. The surface free energy γ of the Pd_xTi_{1-x}H_y(111) surfaces (with adsorbates) is used to evaluate the surface stability in the solution as follows:

$$\gamma_{\rm PdH} = \frac{1}{2A} (G_{\rm PdH(slab)} - N_{\rm (slab)} \mu_{\rm PdH(bulk)})$$
(6.2)

$$\gamma = \frac{1}{A} [G_{(\mathsf{N}_{\mathsf{Pd}}^2, N_{\mathsf{Ti}}^2, N_{\mathsf{H}}^2, N_{\mathsf{ads}}^i)} - G_{(\mathsf{N}_{\mathsf{Pd}}^1, \mathsf{N}_{\mathsf{Ti}}^1, \mathsf{N}_{\mathsf{H}}^1)} - \Delta N_{\mathsf{Pd}} \Delta \mu_{\mathsf{Pd}} - \Delta N_{\mathsf{Ti}} \Delta \mu_{\mathsf{Ti}} - \Delta N_{\mathsf{H}} \Delta \mu_{\mathsf{H}} - \sum_i N_{i(\mathsf{ads})} \mu_{i(\mathsf{ads})} - n_e U - n_e k_{\mathsf{B}} T \mathsf{ln10pH}] - \gamma_{\mathsf{PdH}}$$
(6.3)

where $G_{(N_{Pd}^2, N_{Tl}^2, N_{ads}^2)}$ and $G_{(N_{Pd}^1, N_{Tl}^1, N_{H}^1)}$ are the free energies of structure 2 and structure 1, respectively. Structure 2 is an arbitrary surface with adsorbates and structure 1 is a bare Pd₁₆H₁₆ without adsorbates. $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$, $\Delta \mu_{H}$, and $\mu_{i(ads)}$ are the chemical potential difference of Pd, Ti, H and the chemical potential of adsorbate, respectively. U, pH, and T are the applied potential, pH value, and temperature, respectively.



Figure 6.1: The phase diagram (a) and chemical potential diagram (b) of $Pd_xTi_yH_z$.

The possible Pd and Ti chemical potentials for the Pd-Ti-H system are identified from the chemical potential diagram in Figure 6.1. More than 200 structures are collected from the Materials Project[207] and the Open Quantum Materials Database (OQMD)[208]. The collected structures are then reoptimized with our chosen DFT parameters. The calculated energies are used to construct the Pd-Ti-H phase diagram and chemical potential diagram using the Pymatgen package.[209] The bulk PdH, the H₂ or proton, and the bulk TiPd₃ are assumed to be in equilibrium with $Pd_xTi_{1-x}H_y$ surface because we are interested in high H and Pd concentrations but low Ti concentrations.

The adsorbates species CO^{*}, H^{*} and OH^{*} are assumed to be in equilibrium with CO, H_2 , H_2O , protons and eletrons according to the reactions:

$$CO* \rightleftharpoons CO(g) + *$$
 (6.4)

$$\mathsf{H}^{+} + \mathsf{e}^{-} + * \rightleftharpoons \mathsf{H} * \tag{6.5}$$

$$H_2O(I) + * \rightleftharpoons OH * + H^+ + e^-$$
(6.6)

A rotationally equivariant message-passing neural network, namely PaiNN[137, 210], is applied to speed up the relaxation of the structures. The $Pd_xTi_{1-x}H_y(111)$ surfaces with adsorbates are first calculated by DFT, and we select one single-point structure for every 10 ionic steps, which are fed to the deep learning model. The cutoff radius is set to 5.0 Å. We use ensemble PaiNN models with 8 different architectures (116, 120, 124, 128, 132, 136, 140, 144 node features) to obtain the mean energy and forces and their variances. They are trained using the Adam optimizer and the learning rate is set to 0.0001. The maximum train step is 2,000,000 and the batch size is set to 12. A mixed loss function of energy and forces is used (see Equation D.4) and the balance parameter λ is set to 98%. RMSE of energy and force are calculated by Equation D.5 in the Appendix D.

A multitasking genetic algorithm (MTGA) is carried out to search for the $Pd_xTi_{1-x}H_v(111)$ surfaces (with adsorbates) under various reaction conditions. The surface structures with adsorbates can have different compositions and chemical orderings of the surface with different coverages, types, and mixtures of the adsorbates. The structural diversity is mainly controlled by the operators, which is crucial to determining how to generate new structures. We develop the operators including slab operators that manipulate metal and hydrogen atoms in the slab, adsorbate operators that manipulate adsorbates on the surface, and crossover operator that combines the slab from one structure and adsorbates from another structure. The details can be found in the Appendix D. A set of comparators is used to identify duplicates, including the potential energy comparator, nearest neighbor matrix string comparator in ASE[93], and graph comparator in ACAT[205]. The population size is set to 50. The MTGA converges when new candidates cannot be found anymore in the last three consecutive generations. In the MTGA calculations, the MGDN algorithm (implemented in ACAT)[205] is employed to find the best candidate structures under all considered reaction conditions. After integrating the MTGA and the PaiNN model, an automated active learning workflow based on MyQueue[172] is used to find the global minima.

The search space of surface structures N_{struct} and the number of tasks N_{task} for $Pd_xTi_{1-x}H_y$ (111) with adsorbates are calculated by the following equation 6.7:

$$N_{\text{struct}} = 2^{N_{\text{Pd/Ti(slab)}}} \cdot 2^{N_{\text{H(slab)}}} \cdot (N_{\text{ads}} + 1)^{N_{\text{sites}}}$$
(6.7)

$$N_{\mathsf{task}} = N_T \cdot N_{P_{\mathsf{CO}}} \cdot N_U \cdot N_{\Delta\mu_{\mathsf{Pd}}} \cdot N_{\Delta\mu_{\mathsf{Ti}}} \cdot N_{\kappa} \tag{6.8}$$

where $N_{Pd/Ti(slab)}$ and $N_{H(slab)}$ are the numbers of Pd/Ti and H in the slab without adsorbates, respectively. N_{ads} is 3 including CO*, H*, and OH*. N_{sites} is the number of the adsorption sites. N_T , $N_{P_{CO}}$, N_U , $N_{\Delta\mu_{Pd}}$ and $N_{\Delta\mu_{Ti}}$ are the number of considered temperatures, CO partial pressures, applied potentials, chemical potential differences of Pd and Ti, respectively.



6.3 Results and discussions

Figure 6.2: The phase equilbrium between the $Pd_xTi_{1-x}H_y$ with CO*, H* and OH* adsorbates and CO gas, H₂ gas, liquid H₂O, bulk PdH and bulk TiPd₃.

In order to study the thermodynamic stability of compounds, the Pd-Ti-H ternary phase diagram is calculated as shown in Figure 6.1a. The green circles on the phase diagram show the stable compounds, including Pd, Ti, H₂, TiPd₈, TiPd₅, TiPd₃, TiPd₂, TiPd, Ti₂Pd, TiH₂ and PdH. The unstable phases within 1 eV above the convex hull are shown in the phase diagram, marked by the red squared dots. We assume the Pd-Ti-H slab is in equilibrium with the stable compound PdH, H_2 , and TiPd₃ because we are interested in high H and Pd concentration but low Ti concentration. Figure 6.1b shows the corresponding chemical potential diagram. The total chemical potential of Pd_xTi_yH_z without adsorbates is dependent on the chemical differences $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$ and $\Delta \mu_{H}$. The equilibrium chemical potential of the three stable compounds PdH, H₂ and TiPd₃ is highlighted in the dashed red circle, and their equilibrated chemical difference values of $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$ and $\Delta \mu_{H}$ are -2.249, -7.285 and -3.614 eV, respectively. These terms are used to calculate the surface free energy shown in Equation 6.3. Figure 6.2 is a more straightforward representation of the equilibrium between the $Pd_xTi_{1-x}H_y$ slab with adsorbates and the corresponding stable compounds. The right part of the slab (the blue part) is equilibrated with the bulk PdH, the protons, and the bulk TiPd₃ as described above. The left part (the red part) illustrates the adsorbates are equilibrated with the CO gas, the protons, and the liquid H_2O . In the process of the electrochemical CO_2RR , the HOCO^{*}, CO^{*}, H^{*}, and OH^{*} are all potential adsorbate species that can present on the catalyst surface. However, the adsorption energy of the HOCO^{*} is usually weaker than the other three adsorbates and thus not stable on the surface. So we do not consider the HOCO* adsorption here. The CO*, H*, and OH* are assumed to be in equilibrium with the CO gas, proton/electron pair, and H_2O , respectively (see Equation 6.4, Equation 6.5 and Equation 6.6).

Figure 6.3 shows the process of the global optimization for $Pd_xTi_{1-x}H_y$ with adsorbates CO*, H* and OH* in the active learning workflow, and the corresponding example struc-



Figure 6.3: The process of the global optimization for $Pd_xTi_{1-x}H_y$ with adsorbates CO^{*}, H^{*} and OH^{*} in the active learning workflow, and the corresponding complexity.

tures and complexity are given. We use a $2 \times 2 \times 4$ slab with multiple adsorbates and fix the bottom layer (12 metal atoms, 4 internal hydrogen atoms, 12 adsorption sites, 3 types of adsorbate species). Hence, there exist $2^{20} = 1,048,576$ possible slab configurations and $4^{12} = 16,777,216$ possible adlayer patterns, which constitute a total structural search space of approximately 1.8×10^{13} structures if we ignore the symmetry. Besides, the total number of tasks is 11,250 calculated by Equation 6.8. The total search space is the product of structural search space and the total number of tasks, which is approximately 2.0×10^{17} . The detailed active learning workflow can be found in Figure D.1. Initially, 100 random $Pd_xTi_{1-x}H_v(111)$ surfaces with adsorbates are generated and relaxed by DFT. The calculated end-point structures are collected and fed to the ensemble PaiNN model with 8 different NN architectures. The trained ensemble PaiNN model can be used to optimize new structures generated by the GA operators. During the MTGA calculations, we customize three types of operators that can generate new $Pd_xTi_{1-x}H_y$ surface structures with adsorbates, which is shown in Figure 6.3, namely the slab operators that control the composition and permutation of the metals and internal hydrogen atoms, the adsorbate operators that control the coverage and permutation of the adsorbates, and the crossover operator that combine the adsorbates from one structure and the slab from another structure. The detailed operators can be seen in the GA operators part of the Appendix D. After optimizing a newly generated structure using the PaiNN model, the energy of the optimized structure is used to calculate the surface free energy and thereby the fitness function. The surface free energy dependents chemical potential differences of $\Delta \mu_{\rm Pd}$,

 $\Delta \mu_{\text{Ti}}$, applied potential *U*, temperature *T*, and CO partial pressure P_{CO} adn the used values can be found in Table 6.1. The MGDN algorithm [205] in MTGA is applied to find the candidate structures at each reaction condition. Then the candidate structures and the last generation are picked for DFT relaxation. In order to avoid repeated DFT calculations, the repeated structures are removed by comparing their similarity. The identified unique structures are further optimized by DFT and collected to retrain the PaiNN model. This procedure is repeated until the whole active learning process converges. The convergence condition is that the number of new DFT candidates keeps decreasing until it reaches zero, and new candidates cannot be found anymore in the last 3 iterations as shown in Figure D.7. After convergence, the candidates at all considered reaction conditions are obtained and then used to analyze the activity and selectivity for the CO₂RR and HER.

Table 6.1:	The	values c	of different	state	variables	while	calcu	lating	surface	free	energy

State variable	Values					
Chem. pot. difference of Pd: $\Delta\mu_{\rm Pd}$ (eV)	-2.249, -2.499, -2.749, -2.999, -3.249					
Chem. pot. difference of Ti: $\Delta \mu_{\rm Ti}$ (eV)	-7.285, -7.535, -7.785, -8.035, -8.285					
Applied potential U (V)	0, -0.1, -0.2, -0.3, -0.4, -0.5, -0.6, -0.7, -0.8					
Temperature T (K)	283.15, 298.15, 313.15, 338.15, 353.15					
CO partial pressure P_{CO} (Pa)	0.101325, 10.1325, 1013.25, 5562, 101325					



Figure 6.4: (a) The energy RMSE in the process of active learning. (b) The fitting curve of the DFT energies and the corresponding neural network potential energies of the optimized structures. The green error bars of each point are the uncertainties calculated by ensemble energies.

To evaluate the performance of the active learning, the energy RMSE between the DFT energies and the neural network energies in the process of the active learning is shown in Figure 6.4a. The blue curve shows the energy RMSE rapidly declines in the first several iterations, while it goes down very slowly in the last several iterations. The yellow curve illustrates the energy RMSE without the first iteration in which the structures

are generated randomly. We can find that the energy RMSE rapidly levels off. It can be noticed that active learning mainly contributes to the decrease in the energy RMSE of the GA candidates rather than all structures in the whole search space. This can explain the slow RMSE decline in the last several iterations because the accuracy of the deep learning model cannot improve too much for all structures even though it is already good enough for the potential candidates. Figure 6.4b shows the parity plot between the DFT energies and the neural network potentials for the last iteration. The corresponding error bars of neural network energy variance are also displayed. The energy RMSE is as low as 5.274 meV/atom and the energy variances are so small that the most error bars cannot be seen. The learning curve of the energies in Figure D.4a further illustrates the small energy RMSE and variance. As a comparison, the learning curve of the energies in the first iteration can be seen in Figure D.6a. We can see that both the energy RMSE and variance in the last iteration are greatly decreased compared to the first iteration. The force RMSE is also crucial because it determines the precision of the structure relaxation. Figure D.4b and Figure D.6b display the forces learning curves of the last and the first iteration, respectively. It can be noticed that the same scenario happens as the energy RMSE curves. Both the forces RMSE and variances are greatly decreased. Especially, for the forces variances, they are so small that we almost cannot see them in Figure D.6b. Besides, the energy and forces learning curves of the 8 NN architectures for the first and the last iteration are also shown in Figure D.3 and Figure D.5, respectively, which further illustrate that the precision of energy and forces of the deep learning model have been greatly improved after the active learning.



Figure 6.5: The surface free energy as a function of the state variables between the chemical potential differences of Pd and Ti, applied potentials, temperature, and partial pressure of CO.

To study the effects of the different reaction conditions on the surface free energy, the contour plots of the surface free energy as a function of the chemical potential differences $\Delta \mu_{Pd}$ and $\Delta \mu_{Ti}$, applied potentials U, temperature T, and CO partial pressure P_{CO} are

shown in Figure 6.5. The corresponding heatmaps for candidate structures at the same reaction conditions are shown in Figure D.12. To simplify, the unique number for each structure (the index of the DFT database) is used and the corresponding top view can be found in Figure D.13. When the potential, temperature, and CO partial pressure are fixed at -0.5 V, 298.15 K, and 5562 Pa, respectively, the smaller $\Delta \mu_{Pd}$ and larger $\Delta \mu_{Ti}$ will minimize the surface free energy as shown in Figure 6.5a. At this condition, the candidate structure tends to have high Ti concentration and adsorbate CO* with 25% coverage on the surface as the top view of structure 900 in Figure D.13. When the large $\Delta \mu_{Ti}$ or the small $\Delta \mu_{Pd}$ are fixed at -7.285 eV, -3.249 eV, respectively, under 298.15 K and 5560 Pa as displayed in Figure 6.5b-c, the lower applied potential and smaller $\Delta \mu_{Pd}$ or larger $\Delta \mu_{Ti}$ will make the surface free energy lower. At both conditions, the candidate structure has high Ti concentration and adsorbate H* with high coverage on the surface as the structure 782 shown in Figure D.13. When the CO partial pressure and temperature are fixed at 5562 Pa and 298.15 K, respectively, under the large $\Delta \mu_{Ti}$ =-7.285 eV and the small $\Delta \mu_{\rm Pd}$ =-3.249 eV, as displayed in Figure 6.5d-e, the lower applied potential will minimize the surface free energy. Compared to the applied potential, the temperature and CO partial pressure do not have too much influence on the surface free energy. Similarly, the candidate structure at low potential and different temperatures and CO partial pressure have high Ti concentration and adsorbate H* with high coverage on the surface. When the condition is at large $\Delta \mu_{Ti}$ =-7.285 eV, small $\Delta \mu_{Pd}$ =-3.249 eV and potential=-0.5 V, high CO partial pressure=1 bar and low temperature=0 °C can lower the surface free energy. The candidate structure at this condition has high Ti concentration and adsorbate CO* with 50% coverage arranged in a hexagonal pattern.

To reveal the relations between the stable structures and certain reaction conditions, the surface free energy under several typical reaction conditions is displayed in Figure 6.6. The top views of the corresponding structures are shown at the bottom of each plot. The free energy as a function of the applied potential at four different chemical potential conditions (the vertices in Figure 6.5a) under the room temperature=298.15 K and CO partial pressure=5560 Pa can be found in Figure 6.6a, 6.6b, D.8a, and 6.6d. There are very high concentrations of Ti for all of the stable candidates and the top layers are Ti overlayer pattern when the chemical potential difference is at large $\Delta \mu_{Ti}$ =-7.285 eV and small $\Delta \mu_{Pd}$ =-3.249 eV as shown in Figure 6.6a. Besides, there are 0.25% CO* coverage and very high H* coverage on the surface when the potential is larger than -0.66 V. Otherwise, there is only high H* coverage and no CO* on the surface. After lowering only $\Delta \mu_{Ti}$ to -8.285 eV or increasing only $\Delta \mu_{Pd}$ to -2.249 eV, the same surface free energy plot can be obtained as shown in Figure 6.6b, and Figure D.8a. When the potential is larger than -0.31 V, there are very low Ti concentrations and no Ti on the top layer, and there are only adsorbates CO* on the surface and the coverage is 50%. When the potential is decreased below -0.31 V, the Ti concentration increases and the top layer is in a Ti hexagonal pattern. Besides, CO* coverage is lowered to 25%, and H* begins to appear on the surface. When the potential is further decreased below -0.65 V, there is no CO^{*} anymore and only higher H^{*} coverage on the surface. After lowering



Figure 6.6: (a, b, d) The surface free energy as a function of applied potentials with different chemical potential differences of Pd and Ti at temperature=298.15 K, and CO partial pressure=5560 Pa. (c) The surface free energy as a function of CO partial pressure at fixed $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$, potential=-0.5 V, and temperature=298.15 K. The corresponding most stable structures are shown at the bottom.

 $\Delta \mu_{Ti}$ to -8.285 eV and increasing $\Delta \mu_{Pd}$ to -2.249 eV as shown in Figure 6.6d, the surface free energy is totally higher than that in Figure 6.6a, which is consistent with the result in Figure 6.5a. When the potential is larger than -0.38 V, Ti concentration is very low and no Ti element is on the top layer, and only adsorbates CO* is on the surface with 50% coverage. When the potential is less than -0.38 V, the Ti concentration goes up and the top layer is in a line pattern. The CO* coverage goes down to 25% and H* coverage goes up. The surface free energy as a function of CO partial pressure at $\Delta \mu_{Pd}$ =-3.249 eV, $\Delta \mu_{Ti}$ =-7.285 eV, potential=-0.5 V and temperature=209.15 K is displayed in Figure 6.6c. The Ti concentrations for all candidates are very high and the top layer is overlayer. Furthermore, the H* coverage for all candidates is very high. When the pressure is larger than around 10^4 Pa, the CO* coverage is 50% in a hexagonal pattern. After the pressure is lowered below 10^4 Pa, the CO^{*} coverage is 25%. After the pressure is further lowered below around 5 Pa, the CO* disappears on the surface. The factor of temperature is also studied at $\Delta \mu_{Pd}$ =-3.249 eV, $\Delta \mu_{Ti}$ =-7.285 eV, potential=-0.5 V and CO partial pressure=5562 Pa as shown in Figure D.8b. There is only one candidate with high Ti concentration, high H* coverage, and 25% CO* coverage on the surface. It can be noticed that the slope is very

low for the surface free energy as a function of both CO partial pressure and temperature, which can be attributed to their weaker impact on surface free energy compared to the potential. Besides, the complete surface free energy plots versus potential, CO partial pressure, and temperature are also given as a reference in Figure D.9, Figure D.10 and Figure D.11 in the Appendix D.



Figure 6.7: (a-b) The CO₂RR and HER free energy diagram of active candidates at room temperature=298.15 K and CO partial pressure=5560 Pa. (c) The activity volcano plot of all candidates at potential=-0.5 V and CO partial pressure=5560 Pa. (d) The selectivity towards H_2 and CO₂ for all candidates.

To understand the CO₂RR activity and the selectivity towards H₂ and CO₂, the binding energies and free energies for the obtained candidates with CO* are further calculated and analyzed. We only consider the most stable structures for each composition and the most stable CO* adsorption sites. The details for calculating binding energies can be found in the Appendix D. Figure D.14 shows the free energy diagram of CO₂RR for all candidates. It can be seen that most of the candidates have too strong or too weak adsorption of HOCO* compared to pure PdH (111). It is worth noting that the free energies of HOCO* of Pd₉Ti₇H₁₇+1CO, Pd₅Ti₁₁H₂₀+2CO, Pd₅Ti₁₁H₂₀+1CO and Pd₁₄Ti₂H₁₇+1CO are 0.349, 0.497, 0.570 and 0.595 eV, respectively, which are not too strong or too week, and weaker than 0.606 eV of pure PdH. Furthermore, their free energies of CO* are also not too strong or too weak compared to -0.028 eV of pure PdH, which are -0.244, 0.149, 0.077, and -0.131 eV, respectively. The CO₂RR free energy diagram for them is shown in Figure 6.7a. Hence, they are likely to produce more CO₂ compared to pure PdH. The

HER free energy diagram for all candidates is shown in Figure D.15. The free energies on H* step of Pd₁₄Ti₂H₄+2CO, Pd₁₂Ti₄H₄+3CO, Pd₁₄Ti₂H₄+3CO, Pd₁₄Ti₂H₇+1CO, Pd₁₄Ti₂H₅+3CO, Pd₁₄Ti₂H₁₂+3CO and Pd₉Ti₇H₁₇+1CO are 0.017, 0.033, 0.148, 0.188, 0.286, 0.325 and 0.368 eV, respectively, which are weaker than that of pure PdH (0.430 eV), but not too strong. Therefore, they are likely to produce more H₂ compared to pure PdH. The HER free energy diagram for them is shown in Figure 6.7b. Figure 6.7c shows the CO₂RR activity volcano at -0.5 V of potential and 5560 Pa of CO partial pressure. We can see that Pd₉Ti₇H₁₇+1CO (Pd_{0.56}Ti_{0.44}H_{1.06}+25%CO), Pd₅Ti₁₁H₂₀+2CO Pd₅Ti₁₁H₂₀+1CO (Pd_{0.31}Ti_{0.69}H_{1.25}+25%CO), (Pd_{0.31}Ti_{0.69}H_{1.25}+50%CO), and Pd₁₄Ti₂H₁₇+1CO (Pd_{0.88}Ti_{0.12}H_{1.06}+25%CO) are more active than pure PdH, which is consistent with the result of Figure 6.7c. The selectivity towards H₂ and CO₂ for all candidates is illustrated in Figure 6.7d. A descriptor $\Delta G_{(HOCO*)} - \Delta G_{(H*)}$ is used to describe the trend to generate CO and H2.[189] If we focus on the CO2RR active candidates, all $\Delta G_{(HOCO*)} - \Delta G_{(H*)}$ values for Pd₅Ti₁₁H₂₀+2CO, Pd₅Ti₁₁H₂₀+1CO and $Pd_{14}Ti_2H_{17}$ +1CO and $Pd_9Ti_7H_{17}$ +1CO are negative and then tend to produce more CO₂. It should be noticed that their values are close to 0 eV and thus suitable to generate syngas consisting of CO and H₂. The detailed values can be found in Table D.1 in the Appendix D. Besides, there is on OH* found on all candidate surfaces, which indicates that there is no OH* poisoning.

6.4 Conclusions

In this chapter, a deep learning-assisted multitasking genetic algorithm is used to screen for Pd_xTi_{1-x}H_v surfaces with multiple adsorbates for CO₂RR under different reaction conditions. The ensemble PaiNN model trained by DFT single-point structures can not only greatly speed up the new structure relaxation but also keep a high accuracy of energy and forces. The model can successfully deal with the structural complexity including compositions and chemical orderings of surfaces with different coverages, types, and mixtures of the adsorbates. A genetic algorithm with maximum gain dynamic niching algorithm is used for global optimization of the surface free energy at each reaction condition, which can efficiently handle the complexity of state variables, such as temperature, CO partial pressure, applied potential, and chemical potential differences of Pd and Ti. In order to deal with the complexity of structures and the complexity of state variables simultaneously, an automated active workflow integrated with the deep learning-assisted multitasking genetic algorithm is built. 23 stable structures are finally screened out under different reaction conditions. Among them, Pd_{0.56}Ti_{0.44}H_{1.06}+25%CO, Pd_{0.31}Ti_{0.69}H_{1.25}+50%CO, Pd_{0.31}Ti_{0.69}H_{1.25}+25%CO, and Pd_{0.88}Ti_{0.12}H_{1.06}+25%CO are found to be very active for CO₂RR and suitable to generate syngas.

Chapter 7 Conclusions and Outlook

7.1 Conclusions

In this thesis, Pd-based hydride catalysts for CO_2RR are studied by various computational methods including density functional theory, cluster expansion model, and machine learning potential. Several stable and active Pd-based hydride catalysts are screened out for improving the CO_2RR performance compared to pure PdH(111).

- Transition metal elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re are doped into the PdH(111) surface in different doping configurations to explore their catalytic performance. Ti doping with parallelogram and overlayer configuration and Nb doping with overlayer configuration are found to have better kinetic activities than pure PdH(111). At the same time, Ti and Nb are also possible to generate more CO rather than H₂ compared with pure surface.
- 2. We found 12 stable candidates for PdH_x, which are Pd₆₄, Pd₆₄H₂, Pd₆₄H₄, Pd₆₄H₈, Pd₆₄H₁₀, Pd₆₄H₁₃, Pd₆₄H₃₁, Pd₆₄H₃₉, Pd₆₄H₅₃, Pd₆₄H₆₂, Pd₆₄H₆₃, and Pd₆₄H₆₄. We identify the atomic structures of the PdH_{0.6} phase most likely to produce syngas. The high activity of the PdH_{0.6} surface can be attributed to the fact that H segregation in the PdH_x(111) surface breaks the linear relation between HOCO* adsorbates. In addition, H atoms may weaken the binding energies of all adsorbates.
- For Pd_xM_{1-x}H_y system, 24 active candidates of Pd_xTi_{1-x}H_y and 6 active candidates of Pd_xNb_{1-x}H_y are screened out. Especially, the Pd₁₅Ti₄₉H₆₄ (Pd_{0.23}Ti_{0.77}), Pd₁₂Ti₅₂H₆₀ (Pd_{0.19}Ti_{0.81}H_{0.94}) and Pd₁₁Nb₅₃H₁₆ (Pd_{0.17}Nb_{0.83}H_{0.25}) have good stability and excellent current densities.
- 4. For Pd_xTi_{1-x}H_y with adsorbates system, 23 stable structures with adsorbates are finally screened out under different reaction conditions. Among them, Pd_{0.56}Ti_{0.44}H_{1.06}+25%CO, Pd_{0.31}Ti_{0.69}H_{1.25}+50%CO, Pd_{0.31}Ti_{0.69}H_{1.25}+25%CO, and Pd_{0.88}Ti_{0.12}H_{1.06}+25%CO are found to be very active for CO₂RR and suitable to generate syngas.

Furthermore, all data and codes in this thesis are openly available and can be found in Appendix E.

7.2 Outlook

Even though a bunch of stable Pd-based catalysts have been found to have higher activity than pure PdH(111) surface, there are still several aspects that can be further considered.

1. Explicit solvent and fixing potentials

Our DFT calculations were carried out under vacuum conditions with solvent corrections in order to simplify structural models. However, the explicit solvent environment is more precise and thus can be further considered. Besides, our DFT calculations were implemented in the framework of canonical ensemble, where the electrode's surface charges and thus the fermi level or work function could vary. However, the real electrode potential or work function should be constant. Then, DFT in the framework of a grand canonical ensemble, such as the solvated Jellium method (SJM), can be further considered in the future.

2. Variable lattice constants

We assume that the lattice constants of Pd-base hydrides are unchanged because the atomic radius differences between Pd and introduced metals are not very obvious. However, the strain due to atomic radius difference is likely to have an influence on binding energy. Thus, variable lattice constants can be considered in the future when relaxing structures.

3. Validation of experiments and calculations

The active candidates of Pd-based hydrides in this thesis can be hopefully verified by experiments. Besides, Pd-Ag, Pd-Cu, and Pd-Ni alloy hydrides are reported to be active for CO_2RR in experiments. Our methods can be further extended to these alloy hydrides in the future.

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Appendix A

Supplementary material for metal-doped PdH(111)

This appendix is the supplementary material of Chapter 3, which is based on the supporting information of Paper I.



Figure A.1: The top (a) and side views (b) of crystal structures for pure PdH(111) surface. The blue spheres represent metal Pd atoms and the white spheres are H atoms.



Figure A.2: (a-d) The top and (e-h) side views of crystal structures for PdH(111) surface with adsorbates HOCO*, CO*, H* and OH*, respectively are shown here. The red spheres represent O atoms and the grey spheres are C atoms.

Table A.1: Binding energies (BE, unit is eV) of pure PdH(111) with intermediates HOCO	*,
CO*, H* and OH* in different sites.	

BE for PdH(111)	Sites	HOCO*	CO*	H*	OH*
Pure	top	0.430	-0.363	0.398	1.479
Pure	hollow	0.406	-0.222	0.343	1.248



Figure A.3: The free energy diagram for CO_2RR of pure PdH(111) surface.



Figure A.4: The free energy diagram for HER of pure PdH(111) surface.

Formation energy (eV/atom)	Single	Dimer	Triangle	e Parall.	Island	Overlayer
Sc	-2.683	-2.315	-2.146	-1.978	-2.181	-1.062
Ti	-1.300	-1.200	-1.107	-1.081	-1.131	-1.056
V	0.027	0.059	0.064	0.028	0.127	-0.172
Cr	1.009	0.882	0.903	0.841	1.080	0.804
Mn	1.053	0.986	1.049	0.946	1.210	1.090
Fe	0.963	0.986	1.060	1.013	1.208	1.275
Со	0.485	0.543	0.613	0.664	0.718	0.913
Ni	0.056	0.141	0.216	0.230	0.220	0.379
Cu	-0.005	0.118	0.237	0.314	0.330	0.383
Zn	-0.415	-0.193	-0.005	0.008	-0.016	0.535
Y	-2.959	-2.372	-1.997	-2.132	-2.013	-0.066
Zr	-2.010	-1.723	-1.531	-1.532	-1.571	-0.824
Nb	-0.438	-0.346	-0.241	-0.255	-0.311	-0.364
Мо	0.705	0.584	0.658	0.590	0.788	0.482
Ru	0.567	0.643	0.708	0.717	0.800	0.856
Rh	-0.195	-0.066	-0.009	0.020	0.064	0.182
Ag	-0.048	0.091	0.215	0.291	0.253	0.569
Cd	-0.601	-0.253	0.075	0.184	-0.021	0.991
Hf	-1.955	-1.707	-1.558	-1.484	-1.529	-0.760
Та	-0.379	-0.275	-0.125	-0.166	-0.212	-0.168
W	0.996	0.912	0.932	0.907	0.939	0.942
Re	1.001	0.991	1.137	1.086	1.142	1.325

Table A.2: Formation energies per atom of different transition metal atoms doping on thePdH(111) surface for the different configurations.



Figure A.5: Top1 (T1), top2 (T2) and hollow (H) adsorption sites for single doping configuration.

Table A.3: Binding energies (eV) of HOCO*, CO*, H* and OH* on different adsorption sites for single doping configuration.

BE for single	Sites	HOCO*	CO*	H*	OH*
	top1	0.658	-0.553	1.264	-0.616
Sc	top2	0.818	0.039	0.779	1.750
	hollow	0.648	-0.551	0.524	-0.611
	top1	0.503	-0.786	0.693	-0.324
Ti	top2	0.823	-0.025	0.723	1.716
	hollow	0.523	-0.792	0.516	-0.416
	top1	0.423	-1.022	0.312	-0.242
V	top2	0.748	-0.176	0.684	1.786
	hollow	0.777	-1.020	0.498	-0.246
	top1	0.435	-1.335	0.041	0.081
Cr	top2	0.655	-0.211	0.613	1.692
	hollow	0.563	-1.333	0.423	0.080
	top1	0.491	-1.608	-0.078	0.437
Mn	top2	0.608	-0.241	0.583	0.846
	hollow	0.425	-1.607	-0.212	0.592
	top1	0.420	-1.460	-0.123	0.810
Fe	top2	0.563	-1.330	0.548	0.833
	hollow	0.403	-1.448	-0.194	0.793
Со	top1	0.605	-0.959	0.138	1.205
	top2	0.548	-0.252	0.533	1.330
	hollow	0.614	-0.952	0.282	0.442
	top1	0.647	-0.423	0.625	1.310
Ni	top2	0.567	-0.252	0.531	1.603

	hollow	0.670	-0.478	0.498	1.059
	top1	1.176	-0.191	1.355	1.482
Cu	top2	0.646	-0.134	0.575	1.664
	hollow	0.643	-0.115	0.517	1.470
	top1	1.191	-0.112	1.080	0.671
Zn	top2	0.691	-0.120	0.611	1.294
	hollow	0.691	-0.157	0.507	0.692
	top1	0.473	-0.550	1.223	-0.800
Y	top2	0.787	-0.183	0.780	-0.800
	hollow	0.476	-0.548	0.359	-0.797
	top1	0.350	-0.817	0.701	-0.836
Zr	top2	0.810	-0.022	0.789	-0.851
	hollow	0.351	-0.814	0.496	-0.834
	top1	0.341	-1.009	0.311	-0.414
Nb	top2	0.830	-0.221	-0.139	1.817
	hollow	0.711	-1.011	0.515	-0.422
	top1	0.435	-1.304	-0.013	0.069
Мо	top2	0.789	-0.196	0.732	1.437
	hollow	0.549	-1.304	-0.012	0.069
	top1	0.255	-1.420	-0.231	0.920
Ru	top2	0.632	-1.265	0.608	0.768
	hollow	0.257	-1.401	-0.230	1.261
	top1	0.574	-0.665	0.205	1.499
Rh	top2	0.659	-0.200	0.641	1.380
	hollow	0.563	-0.699	0.509	1.488
	top1	1.416	-0.105	1.622	1.970
Ag	top2	0.675	-0.092	0.603	1.676
	hollow	0.676	-0.118	0.512	1.843
	top1	1.426	-0.143	1.286	1.221
Cd	top2	0.747	-0.093	0.668	-0.523
	hollow	0.750	-0.139	0.593	1.217
	top1	0.434	-0.829	0.716	-0.862
Hf	top2	0.786	-0.019	0.764	1.760
	hollow	0.434	-0.834	0.559	-0.864
Та	top1	0.658	-1.009	0.297	-0.576
	top2	0.835	-0.220	-0.180	1.548
	hollow	0.743	-1.008	0.569	-0.576
W	top1	0.625	-1.184	-0.010	-0.053
	top2	0.816	-0.213	0.727	1.379
	hollow	0.601	-1.182	-0.010	-0.054
	top1	0.666	-0.770	0.046	0.663
Re	top2	0.941	-0.147	0.827	1.392
	hollow	0.604	-0.718	0.046	1.540



Figure A.6: Top1 (T1), top2 (T2), hollow1 (H1) and hollow2 (H2) adsorption sites for dimer doping configuration.

Table A.4: Binding energies (eV) of HOCO*, CO*, H* and OH* on different adsorption sites for dimer doping configuration. (Some of them in the table are not stable, and form other unexpected intermediates on the surfaces. They are thus directly removed and the same is applied in the following other tables.)

BE for dimer	Sites	HOCO*	CO*	H*	OH*
	top1	0.309	-0.507	1.123	-0.796
50	top2	0.903	0.230	0.584	-0.774
30	hollow1	0.254	-0.472	0.234	-0.841
	hollow2	0.017	-0.509	0.091	-0.797
	top1	0.407	-0.751	0.716	-0.526
т	top2	1.013	0.164	0.866	-0.370
11	hollow1	0.368	-0.751	0.418	-0.378
	hollow2	0.512	-0.757	0.384	-0.470
	top1	0.397	-1.016	-0.087	-0.241
V	top2	0.940	0.194	0.864	0.115
V	hollow1	0.409	-1.037	0.324	0.180
	hollow2	0.470	-1.037	0.494	-0.187
	top1	0.265	-1.151	-0.078	-0.370
Cr	top2	0.748	-0.389	0.337	1.852
CI	hollow1	-0.220	-1.136	0.310	0.430
	hollow2	0.492	-1.152	0.493	-0.309
	top1	0.194	-1.394	-0.114	0.388
Mo	top2	0.790	0.021	0.760	1.774
	hollow1	0.106	-1.332	0.264	-0.117
	hollow2	0.842	-1.394	0.324	0.614
	top1	0.449	-1.358	-0.185	0.744

hollow1 0.261 -0.688 0.258 0.600 hollow2 0.903 -1.361 0.195 0.748 Co 10p1 0.627 -0.954 -0.001 1.020 Co 0.635 -0.109 0.667 1.734 hollow1 0.607 -0.334 0.430 1.070 hollow2 0.627 -0.849 0.352 1.089 Ni top1 0.654 -0.491 - 1.288 hollow1 0.652 -0.534 0.546 - hollow1 0.623 -0.180 - 1.155 fop2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.150 0.663 - fop2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - fop2 0.682 0.187 0.452 0.800		top2	0.708	-0.024	0.721	1.792
hollow2 0.903 -1.361 0.195 0.748 top1 0.627 -0.954 -0.001 1.020 top2 0.635 -0.109 0.667 1.734 hollow1 0.607 -0.334 0.430 1.070 hollow2 0.627 -0.349 0.352 1.089 Mi 0.627 -0.534 0.546 - hollow1 0.652 -0.534 0.546 - hollow2 0.616 -0.238 0.592 1.626 hollow2 0.623 -0.118 0.430 1.071 top1 1.227 -0.180 - 1.155 top2 0.752 -0.180 - 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - top1 0.696 -0.121 0.752 -0.804 hollow1 0.792 -0.139 0.800 0.286 hollow		hollow1	0.261	-0.688	0.258	0.600
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hollow2 0.627 -0.849 0.352 1.089 top1 0.654 -0.491 - 1.288 hollow1 0.652 -0.538 0.592 1.626 hollow2 0.623 -0.118 0.430 1.071 hollow2 0.623 -0.118 0.430 1.071 fop1 1.227 -0.160 - 1.155 fop1 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - fup1 0.696 -0.121 0.705 0.463 fup2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - Y fup1 -0.064 -0.389 0.514 -1.102 Mollow1 -0.107 -0.386 -0.013 -0.472 hollow2 0.624 -0.389 0.514 -1.001 <td>Co</td> <td>hollow1</td> <td>0.607</td> <td>-0.334</td> <td>0.430</td> <td>1.070</td>	Co	hollow1	0.607	-0.334	0.430	1.070
Ni top1 0.654 -0.491 - 1.288 hollow1 0.652 -0.534 0.592 1.626 hollow2 0.623 -0.118 0.430 1.071 Cu top1 1.227 -0.180 - 1.155 top2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.011 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.011 -1.001 top2 0.899 0.278 0.568 -0.472 hollow1 0.249 -0.748 0.127		hollow2	0.627	-0.849	0.352	1.089
Ni top2 0.616 -0.238 0.592 1.626 hollow1 0.652 -0.534 0.546 - hollow2 0.623 -0.118 0.430 1.071 Lop1 1.227 -0.180 - 1.155 top2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - Lop1 0.696 -0.121 0.705 0.463 top2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - Lop1 -0.064 -0.389 0.514 -1.102 Lop2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.385 -0.253 -0.984 Lop1 0.249 -0.728 0.781 -1.001 Lop2 0.889 0.278 0.781 -1.001 <t< td=""><td></td><td>top1</td><td>0.654</td><td>-0.491</td><td>-</td><td>1.288</td></t<>		top1	0.654	-0.491	-	1.288
NI hollow1 0.652 -0.534 0.546 - hollow2 0.623 -0.118 0.430 1.071 top1 1.227 -0.180 - 1.155 top2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - Andiow2 0.792 -0.121 0.705 0.463 top1 0.696 -0.121 0.853 - hollow1 0.720 -0.121 0.853 - hollow2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 hollow1 -0.107 -0.386 -0.001 -1.077 hollow1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472	NI;	top2	0.616	-0.238	0.592	1.626
hollow2 0.623 -0.118 0.430 1.071 Cu top1 1.227 -0.180 - 1.155 top2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - Andiow2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.705 0.463 hollow1 0.720 -0.121 0.853 - hollow1 0.720 -0.125 0.604 0.449 ftp1 -0.064 -0.389 0.514 -1.102 ftp2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.894 hollow1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 <td>INI</td> <td>hollow1</td> <td>0.652</td> <td>-0.534</td> <td>0.546</td> <td>-</td>	INI	hollow1	0.652	-0.534	0.546	-
top1 1.227 -0.180 - 1.155 top2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - Zn top1 0.696 -0.121 0.705 0.463 hollow1 0.720 -0.121 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 <td></td> <td>hollow2</td> <td>0.623</td> <td>-0.118</td> <td>0.430</td> <td>1.071</td>		hollow2	0.623	-0.118	0.430	1.071
Cu top2 0.752 -0.050 0.669 1.748 hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - Kop1 0.696 -0.121 0.705 0.463 Kop2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 ftp1 -0.064 -0.389 0.514 -1.102 ftp2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.011 -1.077 hollow1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.249 -0.748 0.127 -1.002 top2 0.989 0.278 0.568 -0.472 hollow1 0.269 -0.748 0.127 -1.002		top1	1.227	-0.180	-	1.155
hollow1 0.788 -0.111 0.842 1.265 hollow2 0.713 -0.115 0.562 - kop1 0.696 -0.121 0.705 0.463 kop2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow2 -0.220 -0.748 0.127 -1.002 top1 0.363 -0.942 0.315 -0.477 hollow2 0.515 -0.942 0.484 -0.412 <	Cu	top2	0.752	-0.050	0.669	1.748
hollow2 0.713 -0.115 0.562 - Iop1 0.696 -0.121 0.705 0.463 Iop2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 Y top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow1 -0.107 -0.385 -0.253 -0.984 top2 0.989 0.278 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.248 -0.749 0.306 -0.694 hollow2 0.515 -0.942 0.315 -0.477 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412<	Cu	hollow1	0.788	-0.111	0.842	1.265
Image top1 0.696 -0.121 0.705 0.463 top2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 hollow1 0.363 -0.942 0.315 -0.477 hollow2 0.515 -0.942 0.484 -0.412 hollow1 0.363 -0.959 0.385		hollow2	0.713	-0.115	0.562	-
Image top2 0.792 -0.139 0.800 0.286 hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 Y top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.249 -0.748 0.127 -1.002 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 Nb top1 0.363 -0.942 0.315 -0.477 hollow2 0.515 -0.942 0.484 -0.412 hollow1 0.363 -0		top1	0.696	-0.121	0.705	0.463
hollow1 0.720 -0.121 0.853 - hollow2 0.798 -0.125 0.604 0.449 top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow1 0.363 -0.942 0.315 -0.477 hollow2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.942 0.484 -0.412 top2 0.515 -0.942 0.484 -0.412	Zn	top2	0.792	-0.139	0.800	0.286
hollow2 0.798 -0.125 0.604 0.449 top1 -0.064 -0.389 0.514 -1.102 top2 0.682 0.187 0.452 -0.800 hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.249 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow1 0.363 -0.942 0.315 -0.477 hollow2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.942 0.484 -0.412 top2 1.104 0.236 0.993 0.526 hollow2 0.515 -0.942 0.484 -0.412	Zn	hollow1	0.720	-0.121	0.853	-
Ytop1-0.064-0.3890.514-1.102top20.6820.1870.452-0.800hollow1-0.107-0.386-0.001-1.077hollow2-0.472-0.385-0.253-0.984top10.249-0.7280.781-1.001top20.9890.2780.568-0.472hollow10.248-0.7490.306-0.694hollow2-0.220-0.7480.127-1.002hollow2-0.220-0.7480.127-1.002hollow10.363-0.9420.315-0.477top21.1040.2360.9930.026hollow10.363-0.9590.3850.146hollow20.515-0.9420.484-0.412top20.9120.1130.3431.869hollow10.259-1.1280.1280.052top20.9120.1130.3431.869hollow10.275-1.339-0.0930.816top20.717-1.129-0.0130.077hollow20.7170.0550.2011.775hollow10.214-0.7010.2451.027hollow10.572-0.6900.2051.451top20.710-0.0520.7351.819hollow10.582-0.7120.5241.129hollow10.582-0.7120.5241.129hollow20.707-0.6840.4911.455<		hollow2	0.798	-0.125	0.604	0.449
Ytop20.6820.1870.452-0.800hollow1-0.107-0.386-0.001-1.077hollow2-0.472-0.385-0.253-0.984Lop10.249-0.7280.781-1.001top20.9890.2780.568-0.472hollow10.248-0.7490.306-0.694hollow2-0.220-0.7480.127-1.002hollow2-0.220-0.7480.127-1.002hollow2-0.220-0.7480.127-0.477top10.363-0.9420.315-0.477top21.1040.2360.9930.026hollow10.363-0.9590.3850.146hollow10.363-0.9590.3850.146hollow20.515-0.9420.484-0.412hollow10.259-1.1280.1280.052hollow10.243-1.1300.3660.492hollow20.717-1.129-0.0130.077Rutop10.275-1.339-0.0930.816hollow10.214-0.7010.2451.027hollow10.572-0.6900.2051.451hollow21.042-1.339-0.1440.829Rutop20.710-0.0520.7351.819hollow10.582-0.7120.5241.129hollow10.582-0.7120.5241.1455hollow20.707-0		top1	-0.064	-0.389	0.514	-1.102
hollow1 -0.107 -0.386 -0.001 -1.077 hollow2 -0.472 -0.385 -0.253 -0.984 Lop1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow1 0.363 -0.942 0.315 -0.477 top2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.942 0.315 -0.477 top2 1.104 0.236 0.933 0.026 hollow1 0.363 -0.942 0.484 -0.412 top2 0.912 0.113 0.343 1.869 hollow2 0.717 -1.129 -0.013 0.077	v	top2	0.682	0.187	0.452	-0.800
hollow2 -0.472 -0.385 -0.253 -0.984 top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 hollow1 0.363 -0.942 0.315 -0.477 top2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.942 0.484 -0.412 top2 0.515 -0.942 0.484 -0.412 hollow2 0.912 0.113 0.366 0.492 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.29 -0.013 0.77 <td>T</td> <td>hollow1</td> <td>-0.107</td> <td>-0.386</td> <td>-0.001</td> <td>-1.077</td>	T	hollow1	-0.107	-0.386	-0.001	-1.077
Image: top1 0.249 -0.728 0.781 -1.001 top2 0.989 0.278 0.568 -0.472 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 hollow1 0.363 -0.942 0.315 -0.477 hollow1 0.363 -0.959 0.385 0.146 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 top1 0.259 -1.128 0.128 0.052 hollow1 0.243 -1.130 0.366 0.492 hollow1 0.275 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.7		hollow2	-0.472	-0.385	-0.253	-0.984
top2 0.989 0.278 0.568 -0.472 hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 Mb top1 0.363 -0.942 0.315 -0.477 top2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow2 0.515 -0.942 0.484 -0.412 hollow1 0.259 -1.128 0.128 0.052 hollow1 0.243 -1.130 0.343 1.869 hollow2 0.717 -1.129 -0.013 0.077 hollow2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245		top1	0.249	-0.728	0.781	-1.001
hollow1 0.248 -0.749 0.306 -0.694 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 -0.220 -0.748 0.127 -1.002 hollow2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow1 0.259 -1.128 0.128 0.052 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.77 hollow1 0.214 -0.701 0.245	7r	top2	0.989	0.278	0.568	-0.472
hollow2 -0.220 -0.748 0.127 -1.002 top1 0.363 -0.942 0.315 -0.477 top2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow2 0.912 0.113 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 Ru top1 0.275 -1.339 -0.093 0.816 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144	21	hollow1	0.248	-0.749	0.306	-0.694
top1 0.363 -0.942 0.315 -0.477 top2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow2 0.912 0.113 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 hollow2 0.717 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 Rh top1 0.572 -0.690 0.205 <		hollow2	-0.220	-0.748	0.127	-1.002
Nb top2 1.104 0.236 0.993 0.026 hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow2 0.515 -0.942 0.484 -0.412 hollow2 0.912 0.113 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow1 0.243 -1.130 0.366 0.492 hollow1 0.275 -1.339 -0.013 0.077 Ru top1 0.275 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow1 0.572 -0.690 0.205 1.451 Rh top1 0.572 -0.690 0.205 1.451 hollow2 0.707 -0.684 0.491 1.455 hollow2 0.707 -0.684 </td <td></td> <td>top1</td> <td>0.363</td> <td>-0.942</td> <td>0.315</td> <td>-0.477</td>		top1	0.363	-0.942	0.315	-0.477
hollow1 0.363 -0.959 0.385 0.146 hollow2 0.515 -0.942 0.484 -0.412 hollow2 0.515 -0.942 0.484 -0.412 Mo top1 0.259 -1.128 0.128 0.052 hollow1 0.243 -1.130 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 hollow2 0.717 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 hollow2 1.042 -1.339 -0.144 0.829 hollow2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491	Nb	top2	1.104	0.236	0.993	0.026
hollow2 0.515 -0.942 0.484 -0.412 top1 0.259 -1.128 0.128 0.052 top2 0.912 0.113 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 hollow2 0.717 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow1 0.214 -0.701 0.245 1.027 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 Rh top1 0.572 -0.690 0.205 1.451 hollow2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491		hollow1	0.363	-0.959	0.385	0.146
top1 0.259 -1.128 0.128 0.052 top2 0.912 0.113 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 hollow2 0.717 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 Rh top1 0.572 -0.690 0.205 1.451 Rh top2 0.710 -0.052 0.735 1.819 Rh top2 0.707 -0.684 0.491 1.455 hollow2 0.707 -0.684 0.491 1.455		hollow2	0.515	-0.942	0.484	-0.412
Mo top2 0.912 0.113 0.343 1.869 hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 hollow2 0.717 -1.339 -0.093 0.816 Ru top1 0.275 -1.339 -0.093 0.816 hollow1 0.214 -0.701 0.245 1.027 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 Rh top1 0.572 -0.690 0.205 1.451 Rh top2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		top1	0.259	-1.128	0.128	0.052
hollow1 0.243 -1.130 0.366 0.492 hollow2 0.717 -1.129 -0.013 0.077 Ru top1 0.275 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 hollow2 1.042 -1.339 -0.144 0.829 Rh top1 0.572 -0.690 0.205 1.451 hollow2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455	Mo	top2	0.912	0.113	0.343	1.869
hollow2 0.717 -1.129 -0.013 0.077 top1 0.275 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 hollow2 0.572 -0.690 0.205 1.451 top2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451	WO	hollow1	0.243	-1.130	0.366	0.492
top1 0.275 -1.339 -0.093 0.816 top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 Rh top1 0.572 -0.690 0.205 1.451 hollow1 0.572 -0.690 0.205 1.451 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		hollow2	0.717	-1.129	-0.013	0.077
top2 0.717 0.055 0.201 1.775 hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 hollow2 0.572 -0.690 0.205 1.451 top2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		top1	0.275	-1.339	-0.093	0.816
hollow1 0.214 -0.701 0.245 1.027 hollow2 1.042 -1.339 -0.144 0.829 kop1 0.572 -0.690 0.205 1.451 kop2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451	Ru	top2	0.717	0.055	0.201	1.775
hollow2 1.042 -1.339 -0.144 0.829 top1 0.572 -0.690 0.205 1.451 top2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		hollow1	0.214	-0.701	0.245	1.027
top1 0.572 -0.690 0.205 1.451 top2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		hollow2	1.042	-1.339	-0.144	0.829
top2 0.710 -0.052 0.735 1.819 hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		top1	0.572	-0.690	0.205	1.451
hollow1 0.582 -0.712 0.524 1.129 hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451	Rh	top2	0.710	-0.052	0.735	1.819
hollow2 0.707 -0.684 0.491 1.455 top1 1.497 -0.100 - 1.451		hollow1	0.582	-0.712	0.524	1.129
top1 1.497 -0.100 - 1.451		hollow2	0.707	-0.684	0.491	1.455
		top1	1.497	-0.100	-	1.451
Ag top2 0.884 0.101 0.768 1.887	Aa	top2	0.884	0.101	0.768	1.887

	hollow1	0.849	-0.104	0.758	1.492
	hollow2	0.779	-0.117	0.520	1.769
	top1	0.933	-0.125	0.816	0.550
Cd	top2	0.970	-0.041	0.911	0.569
Cu	hollow1	0.934	-0.120	0.765	0.521
	hollow2	0.871	-0.132	0.593	0.898
	top1	0.276	-0.731	0.787	-1.001
LIF	top2	0.981	0.283	0.570	-0.701
	hollow1	0.239	-0.752	0.453	-0.679
	hollow2	0.229	-0.753	0.428	-1.002
	top1	0.348	-0.942	0.247	-0.719
То	top2	1.173	0.350	0.994	-0.066
Id	hollow1	0.330	-0.942	0.564	-0.119
	hollow2	0.305	-0.896	0.581	-0.656
	top1	0.380	-1.053	0.127	-0.085
10/	top2	0.932	-0.013	0.358	1.827
vv	hollow1	0.379	-1.050	0.366	0.632
	hollow2	1.088	-1.062	0.099	-0.085
De	top1	0.507	-1.090	-0.001	0.487
	top2	0.846	-0.050	0.667	1.660
NC	hollow1	0.401	-0.270	0.449	1.025
	hollow2	0.830	-1.104	-0.006	0.436



Figure A.7: Top1 (T1), top2 (T2), hollow1 (H1) and hollow2 (H2) adsorption sites for triangle doping configuration.

Table A.5: Binding energies (eV) of HOCO*, CO*, H* and OH* on different adsorption sites for triangle doping configuration.

BE for triangle	Sites	HOCO*	CO*	H*	OH*
	top1	0.108	-0.581	1.034	-0.910
C.	top2	0.903	-0.335	0.867	-0.836
30	hollow1	0.172	0.345	0.155	-0.351
	hollow2	0.106	-0.634	0.301	-0.919
	top1	0.240	-0.775	0.643	-0.673
т	top2	0.704	0.019	0.736	-0.098
11	hollow1	0.238	-0.787	0.336	0.283
	hollow2	0.345	-0.827	0.378	-0.734
	top1	0.181	-1.069	-0.305	-0.485
	top2	0.719	-0.864	0.726	-0.322
V	hollow1	0.155	-1.041	0.100	0.156
	hollow2	0.066	-1.097	0.357	-0.491
	top1	0.282	-1.271	-	-0.629
Cr	top2	0.595	-0.363	0.683	1.785
	hollow1	0.049	-1.341	0.313	0.556
	hollow2	-0.162	-1.345	0.222	-0.629
	top1	0.166	-1.523	-0.388	-0.193
Mo	top2	0.524	-0.290	0.499	1.730
	hollow1	0.089	-1.546	0.303	0.692
	hollow2	0.568	-1.555	0.082	-0.143
	top1	0.207	-1.468	-0.343	0.667
Fo	top2	0.529	-0.065	0.657	1.458
ГЕ	hollow1	0.104	-1.140	0.284	1.084
	hollow2	0.767	-1.463	0.030	0.603
	top1	0.605	-0.869	-0.121	1.111
Co	top2	0.593	-0.222	0.637	1.712
	hollow1	0.517	-0.844	0.430	1.736
	hollow2	0.656	-1.112	0.133	-
	top1	0.604	-0.531	-	1.342
Ni	top2	0.554	-0.283	0.547	1.584
	hollow1	0.593	0.129	0.603	1.537
	hollow2	0.517	-0.538	0.258	-
	top1	1.263	-0.188	1.418	1.399
Cu	top2	0.835	-0.017	0.783	1.682
	hollow1	1.267	-0.104	0.945	1.217
	hollow2	0.837	-0.115	0.560	-
Zn	top1	0.506	-0.126	0.511	0.260
	top2	0.642	-0.290	0.724	-0.047
	hollow1	0.501	-0.119	1.276	0.315
	hollow2	0.615	-0.148	0.546	0.264
	top1	-0.865	-0.553	0.071	-1.563
v	top2	-0.882	-0.452	0.917	-1.432
	hollow1	-0.542	0.273	0.071	-0.803

	hollow2	-0.439	-0.550	-0.887	-1.642
_	top1	0.005	-0.694	0.497	-1.119
	top2	0.327	0.207	0.696	-0.721
Zr	hollow1	0.161	-0.692	0.347	-0.153
	hollow2	-0.097	-0.820	0.117	-1.185
	top1	0.278	-0.917	0.382	-0.658
NIL	top2	0.809	0.141	0.825	-0.310
IND	hollow1	0.254	-0.955	0.316	0.374
	hollow2	0.167	-0.949	0.382	-0.657
	top1	0.432	-1.285	0.066	-0.370
Mo	top2	0.802	0.201	0.798	1.865
INIO	hollow1	0.244	-1.235	0.455	0.759
	hollow2	0.178	-1.234	0.107	-0.353
	top1	0.194	-1.374	-0.164	0.717
Du	top2	0.771	-0.045	0.745	1.860
Ru	hollow1	0.223	-0.408	0.437	0.794
	hollow2	1.027	-1.372	-0.170	0.710
	top1	0.457	-0.681	0.209	1.434
Dh	top2	0.734	-0.135	0.729	1.797
	hollow1	0.561	-0.001	0.502	1.109
	hollow2	0.622	-0.698	0.434	-
	top1	1.549	-0.100	1.121	1.471
A a	top2	0.929	0.100	0.823	1.905
Ay	hollow1	1.554	-0.094	1.123	1.516
	hollow2	0.870	-0.111	0.671	-0.419
	top1	0.802	-0.127	0.426	0.452
Cd	top2	0.853	-0.168	0.866	0.400
Cu	hollow1	0.638	-0.116	0.997	0.496
	hollow2	0.748	-0.136	0.582	-
	top1	0.049	-0.680	0.535	-1.047
Цf	top2	0.360	0.269	0.890	-0.668
1.11	hollow1	0.271	-0.683	0.491	-0.040
	hollow2	-0.010	-0.758	0.336	-1.141
	top1	0.159	-1.020	0.181	-0.921
Та	top2	0.770	0.079	0.813	-0.067
1a	hollow1	0.175	-1.023	0.579	0.407
	hollow2	-0.003	-1.034	0.359	-0.885
	top1	0.485	-1.150	0.081	-0.324
W	top2	0.888	0.173	0.596	1.838
	hollow1	0.474	-1.110	0.577	1.263
	hollow2	0.347	-1.149	0.071	-0.325
	top1	0.136	-1.324	-0.183	0.026
Re	top2	0.793	0.025	0.743	1.762
	hollow1	0.221	-1.346	0.772	1.041
	hollow2	1.022	-1.336	-0.189	-0.048



Figure A.8: Top1 (T1), top2 (T2), hollow1 (H1), hollow2 (H2) and hollow3 (H3) adsorption sites for parallelogram doping configuration.

Table A.6: Binding energies (eV) of HOCO*, CO*, H* and OH* on different adsorption sites for parallelogram doping configuration.

BE for parallel.	Sites	HOCO*	CO*	H*	OH*
	top1	-0.209	-0.548	0.282	-1.664
	top2	0.628	-0.538	0.066	-1.316
Sc	hollow1	-0.076	-0.687	-0.115	-1.437
	hollow2	-0.345	-0.817	-0.050	-1.226
	hollow3	-0.618	-0.878	0.341	-1.666
	top1	0.095	-0.724	0.646	-0.553
	top2	0.925	0.133	0.829	1.817
Ti	hollow1	0.403	-0.744	0.308	-0.006
	hollow2	0.095	-0.730	0.249	-0.454
	hollow3	0.428	-0.721	0.646	-0.555
	top1	0.179	-0.910	0.473	-0.121
	top2	0.768	-0.083	0.746	-0.277
V	hollow1	0.230	-1.027	0.205	0.110
	hollow2	0.117	-0.985	0.240	-0.264
	hollow3	0.519	-0.883	0.560	-0.151
	top1	0.007	-1.128	-	-0.027
	top2	0.639	-1.160	0.659	0.819
Cr	hollow1	0.094	-1.409	0.141	0.116
	hollow2	-0.003	-1.042	0.137	-0.392
	hollow3	0.511	-1.128	0.209	-0.509
	top1	0.092	-1.201	0.165	0.529
	top2	0.637	-0.289	0.789	1.199
Mn	hollow1	0.085	-1.380	0.324	0.109

	hollow2	0.092	-1.320	0.261	0.151
	hollow3	0.795	-1.200	-0.016	0.243
	top1	0.477	-1.239	0.303	0.662
	top2	0.626	-0.228	0.730	1.685
Fe	hollow1	-0.050	-1.372	0.214	0.401
	hollow2	0.098	-1.373	0.253	0.156
	hollow3	0.780	-1.143	-0.202	0.768
	top1	0.214	-1.105	0.192	0.766
	top2	0.335	-0.515	0.381	1.395
Со	hollow1	0.020	-1.376	0.114	0.737
	hollow2	0.201	-1.243	0.041	0.329
	hollow3	0.336	-1.253	0.369	0.967
	top1	0.633	-0.544	0.610	1.268
	top2	0.449	-0.310	0.570	1.549
Ni	hollow1	0.657	-0.370	0.493	0.758
	hollow2	0.617	-0.459	0.331	0.731
	hollow3	0.433	-0.113	0.440	1.005
	top1	1.203	-0.206	0.593	1.282
	top2	0.790	-0.088	0.740	1.671
Cu	hollow1	1.241	-0.117	0.773	0.725
	hollow2	0.825	-0.114	0.597	0.781
	hollow3	0.789	-0.116	0.550	1.282
	top1	0.439	-0.168	0.491	0.250
	top2	0.669	-0.461	0.547	0.508
Zn	hollow1	0.390	-0.055	0.586	0.100
	hollow2	0.723	-0.123	0.549	-0.043
	hollow3	0.639	-0.165	0.565	0.233
	top1	-0.482	-0.575	0.863	-1.051
	top2	-1.061	-1.382	-1.104	-1.221
Y	hollow1	-0.776	-0.848	-0.398	-1.785
	hollow2	0.020	-0.572	-1.086	-1.433
	hollow3	-0.362	-0.579	-0.868	-1.052
	top1	0.202	-0.698	0.636	-1.104
	top2	0.515	-0.423	0.554	-0.554
Zr	hollow1	1.142	-0.482	0.550	-0.307
	hollow2	0.048	-0.419	0.439	-0.690
	hollow3	-0.018	-0.503	0.495	-1.115
Nb	top1	0.127	-0.778	0.451	-0.369
	top2	0.970	0.041	0.927	-0.565
	hollow1	0.400	-0.800	0.440	0.426
	hollow2	0.150	-0.856	0.341	-0.227
	hollow3	0.659	-0.779	0.729	-0.349
	top1	-0.081	-1.064	0.207	0.203
	top2	0.795	-0.154	0.807	-0.408
Мо	hollow1	0.214	-1.347	0.462	0.535

	hollow2	-0.083	-1.111	0.206	-0.106
	hollow3	0.036	-1.042	0.498	0.204
	top1	0.297	-1.340	-0.097	0.964
	top2	0.751	-1.215	0.760	1.476
Ru	hollow1	0.193	-1.389	-0.215	0.505
	hollow2	0.038	-1.394	0.144	0.445
Ru Rh Ag Cd Hf Ta W	hollow3	1.123	-1.340	-0.099	1.022
	top1	0.494	-0.738	0.184	1.444
	top2	0.742	-0.146	0.756	1.810
Rh	hollow1	0.544	-0.794	0.473	1.226
	hollow2	0.611	-0.749	0.398	1.248
	hollow3	0.795	-0.678	0.496	1.517
	top1	1.561	-0.104	0.727	1.731
	top2	0.947	0.039	0.853	-
Ag	hollow1	1.563	-0.105	1.109	1.057
	hollow2	0.989	-0.114	0.905	1.423
	hollow3	0.946	-0.126	0.668	1.624
	top1	0.374	-0.453	0.316	0.297
	top2	0.642	-0.542	0.613	-0.962
Cd	hollow1	-0.772	-0.442	1.167	0.086
	hollow2	0.469	-0.265	0.610	-0.067
	hollow3	0.582	-0.424	0.316	0.352
	top1	-0.164	-0.816	0.512	-1.227
	top2	0.694	-0.327	0.660	-0.343
Hf	hollow1	0.276	-0.058	0.568	-0.467
	hollow2	-0.166	-0.531	0.324	-0.745
	hollow3	-0.057	-0.624	0.232	-1.227
	top1	0.194	-0.725	0.445	-0.404
	top2	1.024	0.070	0.979	-0.693
Та	hollow1	0.303	-0.780	0.624	-0.410
	hollow2	0.157	-0.851	0.190	-0.289
	hollow3	0.695	-0.725	0.446	-0.424
	top1	-0.251	-1.066	0.120	0.020
	top2	0.889	-0.602	-0.134	0.995
W	hollow1	0.248	-1.211	0.059	0.119
	hollow2	-0.251	-1.157	-0.325	-0.461
	hollow3	-0.015	-1.065	0.121	0.020
	top1	0.343	-1.208	-0.076	0.518
	top2	0.705	-0.768	0.619	1.258
Re	hollow1	0.456	-1.253	-0.089	0.781
	hollow2	-0.251	-1.485	-0.295	-0.050
	hollow3	0.833	-1.207	-0.081	0.471



Figure A.9: Top1 (T1), top2 (T2), top3 (T3), hollow1 (H1) and hollow2 (H2) adsorption sites for island doping configuration.

Table A.7: Binding energies (eV) of HOCO*, CO*, H* and OH* on different adsorption sites for island doping configuration.

BE for island	Sites	HOCO*	CO*	H*	OH*
	top1	-0.388	-0.539	0.833	-1.166
	top2	0.387	-0.451	0.862	-0.854
Sc	top3	1.032	-0.500	0.399	-1.291
	hollow1	0.399	-0.449	0.692	-0.856
	hollow2	-0.597	-0.537	0.443	-1.091
	top1	0.107	-0.795	0.632	-0.751
	top2	0.328	-0.739	0.592	-0.563
Ti	top3	0.850	-0.821	0.815	-0.754
	hollow1	0.316	-0.731	0.584	-0.561
	hollow2	-0.017	-0.741	0.064	-0.682
	top1	0.081	-1.080	0.271	-0.203
	top2	0.556	-1.131	0.163	-0.423
V	top3	0.816	-0.886	0.063	-0.209
	hollow1	0.220	-1.132	0.064	-0.422
	hollow2	0.221	-1.131	0.061	-0.380
	top1	0.112	-0.972	0.294	-0.217
	top2	0.128	-1.457	-0.322	-0.382
Cr	top3	0.520	-1.408	-0.416	-0.056
	hollow1	0.185	-1.458	0.117	-0.352
	hollow2	0.174	-1.464	-0.416	-0.494
	top1	-0.289	-2.025	-0.099	-0.451
	top2	-0.341	-2.141	-0.447	-0.075
Mn	top3	0.341	-1.213	-0.753	-0.253

	hollow1	0.240	-1.673	-0.018	-0.148
	hollow2	-0.167	-1.823	-0.479	-0.687
	top1	-0.160	-1.358	0.056	-0.028
	top2	0.086	-1.718	-0.412	0.433
Fe	top3	0.407	-1.150	0.511	0.608
	hollow1	-0.073	-1.719	-0.005	0.061
Fe Co Ni Cu Zn Y Zr Zr	hollow2	0.140	-1.600	-0.304	-0.446
	top1	0.470	-0.900	0.254	0.852
	top2	0.246	-1.205	-0.205	0.797
Со	top3	0.538	-0.706	0.612	1.291
	hollow1	0.255	-1.208	0.099	0.797
Co Ni Cu Zn	hollow2	0.299	-1.205	0.145	0.558
	top1	0.675	-0.494	0.682	1.297
	top2	0.725	-0.433	-	1.314
Ni	top3	0.597	-0.226	0.614	1.081
	hollow1	0.615	-0.428	0.380	1.142
	hollow2	0.706	-0.339	0.357	-
	top1	1.221	-0.253	0.531	1.310
	top2	1.177	-0.241	-	1.220
Cu	top3	0.731	-0.095	0.632	1.552
	hollow1	0.725	-0.120	0.437	0.906
	hollow2	1.196	-0.117	0.531	-
	top1	0.541	-0.114	0.698	0.499
	top2	0.756	-0.117	0.553	0.262
Zn	top3	0.847	-0.136	0.729	0.145
	hollow1	0.768	-0.123	0.679	0.285
	hollow2	0.530	-0.123	0.634	0.132
	top1	-2.768	-2.816	-1.381	-2.649
	top2	-1.017	-1.704	-2.213	-2.171
Y	top3	-2.765	-2.839	-0.183	-2.099
	hollow1	-1.240	-1.321	-	-2.172
	hollow2	-2.118	-2.836	-2.213	-3.988
	top1	-1.450	-1.274	-0.603	-2.611
	top2	0.058	-0.666	0.746	-1.484
Zr	top3	0.467	-1.387	0.217	-2.610
	hollow1	-0.061	-0.672	0.494	-1.040
	hollow2	-1.399	-0.589	0.240	-1.403
	top1	0.149	-0.945	0.332	-0.659
	top2	0.225	-0.902	0.246	-0.408
Nb	top3	0.531	-0.939	0.193	-0.175
	hollow1	0.217	-0.900	0.246	-0.405
	hollow2	-0.186	-0.852	0.193	-0.432
	top1	0.121	-0.761	0.325	-0.218
	top2	0.246	-1.530	-0.215	-0.288
Mo	top3	-0.458	-1.094	-0.056	-0.276

	hollow1	-0.066	-1.530	-0.215	-0.271
	hollow2	0.387	-1.607	-0.044	-0.607
	top1	0.328	-1.208	-0.008	0.565
	top2	0.345	-1.384	-0.098	0.950
Ru	top3	0.490	-0.600	-0.508	1.115
	hollow1	0.075	-1.388	-0.283	0.637
Ru Rh Ag Cd Hf Ta W	hollow2	0.072	-1.404	-0.085	0.111
	top1	0.535	-0.674	0.262	1.402
	top2	0.374	-0.860	0.121	1.288
Rh	top3	0.721	-0.089	0.803	1.895
	hollow1	0.377	-0.863	0.290	1.307
	hollow2	0.461	-0.824	0.418	1.199
	top1	1.570	-0.092	1.745	1.316
	top2	1.497	-0.108	0.682	-
Ag	top3	1.027	0.139	0.901	-
	hollow1	1.026	-0.123	0.731	-
	hollow2	1.526	-0.114	0.682	-
	top1	0.763	-0.119	0.675	0.729
	top2	1.002	-0.150	0.706	0.480
Cd	top3	0.959	-0.132	0.624	-0.788
	hollow1	1.000	-0.155	-0.562	0.712
	hollow2	0.961	-0.139	0.623	0.481
	top1	-1.136	-0.702	-0.300	-2.311
	top2	-0.172	-0.696	0.724	-1.484
Hf	top3	0.328	-1.016	-0.093	-2.318
	hollow1	-0.270	-0.683	0.674	-1.483
	hollow2	-1.270	-1.021	0.166	-1.236
	top1	-0.210	-1.171	0.028	-1.297
	top2	0.077	-0.919	0.161	-0.751
Та	top3	1.016	-0.114	0.254	-1.301
	hollow1	0.068	-0.918	0.163	-0.751
	hollow2	-0.411	-1.170	0.256	-0.540
	top1	-0.061	-0.468	-1.052	-0.875
	top2	0.039	-1.459	0.194	-0.101
W	top3	-0.026	-0.853	-0.586	1.411
	hollow1	0.360	-1.158	-0.641	-0.095
	hollow2	0.053	-1.135	-0.586	-0.434
	top1	-0.019	-0.592	0.320	0.174
	top2	0.121	-1.414	-0.565	0.444
Re	top3	0.608	-0.452	0.474	1.250
	hollow1	0.327	-1.410	-0.552	0.380
	hollow2	0.220	-1.336	-0.067	0.027



Figure A.10: Top (T) and hollow (H) adsorption sites for overlayer doping configuration.

Table A.8:	Binding	energies	(eV) c	of HOCO*,	CO*,	H*	and	OH*	on	different	adsorp	otion
sites for ov	erlayer d	oping con	figurat	tion.								

BE for overly.	Sites	HOCO*	CO*	H*	OH*
80	top	-4.344	-3.911	-3.463	-5.161
30	hollow	-5.407	-4.877	-4.458	-5.790
Ti	top	0.359	-0.711	0.793	-0.613
	hollow	0.174	-0.710	-0.020	-0.528
V	top	0.184	-0.927	0.367	-0.247
v	hollow	0.187	-0.923	0.239	0.094
Cr	top	-0.018	-1.262	0.193	-0.026
	hollow	-0.016	-1.264	0.266	0.315
Mp	top	-0.216	-1.587	0.067	-0.610
	hollow	-0.479	-0.653	0.250	0.460
Fo	top	-1.566	-1.639	-0.033	-0.057
Гe	hollow	-1.500	-2.037	0.244	-0.800
Co	top	-0.734	-1.266	0.126	0.200
	hollow	-0.828	-1.953	0.253	-0.418
Nii	top	-0.438	-0.999	0.387	0.930
	hollow	0.041	-0.616	0.267	-0.469
Cu	top	0.974	-0.333	1.222	-
Cu	hollow	1.076	-0.089	0.920	1.001
Zn	top	-1.898	-2.973	-2.300	-3.155
ΔΠ	hollow	-2.029	-2.678	-1.919	-2.864
v	top	-16.174	-9.814	-	-10.373
I	hollow	-15.721	-16.347	-16.096	-13.788
Zr	top	-1.252	-0.749	-0.041	-1.945
	hollow	-1.578	-0.751	0.105	-1.784
Nb	top	0.519	-0.680	0.309	-0.465
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	hollow	0.210	-0.677	0.455	0.140
Mo	top	0.304	-1.156	0.010	-0.174
MO	hollow	0.077	-1.155	0.420	0.390
Bu	top	-0.028	-1.631	-0.194	0.627
Ru	hollow	-0.148	-0.818	0.269	0.716
Dh	top	0.313	-0.810	0.175	1.350
	hollow	0.329	-1.007	0.397	1.597
٨٩	top	1.363	-0.218	1.581	-
Ay	hollow	-	-0.185	1.066	-
Cd	top	-4.891	-5.273	-5.416	-4.877
Cu	hollow	-4.618	-5.579	-5.213	-5.237
Шf	top	-0.567	-0.913	0.018	-1.879
111	hollow	-1.531	-0.912	-0.083	-1.822
Та	top	0.171	-0.949	-0.052	-0.898
Ia	hollow	-0.171	-0.949	0.409	-0.075
۱۸/	top	0.083	-1.284	-0.274	-0.489
vv	hollow	-0.206	-1.284	0.516	-0.028
Po	top	0.133	-1.477	-0.240	0.101
Re	hollow	-0.533	-1.495	-0.164	-0.139

Table A.9: Contributions to the free energy corrections for different intermediates using the vdw-BEEF functional.

Intermediate	E _{ZPE} (eV)	∫ <i>C_pd7</i> (eV)	- T^*S (eV)	Total (eV)
HOCO*	0.657	0.091	-0.162	0.586
CO*	0.186	0.080	-0.156	0.110
H*	0.190	0.003	-0.004	0.189
OH*	0.355	0.056	-0.103	0.308

Table A.10: DFT energies, zero point energy, heat capacity correction, entropy correction, and final free energies of different gas species.

Species	E _{DFT} (eV)	E _{ZPE} (eV)	∫ C _p d7 (eV)	- <i>T*S</i> (eV)	Free energy (eV)
H ₂	-7.158	0.274	0.091	-0.402	-7.196
CO ₂	-18.459	0.306	0.099	-0.662	-18.718
H_2O	-12.833	0.572	0.104	-0.669	-12.827
CO	-12.118	0.132	0.091	-0.668	-12.564

Single	$\Delta G_{\mathrm{HOCO}*}$	$\Delta G_{\rm CO*}$	ΔG_{H*}	$\Delta G_{\text{OH}*}$	$\Delta G_{\mathrm{HOCO}*} - \Delta G_{\mathrm{H}*}$
Pure	0.820	0.216	0.501	1.581	0.319
Sc	1.062	0.026	0.682	-0.283	0.380
Ti	0.917	-0.213	0.674	-0.083	0.242
V	0.837	-0.443	0.470	0.087	0.368
Cr	0.849	-0.756	0.199	0.413	0.650
Mn	0.839	-1.029	-0.054	0.770	0.893
Fe	0.817	-0.881	-0.036	1.126	0.852
Со	0.962	-0.380	0.296	1.538	0.666
Ni	0.981	0.101	0.656	1.392	0.325
Cu	1.057	0.388	0.675	1.803	0.382
Zn	1.105	0.422	0.665	1.004	0.439
Y	0.887	0.029	0.517	-0.467	0.370
Zr	0.764	-0.238	0.654	-0.518	0.110
Nb	0.755	-0.432	0.019	-0.089	0.736
Мо	0.849	-0.725	0.145	0.402	0.703
Ru	0.669	-0.841	-0.073	1.101	0.741
Rh	0.977	-0.120	0.363	1.713	0.614
Ag	1.089	0.461	0.670	2.009	0.420
Cd	1.161	0.436	0.751	-0.190	0.410
Hf	0.848	-0.255	0.717	-0.531	0.131
Та	1.072	-0.430	-0.022	-0.243	1.094
W	1.015	-0.605	0.148	0.279	0.867
Re	1.018	-0.191	0.204	0.996	0.813

Table A.11: Gibbs free energy difference (eV) of intermediates HOCO^{*}, CO^{*}, H^{*} and OH^{*}, and describer $\Delta G_{\text{HOCO*}} - \Delta G_{\text{H*}}$ for single doping configuration.

Dimer	$\Delta G_{\mathrm{HOCO}*}$	$\Delta G_{\rm CO*}$	ΔG_{H*}	$\Delta G_{\text{OH}*}$	$\Delta G_{\mathrm{HOCO}*} - \Delta G_{\mathrm{H}*}$
Pure	0.820	0.216	0.501	1.581	0.319
Sc	0.431	0.070	0.249	-0.508	0.182
Ti	0.782	-0.178	0.542	-0.193	0.240
V	0.811	-0.458	0.071	0.092	0.740
Cr	0.194	-0.573	0.080	-0.037	0.114
Mn	0.520	-0.815	0.044	0.216	0.477
Fe	0.675	-0.782	-0.027	0.933	0.702
Co	1.021	-0.375	0.157	1.353	0.864
Ni	1.030	0.045	0.588	1.404	0.442
Cu	1.127	0.399	0.720	1.488	0.407
Zn	1.110	0.440	0.762	0.619	0.347
Y	-0.058	0.190	-0.095	-0.769	0.037
Zr	0.194	-0.170	0.285	-0.669	-0.091
Nb	0.777	-0.380	0.473	-0.144	0.304
Мо	0.657	-0.551	0.145	0.385	0.512
Ru	0.628	-0.760	0.014	1.149	0.614
Rh	0.986	-0.133	0.363	1.462	0.623
Ag	1.193	0.462	0.678	1.784	0.515
Cd	1.285	0.447	0.751	0.854	0.535
Hf	0.643	-0.174	0.586	-0.669	0.058
Та	0.719	-0.363	0.405	-0.386	0.314
W	0.793	-0.483	0.257	0.248	0.537
Re	0.815	-0.525	0.152	0.769	0.663

Table A.12: Gibbs free energy difference (eV) of intermediates HOCO^{*}, CO^{*}, H^{*} and OH^{*}, and describer $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ for dimer doping configuration.

Triangle	$\Delta G_{\mathrm{HOCO}*}$	$\Delta G_{\rm CO*}$	ΔG_{H*}	$\Delta G_{\text{OH}*}$	$\Delta G_{\rm HOCO*} - \Delta G_{\rm H*}$
Pure	0.820	0.216	0.501	1.581	0.319
Sc	0.520	-0.055	0.313	-0.586	0.207
Ti	0.652	-0.248	0.494	-0.401	0.158
V	0.480	-0.518	-0.147	-0.158	0.627
Cr	0.252	-0.766	0.380	-0.296	-0.128
Mn	0.503	-0.976	-0.230	0.140	0.732
Fe	0.518	-0.889	-0.185	0.936	0.703
Со	0.931	-0.533	0.037	1.444	0.893
Ni	0.931	0.041	0.416	1.675	0.515
Cu	1.249	0.391	0.718	1.550	0.531
Zn	0.915	0.289	0.669	0.286	0.246
Y	-0.468	0.026	-0.729	-1.309	0.261
Zr	0.317	-0.241	0.275	-0.852	0.042
Nb	0.581	-0.376	0.474	-0.325	0.107
Мо	0.592	-0.706	0.224	-0.037	0.368
Ru	0.608	-0.795	-0.012	1.043	0.621
Rh	0.871	-0.119	0.367	1.442	0.504
Ag	1.284	0.468	0.829	1.804	0.455
Cd	1.052	0.411	0.584	0.733	0.467
Hf	0.404	-0.179	0.494	-0.808	-0.090
Та	0.411	-0.455	0.339	-0.588	0.072
W	0.761	-0.571	0.229	0.008	0.532
Re	0.550	-0.767	-0.031	0.285	0.581

Table A.13: Gibbs free energy difference (eV) of intermediates HOCO^{*}, CO^{*}, H^{*} and OH^{*}, and describer $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ for triangle doping configuration.

Parall.	$\Delta G_{\mathrm{HOCO}*}$	$\Delta G_{\rm CO*}$	ΔG_{H*}	$\Delta G_{\text{OH}*}$	$\Delta G_{\mathrm{HOCO}*} - \Delta G_{\mathrm{H}*}$
Pure	0.820	0.216	0.501	1.581	0.319
Sc	-0.204	-0.299	0.043	-1.333	-0.247
Ti	0.509	-0.165	0.407	-0.222	0.102
V	0.531	-0.448	0.363	0.056	0.168
Cr	0.411	-0.830	0.295	-0.176	0.116
Mn	0.499	-0.801	0.142	0.442	0.357
Fe	0.364	-0.794	-0.044	0.489	0.408
Co	0.434	-0.797	0.199	0.662	0.235
Ni	0.847	0.035	0.489	1.064	0.358
Cu	1.203	0.373	0.708	1.058	0.495
Zn	0.804	0.118	0.649	0.290	0.155
Y	-0.647	-0.803	-0.946	-1.452	0.299
Zr	0.396	-0.119	0.597	-0.782	-0.201
Nb	0.541	-0.277	0.499	-0.232	0.043
Мо	0.331	-0.768	0.364	-0.075	-0.033
Ru	0.452	-0.815	-0.057	0.778	0.510
Rh	0.908	-0.215	0.342	1.559	0.566
Ag	1.360	0.453	0.826	1.390	0.534
Cd	-0.358	0.037	0.474	-0.629	-0.831
Hf	0.248	-0.237	0.390	-0.894	-0.142
Та	0.571	-0.272	0.348	-0.360	0.223
W	0.163	-0.632	-0.167	-0.128	0.330
Re	0.163	-0.906	-0.137	0.283	0.300

Table A.14: Gibbs free energy difference (eV) of intermediates HOCO^{*}, CO^{*}, H^{*} and OH^{*}, and describer $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ for parallelogram doping configuration.

Island	$\Delta G_{\mathrm{HOCO}*}$	$\Delta G_{\rm CO*}$	ΔG_{H*}	$\Delta G_{\text{OH}*}$	$\Delta G_{\mathrm{HOCO}*} - \Delta G_{\mathrm{H}*}$
Pure	0.820	0.216	0.501	1.581	0.319
Sc	-0.183	0.040	0.557	-0.958	-0.739
Ti	0.397	-0.242	0.222	-0.421	0.175
V	0.495	-0.553	0.219	-0.090	0.276
Cr	0.526	-0.885	-0.258	-0.161	0.784
Mn	0.073	-1.562	-0.595	-0.354	0.667
Fe	0.254	-1.140	-0.254	-0.113	0.508
Со	0.660	-0.629	-0.047	0.891	0.707
Ni	1.011	0.085	0.515	1.414	0.495
Cu	1.139	0.326	0.595	1.239	0.544
Zn	0.944	0.443	0.711	0.465	0.233
Y	-2.354	-2.260	-2.055	-3.655	-0.300
Zr	-1.036	-0.808	-0.445	-2.278	-0.591
Nb	0.228	-0.366	0.351	-0.326	-0.123
Мо	-0.044	-1.028	-0.057	-0.274	0.013
Ru	0.486	-0.825	-0.350	0.444	0.836
Rh	0.788	-0.284	0.279	1.532	0.509
Ag	1.440	0.456	0.840	1.649	0.601
Cd	1.177	0.424	-0.404	-0.455	1.581
Hf	-0.856	-0.442	-0.142	-1.985	-0.714
Та	0.003	-0.592	0.186	-0.968	-0.183
W	0.353	-0.880	-0.894	-0.542	1.247
Re	0.395	-0.835	-0.407	0.360	0.802

Table A.15: Gibbs free energy difference (eV) of intermediates HOCO^{*}, CO^{*}, H^{*} and OH^{*}, and describer $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ for island doping configuration.

Overlayer $\Delta G_{\text{HOCO}*}$		$\Delta G_{\rm CO*}$	ΔG_{H*}	$\Delta G_{\mathrm{OH}*}$	$\Delta G_{\mathrm{HOCO}*} - \Delta G_{\mathrm{H}*}$
Pure	0.820	0.216	0.501	1.581	0.319
Sc	-4.993	-4.298	-4.300	-5.457	-0.693
Ti	0.588	-0.132	0.138	-0.280	0.450
V	0.598	-0.348	0.397	0.086	0.201
Cr	0.396	-0.685	0.351	0.307	0.045
Mn	-0.065	-1.008	0.225	-0.277	-0.290
Fe	-1.152	-1.458	0.125	-0.467	-1.277
Co	-0.414	-1.374	0.284	-0.085	-0.699
Ni	-0.024	-0.420	0.425	-0.136	-0.450
Cu	1.388	0.246	1.078	1.334	0.310
Zn	-1.615	-2.394	-2.142	-2.822	0.526
Y	-15.760	-15.768	-15.938	-13.455	0.177
Zr	-1.164	-0.172	0.117	-1.612	-1.281
Nb	0.624	-0.101	0.467	-0.132	0.157
Мо	0.491	-0.577	0.168	0.159	0.323
Ru	0.266	-1.052	-0.036	0.960	0.303
Rh	0.727	-0.428	0.333	1.683	0.394
Ag	1.777	0.361	1.224	1.841	0.553
Cd	-4.477	-5.000	-5.258	-4.904	0.782
Hf	-1.117	-0.334	0.075	-1.546	-1.192
Та	0.243	-0.370	0.106	-0.565	0.137
W	0.208	-0.705	-0.116	-0.156	0.325
Re	-0.119	-0.916	-0.082	0.194	-0.037

Table A.16: Gibbs free energy difference (eV) of intermediates HOCO^{*}, CO^{*}, H^{*} and OH^{*}, and describer $\Delta G_{\text{HOCO}*} - \Delta G_{\text{H}*}$ for overlayer doping configuration.



Figure A.11: The formation of two bonds consisting of C-metal and O-metal and the metal atom is the same one for HOCO* on the doped PdH(111) surface.



Figure A.12: The scaling relation of intermediates on doped PdH(111) with different elements between HOCO* and OH* in different doping configurations. The red line is fitted by Fe, Co, Ni, Cu, Ru, Rh, and Ag-doped PdH(111) due to the formation of one bond for HOCO* on the surface. The blue line is fitted by all element doped PdH(111).



Figure A.13: The scaling relation of intermediates on doped PdH(111) with different elements between CO* and H* in different doping configurations.



Figure A.14: The logarithm of partial current density j of CO* as a function of temperature for Ti doping with parallelogram configuration.

Elements	Bond length of overlayer of doped surfaces	Bonds length of bulk metals
Sc	2.926	3.237
Ti	2.926	2.860
V	2.926	2.615
Cr	2.926	2.459
Mn	2.926	2.481
Fe	2.926	2.448
Со	2.926	2.479
Ni	2.927	2.502
Cu	2.926	2.590
Zn	2.926	2.951
Y	2.926	3.546
Zr	2.926	3.186
Nb	2.926	2.882
Мо	2.926	2.729
Ru	2.926	2.664
Rh	2.926	2.716
Ag	2.926	2.967
Cd	2.926	3.367
Hf	2.926	3.122
Та	2.926	2.868
W	2.926	2.748
Re	2.926	2.759

Table A.17: The average bond lengths of the first metal layer of doped surfaces in the configuration of overlayer and bulk metals. Different degrees of lattice mismatch can be seen for overlayer configuration.

Donante	Single		Din	Dimer		Triangle	
Dopunto	C-M	O-M	C-M	O-M	C-M	O-M	
Sc	2.150	2.123	2.063	2.129	2.055	2.113	
Ti	2.020	2.129	2.214	2.013	2.234	2.063	
V	1.963	2.117	2.129	2.083	2.047	2.054	
Cr	1.931	2.166	2.056	2.092	2.022	2.041	
Mn	1.984	2.392	1.966	2.039	1.967	2.045	
Fe	1.974	2.532	2.010	2.781	2.036	2.815	
Со	2.056	2.856	1.974	2.775	1.954	2.766	
Ni	2.054	2.852	2.056	2.846	2.046	2.845	
Cu	2.061	2.853	2.061	2.859	2.070	2.871	
Zn	2.061	2.855	2.083	2.120	2.076	2.106	
Y	2.328	2.255	2.074	2.287	2.087	2.245	
Zr	2.171	2.241	2.179	2.195	2.186	2.217	
Nb	2.100	2.256	2.295	2.251	2.118	2.262	
Мо	2.056	2.314	2.172	2.232	2.038	2.144	
Ru	2.142	2.955	2.103	2.874	2.097	2.889	
Rh	2.058	2.884	2.047	2.857	2.055	2.875	
Ag	2.054	2.847	2.063	2.859	2.075	2.866	
Cd	2.059	2.854	2.074	2.869	2.285	2.443	
Hf	2.151	2.198	2.16	2.167	2.165	2.179	
Та	2.227	2.842	2.108	2.297	2.098	2.208	
W	2.170	2.574	2.174	2.216	2.020	2.122	
Re	2.124	2.404	2.096	2.190	2.137	2.906	

Table A.18: The C-Metal (C-M) and O-Metal (O-M) bond lengths (Å) of HOCO* on doped surfaces in the configurations of single, dimer, and triangle, respectively.

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Dopants -	Parall.		Isla	Island		Overlayer	
	C-M	O-M	C-M	O-M	C-M	O-M	
Sc	2.061	2.098	2.404	2.077	2.333	2.046	
Ti	2.259	2.032	2.247	2.062	2.307	2.059	
V	2.094	1.999	2.141	2.104	2.146	2.119	
Cr	2.025	2.069	2.057	2.081	2.042	2.072	
Mn	1.967	2.051	1.985	2.756	1.958	2.000	
Fe	2.021	2.784	1.924	2.030	1.895	1.954	
Co	1.931	2.757	1.972	2.800	1.851	1.973	
Ni	2.061	2.854	2.051	2.846	1.909	2.084	
Cu	2.059	2.851	2.063	2.847	2.012	2.822	
Zn	2.074	2.106	2.072	2.122	2.056	2.922	
Y	2.140	2.253	2.470	2.361	2.559	2.237	
Zr	2.185	2.213	2.224	2.225	2.316	2.092	
Nb	2.304	2.191	2.303	2.205	2.310	2.234	
Мо	2.165	2.196	2.066	2.340	2.166	2.203	
Ru	2.110	2.881	2.072	2.549	2.091	2.904	
Rh	2.055	2.863	2.064	2.885	2.059	2.860	
Ag	2.066	2.868	2.057	2.841	2.270	3.090	
Cd	3.760	3.417	2.276	2.492	2.298	2.438	
Hf	2.397	2.097	2.272	3.423	2.276	2.045	
Та	2.239	2.122	2.291	2.153	2.284	2.184	
W	2.161	2.167	2.216	2.216	2.143	2.139	
Re	2.087	2.143	2.130	2.910	2.062	2.116	

Table A.19: The C-Metal (C-M) and O-Metal (O-M) bond lengths (Å) of HOCO* on doped surfaces in the configurations of parallelogram, island, and overlayer, respectively.



Figure A.15: O-Metal (O-M) bond lengths (Å) of HOCO* on doped surfaces in the different configurations.



Figure A.16: Charge density difference with (a) Ti doping, (b) W doping, and (c) Cu doping in the single dopant configuration. Their O-M bond lengths are 2.123, 2.574, and 2.853 Å, respectively. The blue spheres are Pd atoms, the small white spheres represent H atoms, the red spheres are O atoms, and the small grey spheres are C atoms. Isosurface value is set as 0.003 e Å⁻³.



Figure A.17: Histogram of O-M bonds (Å) in the configurations of single, dimer, triangle, parallelogram, island, and overlayer.

Bond formation analysis

We list the C-Metal (C-M) and O-Metal (O-M) bond lengths of HOCO* on doped surfaces in different configurations as shown in Table A.18 and A.19. It can be found that C-M bonds are always around 2.0 Å, which illustrates that the C atom can always form a chemical bond on the surface. However, O-M bond length varies a lot, ranging from 1.8 to 3.0 Å, which means that the O atom can form a chemical bond on the doped surfaces in some cases, and does not bond to the surfaces in other cases. Figure A.16 shows the charge density difference of HOCO* adsorbed with a single Ti, W, and Cu dopant. When the bond length is 2.123 Å, there is a clear charge transfer between the O and the M atom. The charge transfer still exists but is weaker when the O-M bond length is longer (2.574 Å). However, there is no obvious charge transfer when the O-M is much longer (2.853 Å). Figure A.17 displays the bond length distribution in different configurations. It can be seen that no O-M bond lengths between 2.625 and 2.750 Å are found and there may be a bond length threshold between them. Here, we define the threshold as 2.7 Å, which means that the chemical bond would form when the bond length is less than 2.7 A. As shown in Figure A.15, we can find that the O-M bonds do not form on Fe, Co, Ni, Cu, Ru, Rh, and Ag-doped surfaces in all doping configurations in a very large number of cases, which displays that it is much easier to only form C-M bond for them. However, for other element doping, they tend to form both C-M and O-M bonds on their doped surfaces in most cases. In most cases, the O-M bond length is either around 2.0-2.3 Å or around 2.8-3.0 Å, and slightly changing the O-M distance determining whether there are one or two bonds will not significantly affect our classification. Besides, it can be noticed that the binding energies of HOCO* vary as the doping configurations change. This may be because HOCO* has more degrees of freedom of movement due to its asymmetric structures, which causes a wider binding energy distribution.

Pourbaix diagrams

In order to study stability at electrochemical conditions we calculate Pourbaix diagrams. Free energy calculations of dissolved metal ions are obtained from the following equations: [178, 179, 211]

$$\operatorname{Pd}_{(s)} \longrightarrow \operatorname{Pd}^{2+} + 2 e^{-} \qquad E_0 = 0.951$$
 (A.1)

$$G_{Pd^{2+}} = E_{Pd(bulk)} + 2E_0 + 0.0592 \cdot \log[Pd^{2+}]$$
(A.2)

$$Nb_{(s)} \longrightarrow Nb^{3+} + 3e^{-}$$
 $E_0 = -1.099$ (A.3)

$$G_{\rm Nb^{3+}} = E_{\rm Nb(bulk)} + 3 E_0 + 0.0592 \cdot \log[\rm Nb^{3+}]$$
(A.4)

$$Ti_{(s)} \longrightarrow Ti^{2+} + 2e^{-} \qquad E_0 = -1.628 \tag{A.5}$$

$$G_{\text{Ti}^{2+}} = E_{\text{Ti}(\text{bulk})} + 2E_0 + 0.0592 \cdot \log[\text{Ti}^{2+}]$$
(A.6)

$$\operatorname{Ti}^{3+} + \mathrm{e}^{-} \longrightarrow \operatorname{Ti}^{2+} \qquad E_0 = -0.369$$
 (A.7)

$$G_{\mathsf{T}i^{3+}} = G_{\mathsf{T}i^{2+}} + E_0 + 0.0592 \cdot \log \frac{[\mathsf{T}i^{3+}]}{[\mathsf{T}i^{2+}]}$$
(A.8)

The corrosion process of doped PdH(111) is considered as follows:

$$\mathsf{Pd}_{x}\mathsf{M}_{y}\mathsf{H}_{z} \longrightarrow \mathsf{Pd}_{x}\mathsf{M}_{y-1}\mathsf{H}_{z-1} + \mathsf{M}^{n+} + \mathsf{H}^{+} + (\mathsf{n}+1)\,\mathsf{e}^{-} \tag{A.9}$$

$$G_{\text{dissolution}} = G_{\text{Pd}_{x}\text{M}_{y-1}\text{H}_{z-1}} + G_{\text{Ti}^{3+}} + 0.5 \cdot G_{\text{H}_{2}} - (n+1) \cdot eU - k_{\text{B}} \cdot T \cdot pH \cdot \ln(10)$$
(A.10)

where $Pd_xM_yH_z$ is bare surface of doped PdH(111). $Pd_xM_{y-1}H_{z-1}$ represents the surface after dissolving a metal atom and one hydrogen atom and M^{n+} represents dissolved metal ion. According to this equation, we can calculate the free energy of the dissolving metal ion.



Figure A.18: Surface stability of HOCO*, CO*, H*, OH*, Ti²⁺, Ti³⁺, and bare Ti doped PdH(111) surface at pH = 0 in the configuration of parallelogram. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.



Figure A.19: Surface Pourbaix diagram of Ti doped PdH(111) in the configuration of parallelogram. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.


Figure A.20: Surface stability of HOCO*, CO*, H*, OH*, Ti²⁺, Ti³⁺, and bare Ti doped PdH(111) surface at pH = 0 in the configuration of overlayer. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.



Figure A.21: Surface Pourbaix diagram of Ti-doped PdH(111) in the configuration of overlayer. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.



Figure A.22: Surface stability of HOCO*, CO*, H*, OH*, Nb³⁺, and bare Nb doped PdH(111) surface at pH = 0 in the configuration of overlayer. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.



Figure A.23: Surface Pourbaix diagram of Nb-doped PdH(111) in the configuration of overlayer. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.



Figure A.24: Surface stability of HOCO*, CO*, H*, OH*, Pd²⁺, and bare PdH(111) surface at pH = 0. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.



Figure A.25: Surface Pourbaix diagram of pure PdH(111) surface. Temperature is at 298.15 K and the metal ion concentration is considered as 10^{-6} M.

Appendix B

Supplementary material for PdH_x(111)

This appendix is the supplementary material of Chapter 4, which is based on the supporting information of Paper II.

Calculation details

In this work, only the (111) surface of PdH_x is studied as it is energetically the most stable surface and it is exposed on octahedral nanoparticles having the highest activity and selectivity for the CO₂RR. We adopt a 4×4 supercell model of the PdH_x(111) with four bilayers. Each bilayer is composed of one Pd atomic layer and one H or X (vacancy) atomic layer, and the bottom two bilayers are fixed during relaxation. An approximate 15 Å vacuum layer is set in the z-direction to avoid interactions of separated periodic slab images due to periodic boundary conditions. Furthermore, A series of energy corrections are used to further promote the accuracy of energies, in this work. A +0.15 eV correction per C=O, +0.15 eV correction for HOCO*, and +0.1 eV correction for H₂ are applied for systematic overbinding corrections with the BEEF-vdw functional in all calculations.[174, 175, 189] In terms of implicit solvent stabilization effect at the water-catalyst interface, -0.25 eV correction for HOCO* and -0.1 eV correction for CO* are utilized, respectively.[40] The influence of the electric field on the free energy of the adsorbates at the electrochemical interface of catalysis is not considered in our calculations.

In order to obtain the convex hull of PdH_x , the mixing energy E_{Mixing} is calculated by the following definition:

$$E_{\mathsf{Mixing}} = E_{\mathsf{PdH}_x} - xE_{\mathsf{PdH}} - (1-x)E_{\mathsf{Pd}}$$
(B.1)

where E_{PdH_x} denotes the energy of PdH_x when the H concentration, *x*, is between 0 and 1. E_{PdH} means the energy of PdH when H concentration is 1, while E_{Pd} is the energy of pure Pd when H concentration is 0.

The binding energies E_{b} of intermediates in this work are calculated by the following equation:

$$E_{\mathsf{b}} = E_{*+\mathsf{ads}} - E_{*} - E_{\mathsf{ads}} \tag{B.2}$$

where E_{*+ads} is the total DFT energy of slab and adsorbate. E_* denotes the energy of the clean slab and E_{ads} denotes the energy of the adsorbate with respect to gas phase molecules.

The Gibbs free energy (G) is divided into four parts according to the following definition:

$$G = E_{\mathsf{DFT}} + E_{\mathsf{ZPE}} + \int C_p \mathsf{d}T - TS$$
(B.3)

where E_{DFT} denotes the DFT energy with correction. E_{ZPE} denotes the zero-point energy. C_p , T and S are the heat capacity, temperature, and entropy. The free energy calculations of the slabs with adsorbate use the harmonic approximation via calculations of vibrational frequencies, while gas-phase species are calculated within the ideal gas approximation. The detailed terms are listed in Table A.9 and Table A.10. The computational hydrogen electrode (CHE) model[168] is used to avoid calculations of solvated protons.

The ensembles from BEEF-vdW are calculated to estimate binding energy errors and plot error ellipses, which represent the covariance. Each DFT ensemble calculation will generate 2000 energy values and then they can be used to calculate ensemble binding

energies with 2000 values. The covariance matrix $cov(\Delta E_x, \Delta E_y)$ of two column ensemble binding energies of adsorbates A^{*} and B^{*} is calculated the following equation:[212]

$$\mathbf{cov}(\Delta E_x, \Delta E_y) = \begin{bmatrix} var(x) & cov(x, y) \\ var(x, y) & var(y) \end{bmatrix}$$
(B.4)

where ΔE_x and ΔE_y denote the ensemble binding energies of adsorbates A* and B*, respectively. var(x) and var(y) are the variances and can be expressed as var(x) = cov(x, x) and var(y) = cov(y, y). In addition, var(x, y) is the covariance of the two-column ensemble binding energies. The covariance matrix can be decomposed into eigenvalues and eigenvectors by single-value decomposition according to the following equation:

$$\mathbf{cov}(\Delta E_x, \Delta E_y) = U\Sigma U^*, \quad \Sigma = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}, \quad U = \begin{bmatrix} x1 & y1 \\ x2 & y2 \end{bmatrix}$$
(B.5)

where U is the orthogonal eigenvector, which maximizes the description of correlation. σ represents the eigenvalues in the diagonal, which utilizes the size or weight in each orthogonal orientation. The eigenvalues can be normalized into the parameters of the ellipse equation $(\frac{x^2}{a_{\sigma}^2} + \frac{y^2}{b_{\sigma}^2} = 1)$. Their parameters can be obtained by the equation:

$$\alpha_{\sigma} = \sqrt{a * \chi^2(\text{fractile}, \mathsf{d}f)}, \quad \alpha \in a, b$$
(B.6)

where α_{σ} denotes the parameters of the ellipse and χ denotes the chi-squared probability density function with d*f* degrees of freedom. [212]



Figure B.1: The flowchart of active learning cluster expansion of $PdH_x(111)$ surface to find candidates from DFT convex hull.



Figure B.2: (a) The linear fitting plot of cluster expansion energy and DFT energy using 2-body configuration. (b) ECIs distribution obtained from cluster expansion 2-body fitting. (c) The linear fitting plot of cluster expansion energy and DFT energy using a 3-body configuration. (d) ECIs distribution obtained from cluster expansion 3-body fitting.



Figure B.3: The Monte Carlo simulated annealing for each H concentration in round 1 of ALCE. The x-axis shows indices of temperatures and they are 1e10, 10000, 6000, 4000, 2000, 1500, 1000, 800, 700, 600, 500, 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 2, and 1 K.



Figure B.4: The linear fitting plot between cluster expansion energy and DFT energy for (a) round 2, (b) round 3, (c) round 4, and (d) round 5.



Figure B.5: The linear fitting plot between cluster expansion energy and DFT energy for (a) round 6, (b) round 7, (c) round 8, and (d) round 9.



Figure B.6: The DFT convex hull curves of mixing energy as a function of H concentration in round 1, (b) round 2, (c) round 3, and (d) round 4.



Figure B.7: The DFT convex hull curves of mixing energy as a function of H concentration in round 5, (b) round 6, (c) round 7, and (d) round 8.



Figure B.8: The H concentration of each layer as a function of the total concentration of H for the structures of final candidates.



Figure B.9: The H concentration plots of each layer as a function of the total concentration of H for the slab with adsorbates HOCO*, CO*, OH*, and H*, respectively.



Figure B.10: The side view and the top view of surface (a-b) PdH_{64} , (c-d) PdH_{63} , (e-f) PdH_{39} and (g-h) PdH_{31} . The blue spheres are Pd atoms and the white spheres represent H atoms.



Figure B.11: (a) The $4 \times 4 \times 1$ PdH_x(111) structures with one missing layer from bottom to top layer and (b) their corresponding DFT energies. The dashed area is the sublayer corresponding to the 2nd layer.



Figure B.12: (a) The $1 \times 1 \times 4$ PdH_x(111) structures with one missing layer from bottom to top layer and (b) corresponding DFT energies. The dashed area is the sublayer corresponding to the 2nd layer.



Figure B.13: The binding energy relations with error ellipsoids between adsorbates HOCO^{*}, CO^{*}, OH^{*} and H^{*}. The error ellipsoids represent the confidence interval of binding energies. The black horizotal and vertical lines show $\Delta G_{H*} = 0$ and $\Delta G_{CO*} = 0$, repectively.



Semi-grand canonical Monte Carlo calculation

Figure B.14: The top view of 20×20 supercell surface of PdH_x (111). The blue spheres are Pd atoms and the small white spheres represent H atoms.

A semi-grand canonical Monte Carlo is implemented to study H chemical potential as a function of H concentration of $PdH_x(111)$ surface. The 20×20 supercell surface is utilized as shown in Figure B.14. The chemical potentials of H are ranging from -4.5 to -3.0, and 200 even points are generated between them. The chemical potential (μ_{H_2}) of H₂ is dependent on temperature and the partial pressure of H₂, which can be expressed as the following equation: [183]

$$\mu_{\mathsf{H}_2}(T, p_{\mathsf{H}_2}) = \mu_{\mathsf{H}_2}^{\mathsf{0}}(T) + k_{\mathsf{B}}T \ln \frac{p_{\mathsf{H}_2}}{p_{\mathsf{H}_2}^{\mathsf{0}}} \tag{B.7}$$

where $\mu_{H_2}^0(T)$ is the temperature-dependent H₂ chemical potential at the reference pressure and $p_{H_2}^0$ is the reference pressure. k_B is the Boltzmann constant.

Figure B.15 shows H chemical potential as a function of the concentration of H at different temperatures for $PdH_x(111)$ surface. The concentration of H gradually goes up as H chemical potential increases and the effect of temperature is small. It can be seen that the equilibrium concentration of H between internal H of the surface and H₂ gas is around 0.6 at room temperature at standard pressure. The pressure of H₂ and temperature as a function of the concentration of H are studied as shown in Figure B.16. Under the same pressure, the concentration of H₂ will be lower if the temperature is higher. Under the same temperature, the concentration of H₂ will be higher if the pressure is higher. It can be found that the maximum H concentration is around 60%.



Figure B.15: H chemical potential as a function of H concentration of $PdH_x(111)$ at different temperatures at standard pressure. The dashed red line is the chemical potential of the half of H₂ at room temperature at standard pressure.



Figure B.16: (a) The H₂ pressure as a function of H concentration of $PdH_x(111)$ at different temperatures. (b) The temperature as a function of H concentration at different H₂ pressures.

Phase transformation calculation

Phase transformation from metal Pd to PdH_x is theoretically explored at an experimental pH value of 7.3. There exist two different phases of palladium hydride, α -PdH_x and β -PdH_x. [213] α -PdH_x has a low H/Pd ratio, while β -PdH_x has a high H/Pd ratio. Experimentally, Pd can be transformed into palladium hydride by applying a potential during the electrochemical process. Chen et al. reported that their X-ray absorption spectroscopy and in-situ X-ray diffraction were used to identify the transformation of Pd to palladium hydride and the phase transformation finished at -0.5 V vs. RHE.[58] Gao et. al. experimentally reported the phase transformation potential was between -0.2 and -0.5 V vs. RHE through in situ synchrotron radiation XRD patterns.[180] Diercks et al. experimentally reported that H concentration was increasing until the applied potential was around -0.8 V vs. RHE via electrochemical measurements and the maximum concentration of H is around 0.55-0.6.[181] Here, we theoretically study the phase transformation via the Pourbaix diagram. The free energy difference (ΔG) is calculated according to equations (B.8) and (B.9) as follows:

$$\mathsf{Pd}_{64}\mathsf{H}_{64} \longleftrightarrow \mathsf{Pd}_{64}\mathsf{H}_x + (64\text{-}x) \cdot (\mathsf{H}^+ + \mathsf{e}^-) \tag{B.8}$$

$$\Delta G = G_{\mathsf{Pd}_{64}\mathsf{H}_x} - G_{\mathsf{Pd}_{64}\mathsf{H}_{64}} + \frac{1}{2}(64 - x)\mu_{\mathsf{H}_2} + (64 - x) * eU - (64 - x) * k_{\mathsf{B}}T * pH * \mathsf{In}(10)$$
(B.9)

where $G_{Pd_{64}H_x}$ and $G_{Pd_{64}H_{64}}$ are the free energies of $Pd_{64}H_x$ and $Pd_{64}H_{64}$, respectively. U is the applied potential and pH is the pH value. U_{SHE} can be transformed via $U_{RHE} = U_{SHE} + k_BT * pH * \ln(10)$.



Figure B.17: (a-i) Partial density of states of d-band for all candidates' bare slabs. The blue zones mean below the corresponding d band center.



Figure B.18: The H concentration of all candidates as a function of d-band center for bare slabs. The red line is the linear fit line and the corresponding R-squared error is shown in the bottom left corner.



Figure B.19: (a-i) Partial density of states of the d-band for all candidates' slabs with HOCO*. The blue zones mean below the corresponding d band center.



Figure B.20: (a) The H concentration of all candidates as a function of the d-band center for slabs with HOCO*. (b) The HOCO* binding energy as a function of the d-band center. The red line is the linear fit line and the corresponding R-squared error is shown in the bottom left corner.



Figure B.21: (a-i) Partial density of states of the d-band for all candidates slabs with CO*. The blue zones mean below the corresponding d band center.



Figure B.22: (a) The H concentration of all candidates as a function of the d-band center for slabs with CO*. (b) The CO* binding energy as a function of the d-band center. The red line is the linear fit line and the corresponding R-squared error is shown in the bottom left corner.

Surface	H concentration	E_{HOCO*}	$E_{\rm CO*}$	E_{H*}	E_{OH*}
Pd ₆₄	0.000	-0.179	-1.838	-0.366	0.525
$Pd_{64}H_2$	0.031	-0.168	-1.775	-0.405	0.419
$Pd_{64}H_4$	0.062	-0.063	-1.768	-0.399	0.441
$Pd_{64}H_8$	0.125	0.096	-1.596	-0.346	0.619
$Pd_{64}H_{10}$	0.156	0.310	-1.517	-0.323	0.729
$Pd_{64}H_{13}$	0.203	0.374	-1.050	-0.280	1.021
$Pd_{64}H_{31}$	0.484	0.373	-1.022	0.111	1.264
$Pd_{64}H_{39}$	0.609	0.272	-0.756	-0.227	1.333
$Pd_{64}H_{53}$	0.828	0.678	-0.896	0.137	1.153
$Pd_{64}H_{62}$	0.969	0.707	-0.320	0.512	1.144
$Pd_{64}H_{63}$	0.984	0.586	-0.187	0.210	1.430
$Pd_{64}H_{64}$	1.000	0.381	-0.360	0.295	1.443

Table B.1: Binding energies of adsorbates HOCO*, CO*, H* and OH*, and corresponding H concentration at the most stable site for all candidate surfaces.

Table B.2: Free energies of adsorbates HOCO*, CO*, H* and OH*, and corresponding H concentration at the most stable site for all candidate surfaces.

Surface	H concentration	G_{HOCO*}	$G_{\text{CO}*}$	G_{H*}	G_{OH*}
Pd ₆₄	0.000	0.235	-1.259	-0.208	0.858
$Pd_{64}H_2$	0.031	0.246	-1.196	-0.247	0.752
$Pd_{64}H_4$	0.062	0.351	-1.189	-0.241	0.774
$Pd_{64}H_8$	0.125	0.510	-1.017	-0.188	0.952
$Pd_{64}H_{10}$	0.156	0.724	-0.938	-0.165	1.062
$Pd_{64}H_{13}$	0.203	0.788	-0.471	-0.122	1.354
$Pd_{64}H_{31}$	0.484	0.787	-0.443	0.269	1.597
$Pd_{64}H_{39}$	0.609	0.686	-0.177	-0.069	1.666
$Pd_{64}H_{53}$	0.828	1.092	-0.317	0.295	1.486
$Pd_{64}H_{62}$	0.969	1.121	0.259	0.670	1.477
$Pd_{64}H_{63}$	0.984	1.000	0.392	0.368	1.763
$Pd_{64}H_{64}$	1.000	0.795	0.219	0.453	1.776

Appendix C

Supplementary material for PdMH(111)

This appendix is the supplementary material of Chapter 5, which is based on the supporting information of Paper III.



Figure C.1: The flowchart of the active learning cluster expansion model equipped with Monte Carlo simulated annealing and the subsequent screening processes.



Figure C.2: The linear fitting plot between CE energy and DFT energy for iteration 1 of $Pd_xTi_{1-x}H_y$.



Figure C.3: The linear fitting plot between CE energy and DFT energy for (a) iteration 2, (b) iteration 3, (c) iteration 4 and (d) iteration 5 for $Pd_xTi_{1-x}H_y$.



Figure C.4: The linear fitting plot between CE energy and DFT energy for (a) iteration 6, (b) iteration 7, (c) iteration 8 and (d) iteration 9 for $Pd_xTi_{1-x}H_y$.



Figure C.5: The linear fitting plot between CE energy and DFT energy for (a) iteration 10 and (b) iteration 11 for $Pd_xTi_{1-x}H_y$.



Figure C.6: The DFT convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 1, (b) iteration 2, (c) iteration 3 and (d) iteration 4 for $Pd_xTi_{1-x}H_y$.



Figure C.7: The DFT convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 5, (b) iteration 6, (c) iteration 7 and (d) iteration 8 for $Pd_xTi_{1-x}H_y$.



Figure C.8: The DFT convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 9, (b) iteration 10 and (c) iteration 11 for $Pd_xTi_{1-x}H_y$.



Figure C.9: Volume of DFT convex hull as a function of the number of iterations for $Pd_xTi_{1-x}H_y$.



Figure C.10: The CE convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 1, (b) iteration 2, (c) iteration 3 and (d) iteration 4 for $Pd_xTi_{1-x}H_y$.



Figure C.11: The CE convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 5, (b) iteration 6, (c) iteration 7 and (d) iteration 8 for $Pd_xTi_{1-x}H_y$.



Figure C.12: The CE convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 9, (b) iteration 10 and (c) iteration 11 for $Pd_xTi_{1-x}H_y$.



Figure C.13: (a) The 3D CE convex hull of formation energy as a function of H concentration and Pd concentration in iteration 12 and the corresponding (b) top view and (c) main view and (d) side view for $Pd_xTi_{1-x}H_y$.



Figure C.14: Free energy diagram of CO_2RR of all candidates after CO* filter in the stage 4 in the screening workflow for $Pd_xTi_{1-x}H_y$.



Figure C.15: Free energy diagram of HER of all candidates after CO^{*} filter in the stage 4 in the screening workflow for $Pd_xTi_{1-x}H_y$.



Figure C.16: The scaling relations of different adsorbates for all candidates after CO* filter in stage 4 in the screening workflow for $Pd_xTi_{1-x}H_y$. The candidates marked by blue, red, yellow, and black are active for CO_2RR , which comes from the activity volcano plot.



Figure C.17: Distribution of atom Pd, Ti and H of all candidates within the cutoff sphere as a function of (a) the OH* and (b) the H* binding energies for $Pd_xTi_{1-x}H_y$.



Figure C.18: Selectivity plot toward CO and H_2 for $Pd_xTi_{1-x}H_y$. Active candidates for CO_2RR are marked.



Figure C.19: The top (a) and the side view (c) of PdH (111) with water layer. The top (b) and the side view (d) of PdH (111) with OH* and water layer.

In order to see if there is OH* poisoning, the stabilization energy is calculated for OH* on PdH(111) with one water layer. The stabilization energy of OH* adsorbate is calculated as follows:

$$\Delta_{\mathsf{stab}}^{\mathsf{W}} E(\mathsf{OH}*) = \Delta_{\mathsf{b}} E(\mathsf{OH}*) - \Delta_{\mathsf{b}}^{\mathsf{W}} E(\mathsf{OH}*)$$
(C.1)

where $\Delta_{b}^{W}E(OH*)$ is the adsorption energy when the water layer is presented, which is obtained by the following equation:

$$*|(N-1)\mathsf{H}_2\mathsf{O} + \mathsf{H}_2\mathsf{O} \rightleftharpoons \mathsf{OH}*|(N-1)\mathsf{H}_2\mathsf{O} + \frac{1}{2}\mathsf{H}_2$$
(C.2)

 $\Delta_{b}^{W}E(OH*)$ can be given by:

$$\Delta_{b}^{W} E(OH*) = E(OH*|(N-1)H_{2}O) + \frac{1}{2}E(H_{2}) - E(*|(N-1)H_{2}O) - E(H_{2}O)$$
 (C.3)

where $E(*|(N-1)H_2O)$ is calculated as:

$$E(*|(N-1)H_2O) = E(*|NH_2O) - E(H_2O_{WL})$$
(C.4)

where $E(H_2O_{WL})$ is given by:

$$E(H_2O_{WL}) = E(H_2O) + \frac{1}{N}\Delta E_{WL} = \frac{1}{N}\left(E(*|NH_2O) - E(*)\right)$$
(C.5)

The top view and the side view of PdH (111) with water layer and PdH (111) with OH* and water layer can be seen in Figure C.19. The OH* stabilization energy is calculated as 0.356 eV. The stabilization energy correction and zero point energy (0.355 eV) are considered for calculations of OH* binding energy in Figure C.16 and C.34.



Figure C.20: The linear fitting plot between CE energy and DFT energy of iteration 1 for $Pd_xNb_{1-x}H_y$.



Figure C.21: The linear fitting plot between CE energy and DFT energy for (a) iteration 2, (b) iteration 3, (c) iteration 4 and (d) iteration 5 for $Pd_xNb_{1-x}H_y$.



Figure C.22: The linear fitting plot between CE energy and DFT energy for (a) iteration 6, (b) iteration 7, (c) iteration 8 and (d) iteration 9 for $Pd_xNb_{1-x}H_y$.



Figure C.23: The linear fitting plot between CE energy and DFT energy for (a) iteration 10, (b) iteration 11 and (c) iteration 12 for $Pd_xNb_{1-x}H_y$.


Figure C.24: The DFT convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 1, (b) iteration 2, (c) iteration 3 and (d) iteration 4 for $Pd_xNb_{1-x}H_y$.



Figure C.25: The DFT convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 5, (b) iteration 6, (c) iteration 7 and (d) iteration 8 for $Pd_xNb_{1-x}H_y$.



Figure C.26: The DFT convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 9, (b) iteration 10 and (c) iteration 11 for $Pd_xNb_{1-x}H_y$.



Figure C.27: Volume of DFT convex hull as a function of the number of iterations for $Pd_xNb_{1-x}H_y$.



Figure C.28: The CE convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 1, (b) iteration 2, (c) iteration 3 and (d) iteration 4 for $Pd_xNb_{1-x}H_y$.



Figure C.29: The CE convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 5, (b) iteration 6, (c) iteration 7 and (d) iteration 8 for $Pd_xNb_{1-x}H_y$.



Figure C.30: The CE convex hull curves of formation energy as a function of H concentration and Pd concentration in iteration 9, (b) iteration 10, (c) iteration 11 and (d) iteration 12 for $Pd_xNb_{1-x}H_y$.



Figure C.31: (a) The 3D CE convex hull of formation energy as a function of H concentration and Pd concentration in iteration 12 and the corresponding (b) top view and (c) main view and (d) side view for $Pd_xNb_{1-x}H_y$.



Figure C.32: Free energy diagram of CO_2RR of all candidates after CO* filter in the stage 4 in the screening workflow for $Pd_xNb_{1-x}H_y$.



Figure C.33: Free energy diagram of HER of all candidates after CO^{*} filter in the stage 4 in the screening workflow for $Pd_xNb_{1-x}H_y$.



Figure C.34: The scaling relations of different adsorbates for all candidates after CO^{*} filter in the stage 4 in the screening workflow for $Pd_xNb_{1-x}H_y$. The candidates marked by blue and red are active for CO_2RR , which comes from the activity volcano plot.



Figure C.35: Distribution of atom Pd, Nb and H of all candidates within the cutoff sphere as a function of (a) the OH* and (b) the H* binding energies for $Pd_xNb_{1-x}H_y$.



Figure C.36: Selectivity plot toward CO and H_2 for $Pd_xNb_{1-x}H_y$. Active candidates for CO_2RR are marked.

Appendix D

Supplementary material for PdTiH(111) with adsorbates

This appendix is the supplementary material of Chapter 6, which is based on the supporting information of Paper IV.

Computational details

The free energy calculation for CO₂RR is given by:

$$CO_2(g) + * + H^+ + e^- \longleftrightarrow HOCO*$$
 (D.1)

$$HOCO* + H^{+} + e^{-} \longleftrightarrow CO* + H_2O(I)$$
 (D.2)

$$CO* \longleftrightarrow CO(g) + *$$
 (D.3)

When calculating the binding energies, HOCO^{*}, H^{*}, and OH^{*} replace the position of one CO^{*} on the surface, respectively. All sites are considered if there are multiple CO^{*} on the surface, and the most stable site for each adsorbate is used to calculate the binding energy and free energy. For candidates 119, 165, 479, 594, 695, 715, 774, 803, 849, and 900, an extra OH^{*} is also added on the hollow site of existing CO^{*} to calculate the free energy of CO₂RR, and only the most stable sites are used in this work.

After propagating backward a loss function to calculate the gradient of the parameters, the neural networks (NNs) parameters are optimized by the Adam optimizer according to the gradients. The loss function \mathcal{L} is a combination of energy and forces loss function as follows:

$$\mathcal{L} = \frac{1-\lambda}{N} \sum_{i=1}^{N} \left(\hat{E}_i - E_i \right)^2 + \frac{\lambda}{NM} \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{3} \left(\hat{F}_i^{jk} - F_i^{jk} \right)^2$$
(D.4)

where λ is an empirical parameter to control the balance between energy and forces loss function. *N* is the number of images and *M* is the number of atoms in a image. \hat{E}_i and E_i are the NNs and DFT energy of image *i*, respectively. \hat{F}_i^{jk} and F_i^{jk} are the NNs and DFT forces of atom *j* in the *k* direction. Root mean squared errors (RMSE) of energy and force between DFT and NNs predictions are calculated by:

$$E_{\text{RMSE}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(\hat{E}_{i} - E_{i}\right)^{2}}$$

$$F_{\text{RMSE}} = \sqrt{\frac{1}{3NM} \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{3} \left(\hat{F}_{i}^{jk} - F_{i}^{jk}\right)^{2}}$$
(D.5)



Figure D.1: The active learning workflow of machine learning with GA for the global optimization of $Pd_xTi_{1-x}H_y$ with CO*, H*, and OH* adsorbates.

GA opterators

The GA operators in this work can be categorized into three types: slab operators, adsorbate operators, and crossover operator as shown in Figure D.2. Slab operators include *InternalHydrogenAddition* operator that randomly removes one internal hydrogen in the slab, *InternalHydrogenRemoval* operator that randomly adds one hydrogen into a vacancy site in the slab, *InternalHydrogenRemoval* operator that randomly adds one hydrogen into a vacancy site in the slab, *InternalHydrogenMoveToUnoccupied* operator that randomly moves one internal hydrogen to another vacancy site in the slab, *InternalMetalPermutation* operator that randomly swaps the positions of Ti and Pd in the slab and *InternalMetalComposition* operator that randomly mutates Ti into Pd or mutates Pd into Ti in the slab. Adsorbate operators include *AdsorbateAddition* operator that adds one random adsorbate on a random available adsorption site, *AdsorbateRemoval* operator that removes one random adsorbate from a random occupied site, *AdsorbateSwapOccupied* operator that randomly swaps positions of two types of adsorbates, *AdsorbateMoveToUnoccupied* operator that moves one random adsorbate to a random available site. The crossover operator includes *AdsorbateCutSpliceCrossover* operator that randomly combines the slab from structure 1 and adsorbates from structure 2.



Figure D.2: The GA operators for operating adsorbates, internal hydrogens, and metal atoms of the slab.



Figure D.3: The energy RMSE (meV/atom) and forces RMSE (meV/Å) in different architectures for the first iteration as a function of the number of training steps.



Figure D.4: The learning curves of the average and variance of the energy RMSE (meV/atom) and forces RMSE (meV/Å) for the first iteration as a function of the number of training steps.



Figure D.5: The energy RMSE (meV/atom) and forces RMSE (meV/Å) in different architectures for the last iteration as a function of the number of training steps.



Figure D.6: The learning curves of the average and variance of the energy RMSE (meV/atom) and forces RMSE (meV/Å) for the last iteration as a function of the number of training steps.



Figure D.7: The number of new candidates as a function of the number of active learning iterations.



Figure D.8: (a) The surface free energy as a function of applied potential at $\Delta \mu_{Pd}$ =-2.249 eV, $\Delta \mu_{Ti}$ =-7.285 eV, temperature=298.15 K, and CO partial pressure=5560 Pa. (b) The surface free energy as a function of temperature at fixed $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$, potential=-0.5 V, and CO partial pressure=5560 Pa. The corresponding most stable structures are shown at the bottom.



Figure D.9: The surface free energy as a function of applied potential with 25 different chemical potential differences of Pd and Ti at the room temperature=298.15 K and CO partial pressure=5560 Pa.



Figure D.10: The surface free energy as a function of partial pressure of CO with 25 different chemical potential differences of Pd and Ti at the room temperature=298.15 K and applied potential=-0.5 V.



Figure D.11: The surface free energy as a function of temperature with 25 different chemical potential differences of Pd and Ti at applied potential=-0.5 V and CO partial pressure=5560 Pa. The candidates marked by red dashed squares are active for CO_2RR .



Figure D.12: The candidate structures at the different reaction conditions between the chemical potential differences of Pd and Ti, applied potentials, temperature, and partial pressure of CO.



Figure D.13: The top views of all candidate structures at the different reaction conditions: the chemical potential differences of Pd and Ti, applied potentials, temperature, and partial pressure of CO. The top views of active structures for CO_2RR are embedded in the figure.



Figure D.14: The CO₂RR free energy diagram of all candidates at room temperature=298.15 K and CO partial pressure=5560 Pa.



Figure D.15: The HER free energy diagram of all candidates at room temperature=298.15 K and CO partial pressure=5560 Pa.

Table D.1: The free energies and binding energies for candidates at the most stabl
site. The colonms are the candidate structures with CO*, the indices in the database, th
binding energy of HOCO* and CO*, the free energy difference of HOCO*, CO* and H
and describer $\Delta G_{HOCO*} - \Delta G_{H*}$.

Structures	Index	E_{HOCO*}	$E_{\rm CO*}$	ΔG_{HOCO}	$_* \Delta G_{\rm CO*}$	G_{H*}	$\Delta G_{\text{HOCO}*}$ - $\Delta G_{\text{H}*}$
Pure	0	0.192	0.059	0.606	-0.028	0.430	0.175
Pd ₁₄ Ti ₂ H ₄ +3C	O 101	0.944	-0.182	1.358	-0.269	0.148	1.211
Pd ₁₄ Ti ₂ H ₆ +2C	O 119	0.445	-0.690	0.859	-0.777	0.717	0.142
Pd ₁₄ Ti ₂ H ₅ +2C	O 165	0.381	-0.758	0.795	-0.845	0.606	0.188
Pd ₁₄ Ti ₂ H ₇ +1C	O 479	0.542	-0.149	0.956	-0.236	0.188	0.769
Pd ₁₄ Ti ₂ H ₅ +3C	O 532	0.731	-0.575	1.145	-0.662	0.286	0.859
Pd ₁₂ Ti ₄ H ₄ +3C	O 539	0.614	-0.350	1.028	-0.437	0.033	0.995
Pd ₁₄ Ti ₂ H ₄ +2C	O 594	0.220	-0.381	0.634	-0.468	0.017	0.617
Pd ₉ Ti ₇ H ₁₆ +1C	O 695	-1.381	-1.503	-0.967	-1.590	-0.814	-0.154
Pd ₉ Ti ₇ H ₁₇ +1C	0 175	-0.065	-0.157	0.349	-0.244	0.368	-0.019
Pd ₁₄ Ti ₂ H ₆ +3C	O 764	0.735	-0.642	1.149	-0.729	0.733	0.416
Pd ₁₄ Ti ₂ H ₁₇ +10	CO 774	0.181	-0.044	0.595	-0.131	0.702	-0.107
Pd ₅ Ti ₁₁ H ₁₈ +1C	CO 803	-1.281	-1.429	-0.867	-1.516	-0.823	-0.043
Pd ₁₄ Ti ₂ H ₁₂ +30	CO 825	0.837	-0.151	1.251	-0.238	0.325	0.926
Pd ₅ Ti ₁₁ H ₂₀ +20	CO 849	0.083	0.236	0.497	0.149	0.768	-0.271
Pd ₅ Ti ₁₁ H ₂₀ +1C	C 900	0.157	0.164	0.571	0.077	0.905	-0.334

Appendix E

Data and code availability

This appendix includes data and code availability in this thesis, which is openly available.

Data availability

- The data that support the findings in Chapter 3 are openly available in DTU Data Repository at https://doi.org/10.11583/DTU.17263532.
- 2. The data that support the findings in Chapter 4 are openly available in DTU Data Repository at https://doi.org/10.11583/DTU.21325017.
- The data that support the findings in Chapter 5 are openly available in DTU Data Repository at https://doi.org/10.11583/DTU.23798751.
- 4. The data that support the findings in Chapter 6 are openly available in Zenodo Repository at https://doi.org/10.5281/zenodo.8191834.

Code availability

All codes for plot, pre-processing, post-processing, GA operators, and workflow in this thesis are openly available in the Gitlab repository named *Pcat*: https://gitlab.com/ changzhiai/pcat.

Included publications

Paper I

Metal-doped PdH(111) catalysts for CO₂ reduction Changzhi Ai, Tejs Vegge and Heine Anton Hansen *ChemSusChem*, **2022**, 15, e202200008



Metal-Doped PdH(111) Catalysts for CO₂ Reduction

Changzhi Ai,^[a] Tejs Vegge,^[a] and Heine Anton Hansen^{*[a]}

PdH-based catalysts hold promise for both CO₂ reduction to CO and the hydrogen evolution reaction. Density functional theory is used to systematically screen for stability, activity, and selectivity of transition metal dopants in PdH. The transition metal elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re are doped into PdH(111) surface with six different doping configurations: single, dimer, triangle, parallelogram, island, and overlayer. We find that

Introduction

Emission of the greenhouse gas carbon dioxide (CO₂) has increased rapidly with the development of industrialization in the past decades. A long-term goal of the Paris Agreement was proposed to achieve a balance between CO₂ emissions from the combustion of traditional fossil fuels and removals of the greenhouse gas, and it is urgent to limit global warming to 1.5 °C by the year 2100.^[1,2] In order to overcome this challenge, the three strategies of decarbonization, carbon sequestration, and carbon recycling will play crucial roles in mitigating net CO2 emissions.^[2] The CO₂ utilization technology of the electrochemical CO₂ reduction reaction (CO₂RR) is considered as a promising strategy to convert CO₂ into valuable chemicals as it is not only beneficial to carbon recycling but also conducive to increasing chemical energy storage.^[3] So far, significant efforts have been made to reduce CO_2 to C_1-C_3 products including formic acid (HCOOH),^[4] carbon monoxide (CO),^[5] methane ethylene (C_2H_4) ,^[7] methylglyoxal (CH₄),^[6] $(C_{3}H_{4}O_{2})$,^[8] acetaldehyde,^[9] and alcohols.^[10] Among them, CO is one of the most potential products due to the transfer of only two electrons, which leads to higher energy conversion efficiency compared to other products with more electron transfer.[11] More importantly, the hydrogen evolution reaction (HER) usually occurs together with the electrochemical reduction of CO_2 , CO, and H_2 , which are the main components of syngas, can be effectively synthesized into liquid hydrocarbons via the Fischer-Tropsch processes.^[11,12] Therefore, CO is an important

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several dopants, such as Ti and Nb, have excellent predicted catalytic activity and CO_2 selectivity compared to the pure PdH hydride. In addition, they display good stability due to their negative doping formation energy. The improved performance can be assigned to reaction intermediates forming two bonds consisting of one C–Metal and one O–Metal bond on the PdH surface, which break the scaling relations of intermediates, and thus have stronger HOCO* binding facilitating CO_2 activation.

feedstock in industry and it could be crucial to explore efficient catalysts for conversion from CO_2 to CO.

Many previous studies have been done to study metal catalysts for the CO₂RR. Gold (Au),^[13,14] silver (Ag),^[15,16] and copper (Cu)^[17] have been the most widely studied for the electrochemical CO₂RR and show good performance for CO production. Au nanoparticles formed from thick Au oxide films were reported to have high selectivity for CO₂ reduction to CO at 140 mV overpotential and they kept their activity for no more than 8 h.^[18] Kim et al. reported Ag nanoparticles supported on carbon has good Faradaic efficiency and low overpotential.^[16] Raciti et al. reported that Cu nanowires produced by electrochemical reduction are highly active and selective for the CO₂RR to CO at an overpotential of 0.3 V.^[17] However, Au, Ag and Cu cannot tune the desired CO/H₂ ratio with high CO₂RR catalytic activity.^[11,19] In addition, metal-nitrogen-carbon (M-N-C) electrocatalysts with high faradaic efficiencies for CO generation are also popular in the field of CO₂RR. Among them, Fe-N-C electrocatalyst shows high selectivity and CO formation activity at low overpotentials (0.3 to 0.5 V). Ni-N-C electrocatalyst exhibits good selectivity and activity at higher overpotentials because it is more favorable toward the HER. Co-N-C electrocatalyst has a lower selectivity for CO throughout the entire potential range.^[20] Palladium (Pd) was reported to be a potential candidate catalyst for CO2RR to CO by Gao et al. in 2015.^[21] Moreover, Chen et. al. thought the Pd catalyst was more suitable to produce syngas (CO₂ and H₂) compared to other metals, and that the reason why Pd showed good activity and selectivity in the process of electrochemical CO2RR was the Pd metal catalyst was transformed into palladium hydride (PdH).^[11] The formation of PdH would significantly improve Faradaic efficiencies of production of CO and H₂. Furthermore, the PdH(111) surface experimentally exhibited higher current density and Faradaic efficiency compared with other crystal surfaces.^[11] Subsequently, in order to further improve the performance of PdH, several approaches, such as applying transition metal nitrides as promising supports and using bimetallic catalysts has been explored in recent years.^[22]

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In this work, density functional theory (DFT) simulations are performed to study transition metal-doped PdH catalysts. Due to the difficult formation of forming HOCO* on the pure PdH(111), we explore the possibility of lowering the HOCO* formation energy through doping transition metal elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re into the PdH(111) surface in different configurations to systematically study their properties. First, the doping formation energies are calculated to illustrate the stability of different doped surfaces. Then, the scaling relations between reaction intermediates, free energy diagrams, and kinetic model were carried out to explore the CO₂RR catalytic activities after doping. Finally, selectivity toward CO₂RR and HER was also studied to describe the competition between CO₂ and H₂.

Computational Details

All calculations in this work are carried out with spin-polarized density functional theory simulations using the Vienna ab initio simulation package (VASP, version 5.4)[23-26] and the Atomic Simulation Environment (ASE, version 3.2).[27,28] The effects of exchange and correlation are approximated by using the Bayesian error estimation functional with van der Waals correlation (BEFF-vdW).^[29] The ionic cores are treated using the projector augmented wave (PAW) method^[30] and the wave functions are expanded in a plane waves basis set. A cutoff energy is set as 400 eV and a Gaussian smearing of 0.05 eV is used for the electronic states. In order to remove the electrostatic dipole-dipole interaction between periodically repeated surface slabs, the dipole correction is used in the direction perpendicular to the slab in all calculations. All calculation processes, data col- lection and analysis are performed in a custom build workflow and a computational database is freely available in the DTU Data Repository.[31]

Bulk PdH is in the rock salt (NaCl) crystal structure and the (111) surface, which is energetically the most stable, is considered in this work. A 3×3 supercell model of the PdH(111) with six bilayers is built and each bilayer consists of one Pd atomic layer and one H atomic layer, where the bottom three bilayers are fixed in their bulk positions during optimization. A 3×3×1 Monkhorst-pack grid^[32] of *k*-points is applied to sample the first Brillouin zone of the PdH(111) slab. The convergence threshold of Hellman-Feynman force is set to 0.01 eV $Å^{-1}$ and the energy convergence criteria on each atom was set to 10^{-6} eV atom⁻¹. A vacuum layer of about 15 Å is adopted in z direction to separate periodic slab images and avoid interactions between them. In order to further improve accuracy, a +0.15 eV correction per C=O is applied for systematic overbinding corrections with the BEEF-vdW functional, +0.15 eV for HOCO* and +0.1 eV for H₂.^[33,34] For solvent stabilization correction at the watercatalyst interface, -0.25 eV for HOCO^{*} and -0.1 eV for CO^{*} are used in all calculations, respectively.^[35] The effects of the electric field at the electrochemical interface of catalysis on the free energy of the adsorbates are ignored in this treatment.

The formation energies of PdH doped with transition metals are calculated according to the following definition:

$$E_{\rm form} = E_{\rm nM-doped} - E_{\rm pure} - n\mu_{\rm M} + n\mu_{\rm Pd} \tag{1}$$

where $E_{nM-doped}$ denotes the energy of doping the PdH(111) slab with n metal atoms, while pure is the energy of the pure undoped

PdH(111) slab. μ_M and μ_{Pd} represent the chemical potential of doped metal atom and Pd, respectively.

The binding energies $E_{\rm b}$ of different intermediates in this work are given by the following equation:

$$E_{\rm b} = E_{\rm *+intermediate} - E_{\rm *} - E_{\rm intermediate}$$
(2)

where $E_{*+\text{intermediate}}$ is the total DFT energy of slab and intermediate. E_* and $E_{\text{intermediate}}$ are the energies of clean slab and intermediate with respect to gas phase molecules, respectively.

The calculation of Gibbs free energy (G) is done using Equation (3):

$$G = E_{\rm DFT} + E_{\rm ZPE} + \int C_{\rm p} dT - TS$$
(3)

where E_{DFT} represents the DFT energy with overbinding correction and solvent stabilization correction. E_{ZPE} represents the zero-point energy of the species. C_p and S are the heat capacity and entropy, respectively, and T is temperature. E_{ZPE} , C_p and the entropy of slabs are obtained from statistical mechanics using the harmonic approximation throughout calculations of vibrational frequencies. We assume that variations in these terms are small compared with that of binding energies and thus the energies of these terms for pure PdH(111) are applied to other surfaces as listed in Table S9 in the Supporting Information. Gas-phase species are obtained by ideal gas methods and the corresponding free energies listed in Table S10.

The reaction mechanism for CO_2 reduction to CO in this work is considered as follows:^{[19]}

$$CO_2(g) + * + H^+ + e^- \rightleftharpoons HOCO^*$$
 (4)

$$HOCO^* + H^+ + e^- \rightleftharpoons CO^* + H_2O(I)$$
(5)

$$CO^* \rightleftharpoons CO(g) + *$$
 (6)

Reaction free energies are calculated by the computational hydrogen electrode (CHE) model,^[36] which provides an elegant method to avoid calculations of solvated protons. In this model, 0 V is defined based on the reversible hydrogen electrode (RHE). The reaction is defined as in equilibrium at 0 V, at standard pressure:

$$\mathsf{H}^+ + \mathsf{e}^- \to 1/2\mathsf{H}_2 \tag{7}$$

Therefore, the sum of the chemical potential of H^+ and e^- is equal to half of that of gaseous hydrogen. The reaction free energy dependence on the applied potentials are as follows:

$$\Delta G_1 = G_{\text{HOCO}*} - G_* - \mu_{\text{CO}_2(g)} - 1/2\mu_{\text{H}_2^{\circ}} + eU$$
(8)

$$\Delta G_2 = G_{CO*} + {}_{H_2O(I)} - G_{HOCO*} - 1/2\mu_{H_2^{\circ}} + eU$$
(9)

$$\Delta G_3 = G_* + \mu_{\rm CO(g)} - G_{\rm CO*} \tag{10}$$

where the applied potentials are relative to the RHE. ΔG_1 , ΔG_2 and ΔG_3 are the free energy difference of the three step reactions for CO₂RR. G_{HOCO^*} , G_{CO^*} and G_* are the free energies of species HOCO*, CO* and the surface, respectively. $\mu_{CO_2(g)}$, $\mu_{CO(g)}$, $\mu_{H_2O(1)}$ and $\mu_{H_2^*}$ represent the chemical potentials of gaseous CO₂, gaseous CO, liquid H₂O and gaseous H₂, respectively.

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Moreover, experimental vapor pressures are utilized for them in this work. The partial pressures of H₂O and CO are 3534 Pa and 5562 Pa, respectively.^[35] The partial pressure of CO₂ and H₂ are both under standard pressure 101325 Pa.^[35,37] We ignore electric field effects on adsorption energies in this work.

The reaction mechanism for the HER can be described by the following $\mathsf{steps}^{\scriptscriptstyle[38]}$

$$H^{+} + e^{-} + * \rightleftharpoons H^{*} \text{ (Volmer step)} \tag{11}$$

$$H^* + H^+ + e^- \rightleftharpoons H_2(g) + * (Heyrovsky step)$$
(12)

A kinetic model is utilized to study the activity for CO_2 reduction to CO. The net reaction rates of CO_2RR are described as^[39]

$$r_1 = k_1 \theta * p_{CO_2} - \frac{k_1}{K_1} \theta_{HOCO} *$$
 (13)

$$r_2 = k_2 \theta_{\text{HOCO}} * - \frac{k_2}{K_2} \theta_{\text{CO}} *$$
(14)

$$r_{3} = k_{3}\theta_{CO}* - \frac{k_{3}}{K_{3}}\theta*p_{CO}$$
(15)

where k_1 , k_2 , and k_3 represent forward rate constants for the three steps of CO₂RR. K_1 , K_2 , and K_3 are the corresponding equilibrium constants and backward rate constants can be calculated by forward rate constant over the corresponding equilibrium constants. For example, backward rate constant is equal to k_1/K_1 . p and θ represent the partial pressure and surface coverage, respectively. For the electrochemical step 1 and step 2 with coupled electron proton transfer, the forward rate constants are denoted as

$$k_{i=1,2} = A' exp\left(-\frac{\beta e(U-U_i^0)}{k_B T}\right)$$
(16)

where the pre-exponential factor A' is a material independent constant. A value of $A' = 3.6 \times 10^4 \text{ s}^{-1}$ is used as in previous work.^[39] k_B is the Boltzmann constant and β is a symmetry factor which is set as 0.5 here. U_i^0 is the reversible potential of reaction step *i*

$$U_i^0 = -\frac{\Delta G_i}{e} \tag{17}$$

where ΔG_i is the reaction free energy difference at zero voltage (vs. RHE) calculated by DFT using the CHE model. The corresponding equilibrium constants are given by

$$K_{i} = \exp\left(-\frac{e(U - U_{i}^{0})}{k_{B}T}\right)e$$
(18)

For the chemical step 3 with no electron or proton transfer, the rate constant is approximated as

$$k_{3} = \nu \exp\left(-\frac{\mathsf{E}_{\rm CO}*}{k_{\rm B}T}\right) \tag{19}$$

where E_{CO^*} represents the binding energy of intermediate CO*. A typical pre-exponential factor ν is 10¹³ s⁻¹.

Results and Discussion

Before investigating transition metal element dopants, the pure PdH(111) surface is first studied by DFT with the BEEF-vdW functional. The crystal constants of optimized bulk PdH are a =b=c=4.138 Å, which is well consistent with the experimental result of 4.090 Å.^[40] Figure S1 shows the top and side view of pure PdH(111) structures. The PdH(111) slab is built by optimized bulk PdH and its lattice constants are a=b=8.778 Å and c = 27.140 Å. The top and side views of pure PdH(111) with adsorbates HOCO*, CO*, H* and OH* are shown in Figure S2. We notice that HOCO*, CO* and OH* tend to adsorb on the top site of PdH, while H* prefers to adsorb on the hollow site according to their binding energies in Table S1. Figure S3 demonstrates the CO₂RR free energy diagram of PdH(111) at 0 V (vs. RHE), at room temperature. The free energies of the HOCO*, CO* and CO intermediates in this diagram are 0.820, 0.216 and 0.123 eV, respectively. Because the HOCO* formation step has the highest free energy, this reaction step is the potential-limiting step on pure PdH(111). This is consistent with the DFT results of 0.67 eV for the HOCO* step found by by Sheng et al. using the PW91 functional.^[11] At the same time, the HER free energy diagram of PdH(111) at 0 V (vs. RHE) is also shown in Figure S4 and the free energy of the Volmer step is 0.501 eV, which is lower than 0.820 eV for CO₂RR. Therefore, the CO₂RR steps are thermodynamically more difficult than the HER steps for pure PdH. Experiments by Sheng et al. found that the CO/H₂ ratio is always lower than 1 at different potentials and thus show CO has a lower proportion, which has good agreement with computational results.^[11]

In order to improve the CO2RR performance of PdH, the impact of doping transition metal elements into the PdH(111) surface is explored below. As displayed in Figure 1, we try to dope different elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W and Re into the PdH(111) surface in different doping configurations which we demote as: single, dimer, triangle, parallelogram, island and overlayer, respectively. Their formation energies per dopant atom in the different doping configurations is first calculated and shown in Table S2 and in Figure 2. We find, in most cases, that the overlayer doping is the most unstable, while single doping is the most stable when an element is doped in different

Figure 1. Top views of doping PdH(111) surface in different doping configurations: (a) single, (b) dimer, (c) triangle, (d) parallelogram, (e) island and (f) overlayer. The blue spheres are Pd atoms, the small white spheres represent H atoms and the grey spheres represent dopant atoms



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Figure 2. Formation energies of doping PdH(111) with different elements in different doping configurations.

configurations. Moreover, the doping formation energies of Sc, Ti, Zn, Y, Zr, Nb, Hf and Ta in all doping configurations are negative except overlayer doping of Zn. This demonstrates that Sc, Ti, Zn, Y, Zr, Nb, Hf and Ta are easier to be doped into PdH compared to other elements. We note that for the largest dopants: Sc, Zn, Y, Zr, Ag, Cd, and Hf significant destabilization of the overlayer structure compared to single dopant by more than 1 eV can be observed. This is likely caused by the increased strain with the full overlayer.

The CO₂RR free energy diagrams of doping PdH(111) with different elements in different configurations are calculated to explore the possibility of lowering the potential-limiting HOCO* step as displayed in Figure 3. The free energies are calculated using the most stable adsorption sites according to the binding energies in Tables S3-S8 and the corresponding specific free energies are listed in Tables S11–S16 in the Supporting Information. For single atom doping of PdH(111), Fe, Zr, Nb and Ru doping effectively decrease the free energy of the HOCO* step by -0.003, -0.06, -0.07, and -0.15 eV, respectively, compared to the pure PdH. However, the doping formation energies of Fe and Ru are positive and thus unstable. Therefore, the candidates for lowering the HOCO* step are Nb and Zr doped PdH for doping with a single atom. For dimer doping of PdH(111), the free energies of HOCO* step of Sc, Ti, V, Cr, Mn, Fe, Y, Zr, Nb, Mo, Ru, Hf, Ta, W and Re are downhill relative to undoped PdH. Their free energy differences with respect to PdH are -0.39, -0.04, -0.01, -0.63, -0.30, -0.143, -0.88, -0.63, -0.04, -0.16, -0.19, -0.18, -0.10, -0.03, and -0.01 eV, respectively. Among them, Sc, Ti, Zr, Nb, Hf and Ta are stable according to their doping formation energies, and thus they are possible candidates for CO2RR for this case. Doping with Y dimers is neglected due to structural distortion upon optimization. Still, for the triangle doping, Sc, Ti, V, Cr, Mn, Fe, Zr, Nb, Mo, Ru, Hf, Ta, W and Re doping leads to a free energy reduction of the potential-limiting step, and the free energy differences compared to pure PdH(111) are - 0.30, -0.17, -0.34, -0.57, -0.32, -0.30, -0.50, -0.24, -0.23, -0.21, -0.42, -0.41, -0.06 and -0.27 eV, respectively (Y doping is removed due to large structure distortion). The ones that could be stable are still



Figure 3. Free energy diagrams of doped PdH(111) with doping elements in different configurations.

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Sc-, Ti-, Zr-, Nb-, Hf- and Ta-doped PdH. Similarly, there are more doping elements that can lower the potential-limiting step: Sc, Ti, V, Cr, Mn, Fe, Co, Zr, Nb, Mo, Ru, Hf, Ta, W and Re in the parallelogram configuration. Their free energy differences with respect to PdH are -1.02, -0.31, -0.29, -0.41, -0.32, -0.46, -0.39, -0.42, -0.28, -0.49, -0.37, -0.57, -0.25, -0.66, and -0.66 eV, respectively. In the parallelogram configuration Zn, Y and Cd doping are discarded due to large structural distortion. Again, the most promising stable candidates are Sc, Ti, Zr, Nb, Hf and Ta dopants. It is worth to notice that Sc doping in this case greatly decreases the HOCO* step and the line connecting HOCO* to CO* in the free energy diagram intersects with lines from other dopants. This illustrates that Sc doping clearly breaks the scaling relation between HOCO* and CO*. For the case of island doping, the free energies of Sc, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, Ru, Rh, Ta, W and Re are downhill compared with that of the undoped PdH(111), and the free energy differences are -1.002, -0.423, -0.325, -0.293, -0.747, -0.565, -0.160, -0.592, -0.864, -0.333, -0.032, -0.817, -0.466 and -0.424 eV, respectively. Y, Zn, Zr, Cd and Hf doping are discarded due to large structure distortion in the island configuration. However, the stable dopants are Sc, Ti, Nb and Ta in the light of their negative formation energies. In the last configuration of overlayer doping, several structures are not stable after binding the reaction intermediates including Sc, Y, Zn, Zr, Cd and Hf overlayer surfaces. This may again be related to the large size of these dopants and the corresponding lattice mismatch that can be seen in Table S17, and thus they are removed in this case. Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, Ta, W and Re doping can effectively reduce the free energy of HOCO* step and the free energy differences are -0.232, -0.222, -0.423, -0.884, -1.971, -1.234, -0.844, -0.196, -0.329, -0.554, -0.093, -0.577, -0.611 and -0.939 eV, respectively, but only Ti, Nb, Ta and V doping are the stable ones. The candidates of different configurations for CO2RR are finally summarized in Table 1. Overall, we find that Ti, Sc, Nb, Zr, Hf and Ta doping of PdH(111) are promising dopant candidates in most configurations.

The scaling relations of intermediates on doped PdH(111) with different elements in different doping configurations are further studied to understand catalytic performance. Taking the top site adsorption as an example, the structures of the surface with HOCO*, CO*, H* and OH* are displayed in Figure 4a–d. The binding energies in the most stable sites are, however, applied in the following analysis with the corresponding data listed in Tables S3–S8. Figure 5 shows the scaling relation between HOCO* and CO* in the six dopant configurations. We use R², a

Table 1. Possible candidates for different PdH(111) doping configurations according to free energy diagrams.				
Doping configurations	Possible candidates			
single dimer triangle parallelogram island overlayer	Nb, Zr Sc, Ti, Nb, Zr, Hf, Ta Sc, Ti, Nb, Zr, Hf, Ta Sc, Ti, Nb, Zr, Hf, Ta Sc, Ti, Nb, Ta Ti, Nb, Ta, V			



Figure 4. Structures of intermediates (a) HOCO* (one bond), (b) CO*, (c) H* and (d) OH* on the top sites of a doped PdH(111) surface. (e) HOCO* forms two bonds with PdH(111). The blue spheres are Pd atoms, the small white spheres represent H atoms, the big grey spheres represent dopant atoms, the red spheres are O atoms, and the small grey spheres are C atoms. (f) Charge density difference figure for HOCO* with two bonds. The blue region represents charge depletion while the yellow region means charge accumulation.

statistical measure that represents the proportion of the variance between two variables, to describe how well a linear scaling relation is fitted, and a good fit has R² close to 1. In Figure 5a-f, Fe, Co, Ni, Cu, Ru, Rh and Ag doping are marked in red dots and the corresponding fitted lines are also shown in red. They display clear linear scaling relations in all configurations with R² values 0.84, 0.88, 0.89, 0.96, 0.97 and 0.86, respectively. This is because they all form only a C-metal bond on the top of one dopant in all doping configurations according to optimized HOCO* structures as shown in Figure 4a. The fitted lines of the six doping cases using all doping elements are displayed by the blue lines. They show much lower R² values of 0.42, 0.36, 0.51, 0.48, 0.41, and 0.80, respectively. This is because the surfaces doped with Sc, Ti, Nb, Zr, Zn, V, Mn, Mo, Cr, Hf, Cd, W, Ta, and Re mostly tend to form two bonds to the surface consisting of a C-Metal (C-M) and an O-Metal (O-M) on two different metal atoms for HOCO* on the surface as displayed in Figure 4e. A small part of them, however, forms two bonds to the same metal atom as shown in Figure S11. All structures are summarized in the database in the supporting information and the corresponding formation of two bonds can be found in the database. The C-M and O-M bond lengths of HOCO* on the doped surfaces in different configurations are listed in Tables S18 and S19, and O-M bond lengths are summarized in figure S15. We have chosen a surface-oxygen distance of 2.7 Å to determine whether a bond is formed between the O in HOCO and the surface because few surfaces have O-M bond lengths between 2.4 and 2.8 Å. A more detailed discussion is given in the supporting information. For example, Figure 4f shows the charge density difference for HOCO* on the Ti parallelogram doped surface, which clearly demonstrates that two bonds form to the surface. The bond length of C-Ti is 2.259 Å and the bond length of O-Ti is 2.032 Å. We therefore conclude the formation of two bonds breaks the previous single C-Metal scaling relations and thus reduces the R². Furthermore, the dopant structures resulting in the formation of two bonds show stronger HOCO* binding with the surface compared to their CO* binding energy, which may be the reason the free energies of the HOCO* step with the two bonds are relatively 2, 10, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cssc.202200008 by Royal Danish Library, Wiley Online Library on [27/08/2023]. See the Terms and Conditions (https://oinleibrary.wiley.com/terms -and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

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Figure 5. Scaling relation of intermediates on doped PdH(111) with different elements between HOCO* and CO* in different dopant configurations. The red line is fitted to Fe, Co, Ni, Cu, Ru, Rh and Ag doped PdH(111) where HOCO* forms one bond to the surface. The blue line is fitted to all doped PdH(111).

low in Figure 3. Figure S12 shows the scaling relations of adsorbates HOCO* vs. OH* in different doping configurations. Similarly, for the surfaces doped with Fe, Co, Ni, Cu, Ru, Rh, and Ag, their HOCO* binding energies can scale linearly with the OH* energies, and the R² values are 0.81, 0.82, 0.81, 0.63, 0.77 and 0.83 in different doping configurations, respectively. However, their scaling relations of total metal element doped surfaces have worse R² values of 0.03, 0.46, 0.62, 0.60, 0.80, 0.50, respectively. This could also be attributed to the formation of the two bonds of HOCO* on the surfaces as we described before. The scaling relations between CO* and H* intermediates on doped PdH(111) surfaces in different doping configurations are also shown in Figure S13. The CO* and H* intermediates display good scaling relations with R² values of 0.68, 0.80, 0.74, 0.66, 0.78 and 0.49. This can be attributed to the fact that only one atom in CO* and H* interacts with the surfaces.

In order to further study the kinetic activity of doped PdH(111), a kinetic model is utilized. In Figure 6, the activity volcano of doped PdH(111) for CO₂RR in different doping configurations are given. It is seen that the kinetic activities depend on the binding energies of both HOCO* and CO*. The partial pressure of CO₂ and CO are 101325 Pa and 5562 Pa, respectively, and the overpotential (the difference between the applied potential and the equilibrium potential calculated with the BEEF–vdW functional) is set to 0.3 V. It can be noted that Ti, Sc, Nb and Zr demonstrate excellent catalytic activities in different doping configurations. Among them, Sc doping with dimer, triangle and parallelogram configuration are close to the center of the volcano and thus show good activities. However,

according to binding energy in Figure S12, OH* binding of Sc, Zr and Hf are so strong on the PdH surface, which will cause OH* poisoning. Besides, we notice that Ti doping with parallelogram and overlayer configuration and Nb doping with overlayer configuration are also closer to the center of the volcano compared to PdH. Furthermore, the free energies of OH* are smaller than 0.3 eV and thus will not be poisoned at 0.3 V overpotential. Therefore, they are expected to have better kinetic activities than pure surface. However, we can find that CO* binding of Ti and Nb doping are stronger than pure PdH, which limits their kinetic activities at room temperature due to slow CO desorption. In order to further improve CO* activities of noneletrochemical step, one could increase the temperature. As shown in Figure S14, we take Ti doping in the parallelogram configuration as an example. With the temperature increasing, the partial current density of CO* would increase and $7.72 \mbox{ mA cm}^{-2}$ can be achieved at 350 K. In addition, we calculate the surface stability and the corresponding Pourbaix diagram^[41,42] of HOCO*, CO*, H*, OH*, metal ion dissolution, for PdH(111) surfaces including Ti doping in parallelogram and overlayer configurations, Nb doping with overlayer configurations, and pure PdH(111) as displayed in Figures S20-S25. The detailed methods are given in the supporting information. It is noticed that ion dissolution is unfavorable when the potential is less than or equal to -0.304, -0.290, -0.224 and 1.017 V at pH=0 for these four configurations, and the dissolution potential will be more negative as pH increases. This means that these three doped surfaces are stable under negative bias typically required for CO₂ reduction, but that stability might be an issue above the working potential.

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Figure 6. Activity volcano plots of doped PdH(111) with different elements for CO₂RR at 0.3 V overpotential in different dopant configurations.

Figure 7 illustrates the selectivity for CO2RR and HER of doped PdH(111) in different doping configurations with the corresponding data listed in Tables S3–S8. We apply $\Delta G_{\text{HOCO}*}$ – $\Delta G_{\text{H*}}$ as a descriptor to demonstrate the trend of producing CO₂ and H₂. When the value of $\Delta G_{\text{HOCO}*}$ – $\Delta G_{\text{H*}}$ is more negative, it indicates that there would be higher selectivity toward CO₂RR. Otherwise, the more positive value of $\Delta G_{\text{HOCO}*}$ – $\Delta G_{\text{H*}}$ represents the higher selectivity toward HER. We find that a majority of elements doped PdH in different doping configuration will generate more H₂ than CO according to Figure 7. However, some overlayer doping such as, Sc, Mn, Fe, Co, Ni and Zr prefer to generate more CO. It is worth noting that the values for Ti and Nb doping are more negative than for pure PdH(111) in



Figure 7. Selectivity plot for CO_2RR and HER of doped PdH(111) with elements in different dopant configurations.

most doping configurations and thus tend to produce more CO.

Conclusions

Density functional theory calculations have been applied to study the CO₂RR and the competing HER of PdH(111). 22 transition metal elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W and Re are doped into the PdH(111) surface in different doping configurations to explore their catalytic performance. Doping formation energies show Sc, Ti, Zn, Y, Zr, Nb, Hf and Ta dopants are easier to dope into the surface. Free energy diagrams identify Ti, Sc, Nb, Zr, Hf and Ta as possible doping candidates which lower the HOCO* limiting step for the CO₂RR. The scaling relations of HOCO* vs. CO* binding energies in different doping configurations display well-defined scaling relations for Fe, Co, Ni, Cu, Ru, Rh and Ag doping because HOCO* and CO* intermediates all form a single C-Metal on the surfaces. However, the formation of the two bonds consisting of one C-Metal and one O-Metal bond break the scaling relation for other dopants, which is the reason why these dopants have strong HOCO* binding compared to the CO* binding. According to kinetic volcano plots, Ti doping with parallelogram and overlayer configuration and Nb doping with overlayer configuration are further found to have better kinetic activities than pure PdH(111) at a low overpotential of 0.3 V. At the same time, Ti and Nb are also possible to generate more CO compared with pure surface based on their selectivity toward the CO₂RR and HER.



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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in DTU Data Repository at https://doi.org/10.11583/DTU.17263532, reference number 17263532.

Keywords: Density functional theory \cdot palladium hydride \cdot doping \cdot scaling relations \cdot kinetic activity

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Paper II

Impact of hydrogen concentration for CO_2 reduction on PdH_x : A combination study of cluster expansion and kinetics analysis

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Impact of Hydrogen Concentration for CO_2 Reduction on PdH_x: A Combination Study of Cluster Expansion and Kinetics Analysis

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Abstract

Pd hydride has shown better electrochemical CO_2 reduction reaction (CO_2RR) performance compared to metal Pd implying that H in the PdH_x surface plays a vital role in affecting the performance. Using density functional theory (DFT) calculations in combination with active learning cluster expansion and Monte Carlo simulated annealing we identify 12 stable PdH_x(111) configurations on the DFT convex hull and investigate the binding energies of intermediates in the CO₂RR and the competing hydrogen evolution reaction. Through analysis of intermediate binding energies and a microkinetic model, we identify the atomic structures of the PdH_x phase most likely to produce syngas. The high activity of the PdH_{0.6} surface can be attributed to the fact that H segregation in the PdH_x(111) surface breaks the linear relation between HOCO^{*} and CO^{*} adsorbates.

1 Introduction

The primary driver of global climate change is carbon dioxide (CO_2) emissions in the world nowadays. It is widely recognized that it is urgent to reduce CO_2 emissions as parties to the Paris Agreement agreed "the increase in the global average temperature to well below 2 °C above preindustrial levels and to pursue efforts to limit the temperature increase to below 1.5 °C above pre-industrial levels." [1, 2] Conversion and utilization of CO_2 is considered as a possible scheme to mitigate these emissions. Several technologies to realize the CO_2 reduction exist, such as electrocatalysis, thermocatalysis, photocatalysis, and biocatalysis. Among them, the electrochemical CO_2 reduction reaction (CO_2RR) is one of the most promising approaches for converting CO_2 to

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valuable fuels and chemicals[3]. In fact, the electrochemical processes of CO_2RR would involve multiple electron/proton transfer, which can generate different common products, such as 2, 6, 8, and 12 electrons for the formation of CO, CH₃OH, CH₄ and C₂H₅OH.[4–6] In general, longer reaction pathways that accompany more electron/proton transfers have lower energy conversion efficiency than shorter pathways. Converting CO₂ into the CO product only needs two electron/proton transfers during the electrochemical reaction process and thus has higher energy conversion efficiency, which shows great potential for industrial applications. However, high overpotential is generally required due to the high stability of CO₂. Under the high overpotential, the competitive hydrogen evolution reaction (HER) will also likely produce H₂. Many efforts have been made to suppress the HER, such as designing various electrocatalysts, electrodes, and so on, to promote high selectivity for the CO₂RR.[7] An alternative to finding highly selective catalysts is to tune the CO/H₂ ratio. This is because CO and H₂, the main components of syngas, can be used as downstream reactants to synthesize many basic organic chemicals and intermediates through the Fischer–Tropsch processes.[8] Therefore, it is necessary to find efficient electrocatalysts to produce syngas with a suitable CO/H₂ ratio.

The Faradaic efficiency and chemical selectivity of the CO_2RR are strongly related to the structure and chemical nature of the electrocatalysts as well as the electrolysis conditions, such as the applied potential.[9] Over the past decades, many works have been devoted to studying metal catalysts as they exhibit good catalytic activity for the $CO_2RR[10, 11]$ Copper (Cu) is the only metal catalyst that can realize significant C-C coupling to produce multiple hydrocarbons, in addition to methane, formic acid, hydrogen, and CO.[10] Among them, up to 20% CO Faradaic efficiency can be reached at -0.85 V versus the reversible hydrogen electrode (RHE), which can be attributed to its moderate adsorption energy for carbon monoxide. [10, 12, 13] Gold (Au) nanoparticle electrocatalyst can exhibit a highly selective electrocatalytic reduction of CO_2 to CO, and the maximum selectivity can reach 90% Faradaic efficiency at -0.67 V vs. RHE when the size of the nanoparticle is 8 nm.[14] Furthermore, the selectivity can be higher, reaching 97% CO Faradaic efficiency toward CO at -0.52 V vs. RHE when Au nanoparticles are embedded in a matrix of butyl-3-methylimidazolium hexafluorophosphate. [14] A nanoporous silver (Ag) electrocatalyst was also reported to be able to reduce CO_2 to CO with about 92% selectivity under moderate overpotentials of less than -0.5 V vs. RHE, which is 3000 times higher than its polycrystalline counterpart.[15] Non-noble metal Zinc (Zn) has recently been illustrated to be a potential alternative to Au and Ag for reducing CO_2 to CO due to its abundant reserves. A hierarchical hexagonal Zn catalyst was reported to have high selectivity up to 95% CO production at -0.95 V vs. RHE when using a CO₂-saturated 0.5 M KCl electrolyte. [16] Therefore, Cu has modest CO Faradaic efficiency and selectivity, and even though Au, Ag, and Zn selectively produce CO, they can not generate the favorable CO/H_2 ratio with efficient CO_2RR activity.[17]

Recently, metallic palladium (Pd) electrocatalyst has received attention for reducing CO₂ to

CO; it not only exhibits good selectivity and activity but also can split CO and H₂ simultaneously to synthesize gas with an adjustable H_2 to CO ratios.[17] Pd is usually considered as a favorable HER catalyst, but it can also produce CO at a very similar ratio to H_2 .[18] Chen et al. revealed that carbon-supported palladium (Pd/C) nanoparticles can generate CO and H_2 simultaneously in an aqueous electrolyte with a tunable CO/H_2 ratio from 0.5 to 1, which is a favorable ratio range to perform Fischer–Tropsch reaction that already exists in the industrial processes. [18] Chen et al. continued to explore the influence of different facets of Pd with cubic and octahedral particles dominated by Pd(100) and Pd(111) surfaces, respectively.[17] Their results show that the octahedral Pd particles have better activity and selectivity than cubic Pd particles, and both can produce suitable CO/H₂ ratios between 1 and 2, which are desirable ratios for Fischer–Tropsch process. It is worth noting that experiments show that a key factor of the high performance is because Pd particles are transformed to Pd hydrides (PdH).[17, 19] In fact, there could exist different concentrations of H in Pd hydrides (PdH_x) controlled by the applied potential, which has an important influence on the CO_2RR performance. [19, 20] Experiments only give the relation between the applied potential and CO₂RR performance and corresponding DFT calculations have only compared the performance of pure Pd and stoichiometric PdH. However, the best concentration of H of PdH_x surface for CO_2 reduction to CO is not given and it is unclear whether there is a saturation concentration of H.

Some previous theoretical efforts have been done to study CO_2RR or HER properties of PdH_x . Chen et al. reported the free energy diagram of Pd(111) and PdH(111). They concluded that the CO* desorption from metal Pd(111) surface could be the rate-limiting step due to strong CO* binding compared to PdH(111).[17, 18] Chorkendorff and co-workers reported hydrogen adsorption on palladium and palladium hydride at 1 bar. They showed the relation between the adsorption energy of H and surface H coverage on Pd(111) and Pd hydride slabs, and that the H binding energies became weaker as H coverage increased. They thought the adsorption and desorption of H₂ are faster on β -Pd hydride than α -Pd hydride at 1 bar.[21] Erhart et. al. constructed the phase diagrams of bulk Pd hydride and Pd-Au hydride using a cluster expansion and studied their thermodynamic properties.[22] However, these theoretical efforts have not systematically investigated the effect of H concentration on CO_2RR .

This study uses an active learning cluster expansion (ALCE) model equipped with Monte Carlo simulated annealing to search for the stable composition of $PdH_x(111)$ surfaces. Energies calculated by density functional theory (DFT) are used to train the ALCE model and find the ground state CE structures of each H concentration of PdH_x from the CE convex hull. Furthermore, we perform DFT relaxation to verify the CE convex hull and finally get the DFT convex hull to identify the ground state DFT candidates. Once the stable candidates are found, the CO₂RR activity and selectivity are further studied. As a result, PdH, PdH_{0.97}, and PdH_{0.60} are finally screened out to be the most active candidates and able to generate CO/H₂ with suitable ratios.

2 Computational details

All spin-polarized density functional theory (DFT) calculations are carried out to train the cluster expansion model and calculate adsorption energies using the atomic simulation environment (ASE) [23, 24] and the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method.[25–27] The Bayesian error estimation functional with van der Waals correlation (BEEF-vdW) ensemble is used for exchange and correlation functional, which performs quite well for chemisorption processes.[28] The first Brillouin zone is sampled by a $3 \times 3 \times 1$ Monkhorst-pack grid[29]. 400 eV is set for cutoff energy. The dipole correction is utilized in the z direction to remove the electrostatic dipole-dipole interaction due to periodically repeated surface slabs in all calculations. The structures are relaxed until all Hellman-Feynman forces are less than 0.01 eV/Å and the energy convergence criterion is within 10^{-6} eV. More DFT calculation details can be found in the supporting information.

All cluster expansion (CE) calculations in this work are performed with the Cluster Expansion in the Atomic Simulation Environment software package (CLEASE) developed by Chang et. al.[30] CE can greatly decrease the computational cost by mapping the first principles results onto a Hamiltonian that is fast to evaluate. The main idea of CE is to express the scalar physical quantity $q(\boldsymbol{\sigma})$ of crystal structure, which here is the electronic energy, as its configuration $\boldsymbol{\sigma}$ that is an N-dimensional vector consisting of site variables. It can be expressed as a linear expansion of cluster functions:[30, 31]

$$q(\boldsymbol{\sigma}) = \mathbf{J}_0 + \sum_{\alpha} \mathbf{m}_{\alpha} \, \mathbf{J}_{\alpha} \, \phi_{\alpha} \tag{1}$$

Where J_{α} denotes the effective cluster interaction (ECI) per occurrence, which must be fitted. J_0 is the ECI of an empty cluster. m_{α} denotes the multiplicity factor illustrating the number of α per atom and correlation function ϕ is the average value of the cluster functions in cluster α . m_{α} and ϕ can be calculated from the crystal structure. The equation can be simplified as follows:

$$\mathbf{q} = \mathbf{X}\,\boldsymbol{\omega} \tag{2}$$

where **X** is the correlation functions matrix and ω is a column vector of ECI values. **q** denotes a column vector of energies here.

ECIs are fitted by the ordinary least squares method with regularization. We utilize l1 regularization to avoid overfitting by adding a regularization term as follows:

$$\min_{\omega} \|\mathbf{X}\boldsymbol{\omega} - \mathbf{q}\|_2^2 + \lambda \|\boldsymbol{\omega}\|_1 \tag{3}$$

where λ is the regularization constant and $\|\omega\|_1$ is the *l1*-norm of the column vector ω . Furthermore, 10-fold cross validation is used to evaluate the prediction performance of the model in order to improve the model reliability.

Monte Carlo simulated annealing at each H concentration of PdH_x is performed in order to search for the ground state structure of each concentration, which is carried out in CLEASE. The standard Metropolis Monte Carlo at each temperature during simulated annealing is used and has the acceptance probability \mathcal{P}_{acc} as follows:[30]

$$\mathcal{P}_{\rm acc} = \min\left\{1, \, \exp\left(\frac{-(E_{\rm new} - E_{\rm old})}{k_{\rm B}T}\right)\right\} \tag{4}$$

Where E_{new} and E_{old} are the energies of new and old structures, respectively. k_{B} is the Boltzmann constant and T denotes temperature. The temperatures are set as 10^{10} , 10000, 6000, 4000, 2000, 1500, 1000, 800, 700, 600, 500, 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 2 and 1 K. For each temperature, 1000 Monte Carlo sweeps are applied (1 sweep includes N steps, where N is the number of atoms.)

The elementary reactions for CO_2RR in this work are considered as follows: [17, 32]

$$CO_2(g) + * + H^+ + e^- \longleftrightarrow HOCO*$$
 (5)

$$HOCO* + H^+ + e^- \longleftrightarrow CO* + H_2O(l)$$
(6)

$$CO* \longleftrightarrow CO(g) + *$$
 (7)

The elementary reactions for the HER can be considered by the following: [33]

$$H^+ + e^- + \ast \longleftrightarrow H \ast \quad (Volmer step) \tag{8}$$

$$H^* + H^+ + e^- \longleftrightarrow H_2(g) + * \quad (Heyrovsky step) \tag{9}$$

A kinetic model is applied to analyze the activity for the CO_2 reduction to CO. The net reaction rates of three elementary reactions are illustrated as[32, 34]

$$\mathbf{r}_1 = \mathbf{k}_1 \,\theta_* \mathbf{p}_{\mathrm{CO}_2} - \frac{\mathbf{k}_1}{\mathbf{K}_1} \,\theta_{\mathrm{HOCO}*} \tag{10}$$

$$\mathbf{r}_2 = \mathbf{k}_2 \,\theta_{\mathrm{HOCO}*} - \frac{\mathbf{k}_2}{\mathbf{K}_2} \,\theta_{\mathrm{CO}*} \tag{11}$$

$$r_3 = k_3 \,\theta_{CO*} - \frac{k_3}{K_3} \,\theta_* \,p_{CO}$$
 (12)

where k_1 , k_2 , k_3 denote forward rate constants of the three elementary reactions for CO₂RR. K_1 , K_2 , K_3 represent the corresponding equilibrium constants. p and θ represent the corresponding partial pressure and surface coverage, respectively. Experimental vapor pressures are utilized for them in this work. The partial pressure of H₂O is 3534 Pa and CO partial pressure is 5562 Pa.[35] The partial pressure of both CO₂ and H₂ are under standard pressure 101325 Pa.[10, 35]. Further details for the calculations for Gibbs free energy and the kinetic model can be found in our previous work and the supporting information.[34]



Figure 1: (a) The side view and (b) the top view of $PdH_x(111)$ surface that take H concentration of 50% as an example. The blue spheres are Pd atoms, the white spheres represent H atoms, and the red spheres are H vacancies.

3 Results and discussion

To illustrate the structures of the $PdH_x(111)$ surface, we take an H concentration of 50% as an example here and display the side and top views in Figure 1. The structure has four bilayers, including 16 Pd atoms and up to 16 H atoms. It can be seen that PdH_x has a Pd atom (blue spheres) framework, with the smaller H atoms (white spheres) filling octahedral sites between the larger Pd atoms. Red virtual atoms show H vacancies. The $PdH_x(111)$ slab is cut from the optimized bulk PdH with the crystal constants a = b = c = 4.138 Å and the slab size is $4 \times 4 \times 4$ with a = b = 11.704 and c = 28.362 Å. Here, we ignore the crystal constants variation when the H concentrations change because they vary only in a small range, approximately 0.2 Å from 0 to 1 for H concentration, which is less than 5% of the lattice constants of PdH.[36] Besides, previous work reported the strain of PdH only has a small impact on the performance of CO₂RR and HER.[37]

There can be up to 64 H atoms in the $PdH_x(111)$ surface as shown in Figure 1. It is impossible to run DFT calculations for all the possible structures (2⁶⁴ neglecting symmetry). Instead, we utilize an active learning cluster expansion (ALCE) surrogate method. The workflow of the ALCE for $PdH_x(111)$ is shown in Figure S1. After defining the CE settings, we generate 50 random H concentration structures of PdH_x to form the initial database pool and then relax the structures to get their DFT energies, which can be used to train the CE model and get the initial ECI values. If the root mean square error (RMSE) between DFT energies and CE energies is less than 5 meV/atom, we consider the CE model converged. Otherwise, more random structures will be generated and run by DFT, which are finally added to the database pool to verify if the CE model is converged. Once we have the converged the CE model, Monte Carlo simulated annealing (MCSA) with the CE calculator is performed to search for ground state structures for each H concentration of PdH_x , which gives 63 MCSA in total because the numbers of H range from 0 to 64 (concentration from 0 to 1) except pure slabs Pd(111) and PdH(111). The CE convex hull can be calculated according to all ground state structures at each concentration of H of PdH_x . Theoretically, the stable structures could be found from the vertices of the CE convex hull at this point. However, considering the uncertainty of the processes, the obtained ground state structures should be verified by DFT calculations. Therefore, the possible stable candidates of the CE convex hull are further collected, relaxed by DFT calculations, and finally added to the database pool to continue the next new round. At the same time, the DFT convex hull is also carried out until its convergence. The criterion of convergence is defined that the shape of the DFT convex hull will not change for three rounds. After that, the final stable candidates can be found according to converged DFT convex hull and their CO_2RR activity and selectivity toward CO and H₂ are further studied.



Figure 2: (a) The linear fitting plot of CE energy and DFT energy for 50 random structures. (b) The ECIs distribution obtained from cluster expansion fitting. (c) The DFT convex hull curve of mixing energy as a function of H concentration in round 9. (d) The H concentration of each layer as a function of the total concentration of H for the structures of the DFT lowest energies in each concentration.

To study stable compositions of $PdH_x(111)$, CE calculations are performed using the CLEASE package. Figure 2a shows the linear fitting between CE energies (E_{CE}) and DFT energies (E_{DFT}) when we have 50 random structures in round 1. It can be seen that both 10-fold cross validation

error and RMSE are really small, 1.043 meV/atom and 0.450 meV/atom, respectively, which illustrates that the CE model is really good for the $PdH_x(111)$ surface. The ECI value distribution as a function of cluster diameter (1st, 2nd, 3rd, or 4th nearest neighbor) is displayed in Figure 2b. It can be noticed that the ECIs of 0, 1, and 2-bodies are larger, while there are more 3-body and 4-body ECI values closer to 0. To avoid overfitting, we choose to use up to 4-body interactions and neglect high terms. To get accurate stable compositions, ALCE is carried out to deal with the uncertainty of the CE. After 9 rounds, the vertices of the DFT convex hull are unchanged in the last three rounds, which means the convex hull is converged. In addition, the fitting RMSEs remain small during the 9 rounds as displayed in Figure S4 and Figure S5, meaning that the CE models remain good. For each round, simulated annealing at each H concentration is calculated to find ground state structures as the example round 1 in Figure S3. As shown in Figure 2c, 12 stable candidates can be finally obtained and are marked by black crosses. They are Pd_{64} , $Pd_{64}H_2, Pd_{64}H_4, Pd_{64}H_8, Pd_{64}H_{10}, Pd_{64}H_{13}, Pd_{64}H_{31}, Pd_{64}H_{39}, Pd_{64}H_{53}, Pd_{64}H_{62}, Pd_{64}H_{63} \ and \ address address$ $Pd_{64}H_{64}$ and the corresponding H concentrations are 0, 0.0313, 0.0625, 0.1250, 0.1563, 0.2031, 0.4844, 0.6094, 0.8281, 0.9688, 0.9844 and 1, respectively. The side and the top view of optimized example structures among them can be found in Figure S10. Figure 2d shows the H distributions of each layer as a function of total concentrations of H in the slabs for the slabs of the DFT lowest energies in each concentration. The first layer is first filled up with H, then the fourth and third layers are filled up, respectively. Finally, the sublayer (second layer) will be finally filled at last. Possible artifacts due to the finite thickness of the model slab should be considered. To further confirm our conclusion, the $PdH_x(111)$ structures with more atomic layers with one missing layer are explored as displayed in Figure S11 and S12 in the supporting information. It can still be found that removing the sublayer H has the lowest energy and thus will be filled at last, independent of the slab thickness. In addition, semi-grand canonical Monte Carlo calculations are implemented to study H chemical potential, temperature, and pressure influence on H concentration as shown in Figure S14, S15 and S16 and the corresponding analysis can be found in the supporting information. Besides, all bare candidates surfaces are used to study the Pourbaix diagram and the phase transformation process from Pd to PdH under the applied potential in Figure 5c-d assuming the surface to be in equilibrium with protons and electrons at all potentials. The corresponding computational details can be found in the supporting information. Figure 5c shows the relative free energy of surface structure as a function of potential at pH 7.3, where the H concentration increases when the larger potentials are applied. The corresponding H concentration as a function of applied potential is shown in Figure 5d. This displays metal Pd can be completely transformed to Pd hydride at a potential of about -0.6 V vs. RHE assuming the surface is in equilibrium with protons and electrons. However, characterization of Pd aerogels by Schmidt and co-workers suggests H concentration is saturated around 60% already at -0.1 V, [20] which suggests the surface can be in equilibrium with H_2 gas rather than protons and electrons. In that case, the $Pd_{64}H_{39}$



surface is likely the active surface for CO production.

Figure 3: (a) Adsorption sites schematic diagram on $PdH_x(111)$ surface. (b) Binding energies of HOCO^{*}, CO^{*}, OH^{*}, and H^{*} as a function of H concentration. (c) Cutoff sphere schematic diagram of adsorbate on $PdH_x(111)$ surface. (d) Free energy diagram of CO₂RR of candidates. The insets show HOCO^{*} and CO^{*} adsorption surface structures. The blue spheres are Pd atoms, the small white spheres represent H atoms, the grey spheres are C atoms, the red spheres are O atoms and the small green spheres denote adsorption sites.

After identifying stable candidates on the DFT convex hull, their CO_2RR and HER performances are further studied. Figure 3a shows the different adsorption sites of a random structure, which are displayed in small green spheres. They are automatically found according to local similarity, which compares the similarity of local structure as displayed in Figure 3c. The similarity is defined by comparing the neighbor list information of each adsorbate within a 2.8 Å cutoff sphere, including numbers of neighbor atoms, neighbor element types, and distance lists between adsorbate and neighbor atoms. We consider they are the same adsorption site if the similarity is 1; otherwise, they are different sites. Here only the top site, fcc site, and hcp site are considered, and the fcc sites very close to H atoms (less than 1 Å) are not considered because adsorbates located in these sites can easily react with the neighboring H. We do not consider bridge sites because they are

unstable. All information on surface structures with adsorbates on all unique sites can be found in our database. [38] Binding energies of adsorbates of HOCO^{*}, CO^{*}, OH^{*} and H^{*} on the most stable sites of all PdH_x candidates are shown in Figure 3b and the corresponding data can be found in Table S3. It can be seen that the binding energies of all adsorbates gradually increase as the concentration of H goes up from 0 to 1, especially for the adsorbate CO^* . The CO_2RR free energy diagram of all candidates with adsorbates on the most stable sites is displayed in Figure 3d, and the corresponding data can be found in Table S4. We notice that most surfaces have very negative binding energies and thus have strong CO^{*} binding, which results in CO^{*} poisoning, especially for candidates with low H concentration. For example, the free energies of Pd_{64} , $Pd_{64}H_2$, $Pd_{64}H_4$, Pd₆₄H₈ and Pd₆₄H₁₀ at CO* step are -1.259, -1.196, -1.189, -1.017 and -0.938 eV, respectively. They have so strong CO^{*} binding that CO^{*} is very hard to release from the surface, which is the reason why CO^{*} poisoning happens. This can also be found in Figure S13e. On the other hand, for candidates with high H concentration, their free energies at HOCO^{*} are very high. For example, the free energy of $Pd_{64}H_{62}$ at the HOCO^{*} step is 1.121 eV, which is too weak to bind HOCO^{*} at low overpotential. Therefore, the ideal CO₂RR candidate should have strong HOCO^{*} binding and weak CO^{*} binding. It is worth noting the PdH surface with full H occupation does not have too high HOCO^{*} free energy step (0.79 eV), and weak CO^{*} free energy (0.22 eV) and thus no CO^{*} poisoning. Besides, Pd₆₄H₆₃ has very weak CO^{*} binding, 0.392 eV of CO^{*} free energy, and acceptable HOCO^{*} free energy. $Pd_{64}H_{39}$ has weak HOCO^{*} binding free energy (0.686 eV) and acceptable CO^* adsorption. Thus, $Pd_{64}H_{64}$, $Pd_{64}H_{63}$ and $Pd_{64}H_{39}$ are possible candidates of CO_2RR , which is consistent with the activity volcano in Figure 5a.



Figure 4: Scaling relations for adsorbates on $PdH_x(111)$ configurations on the convex hull.

To further understand the catalytic performance of $PdH_x(111)$ surfaces, the scaling relations between different adsorbates are shown in Figure 4 and the binding energy relations with error ellipsoids can be found in Figure S13. The relations E_{CO*} vs. E_{HOCO*} , E_{OH*} vs. E_{HOCO*} , E_{OH*} vs. E_{CO*} , E_{H*} vs. E_{CO*} , E_{H*} vs. E_{CO*} , E_{OH*} vs. E_{HOCO*} , E_{OH*} vs. E_{CO*} , E_{H*} vs. E_{CO*} , E_{H*} vs. E_{OH*} are displayed in 4a-f, respectively, and their R^2 values are given, which is a statistical measure to illustrate how well the linear scaling relations are fitted. For the ideal scaling relation, the R^2 value is close to 1. Otherwise, it is worse if the R^2 value is close to 0. We can see that their R^2 values are 0.72, 0.65, 0.68, 0.87, 0.77, and 0.60, respectively, which demonstrates that they have good scaling relations. However, it can also be noticed that there are some obvious outliers. For example, $Pd_{64}H_{39}$ in Figure 4f is far from the best-fit line. This might be attributed to H segregation, which breaks the scaling relation. The H concentration distribution plots of clean surfaces and surfaces with adsorbates are displayed in Figure S8 and Figure S9 in the supporting information. It can be noticed that there are fewer H atoms in the 1st layer and more H atoms in the 2nd layer for OH*, while more H is in the 1st layer and less H is in the 2nd layer compared to that of the clean surface for $Pd_{64}H_{39}$.



Figure 5: (a) Activity volcano plot of $PdH_x(111)$ candidates for CO_2RR at -0.5 V overpotential. (b) Selectivity plot toward CO and H₂. (c) Stability of ground state structures at pH 7.3. (d) The concentration of H as a function of potentials. The dashed line shows the saturation of H if the surface is in equilibrium with H₂ at 1 bar.

A kinetic model explores the CO_2RR activity for the $PdH_x(111)$ surfaces. Figure 5a shows

the activity volcano at -0.5 V overpotential at room temperature. The current density depends on both $E_{\text{HOCO}*}$ and $E_{\text{CO}*}$, which is more accurate than a single descriptor. We notice that PdH_x with low H concentration is far away from the apex of the volcano due to the strong CO binding, which means they have poor kinetic activity. The completely H-filled $\text{Pd}_{64}\text{H}_{64}$ is the closest to the apex, illustrating that it has the best activity. In addition, $\text{Pd}_{64}\text{H}_{39}$ and $\text{Pd}_{64}\text{H}_{63}$ also exhibit good kinetic activity for higher H concentration. Besides, according to Figure 4b, we can see that the OH* binding energies on $\text{Pd}_{64}\text{H}_{64}$, $\text{Pd}_{64}\text{H}_{39}$ and $\text{Pd}_{64}\text{H}_{63}$ are weak, so OH* will not poison them. Figure 5b shows the selectivity of all candidates toward CO and H₂. We compare the binding energies of the first step of the CO₂RR and the HER. If the binding energy of H* is lower than that of HOCO*, it means HER is thermodynamically prefered over CO₂RR and the catalyst tends to produce more H₂. We notice that all of the candidates tend to generate more H₂ as shown in Figure 5b. Besides, $\text{Pd}_{64}\text{H}_{64}$ is very close to the black dashed line and can produce more CO, and thus its CO/H₂ ratio is closer to components of syngas compared to other candidates.



Figure 6: Distribution of atom Pd and H of all candidates within the cutoff sphere as a function of HOCO^{*}, CO^{*}, OH^{*}, and H^{*} binding energies. The yellow curves are fitted Gaussian distribution of H.

The statistical distribution of all candidates is calculated to reveal the effect of H and Pd on binding energies. Here, the statistical data of binding energies includes all possible adsorption sites on all the candidate surfaces. Figure 6a-d display the frequencies of H, Pd, and the total atoms within a sphere with a 2.8 Å radius centered on the adsorbate as a function of the binding energies of HOCO^{*}, CO^{*}, H^{*} and OH^{*}, respectively. In addition, Figure 6a-b indicate the most favorable binding energy for HOCO^{*} and CO^{*} marked in blue, respectively. We see the tendency that the binding energies for all adsorbates are weaker when there are H atoms within the cutoff sphere of adsorbates. The fitted Gaussian distributions of H are also shown in the yellow curves in Figure 6. Their positions at the center of the peak are 0.60, -0.15, 0.44, and 1.52 eV, respectively, which are relatively weak in their corresponding binding energy distributions. Therefore, it can be concluded that H atoms weaken the binding energies of all adsorbates on PdH_x surface. To further verify the conclusion, the partial density of states (PDOS) of the d-band is calculated. Figure S17 shows the PDOS of the bare surfaces of all candidates, and the corresponding d-band centers are given. It can be seen that d-band centers gradually decrease as H concentrations increase. The linear fit between d-band centers and H concentrations is also shown in Figure S18. The R-squared value is used to describe the degree of their linear relation. The linear relation will be stronger if the R-squared value is closer to 1. The R-squared value is 0.87 in Figure S18 and thus they have strong linear relation. The lower d-band center means weaker binding energy. [39] We further calculate d-band centers for surfaces with HOCO^{*} and CO^{*} to support this. Figure S19 and Figure S22 show the PDOS and d-band center for all candidate surfaces with HOCO* and CO*, respectively. Their corresponding linear fits between H concentrations and d-band centers and between adsorbate binding energies and d-band centers for all surfaces with adsorbates are shown in Figure S20 and Figure S22, respectively. It can be noticed that there are still very good scaling relations between H concentration and d-band centers for surfaces with adsorbates. And their binding energies have a good linear relation with d-band centers. This can be further concluded that increased H concentration can weaken the binding energy.

4 Conclusions

In this work, the effect of H concentration on $PdH_x(111)$ surfaces on the CO₂RR and the HER has been studied using theoretical methods. Active learning cluster expansion equipped with Monte Carlo simulated annealing has been implemented to find stable $PdH_x(111)$ surface candidates. We have obtained 12 stable candidates from converged DFT convex hull, which are Pd_{64} , $Pd_{64}H_2$, $Pd_{64}H_4$, $Pd_{64}H_8$, $Pd_{64}H_{10}$, $Pd_{64}H_{13}$, $Pd_{64}H_{39}$, $Pd_{64}H_{53}$, $Pd_{64}H_{62}$, $Pd_{64}H_{63}$ and $Pd_{64}H_{64}$. We have carried out a method to find adsorption sites and then calculate the binding energies automatically. Their free energies are further calculated, illustrating the $PdH_x(111)$ surfaces with low H concentration have CO* poisoning. The scaling relations between different adsorbates show there are still good linear relations, but the segregation of H may have an influence on their scaling relations. According to the activity volcano, $Pd_{64}H_{64}$, $Pd_{64}H_{63}$ and $Pd_{64}H_{39}$ corresponding H concentrations of 1, 0.97, and 0.60 respectively, show high current densities at an overpotential of 0.5 V. The $Pd_{64}H_{39}$ surface is stable when the surface is in equilbrium with H_2 gas, and the H concentration match well with the experimentally determined 60% H concentration of Pd hydride.[20] Due to the existence of the competitive reactions between CO_2RR and HER, the selectivity plot toward CO and H_2 is calculated and illustrates these three candidates have better CO production compared to others, especially for $Pd_{64}H_{64}$. The statistical distribution of Pd and H atoms in all candidates reveals that H atoms can weaken the binding energies of all adsorbates, which may provide good guidance to tune the binding energy.

Conflicts of Interest

There are no conflicts of interest to declare.

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Keywords

Active learning; Cluster expansion; CO_2 reduction; PdH_x ; H concentration; Scaling relations; Kinetic activity; Selectivity

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Paper III

High-throughput compositional screening of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ hydrides for CO₂ reduction

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High-throughput Compositional Screening of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ Hydride for CO₂ Reduction

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Abstract

Electrochemical experiments and theoretical calculations have shown that Pd-based metal hydrides can perform well for the CO₂ reduction reaction (CO₂RR). Our previous work on doped-PdH showed that doping Ti and Nb into PdH can improve the CO₂RR activity, suggesting that the Pd alloy hydrides with better performance are likely to be found in the Pd_xTi_{1-x}H_y and Pd_xNb_{1-x}H_y phase space. However, the vast compositional and structural space with different alloy hydride compositions and surface adsorbates, makes it intractable to screen out the stable and active $Pd_xM_{1-x}H_y$ catalysts using density functional theory calculations. Herein, an active learning cluster expansion (ALCE) surrogate model equipped with Monte Carlo simulated annealing (MCSA), a CO* binding energy filter and a kinetic model are used to identify promising $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ catalysts with high stability and superior activity. Using our approach, we identify 24 stable and active candidates of $Pd_xTi_{1-x}H_y$ and 6 active candidates of $Pd_xNb_{1-x}H_y$. Among these candidates, the $Pd_{0.23}Ti_{0.77}H$, $Pd_{0.19}Ti_{0.81}H_{0.94}$, and $Pd_{0.17}Nb_{0.83}H_{0.25}$ are predicted to display current densities of approximately 5.1, 5.1 and 4.6 μ A cm⁻² at -0.5V overpotential, respectively, which are significantly higher than that of PdH at 3.7 μ A cm⁻².

1 Introduction

Society still relies heavily on fossil fuels, producing excessive carbon dioxide (CO_2) emissions. CO_2 is the primary greenhouse gas that causes weather anomalies and global warming.[1, 2] Therefore, it is crucial to mitigate CO_2 emissions through various new technologies. On the one hand, it is possible to capture CO_2 that arises from the combustion of fossil fuels and from industries and then sequestrate it in an alternative geological formation.[3] On the other hand, CO_2 can be transformed into valuable fuels and chemicals via catalytic approaches, such as photocatalysis

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and electrocatalysis. Electrochemical CO₂ reduction reaction (CO₂RR) shows great potential to valorize CO₂ as useful fuels or chemicals.[3–5] The utilization of renewable energy sources such as wind and solar energy is gradually increasing to generate electricity, and the utilization cost is decreasing. However, there are still significant challenges for storing the generated electrical energy.[6, 7] To face the challenges, the electrochemical CO₂ reduction is one of the most effective approaches via converting the generated electric energy to chemical energy carriers, such as carbon monoxide (CO), methane (CH₄), ethylene (C₂H₄), ethanol (C₂H₅OH) and propanol (C₃H₇OH). [3, 8, 9] This is an elegant solution that not only decreases the greenhouse effect but also obtains hydrocarbon chemicals when coupled with the utilization of renewable electricity. However, due to the chemical inertness of CO₂, it is very challenging to reduce CO₂ as it requires both energy input and favorable catalysts. Stability, activity, and selectivity of catalysts during the electrochemical process should be considered.[10]

Pure transition metal catalysts are usually stable and active for CO_2RR at room temperature, but their selectivities are quite different. Pure metal catalysts can be grouped into four categories based on their selectivity: (I) Cu is classified as its own category because it is the only metal that can simultaneously reduce CO_2 to multiple hydrocarbons and multi-carbon products such as CH_4 , C_2H_4 and C_3H_7OH . [8, 11–13] (II) Pb, Hg, Tl, and In are most likely to produce formate (HCOO^-) and the Faradaic efficiency of the products are over 90%.[3] (III) Ni, Fe, Pt, and Ti produce H₂ without producing or producing only a very small amount of hydrocarbons (the Faradaic efficiency of H₂ over 90 %) via hydrogen evolution reaction (HER).[3] (IV) Au, Ag, Zn and Pd mainly reduce CO₂ to carbon monoxide (CO). It is worth pointing out that Pd can also produce an almost equal proportion of H_2 while producing CO.[13] We note that both CO and HCOO are 2-electron products from CO₂RR, while CH₄, C₂H₄ and C₃H₇OH are 8-, 12- and 18-electron products, respectively.[14] CO and HCOO⁻ have the shortest reaction pathways, and their energy conversion efficiencies can be very high. On the other hand, the pathways of the higher number of electron products are long, and their conversion efficiencies are usually very low. This is because a long reaction pathway makes the process complex and arduous to manipulate. 9 The conversion efficiency of CO₂RR for synthesizing multiple electron products C2 and C3, in particular, is far from the level viable for practical productions due to the consumption of a lot of electrons and protons and long pathways. [9, 15] In contrast, the Faradaic efficiencies of 2-electron products CO or HCOO⁻ are usually higher than other products due to the short reaction pathways. Compared to liquid $HCOO^-$, CO is a gas that is easier to separate, and thus, reducing CO₂ to CO appears to be more achievable.

Though the Faradaic efficiency for CO formation on Pd is lower than that on Au, Ag, and Zn, Pd can simultaneously generate H_2 at a similar Faradaic efficiency due to the competitive HER. The generated CO and H_2 are the main components of syngas, which can be directly used to synthesize valuable chemical products via the Fischer–Tropsch processes.[3] Several works report that Pd-based catalysts can also produce syngas through electrochemical CO₂RR. Sheng et al. report that carbon-supported Pd nanoparticles (Pd/C) can simultaneously generate syngas with a CO to H₂ ratio between 0.5 and 1.[16] The current density can reach 0.6 mA cm⁻² at -0.7 V overpotential vs. reversible hydrogen electrode (RHE). In this electrochemical process, metal Pd nanoparticles are transformed into Pd hydride (PdH) as observed by in-situ X-ray absorption spectroscopy and in-situ X-ray diffraction. Density functional theory (DFT) calculations showed that PdH weakens the binding energies of both CO^{*} and H^{*}.[16] Zhu et al.[17] illustrated that different facets of Pd nanoparticles have an influence on their performance in CO₂RR to syngas; for example, Pd(111) surface has a higher activity of CO₂RR and better CO selectivity than the Pd(100) surface. The CO partial current density of PdH(111) in their work can reach 17 mA cm⁻² at -0.7 V overpotential vs. RHE, while that of PdH(100) is around 3 mA cm⁻², which is greater than that of commercial Pd catalysts. DFT calculations explain that forming PdH(111) makes CO^{*} desorption no longer difficult and thus improves the activity of CO₂RR.[17]

Liu et al.[18] reported that Pd-modified niobium nitride (Pd/NbN) can produce a much higher partial current density of syngas and larger CO Faradaic efficiency than Pd-modified vanadium nitride (Pd/VN) catalyst and commercial Pd/C catalyst. Among them, the CO partial current density of Pd/NbH is the highest at around $0.7 \,\mathrm{mA \, cm^{-2}}$ at $-0.7 \,\mathrm{V}$ vs. RHE. In-situ X-ray diffraction illustrated the formation of PdH in Pd/NbN, which weakens *CO desorption and enhances the CO_2 conversion to syngas. [18] Lee et al. [19] reported the use of Pd-based bimetallic hydrides for producing syngas using electrochemical CO_2RR approach. The second metal, such as Co_2RR approach. Ni, Cu, Ag, and Pt, was chosen to form alloys with precious metal Pd nanoparticles and concentrations of the second metals were fixed at 25% in their work. After applying potentials, the CoPd, NiPd, CuPd, AgPd, and PtPd alloys were transformed to (CoPd)H, (NiPd)H, (CuPd)H, (AgPd)H, and (PtPd)H, respectively, and their potentials of alloy hydrides formation were -0.322, -0.352, -0.434, -0.544 and -0.544 V vs. RHE, respectively. (AgPd)H, (CuPd)H, (NiPd)H, and (CoPd)H show higher CO partial current density than that of PdH. According to their CO/H_2 ratio, (CuPd)H and (NiPd)H are more suitable to produce syngas with the ratio range between 1 and 2.[19] Our previous study[20] using DFT suggested that among the transition metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Hf, Ta, W, and Re doped into PdH(111) at different doping configurations, Ti and Nb doping yielded a higher performance of CO_2RR than undoped PdH(111). Furthermore, their generated CO and H_2 are suitable for generating syngas, [20] providing clear guidance to further study of Ti- and Nb-Pd alloy hydrides.

In this work, $Pd_xTi_{1-x}H_y(111)$ and $Pd_xNb_{1-x}H_y(111)$ alloy hydrides are systematically studied via a hierarchy of theoretical calculations. Due to the vast search space of composition of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, their stabilities are first explored by an active learning cluster expansion model equipped with Monte Carlo simulated annealing of each concentration.[21] The advantage of this method is to search the ground-state structure at each concentration efficiently. Furthermore, the final ground-state structures are verified by DFT calculations. After obtaining the stable slabs, the most stable absorption sites are further searched for each slab. Finally, a kinetic model is applied to calculate the activity of CO_2RR , and a large number of candidates with catalytic activities better than that of PdH(111) are found. The selectivities are analyzed to see if they are suitable for producing syngas.

2 Computational details

All DFT calculations are performed using the atomic simulation environment (ASE) [22, 23] with the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method.[24–26] The exchange and correlation functional used in this work is the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW) ensemble.[27] The cutoff energy is set to 400 eV and the electronic smearing width is 0.05 eV. A Monkhorst-Pack grid of $3 \times 3 \times 1$ is used to sample the first Brillouin zone.[28] The electronic relaxation is set to stop when the energy difference between two steps is smaller than 10^{-6} eV. The ionic relaxation will converge when all the forces' norms are less than 0.01 eV Å^{-1} . The $Pd_xM_{1-x}H_y$ (111) surface is utilized because PdH (111) surface is the most stable in experiments (M is the metal element Ti or Nb).[17] To remove the electrostatic dipole-dipole interaction in the z direction due to periodic boundary conditions, a vacuum layer of approximately 15 Å is added, and the dipole correction is applied along the z direction. A 4 × 4 surface supercell cell of the $Pd_xM_{1-x}H_y$ (111) is utilized. Four atomic bilayers are used, each consisting of one Pd or M atomic layer (M is Ti or Nb element) and one H or X atomic layer (X denotes H vacancy). We fix the bottom two bilayers in their bulk positions when relaxing the slab.

The Cluster Expansion in the Atomic Simulation Environment software package (CLEASE) is used to implement cluster expansion (CE) calculations of the surface.[29] The initial slabs and corresponding relaxed energies are used to train the CE model, which can quickly predict the energies of the given new structures and thus greatly reduce the computational cost. The physical quantity (here it is the energy) of the material can be expressed as the following equation:[29, 30]

$$q(\boldsymbol{\sigma}) = J_0 + \sum_{\alpha} m_{\alpha} J_{\alpha} \phi_{\alpha} \tag{1}$$

where $q(\boldsymbol{\sigma})$ is the energy of the configuration $\boldsymbol{\sigma}$. J_0 is the effective cluster interaction (ECI) of an empty cluster. J_{α} denotes the ECI of cluster α , which needs to be fitted. m_{α} is the multiplicity factor that means the number of α per atom. ϕ_{α} denotes the correlation function of the cluster α , which is the average value of the cluster functions.[29] Up to 4-body clusters are included in this work, with the cutoff radii of 6.0, 5.0, 4.0 Å for 2-body, 3-body, and 4-body clusters, respectively. Monte Carlo Simulated Annealing (MCSA) is carried out to find the ground-state structure at each concentration. 65×65 MCSAs are implemented in parallel for each active learning iteration (65 H concentrations and 65 metal (Ti or Nb) concentrations in this work). Each MCSA uses standard Metropolis Monte Carlo at decreasing temperatures of 10^{10} , 10000, 6000, 4000, 2000, 1500, 1000, 800, 700, 600, 500, 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 2, and 1 K. 1000 Monte Carlo sweeps are set at each temperature and each sweep has N attempted swaps (N is the number of atoms in the cell). During the MCSA, the acceptance probability $P_{\rm acc}$ can be expressed as:[21, 29]

$$P_{\rm acc} = \min\left\{1, \exp\left(\frac{-\Delta E}{k_{\rm B}T}\right)\right\},\tag{2}$$

where ΔE is the energy difference between the new and the old structures. k_B denotes the Boltzmann constant and T is temperature in kelvin.

The binding energies, E_b , of adsorbates are calculated as:

$$E_b = E_{*+\text{ads}} - E_* - E_{\text{ads}},\tag{3}$$

where E_{*+ads} is the DFT energy of the surface with an adsorbate. E_* is the DFT energy of the clean surface, and E_{ads} is the DFT energy of the adsorbate. The adsorbates include HOCO^{*}, CO^{*}, OH^{*}, and H^{*}. The binding energy calculations of HOCO^{*}, OH^{*}, and H^{*} are referenced to CO₂, H₂, and H₂O gas molecules, respectively, while that of CO^{*} is referenced to CO gas molecule. The stabilization energy and zero point energy are considered when the OH^{*} binding energy is calculated. The stabilization calculation details can be seen in Figure S18 and the corresponding description in the supporting information.

The mixing energy, E_{Mixing} , is calculated to obtain the convex hull of $\text{Pd}_x M_{1-x} H_y$ according to:

$$E_{\text{Mixing}} = E_{\text{Pd}_{x}M_{1-x}H_{y}} - x\mu_{\text{Pd(bulk)}} - (1-x)\mu_{\text{M(bulk)}} - y\frac{1}{2}\mu_{\text{H}_{2}(g)}$$
(4)

where $E_{\mathrm{Pd}_{x}\mathrm{M}_{1-x}\mathrm{H}_{y}}$ is the DFT energy of $\mathrm{Pd}_{x}\mathrm{M}_{1-x}\mathrm{H}_{y}$, where x is the concentration of element Pd and y is the concentration of element H. $\mu_{\mathrm{Pd}(\mathrm{bulk})}$ and $\mu_{\mathrm{M}(\mathrm{bulk})}$ denote the chemical potentials of bulk Pd and bulk metal M, respectively. $\mu_{\mathrm{H}_{2}(\mathrm{g})}$ is the chemical potential of H₂ gas at 1 bar.

The CO_2RR elementary reactions and the corresponding net reaction rate equations of the kinetic model are considered: [17, 20, 31]

$$CO_2(g) + * + H^+ + e^- \longleftrightarrow HOCO*$$
 (5)

$$HOCO* + H^+ + e^- \longleftrightarrow CO* + H_2O(l)$$
(6)

$$CO* \longleftrightarrow CO(g) + *$$
 (7)

$$r_1 = k_1 \theta_* p_{\text{CO}_2} - \frac{k_1}{K_1} \theta_{\text{HOCO}*} \tag{8}$$

$$r_2 = k_2 \theta_{\text{HOCO}*} - \frac{k_2}{K_2} \theta_{\text{CO}*} \tag{9}$$

$$r_3 = k_3 \theta_{\rm CO*} - \frac{k_3}{K_3} \theta_* p_{\rm CO} \tag{10}$$

 k_1 , k_2 and k_3 denote forward rate constants of equations 8, 9 and 10, respectively. K_1 , K_2 and K_3 are the corresponding equilibrium constants. p_{CO_2} is the CO₂ partial pressure of 101 325 Pa. p_{CO} is the CO partial pressure of 5562 Pa. θ denotes the surface coverage.[8, 11]

The HER elementary reactions are considered as:[32]

$$H^{+} + e^{-} + \ast \longleftrightarrow H \ast \quad (Volmer step) \tag{11}$$

$$H_* + H^+ + e^- \longleftrightarrow H_2(g) + * (Heyrovsky step)$$
 (12)

The Gibbs free energy (G) is calculated from:

$$G = E_{\rm DFT} + E_{\rm ZPE} + \int C_p dT - TS$$
⁽¹³⁾

where E_{DFT} , E_{ZPE} , C_p , and S are the DFT energy, the zero point energy, the heat capacity, and entropy, respectively. The free energy calculations of gas-phase species utilize the ideal gas approximation. The harmonic approximation is used to calculate the free energy of the slabs with adsorbate. The free energy calculations of HOCO^{*}, CO^{*}, OH^{*}, and H^{*} are references to CO₂ gas, H₂ gas, and liquid H₂O. A +0.15 eV correction per C=O, +0.15 eV correction for HOCO^{*} and +0.1 eV correction for H₂ are used for systematic overbinding corrections with the BEEF-vdw functional in all calculations.[20, 33] The free energy calculations of the molecules and various adsorbates can be found in Table S1 and Table S2, which are the same as in our previous work.[20] To avoid calculations of solvated protons, the computational hydrogen electrode (CHE) model is used in this work.[34]

3 Results and discussion

The workflow for the screening of stable and active candidates of $Pd_xM_{1-x}H_y$ for the CO₂RR can be divided into the following five stages. The first stage shows the search space of the slabs of each $Pd_xM_{1-x}H_y$. For the $4 \times 4 \times 4$ bare slabs, there are 64 metal sites, which can be occupied by either Pd or the metal M, and 64 hydrogen sites which can be occupied by H or be vacant. Thus, the search space (including symmetrically identical slabs) is $2^{64} \times 2^{64} \approx 3.4 \times 10^{38}$, which is intractable to run DFT calculation for all slabs. To handle the huge search space, the ALCE model equipped with MCSA in parallel is utilized to obtain the ground-state slabs at each concentration. The specific implementation of the ALCE+MCSA can be seen in Figure S1. The ALCE can obtain the accurate surrogate model to speed up the CE energy prediction of the new given slabs, while MCSA is used to obtain the ground-state structures at each concentration quickly. During this stage (the second stage), $100 \sim 200$ stable bare slabs are found according to the DFT convex hull, which is a huge reduction of search space from the original 3.4×10^{38} possible configurations. Since there are several unique adsorption sites for each stable bare surface, a local similarity comparison method is implemented to find unique sites. [21] After finding the unique adsorption sites, CO* adsorbate is added to the bare slabs, and its binding energies are calculated using DFT. During this stage (the third stage), $600 \sim 900$ unique slabs with CO^{*} are found. The kinetic model in the fourth stage can be built to find the active range of CO^{*} binding energies, reducing the number of possibly active slabs down to 200~300. Because the number of slabs is limited at this point, the binding energies of HOCO^{*}, OH^{*}, and H^{*} adsorbates can now be calculated via DFT. In the last stage, the final candidates can be found through the kinetic model dependent on the binding energies of CO^{*} and HOCO^{*} at the most stable adsorption sites. Finally, less than 30 stable and active candidates of $Pd_xM_{1-x}H_y$ are found. All structures for the final candidates with adsorbates can be found in our database.[35]



Figure 1: The workflow of the processes of the screening stable and active candidates of $Pd_xM_{1-x}H_y$ for CO₂RR. The top and side views of an example structure are given for the first 4 stages. The top views of HOCO^{*} and CO^{*} of an example candidate for the last stage. The blue spheres are Pd atoms, and the big grey spheres are metal M atoms (e.g., Ti). The white spheres are H atoms. The small grey spheres in adsorbates are C atoms, and the red spheres are O atoms.

To quickly and accurately obtain the energies of slabs, a good surrogate model is very important. Here, The ALCE method is carried out to train the CE model. The CE candidates are extracted from the CE convex hull and calculated by DFT and then added to the train set of the CE. We re-train the CE model with the new train set and then get new CE candidates from the new CE convex hull. During this process, we focus on the DFT convex hull of each iteration rather than the CE convex hull, which means the CE convex hull will be confirmed by DFT, and thus, the DFT convex hull is more reliable. This differs from other approaches that directly use the convex hull predicted from the surrogate model. As are shown in Figure 2a and Figure 2b, both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ have 12 ALCE iterations. The green curves are 10-fold cross validation (CV) errors that we mainly focus on. The initial 10-fold CV error of $Pd_xTi_{1-x}H_y$ is 10.276 meV/atom as shown in Figure S2, which is a large error because only 50 random structures are in the initial train set. During the process of ALCE, the new structures of 50, 50, 200, 406, 500, 528, 382, 339, 320, 312, and 279 are added into the train set from iteration 2 to iteration 12, respectively. Their fitting



Figure 2: The 10-fold CV or RMSE as a function of ALCE iterations for $Pd_xTi_{1-x}H_y$ (a) and $Pd_xNb_{1-x}H_y$ (b). The linear fitting plots of CE energy and DFT energy of ALCE iteration 12 for (c) $Pd_xTi_{1-x}H_y$ and (d) $Pd_xNb_{1-x}H_y$.

plots can be found in Figure S3, Figure S4 and Figure S5. The 10-fold CV is gradually decreased and finally maintains stable at around 2.0 meV/atom as seen in Figure 2c. A similar case is observed for $Pd_xNb_{1-x}H_y$ in Figure 2b. Its initial 10-fold CV error is as large as 10.276 meV/atom as shown in Figure S20. Then, we add the new structures of 488, 499, 546, 575, 444, 437, 373, 272, 321, 342, and 352 into the train set from iteration 2 to iteration 12, respectively. The 10-fold CV error drop rapidly since iteration 2 and then remain stable at about 3.2 meV/atom, where the fitting plots can be seen in Figure S21, Figure S22, Figure S23, and Figure 2d. Besides, the orange curves in Figure 2a and Figure 2b are the RMSEs of only train sets (without test sets) for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$. They are very small at first and then gradually go up to stable values, and finally, the RMSEs are close to their 10-fold CV errors. This could be because the overfitting is very large at first and gradually decreases as more structures are added to the train set.

To identify stable compositions of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, their CE and DFT convex hull plots are calculated. Before obtaining the CE convex hull, the most stable slabs at each unique H and Pd concentration are first calculated by MCSA. Since there are 65×65 unique concentrations,



Figure 3: The CE convex hull plots of ALCE iteration 12 for (a) $Pd_xTi_{1-x}H_y$ and (b) $Pd_xNb_{1-x}H_y$. The DFT convex hull plots of ALCE iteration 12 for (c) $Pd_xTi_{1-x}H_y$ and (d) $Pd_xNb_{1-x}H_y$.

MCSAs at each concentration are implemented to get 65×65 stable slabs, which can be used to calculate CE convex hull. The points on the vertices of the CE convex hull are likely to be stable compositions considering the uncertainty of the CE model. The possible stable candidates from the CE convex hull need to be verified by the DFT convex hull. To better understand the shape of the convex hull for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, their 3D CE convex hulls in iteration 12 are displayed in the Figure S13 and Figure S31. However, in order to clearly see the specific concentrations of the convex hull, the 2D convex hulls are used in the following. Figure 3a and Figure 3b show the CE convex hull plots of the ALCE final iteration 12 for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, respectively. The CE convex hull of iteration 1-11 of $Pd_xTi_{1-x}H_y$ can be found in Figure S10, Figure S11 and Figure S12, while that of $Pd_xNb_{1-x}H_y$ can be found in Figure S28, Figure S29 and Figure S30. We notice that the CE convex hull of the last iteration is quite different from the initial one, but that of the last several iterations are very similar. This is because the CE model in the beginning is not good enough, and the overfitting is very large. However, the CE model is eventually improved and there is almost no overfitting in the end. It is worth pointing out that this situation is more obvious for the DFT convex hull. Figure 3c and Figure 3d display the DFT convex hull plots of the ALCE in iteration 12 for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, respectively. The previous iterations 1-11 of the DFT convex hull of $Pd_xTi_{1-x}H_y$ are shown in Figure S6, Figure S7 and Figure S8, while that of the DFT convex hull for $Pd_xNb_{1-x}H_y$ are shown in Figure S24, Figure S25 and S26. Since there are very similar tendencies for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, we only take $Pd_xTi_{1-x}H_y$ as an example here. We can notice that the DFT convex hull shapes greatly differ in the first 5 iterations. After that, their shapes become quite similar. Especially the DFT convex hulls for the last 3 iterations are almost identical and thus we conclude that the DFT convex hull is converged. Furthermore, the volume of the DFT convex hull is a more straightforward quantity to understand whether the convex hull is converged. As shown in Figure S9 and S27, we can see that the volume of the DFT convex hull is rapidly going up in the first 5 iterations and finally reaches a stable maximum in the last several iterations, which further verify the converged DFT convex hull. However, we should clarify that it is very difficult to ensure that all the global ground state structures are located for any model at 65×65 concentrations. Even though our ALCE method with MCSA makes DFT convex hull converged, there still exists the rare probability that the true global ground state structures are not found, but the number of them is so few that we do not consider them. Finally, we find 125 stable slabs for $Pd_xTi_{1-x}H_y$ and 116 stable slabs for $Pd_xNb_{1-x}H_y$, which has greatly reduce the search space.



Figure 4: Activity volcano plot of (a) the $Pd_xTi_{1-x}H_y(111)$ candidates and (b) the corresponding partial magnification of black dashed area for CO₂RR at -0.5 V overpotential. Activity volcano plot of (c) the $Pd_xNb_{1-x}H_y(111)$ candidates and (d) the corresponding partial magnification of black dashed area for CO₂RR at -0.5 V overpotential.

In order to further study the CO_2RR activity of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, a kinetic model is built as illustrated in Equation 8, Equation 9 and Equation 10. As shown in Figure 4a and Figure 4c, the activity volcano plots of the $Pd_xTi_{1-x}H_y(111)$ and the $Pd_xNb_{1-x}H_y(111)$ depend on the binding energies of CO^{*} and HOCO^{*} and the color bars show the current density calculated by the kinetic model at $-0.5 \,\mathrm{V}$ overpotential. The white dots in the Figures are all candidates after screening by the CO^{*} filter in stage 4 in Figure 1, and $Pd_xTi_{1-x}H_y(111)$ has 111 candidates and $Pd_xNb_{1-x}H_y(111)$ has 76 candidates. The red dot is the slab of $Pd_{64}H_{64}$, about $3.7\,\mu\mathrm{A\,cm^{-2}}$, used for the comparison. It can be noticed that there are lots of candidates with better CO₂RR activity than that $Pd_{64}H_{64}$ for the $Pd_xTi_{1-x}H_u(111)$ in Figure 4a and they can be seen in the black dashed rectangle. For the $Pd_xTi_{1-x}H_y(111)$, 24 active candidates can be found in detail in the partial magnification in Figure 4b, which can be divided into four categories. The dots marked by blue has comparable current densities $(3.7-4.2 \,\mu A \, cm^{-2})$ compared to the pure $Pd_{64}H_{64}$; the current densities of the dots marked by red, yellow, and black are sequentially better than that of $Pd_{64}H_{64}$. Especially, the current densities of the $Pd_{15}Ti_{49}H_{64}$ and $Pd_{12}Ti_{52}H_{60}$ can reach at about $5.1 \,\mu A \,\mathrm{cm}^{-2}$ that is significant greater than $Pd_{64}H_{64}$. There is no too strong OH^{*} binding on these active candidates as shown in Figure S16 and thus no OH^{*} poisoning. Besides, it can be noticed that the active candidates have a higher concentration of Ti and H. For the $Pd_xNb_{1-x}H_y(111)$, there are fewer active candidates, only 5 comparable slabs, which are shown in the partial magnification Figure 4d. They are Pd₈Nb₅₆H₂₇, Pd₁₂Nb₅₂H₅₆, Pd₁₅Nb₄₉H₂₉, $Pd_{36}Nb_{28}H_{33}$ and $Pd_{11}Nb_{53}H_{16}$, which have high Nb concentration. Especially, the $Pd_{11}Nb_{53}H_{16}$ has the highest current density, $4.6\,\mu\mathrm{A\,cm^{-2}}$. The OH* binding on these active candidates are not too strong and thus do not poison the surfaces as shown in Figure S34. Besides, it is worth mentioning that the candidates of the Pd alloy hydride have much better CO_2RR activity than the corresponding candidates of the doped Pd hydride in our previous work. [20]

In order to further understand the catalytic activities of active $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ candidates, the free energy diagrams of the CO₂RR and HER are shown in Figure 5. The black curves in all Figures are the free energy diagram of pure $Pd_{64}H_{64}$, which is used as a reference. The CO₂RR free energy diagrams in Figure 5a and Figure 5c illustrate that the HOCO* step of $Pd_{64}H_{64}$ is the potential limiting step, which means the free energy of the HOCO* is too high and thus the HOCO* binding is too weak to form efficiently on the surface. We notice that all of the HOCO* steps of the active candidates are lower than that of $Pd_{64}H_{64}$, which results in stronger HOCO* binding on the surface and thus make the reaction 5 easier. Besides, it can be noticed that the majority of active candidates have a stronger binding of CO* than $Pd_{64}H_{64}$, but the binding energy should not be too strong to avoid CO* poisoning. The CO₂RR free energy diagrams of all candidates at stage 4 in Figure 1 are also displayed in Figure S14 and Figure S32, most of them are inactive for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$. This is because either their HOCO* step is so high (the binding is too weak) that it is too difficult to produce HOCO*, or the CO* step



Figure 5: Free energy diagram of (a) CO_2RR and (b) HER of active candidates for the $Pd_xTi_{1-x}H_y(111)$. Free energy diagram of (c) CO_2RR and (d) HER of active candidates for the $Pd_xNb_{1-x}H_y(111)$.

is too low (the binding is too strong)causing CO* poisoning. For the $Pd_{15}Ti_{49}H_{64}$, $Pd_{12}Ti_{52}H_{60}$, and $Pd_{11}Nb_{53}H_{16}$ with high current densities, their HOCO* binding is not weak and the CO* binding is not strong, which is the reason why they are very active. However, the HER free energy diagrams for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ indicate that the candidates that are active for CO₂RR also have better HER performance than $Pd_{64}H_{64}$ as shown Figure 5b and Figure 5d. All of them have lower free energy of the Volmer step compared to the $Pd_{64}H_{64}$, which can improve their HER activity. The HER free energy diagrams of all candidates have stronger binding of H* than $Pd_{64}H_{64}$ and the bindings are not strong, which leads to their high HER activity. However, the candidates with high concentrations of H and Pd have weaker binding of H* than $Pd_{64}H_{64}$ and thus lower HER activity, which is consistent with our previous work.[21] In addition, there are no obvious scaling relations between the binding energies of different adsorbates for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ as shown in Figure S16 and Figure S34, which may be attributed to the high complexity of the composition of the surfaces and the different stable adsorption sites. Figure S19 and Figure S36 describe the selectivity of all candidates toward CO and H₂ for $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, where $\Delta G_{HOCO*} - \Delta G_{H*}$ is used as a descriptor to illustrate the tendency towards CO_2RR and HER. The more positive value of $\Delta G_{HOCO*} - \Delta G_{H*}$ tends to generate more H₂, while the more negative value will produce more CO_2 . It can be seen that a majority of candidates can produce more H₂ than CO_2 and only a small part of candidates can generate more CO_2 .



Figure 6: Distribution of atom Pd, Ti, and H of all candidates within the cutoff sphere as a function of (a) the HOCO^{*} and (b) the CO^{*} binding energies. Distribution of atom Pd, Nb, and H of all candidates within the cutoff sphere as a function of (c) HOCO^{*} and (d) CO^{*} binding energies.

To further reveal the role of each element in affecting the binding energies, the statistical distributions of the binding energy of different adsorbates as a function of the frequency of appearance of each element in a local environment are displayed in Figure 6. The grey rectangle area is the active zone for HOCO^{*} or CO^{*} according to the kinetic model for CO production. Figure 6a and Figure 6b are the distributions of the binding energies of HOCO^{*} and CO^{*} for $Pd_xTi_{1-x}H_y$. Most of the HOCO^{*} binding energies are not in the active zone, and only a small part of elements Ti and H is distributed in this active zone. However, the center of the CO^{*} binding energies is nearly in the middle of the active zone. The distributions of the OH^{*} and H^{*} binding energies for $Pd_xTi_{1-x}H_y$ are also shown in Figure S17. It is worth pointing out that Pd is distributed in the weak binding zone of the HOCO^{*}, CO^{*}, and OH^{*}, which implies that Pd may weaken their binding. This is not

the case for H* distribution as the element Pd is mainly distributed in the center of the zone of the H* binding energies. For the $Pd_xNb_{1-x}H_y$, the distributions of binding energies of HOCO*, CO*, OH* and H* are displayed in Figure 6c-d and Figure S35a-b, respectively. Similar to the $Pd_xTi_{1-x}H_y$, most of the binding energies of the HOCO* are higher than the active zone, and only a tiny part of Ti and H is in the HOCO* active zone. The centers of the distributions for the element Pd, Nb, and H are roughly in the middle of the CO* binding. Their OH* and H* distributions are displayed in Figure S34. The metal element Pd is obviously only in the weak binding zone of the OH* (1.0-2.0 eV), while element Nb is mainly in the strong binding zone of the OH*. This means element Pd may weaken the OH* binding. Pd is mainly distributed in the strong binding zone of the H*. It is worth noting that the frequency of occurrence of element Pd is very low within the local spheres for both $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$, which is much lower than that of Ti/Nb and H. This indicates that the adsorbates binding to elements Ti/Nb and H mainly contribute to the binding energy of the candidates.

4 Conclusions

We have used a surrogate model ALCE+MCSA, a CO* filter, and kinetic model to screen highperformance catalysts of alloy hydrides of $Pd_xTi_{1-x}H_y$ and $Pd_xNb_{1-x}H_y$ for CO₂RR, which greatly reduces the massive search space. Due to the large complexity that includes different compositions of alloy hydrides, different concentrations of metal elements and H of alloy hydrides, different adsorption sites, and different adsorbates, it is impossible to find the stable and active catalysts only using the density functional theory calculation. We utilize the high precision and low overfitting ALCE model with RMSE of about 2 or 3 meV/atoms, and a large amount of MCSA to identify the ground state Pd alloy hydride surfaces from the convex hull. Adsorption sites and binding energies of adsorbates are also accurate as they are also calculated from DFT. Finally, 24 active candidates of $Pd_xTi_{1-x}H_y$ and 5 active candidates of $Pd_xNb_{1-x}H_y$ are screened out according to the kinetic model. Especially, the $Pd_{15}Ti_{49}H_{64}$ ($Pd_{0.23}Ti_{0.77}H$), $Pd_{12}Ti_{52}H_{60}$ $(Pd_{0.19}Ti_{0.81}H_{0.94})$ and $Pd_{11}Nb_{53}H_{16}$ $(Pd_{0.17}Nb_{0.83}H_{0.25})$ have good stability and excellent current densities (approximately 5.1, 5.1 and $4.6 \,\mu A \, \mathrm{cm}^{-2}$, respectively), which are higher than that of $Pd_{64}H_{64}$ at 3.7 µA cm⁻². These are because their HOCO^{*} binding is not too weak, and CO^{*} binding is not too strong. Consequently, three candidates Pd_{0.23}Ti_{0.77}H, Pd_{0.19}Ti_{0.81}H_{0.94} and $Pd_{0.17}Nb_{0.83}H_{0.25}$ are recommended for further experimental investigations.

Data availability

The data including all DFT structures with the adsorbates HOCO^{*}, CO^{*}, H^{*} and OH^{*} on all adsorption sites in this work are available at DTU database: https://doi.org/10.11583/DTU. 23798751

Code availability

All plot, pre-processing, and post-processing codes in this paper are available at the following Gitlab repository named Pcat: https://gitlab.com/changzhiai/pcat.

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Keywords

 CO_2 reduction; $Pd_xM_{1-x}H_y$; Complex hydrides; High-throughput screening; Active learning; Cluster expansion; Kinetic activity; Selectivity.

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Paper IV

Graph neural network-accelerated multitasking genetic algorithm for optimizing $Pd_xTi_{1-x}H_y$ surface under various CO_2 reduction reaction conditions

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Graph Neural Network-Accelerated Multitasking Genetic Algorithm for Optimizing $Pd_xTi_{1-x}H_y$ Surface under Various CO₂ Reduction Reaction Conditions

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Abstract

Palladium (Pd) hydride-based catalysts have been reported to have excellent performance for the CO_2 reduction (CO_2RR) and the hydrogen evolution reactions (HER). Our previous work on doped-PdH and Pd-alloy hydrides showed that Ti-doped and Ti-alloyed Pd hydride could improve the performance of the CO_2 reduction reaction compared to pure Pd hydride. Compositions and chemical orderings of the surfaces with only one adsorbate under certain reaction conditions are linked to their stability, activity, and selectivity towards CO_2RR and HER, as shown in our previous work. In fact, various coverages, types, and mixtures of the adsorbates, as well as state variables such as temperature, pressure, applied potential, and chemical potential, could impact their stability, activity, and selectivity. However, these factors are usually fixed at common values to reduce the complexity of the structures and the complexity of the reaction conditions in most theoretical work. To address the complexities above and the huge search space, we apply a deep learning-assisted multitasking genetic algorithm to screen for $Pd_xTi_{1-x}H_y$ surfaces containing multiple adsorbates for CO_2RR under different reaction conditions. The ensemble deep learning model can greatly speed up the structure relaxations and retain a high accuracy and low uncertainty of energy and forces. The multitasking genetic algorithm simultaneously finds globally stable surface structures at each reaction condition. Finally, 23 stable structures are screened out under different reaction conditions. Among $these, Pd_{0.56}Ti_{0.44}H_{1.06} + 25\%CO, Pd_{0.31}Ti_{0.69}H_{1.25} + 50\%CO, Pd_{0.31}Ti_{0.69}H_{1.25} + 25\%CO, and CO, Pd_{0.5} + 25$ $Pd_{0.88}Ti_{0.12}H_{1.06}+25\%CO$ are found to be very active for CO_2RR and suitable to generate syngas consisting of CO and H₂.

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1 Introduction

The electrochemical CO_2 reduction reaction ($CO_2 RR$) is one of the most attractive approaches to convert CO_2 into chemical fuels and feedstocks.[1] This is because it can reduce the greenhouse gas CO_2 and produce valuable chemicals. Among them, reducing CO_2 to CO is a trendy scheme as its short reaction pathway only requires 2 electron/proton pairs and thus has a high energy conversion efficiency. At the same time, it usually can simultaneously produce H_2 due to the competitive chemical reaction in the process of producing CO.[2] The obtained CO and H_2 are the components of syngas that can be synthesized to other valuable multi-carbon chemicals via the Fischer-Tropsch processes.[3] Many experimental works report that PdH is a promising material to synthesize syngas because of its high CO_2RR and hydrogen evolution reaction (HER) performance. [2, 4–7] The phase transformation from Pd to PdH at reducing potentials weakens the CO binding energy and has been linked to the good syngas production performance on PdH.[2] A series of improved materials based on PdH, such as bimetallic catalysts^[5], single-atom catalysts^[6], and material supports[2], have been explored to improve the Faradaic Efficiency (FE) of the syngas production. However, due to the complexity of locating the relevant atomic structures of the materials, especially for bi/multi-metallic alloy hydrides, it is very challenging to experimentally reveal the relationship between the structures and the FE in the electrochemical CO_2RR . Even though the theoretical calculations are applied to explain the reaction mechanism in the alloy hydride system, the selection of the atomic structures in most theoretical work typically relies on chemical intuition.

Three key factors need to be considered to search for the relevant surface structures while handling the complexity. Firstly, a global optimization method, such as minima hopping[8], simulated annealing [9, 10], or a genetic algorithm (GA)[11-15], need to be utilized to find the global minimum of a property of interest. Secondly, surrogate models, including cluster expansion[16] or machine learning potentials [17, 18] can be used to speed up the calculations. The cluster expansion model can predict the energy of a given structure with good accuracy; however, it is challenging to apply to complex systems, such as a surface with multiple adsorbates potentially in contact with an explicit solvent. Machine learning interatomic potentials have recently gained significant attention due to their computational efficiency and accuracy. They offer a promising alternative to the cluster expansion model for complex chemical systems. Broadly, machine learning potentials can be classified into three categories: kernel methods such as Gaussian approximation potentials[19, 20], descriptor-based feed-forward neural networks (such as the Behler-Parrinello neural network potential[17, 21–23]), and deep neural networks[18, 24]. Among them, deep neural networks, particularly rotationally equivariant message-passing neural networks, have become highly popular owing to their rapid and precise predictions for directional properties, like forces and dipole moments. Notable examples of these models include Nequip[25], MACE[26], and PaiNN[18]. Last, but not least, it is also crucial to determine what physical properties need to be optimized. Structural
stability is usually the property that we should consider optimizing first. There are two common types of stability: thermodynamical compound stability[27] and electrochemical stability[28]. The compound stability is determined by the convex hull of formation energy or mixing energy. It means a structure is thermodynamically stable if it is in its lowest energy state, or in chemical equilibrium with its components. During electrochemical reactions, electrochemical stability is another key factor determining if the material is thermodynamically stable in an aqueous electrochemical system. The most common method is constructing a surface Pourbaix diagram, which plots surface free energy as a function of applied potential and pH value. Besides, the surface free energy can also depend on additional state variables, such as chemical potential, temperature, pressure, etc.

Substantial efforts have been made in Pd-based hydride systems to establish relationships between the structures and the electrochemical performance. [2, 6] Our previous systematic doping study builds the relationship between transition metal doping and the CO_2RR activity. 22 transition metal elements are doped into the PdH(111) surface with different doping configurations, and Ti-doped Pd hydride shows high CO_2RR and HER activity. [29] Based on this information, the Ti-Pd alloy hydride system with a higher complexity is also likely to accommodate very active candidates. Subsequently, the chemical composition of the alloy hydride $Pd_xTi_{1-x}H_y(111)$ surface is searched by cluster expansion method equipped with Monte Carlo simulated annealing according to the compound stability.[30] Some stable $Pd_xTi_{1-x}H_y$ structures are found to be very active for the CO_2RR and the HER. However, the adsorbate coverage and mixtures of different adsorbate species under the electrochemical reaction conditions are ignored during this structure searching process, which is crucial in the electrochemical CO_2RR and HER.[31, 32] It is very challenging to consider the full complexity because the search space increases drastically due to the huge complexities associated with the structure and reaction conditions. Herein, this work focuses on dealing with these complexities to identify relevant structures under diverse reaction conditions quickly and accurately.

In this work, we apply a graph neural network-assisted multitasking genetic algorithm to screen $Pd_xTi_{1-x}H_y$ surface with adsorbates under different CO₂RR conditions. The complex structural configurations result in a huge search space, where a deep learning model is used to speed up the atomic-scale calculations. Structures from DFT relaxations are used to train an ensemble of PaiNN models, and the trained models are utilized to optimize the new structures and calculate their energy uncertainty. The surface free energy is used to evaluate the surface stability, which depends on temperature, CO partial pressure, applied potential, and the chemical potential difference between Pd and Ti. Due to the complexity of the state variables above, a multitasking genetic algorithm employing the maximum gain dynamic niching (MGDN) algorithm [33] is used to search for stable $Pd_xTi_{1-x}H_y$ surface structures with adsorbates are found to be stable under difference difference between Pd and Ti.

ferent reaction conditions. Among them, $Pd_{0.56}Ti_{0.44}H_{1.06}+25\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+50\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+25\%CO$, and $Pd_{0.88}Ti_{0.12}H_{1.06}+25\%CO$ are found to be active for the CO_2RR .

2 Computational details

All density functional theory (DFT) calculations are performed by the Vienna Ab initio Simulation Package (VASP) equipped with the projector augmented wave method.[34, 35] The atomic simulation environment (ASE) is used as the interface to all VASP calculations in this work.[36, 37] The Bayesian error estimation exchange-correlation functional is used with van der Waals correlation (BEEF-vdW) ensemble[38], which is suitable for chemisorption calculations. A $3 \times 3 \times 1$ Monkhorstpack grid of k-points is used to sample the first Brillouin zone, and the energy cutoff is set to 400 eV.[39] The Hellman-Feynman forces and the energy convergence criterion for all structure relaxations are set as $0.01 \text{ eV}/\text{\AA}$ and 10^{-5} eV , respectively. The dipole correction is used in all DFT calculations to remove the electrostatic dipole-dipole interactions in the z direction due to periodical boundary conditions.

The surface free energy is used to construct the fitness function F_i in the GA global optimization. F_i can be calculated as follows:[40]

$$F_i = -(\gamma - \kappa_i * \sigma_i) \tag{1}$$

where κ is a factor that determines the relative weight of the predicted mean and uncertainty, and 0 and 1 are used in our calculations. σ is the standard deviation of the ensemble energies. The surface free energy γ of the $Pd_xTi_{1-x}H_y(111)$ surfaces (with adsorbates) is used to evaluate the surface stability in the solution. It can be represented in the following equations:

$$\gamma_{\rm PdH} = \frac{1}{2A} (G_{\rm PdH(slab)} - N_{\rm (slab)} \mu_{\rm PdH(bulk)})$$
(2)

$$\gamma = \frac{1}{A} [G_{(N_{Pd}^2, N_{Ti}^2, N_H^2, N_{ads}^i)} - G_{(N_{Pd}^1, N_{Ti}^1, N_H^1)} - \Delta N_{Pd} \Delta \mu_{Pd} - \Delta N_{Ti} \Delta \mu_{Ti} - \Delta N_H \Delta \mu_H - \sum_i N_{i(ads)} \mu_{i(ads)} - n_e U - n_e k_B T \ln 10 \text{pH}] - \gamma_{PdH}$$
(3)

where $G_{(N_{Pd}^2, N_{Ti}^2, N_{Ads}^2)}$ and $G_{(N_{Pd}^1, N_{Ti}^1, N_{H}^1)}$ are the free energies of structure 2 and structure 1, respectively. Structure 2 is an arbitrary surface with adsorbates, and structure 1 is a bare $Pd_{16}H_{16}$ without adsorbates. $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$, $\Delta \mu_{H}$, and $\mu_{i(ads)}$ are the chemical potential difference of Pd, Ti, H and the chemical potential of adsorbate, respectively. U, pH, and T are the applied potential, pH, and temperature, respectively.

The possible Pd and Ti chemical potentials for the Pd-Ti-H system are identified from the chemical potential diagram in Figure 1. More than 200 structures are collected from the Materials Project[41] and the Open Quantum Materials Database (OQMD)[42]. The collected structures are then reoptimized with our chosen DFT parameters. The calculated energies are used to construct



Figure 1: The phase diagram (a) and chemical potential diagram (b) of $Pd_xTi_yH_z$.

the Pd-Ti-H phase diagram and chemical potential diagram using the Pymatgen package.[43] The bulk PdH, the H₂ or proton, and the bulk TiPd₃ are assumed to be in equilibrium with $Pd_xTi_{1-x}H_y$ surface because we are interested in high H and Pd concentrations but low Ti concentrations.

The adsorbate species CO^* , H^* , and OH^* are assumed to be in equilibrium with CO, H_2 , H_2O , protons and eletrons according to the reactions:

$$CO* \rightleftharpoons CO(g) + *$$
 (4)

$$\mathbf{H}^+ + \mathbf{e}^- + * \rightleftharpoons \mathbf{H} * \tag{5}$$

$$H_2O(l) + * \rightleftharpoons OH* + H^+ + e^- \tag{6}$$

A rotationally equivariant message-passing neural network, namely the polarizable atom interaction neural network (PaiNN)[18, 44], is applied to speed up the relaxation of the structures. The $Pd_xTi_{1-x}H_y(111)$ surfaces with adsorbates are first calculated by DFT, and we select one singlepoint structure for every 10 ionic steps, which are fed to the deep learning model. The cutoff radius is set to 5.0 Å. We use ensemble PaiNN models with 8 different architectures (116, 120, 124, 128, 132, 136, 140, 144 node features) to obtain the mean energy and forces and their variances. They are trained using the Adam optimizer, and the learning rate is 0.0001. The maximum train step is 2,000,000, and the batch size is 12. A mixed loss function of energy and forces is used (see Equation S4) and the balance parameter λ is set to 98% weight on forces. Root mean squared errors (RMSE) of energy and force are calculated by Equation S5 in the Supporting Information.

A multitasking genetic algorithm (MTGA) is carried out to search for the $Pd_xTi_{1-x}H_y(111)$ surfaces (with adsorbates) under various reaction conditions. The surface structures with adsorbates can have different compositions and chemical orderings of the surface with different coverages, types, and mixtures of the adsorbates. The structural diversity is mainly controlled by the operators, which is crucial to determining how to generate new structures. We develop the operators including slab operators that manipulate metal and hydrogen atoms in the slab, adsorbate operators that manipulate adsorbates on the surface, and crossover operator that combines the slab from one structure and adsorbates from another structure. The details can be found in the Supporting Information. A set of comparators is used to identify duplicates, including the potential energy comparator, nearest neighbor matrix string comparator in ASE[37], and graph comparator in ACAT[33]. The population size is set to 50. The MTGA converges when new candidates cannot be found anymore in the last three consecutive generations. In the MTGA calculations, the maximum gain dynamic niching (MGDN) algorithm (implemented in ACAT)[33] is employed to find the best candidate structures under all considered reaction conditions. After integrating the MTGA and the PaiNN model, an automated active learning workflow based on MyQueue[45] is used to find the global minima.

The search space of surface structures N_{struct} and the number of tasks N_{task} for $\text{Pd}_x \text{Ti}_{1-x} \text{H}_y$ (111) with adsorbates are calculated by the following equation 7:

$$N_{\text{struct}} = 2^{N_{\text{Pd/Ti(slab)}}} \cdot 2^{N_{\text{H(slab)}}} \cdot (N_{\text{ads}} + 1)^{N_{\text{sites}}}$$
(7)

$$N_{\text{task}} = N_T \cdot N_{P_{\text{CO}}} \cdot N_U \cdot N_{\Delta\mu_{\text{Pd}}} \cdot N_{\Delta\mu_{\text{Ti}}} \cdot N_{\kappa} \tag{8}$$

where $N_{\rm Pd/Ti(slab)}$ and $N_{\rm H(slab)}$ are the numbers of Pd/Ti and H in the slab without adsorbates, respectively. $N_{\rm ads}$ is 3 including CO^{*}, H^{*}, and OH^{*}. $N_{\rm sites}$ is the number of the adsorption sites. N_T , $N_{P_{\rm CO}}$, N_U , $N_{\Delta\mu_{\rm Pd}}$ and $N_{\Delta\mu_{\rm Ti}}$ are the number of considered temperatures, CO partial pressures, applied potentials, chemical potential differences of Pd and Ti, respectively.

3 Results and discussion

To study the thermodynamic stability of the compounds, the Pd-Ti-H ternary phase diagram is calculated as shown in Figure 1a. The green circles in the phase diagram show the stable compounds, including Pd, Ti, H₂, TiPd₈, TiPd₅, TiPd₃, TiPd₂, TiPd, Ti₂Pd, TiH₂ and PdH. Unstable phases within 1 eV (above) of the convex hull are shown in the phase diagram, marked by the red squared dots. We assume the Pd-Ti-H slab is in equilibrium with the stable compound PdH, H₂, and TiPd₃ because we are interested in high H and Pd concentration but low Ti concentration. Figure 1b shows the corresponding chemical potential diagram. The total chemical potential of Pd_xTi_yH_z without adsorbates is dependent on the chemical differences $\Delta\mu_{\rm Pd}$, $\Delta\mu_{\rm Ti}$ and $\Delta\mu_{\rm H}$. The equilibrium chemical potential of the three stable compounds PdH, H₂ and TiPd₃ is highlighted in the dashed red circle, and their equilibrated chemical difference values of $\Delta\mu_{\rm Pd}$, $\Delta\mu_{\rm Ti}$ and $\Delta\mu_{\rm H}$ are -2.249, -7.285 and -3.614 eV, respectively. These terms are used to calculate the surface free energy shown in Equation 3. Figure 2 is a more straightforward representation of the equilibrium between the Pd_xTi_{1-x}H_y slab with adsorbates and the corresponding stable compounds. The right part of the slab (the blue part) is equilibrated with the bulk PdH, the protons, and the bulk TiPd₃ as described above. The left (red) part illustrates the adsorbates are equilibrated with the CO gas,



Figure 2: The phase equilibrium between the $Pd_xTi_{1-x}H_y$ with CO^{*}, H^{*} and OH^{*} adsorbates and CO gas, H₂ gas, liquid H₂O, bulk PdH and bulk TiPd₃.

the protons, and the liquid H_2O . In the electrochemical CO_2RR process, the HOCO^{*}, CO^* , H^* , and OH^* are all potential adsorbate species that can present on the catalyst surface. However, the adsorption energy of the HOCO^{*} is usually weaker than the other three adsorbates and thus not stable on the surface. So we do not consider the HOCO^{*} adsorption here. The CO^{*}, H^* , and OH^* are assumed to be in equilibrium with the CO gas, proton/electron pair, and H_2O , respectively (see Equation 4, Equation 5 and Equation 6).

Figure 3 shows the process of the global optimization for $Pd_xTi_{1-x}H_y$ with adsorbates CO^{*}, H^{*} and OH^{*} in the active learning workflow, and the corresponding example structures and complexity are given. We use a $2 \times 2 \times 4$ slab with multiple adsorbates and fix the bottom layer (12 metal atoms, 4 internal hydrogen atoms, 12 adsorption sites, 3 types of adsorbate species). Hence, there exist $2^{20} = 1,048,576$ possible slab configurations and $4^{12} = 16,777,216$ possible adlayer patterns, which constitute a total structural search space of approximately 1.8×10^{13} structures if we ignore the symmetry. Besides, the total number of tasks is 11,250 calculated by Equation 8. The total search space is the product of structural search space and the total number of tasks, which is approximately 2.0×10^{17} . The detailed active learning workflow can be found in Figure S1. Initially, 100 random $Pd_xTi_{1-x}H_y(111)$ surfaces with adsorbates are generated and relaxed by DFT. The calculated end-point structures are collected and fed to the ensemble PaiNN model with 8 different NN architectures. The trained ensemble PaiNN model can be used to optimize new structures generated by the GA operators. During the MTGA calculations, we customize three types of operators that can generate new $Pd_xTi_{1-x}H_y$ surface structures with adsorbates, which is shown in Figure 3, namely the slab operators that control the composition and permutation of the metals and internal hydrogen atoms, the adsorbate operators that control the coverage



Figure 3: The process of the global optimization for $Pd_xTi_{1-x}H_y$ with adsorbates CO^{*}, H^{*}, and OH^{*} in the active learning workflow, and the corresponding complexity.

and permutation of the adsorbates, and the crossover operator that combine the adsorbates from one structure and the slab from another structure. The detailed operators can be seen in the GA operators part of the Supporting Information. After optimizing a newly generated structure using the PaiNN model, the energy of the optimized structure is used to calculate the surface free energy and thereby the fitness function. The surface free energy dependents chemical potential differences of $\Delta \mu_{\rm Pd}$, $\Delta \mu_{\rm Ti}$, applied potential U, temperature T, and CO partial pressure $P_{\rm CO}$ adn the used values can be found in Table 1. The MGDN algorithm [33] in MTGA is applied to find the candidate structures at each reaction condition. Then, the candidate structures and the last generation are picked for DFT relaxation. In order to avoid repeated DFT calculations, the repeated structures are removed by comparing their similarity. The identified unique structures are further optimized by DFT and collected to retrain the PaiNN model. This procedure is repeated until the whole active learning process converges. The convergence condition is that the number of new DFT candidates keeps decreasing until it reaches zero, and new candidates cannot be found anymore in the last 3 iterations, as shown in Figure S7. After convergence, the candidates at all considered reaction conditions are obtained and then used to analyze the activity and selectivity for the CO_2RR and HER.

Table 1: The values of different state variables while calculating surface free energy.

State variable	Values
Chemical potential difference of Pd: $\Delta \mu_{\rm Pd}$ (eV)	-2.249, -2.499, -2.749, -2.999, -3.249
Chemical potential difference of Ti: $\Delta \mu_{\rm Ti}$ (eV)	-7.285, -7.535, -7.785, -8.035, -8.285
Applied potential U (V)	0, -0.1, -0.2, -0.3, -0.4, -0.5, -0.6, -0.7, -0.8
Temperature T (K)	283.15, 298.15, 313.15, 338.15, 353.15
CO partial pressure $P_{\rm CO}$ (Pa)	0.101325, 10.1325, 1013.25, 5562, 101325



Figure 4: (a) The energy RMSE in the process of active learning. (b) The fitting curve of the DFT energies and the corresponding neural network potential energies of the optimized structures. The green error bars of each point are the uncertainties calculated by ensemble energies.

To evaluate the performance of the active learning framework, the energy RMSE between the DFT energies and the neural network energies in the process of the active learning is shown in Figure 4a. The blue curve shows the energy RMSE rapidly declines in the first several iterations while it goes down very slowly in the last several iterations. The yellow curve illustrates the energy RMSE without the first iteration in which the structures are generated randomly. We can find that the energy RMSE rapidly levels off. It can be noticed that active learning mainly contributes to the decrease in the energy RMSE of the GA candidates rather than all structures in the whole search space. This can explain the slow RMSE decline in the last several iterations because the accuracy of the deep learning model cannot improve too much for all structures even though it is already good enough for the potential candidates. Figure 4b shows the parity plot between the DFT energies and the neural network potentials for the last iteration. The corresponding error bars for the neural network energy variances are so small that the most error bars cannot be seen.

The learning curve of the energies in Figure S4a further illustrates the small energy RMSE and variance. For comparison, the learning curve of the energies in the first iteration can be seen in Figure S6a. We can see that both the energy RMSE and variance in the last iteration are significantly decreased compared to the first iteration. The force RMSE is also crucial because it determines the precision of the structure relaxation. Figure S4b and Figure S6b display the forces learning curves of the last and the first iteration, respectively. It can be noticed that the same scenario happens as for the energy RMSE curves. Both the forces RMSE and variances are greatly decreased. Especially for the force variances, they are so small that we almost cannot see them in Figure S6b. Besides, the energy and forces learning curves of the 8 NN architectures for the first and the last iteration are also shown in Figure S3 and Figure S5, respectively, which further illustrate that the precision of energy and forces of the deep learning model have been greatly improved after the active learning.



Figure 5: The surface free energy as a function of the state variables between the chemical potential differences of Pd and Ti, applied potentials, temperature, and partial pressure of CO.

To study the effects of the different reaction conditions on the surface free energy, the contour plots of the surface free energy as a function of the chemical potential differences $\Delta \mu_{\rm Pd}$ and $\Delta \mu_{\rm Ti}$, applied potentials U, temperature T, and CO partial pressure $P_{\rm CO}$ are shown in Figure 5. The corresponding heatmaps for candidate structures at the same reaction conditions are shown in Figure S12. To simplify, the unique number for each structure (the index of the DFT database) is used, and the corresponding top view can be found in Figure S13. When the potential, temperature, and CO partial pressure are fixed at -0.5 V, 298.15 K, and 5562 Pa, respectively, the smaller $\Delta \mu_{\rm Pd}$ and larger $\Delta \mu_{\rm Ti}$ will minimize the surface free energy as shown in Figure 5a. At this condition, the candidate structure tends to have high Ti concentration and adsorbate CO^{*} with 25% coverage on the surface as the top view of structure 900 in Figure S13. When the large $\Delta \mu_{\rm Ti}$ or the small $\Delta \mu_{Pd}$ are fixed at -7.285 eV, -3.249 eV, respectively, under 298.15 K and 5560 Pa as displayed in Figure 5b-c, the lower applied potential and smaller $\Delta \mu_{Pd}$ or larger $\Delta \mu_{Ti}$ will make the surface free energy lower. At both conditions, the candidate structure has high Ti concentration and adsorbate H* with high coverage on the surface as the structure 782 shown in Figure S13. When the CO partial pressure and temperature are fixed at 5562 Pa and 298.15 K, respectively, under the large $\Delta \mu_{Ti}$ =-7.285 eV and the small $\Delta \mu_{Pd}$ =-3.249 eV, as displayed in Figure 5d-e, the lower applied potential will minimize the surface free energy. Compared to the applied potential, the temperature and CO partial pressure do not substantially influence the surface free energy. Similarly, the candidate structure at low potential and different temperatures and CO partial pressure have high Ti concentration and adsorbate H* with high coverage on the surface. When the condition is at large $\Delta \mu_{Ti}$ =-7.285 eV, small $\Delta \mu_{Pd}$ =-3.249 eV and potential=-0.5 V, high CO partial pressure=1 bar and low temperature=0 °C can lower the surface free energy. The candidate structure at this condition has high Ti concentration and adsorbate CO* with 50% coverage arranged in a hexagonal pattern.

To reveal the relations between the stable structures and certain reaction conditions, the surface free energy under several typical reaction conditions is displayed in Figure 6. The top views of the corresponding structures are shown at the bottom of each plot. The free energy as a function of the applied potential at four different chemical potential conditions (the vertices in Figure 5a) under the room temperature=298.15 K and CO partial pressure=5560 Pa can be found in Figure 6a, 6b, S8a, and 6d. There are very high concentrations of Ti for all of the stable candidates and the top layers are Ti overlayer pattern when the chemical potential difference is at large $\Delta \mu_{\rm Ti}$ =-7.285 eV and small $\Delta \mu_{\rm Pd}$ =-3.249 eV as shown in Figure 6a. Besides, there are 0.25% CO* coverage and very high H* coverage on the surface when the potential is larger than -0.66 V. Otherwise, there is only high H* coverage and no CO* on the surface. After lowering only $\Delta \mu_{\rm Ti}$ to -8.285 eV or increasing only $\Delta \mu_{\rm Pd}$ to -2.249 eV, the same surface free energy plot can be obtained as shown in Figure 6b, and Figure S8a. When the potential is larger than -0.31 V, the Ti concentrations are very low with no Ti in the top layer, and there are only CO^{*} adsorbates on the surface and the coverage is 50%. When the potential decreases below -0.31 V, the Ti concentration increases and the top layer is in a Ti hexagonal pattern. Besides, CO^* coverage is lowered to 25% and H^{*} begins to appear on the surface. When the potential decreases below -0.65 V, there is no CO^{*} anymore and only higher H^{*} coverage on the surface. After lowering $\Delta \mu_{\rm Ti}$ to -8.285 eV and increasing $\Delta \mu_{\rm Pd}$ to -2.249 eV as shown in Figure 6d, the surface free energy is higher than that in Figure 6a, which is consistent with the result in Figure 5a. When the potential is larger than -0.38 V, Ti concentration is very low, and no Ti is in the top layer, and only adsorbates CO^{*} is on the surface with 50% coverage. When the potential is less than -0.38 V, the Ti concentration increases, and the top layer is in a line pattern. The CO^* coverage goes down to 25% and H^{*} coverage goes up. The surface free energy as a function of CO partial pressure at $\Delta \mu_{Pd}$ =-3.249 eV, $\Delta \mu_{Ti}$ =-7.285 eV,



Figure 6: (a, b, d) The surface free energy as a function of applied potentials with different chemical potential differences of Pd and Ti at temperature=298.15 K, and CO partial pressure=5560 Pa. (c) The surface free energy as a function of CO partial pressure at fixed $\Delta \mu_{Pd}$, $\Delta \mu_{Ti}$, potential=-0.5 V, and temperature=298.15 K. The corresponding most stable structures are shown at the bottom.

potential=-0.5 V and temperature=209.15 K is displayed in Figure 6c. The Ti concentrations for all candidates are very high and the top layer is an overlayer. Furthermore, the H^{*} coverage for all candidates is very high. When the pressure is larger than around 10^4 Pa, the CO^{*} coverage is 50% in a hexagonal pattern. After the pressure is lowered below 10^4 Pa, the CO^{*} coverage is 25%. After the pressure is lowered below 5 Pa, the CO^{*} disappears from the surface.

The influence of temperature is also studied at $\Delta \mu_{Pd}$ =-3.249 eV, $\Delta \mu_{Ti}$ =-7.285 eV, potential=-0.5 V and CO partial pressure=5562 Pa as shown in Figure S8b. There is only one candidate with high Ti concentration, high H* coverage, and 25% CO* coverage on the surface. It can be noticed that the slope is very low for the surface free energy as a function of both CO partial pressure and temperature, which can be attributed to their weaker impact on surface free energy compared to the potential. Besides, the complete surface free energy plots versus potential, CO partial pressure, and temperature are also given as a reference in Figure S9, Figure S10 and Figure



Figure 7: (a-b) The CO_2RR and HER free energy diagram of active candidates at room temperature=298.15 K and CO partial pressure=5560 Pa. (c) The activity volcano plot of all candidates at potential=-0.5 V and CO partial pressure=5560 Pa. (d) The selectivity towards H₂ and CO₂ for all candidates.

To understand the CO₂RR activity and the selectivity towards H₂ and CO₂, the binding energies and free energies for the obtained candidates with CO^{*} are further calculated and analyzed. We only consider the most stable structures for each composition and the most stable CO^{*} adsorption sites. The details for calculating binding energies can be found in the supporting information. Figure S14 shows the free energy diagram for the CO₂RR for all candidates. It can be seen that most of the candidates have too strong or too weak adsorption of HOCO^{*} compared to pure PdH(111). It is also worth noting that the free energies of HOCO^{*} of Pd₉Ti₇H₁₇+1CO, Pd₅Ti₁₁H₂₀+2CO, Pd₅Ti₁₁H₂₀+1CO and Pd₁₄Ti₂H₁₇+1CO are 0.349, 0.497, 0.570 and 0.595 eV, respectively, which are not too strong or too weak compared to -0.028 eV of pure PdH. Furthermore, their free energies of CO^{*} are not too strong or weak compared to -0.028 eV of pure PdH, which are -0.244, 0.149, 0.077, and -0.131 eV, respectively. The CO₂RR free energy diagram for them is shown in Figure 7a. Hence, they are likely to produce more CO₂ compared to pure PdH. The HER free energy diagram for all candidates is shown in Figure S15. The free energies on H^{*} step of Pd₁₄Ti₂H₄+3CO, Pd₁₂Ti₄H₄+3CO, Pd₁₄Ti₂H₄+3CO, Pd₁₄Ti₂H₇+1CO, Pd₁₄Ti₂H₅+3CO, Pd₁₄Ti₂H₁₂+3CO and

Pd₉Ti₇H₁₇+1CO are 0.017, 0.033, 0.148, 0.188, 0.286, 0.325 and 0.368 eV, respectively, which are weaker than that of pure PdH (0.430 eV), but not too strong. Therefore, they are likely to produce more H₂ compared to pure PdH. The HER free energy diagram for them is shown in Figure 7b. Figure 7c shows the CO₂RR activity volcano at -0.5 V of potential and 5560 Pa of CO partial pressure. We can see that Pd₉Ti₇H₁₇+1CO (Pd_{0.56}Ti_{0.44}H_{1.06}+25%CO), Pd₅Ti₁₁H₂₀+2CO (Pd_{0.31}Ti_{0.69}H_{1.25}+50%CO), Pd₅Ti₁₁H₂₀+1CO (Pd_{0.31}Ti_{0.69}H_{1.25}+25%CO), and Pd₁₄Ti₂H₁₇+1CO (Pd_{0.88}Ti_{0.12}H_{1.06}+25%CO) are more active than pure PdH, which is consistent with the result of Figure 7c. The selectivity towards H₂ and CO₂ for all candidates is illustrated in Figure 7d. A descriptor $\Delta G_{(HOCO*)} - \Delta G_{(H*)}$ is used to describe the trend to generate CO and H₂.[29] If we focus on the CO₂RR active candidates, all $\Delta G_{(HOCO*)} - \Delta G_{(H*)}$ values for Pd₅Ti₁₁H₂₀+2CO, Pd₅Ti₁₁H₂₀+1CO and Pd₁₄Ti₂H₁₇+1CO and Pd₉Ti₇H₁₇+1CO are negative and then tend to produce more CO₂. It should be noticed that their values are close to 0 eV and thus suitable to generate syngas consisting of CO and H₂. The detailed values can be found in Table S1 of the supporting information. Besides, there is no OH* found on any candidate surfaces, which indicates that there is no OH* poisoning.

4 Conclusions

In this work, a deep learning-assisted multitasking genetic algorithm is used to screen for $Pd_xTi_{1-x}H_y$ surfaces with multiple adsorbates for CO_2RR under different reaction conditions. The ensemble PaiNN model trained by DFT single-point structures can not only greatly speed up the new structure relaxation but also keep a high accuracy of energy and forces. The model can successfully deal with the structural complexity including compositions and chemical orderings of surfaces with different coverages, types, and mixtures of the adsorbates. A genetic algorithm with maximum gain dynamic niching algorithm is used for global optimization of the surface free energy at each reaction condition, which can efficiently handle the complexity of state variables, such as temperature, CO partial pressure, applied potential, and chemical potential differences of Pd and Ti. A multitasking genetic algorithm is built to simultaneously deal with the complexity of structures and state variables. 23 stable structures are screened out under different reaction conditions. Among them, $Pd_{0.56}Ti_{0.44}H_{1.06}+25\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+50\%CO$, $Pd_{0.31}Ti_{0.69}H_{1.25}+25\%CO$, and $Pd_{0.88}Ti_{0.12}H_{1.06}+25\%CO$ are found to be very active for CO_2RR compared to pure PdH(111) and suitable to generate syngas.

Data Availability

The data, including a final DFT trajectory and a task file given all reaction conditions, and overall figures of surface free energy versus state variables, and candidate structures under all different reaction conditions are available at Database: https://doi.org/10.5281/zenodo.8191834

Code Availability

All codes for plot, pre-processing, and post-processing in this paper are available at the following Gitlab repository named Pcat: https://gitlab.com/changzhiai/pcat.

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Keywords

 CO_2 reduction; $Pd_xTi_{1-x}H_y$; Surface free energy; Deep learning; Graph neural network; Genetic algorithm.

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