

Copyright Undertaking

This thesis is protected by copyright, with all rights reserved.

By reading and using the thesis, the reader understands and agrees to the following terms:

1. The reader will abide by the rules and legal ordinances governing copyright regarding the use of the thesis.
2. The reader will use the thesis for the purpose of research or private study only and not for distribution or further reproduction or any other purpose.
3. The reader agrees to indemnify and hold the University harmless from and against any loss, damage, cost, liability or expenses arising from copyright infringement or unauthorized usage.

IMPORTANT

If you have reasons to believe that any materials in this thesis are deemed not suitable to be distributed in this form, or a copyright owner having difficulty with the material being included in our database, please contact lbsys@polyu.edu.hk providing details. The Library will look into your claim and consider taking remedial action upon receipt of the written requests.

**ATOMIC-SCALE ENGINEERING AND MECHANISTIC
INSIGHTS INTO NEXT-GENERATION ELECTROCATALYSTS:
A COMPUTATIONAL PERSPECTIVE**

DING KEDA

PhD

The Hong Kong Polytechnic University

2026

The Hong Kong Polytechnic University

Department of Applied Physics

**Atomic-Scale Engineering and Mechanistic Insights into Next-
Generation Electrocatalysts: A Computational Perspective**

DING Keda

**A thesis submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy**

August 2025

CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

_____ **(Signed)**

DING Keda _____ **(Name of student)**

Abstract

This work systematically investigates the electronic structure and catalytic performance of advanced electrocatalyst systems across three representative platforms: curved and vacancy-engineered MoS₂ for the hydrogen evolution reaction (HER), heteronuclear Fe-Co single-atom catalysts (SACs) for the oxygen reduction reaction (ORR), and geminal Cu atom-doped polymeric carbon nitride (Cu/PCN) for CO reduction reaction (CORR). Through in-depth first-principles calculations, we reveal that engineering curvature and sulfur vacancies in MoS₂ narrows the band gap and optimizes the density of states near the Fermi level, which significantly enhancing HER activity. For Fe-Co SACs on 4-fold nitrogen embedded on graphene (FeN₄-C and CoN₄-C), our study illustrates the importance of the loading effect in heteronuclear SACs; and identify the best ORR performance around 16.8% wt. In the case of Cu/PCN, detailed electronic and thermodynamic analyses uncover the mechanisms underlying C₁ (methanol) versus C₂ (ethylene glycol) product selectivity; high concentrations of geminal Cu and CO availability favoring ethylene glycol formation. These findings reveal the atomic-scale engineering and mechanistic insights for the next-generation electrocatalysts.

Publications

1. Ho, T. L., **Ding, K.**, Lyapunov, N., Suen, C. H., Wong, L. W., Zhao, J., ... & Dai, J. Y. (2022). Multi-level resistive switching in SnSe/SrTiO₃ heterostructure based memristor device. *Nanomaterials*, 12(13), 2128.
2. **Ding, K.**, Yang, T., Leung, M. T., Yang, K., Cheng, H., Zeng, M., ... & Yang, M. (2023). Recent advances in the data-driven development of emerging electrocatalysts. *Current Opinion in Electrochemistry*, 42, 101404.
3. Qiu, H., Yang, T., Zhou, J., Yang, K., Ying, Y., **Ding, K.**, ... & Huang, H. (2023). Tunable hydrogen evolution activity by modulating polarization states of ferroelectric BaTiO₃. *Journal of Materials Chemistry A*, 11(13), 7034-7042.
4. Yang, T., **Ding, K.**, Zhou, J., Ma, X., Tan, K. C., Wang, G., ... & Yang, M. (2025). Unravelling Species-Specific Loading Effects on Oxygen Reduction Activity of Heteronuclear Single Atom Catalysts. *Small methods*, 9(5), 2401333.
5. Curvature Effects on Hydrogen Evolution Performance in Two-Dimensional Curved MoS₂. (In preparation)
6. Geminal Copper Atoms Catalyze the Reduction of CO to Ethylene Glycol with High Selectivity. (In preparation)

Acknowledgements

I would like to express my gratitude to everyone who supported me throughout my 4 years Ph.D. journey.

Firstly, I am very grateful to my supervisor, Prof. YANG Ming. During these four years, he gave me so much help, not only in academy, but also in daily life, just like a friend. I struggled with sequelae for almost a year during covid, and my progress is always slow. The first work was a big failure that I even wanted to drop out, however Prof. YANG always encouraged me and never press me. He loves sports and often organized us to go hiking, the scenery made me forget the worries. Every Mid-autumn Festival, he invited the whole group to his home to celebrate and have a big meal. He is so kind and patient that I sometimes feel sorry for I have not made an excellent work.

Secondly, I am very grateful to my co-supervisor, Prof. HUANG Haitao. He also provided selfless help and sincere care in my Ph.D. career. Also, I would like to thank the copyright given by publishers.

Thirdly, I would like to thank Dr. YANG Tong and Dr. YANG Ke. Although they had quite heavy work, they still gave me a lot of technical help, and advice for documents or presentation. In spare time, we sometimes played games or mahjong. YANG Tong and his wife are good cooks and I felt like I was back home when I ate the dishes they cook.

Then, I would like to express my gratitude to my parents, who gave me so much encouragement and always supported my decisions, whatever good or bad.

Finally, I would also like to thank my colleagues and friends, Dr. QIU Haifa, Dr. CHENG Hao, HE Jingyu, WU Hao, ZHENG Chenhang, PANG Guijian and JI Jinsheng, for their support and assistance throughout my research journey.

Table of Contents

Abstract	I
Publications	II
Acknowledgements.....	III
Table of Content.....	IV
List of Figures	VIII
List of Tables	XIV
Chapter 1. Introduction.....	1
1.1 Background	1
1.1.1 The Urgency of Sustainable Energy Conversion and Storage	1
1.1.2. Electrocatalysis in Energy Technologies	2
1.1.3. Limitations of Conventional Bulk Catalysts.....	4
1.1.4. Potential of Atomic-Scale Engineering.....	6
1.2. Key Challenges and Knowledge Gaps.....	7
1.2.1. Catalytic Efficiency Constraints	7
1.2.2. Durability and Selectivity Limitations	10
1.2.3. Insufficient Control of Active Sites at the Atomic Scale	14
1.3. Recent Advances in Material Engineering.....	15
1.3.1. Structural Modifications	15
1.3.2. Species-Specific Loading Engineering	19
1.3.3. Geminal Atom Site Engineering	21
1.4. Motivation and Research Objectives of This Thesis	23
1.5. Thesis Structure	25
References.....	27
Chapter 2. Methodology	34
2.1. Schrödinger Equation.....	34
2.2. Born-Oppenheimer Approximation	36
2.3. Hartree-Fock theory	38

2.4. Density Functional Theory	40
2.4.1. Thomas-Fermi Model	40
2.4.2. Hohenberg-Kohn Theorems	43
2.4.3. Kohn-Sham Equations	44
2.4.4. Exchange-correlation Functional	46
2.4.5. Bloch Theorem.....	49
2.4.6. Plane-Waves and Pseudopotentials	50
2.5. Software Utilized in This Thesis.....	53
2.5.1. VASP	53
2.5.2. VESTA	53
2.6. General Concept of Electrocatalysis Calculation	54
2.6.1. Thermodynamics Determines the Reactivity	54
2.6.2. Kinetics Determines the Selectivity	55
2.6.3. Band Center Theory	56
References.....	58
Chapter 3. Curvature Effects on Hydrogen Evolution Performance in Two-Dimensional Curved MoS ₂	61
3.1. Introduction.....	61
3.2. Computational Methods.....	62
3.2.1. Computational Parameters	62
3.2.2. System Design and Curvature Define.....	62
3.2.3. Catalytic Path and Thermodynamics of HER in Calculation	63
3.2.4. Formation energy	63
3.3. Results and Discussion	64
3.3.1. Structures and Reasonableness	64
3.3.2. HER Activity of MoS ₂ Arcs	69
3.3.3. Electronic Structures Analysis	71
3.3.4. Adsorption and Vacancy Located on the Same Side.....	75
3.4. Conclusions.....	79
References.....	81

Chapter 4. Loading Effects on the Oxygen Reduction Reaction Activity of Heteronuclear Fe-Co Single-Atom Catalysts.....	84
4.1. Introduction.....	84
4.2. Computational methods	85
4.2.1. Computational Parameters	85
4.2.2. System Design and Metal Loading.....	86
4.2.3. Catalytic Path of ORR in Calculation.....	86
4.2.4. Thermodynamics of ORR	86
4.2.5. Energy Center of the Occupied States	87
4.3. Results and Discussion	88
4.3.1. Structures and Stability	88
4.3.2. ORR Activity of Isolated Fe and Co Sites	92
4.3.3. Loading-Dependent Catalytic Behavior	94
4.3.4. Magnetism and Spin State Evolution.....	97
4.3.5 Local Coordination Environment	100
4.3.6. Electronic Structures Analysis	101
4.3.7 Ultra-High Loading and Preoccupation Effects.....	111
4.4. Conclusions.....	118
References.....	121
Chapter 5. Geminal copper atoms catalyzed CO Reduction	124
5.1. Introduction.....	124
5.2. Computational Methods.....	125
5.2.1. Computational Parameters	125
5.2.2. System Design	125
5.2.3. Catalytic Path of Carbon reduction.....	126
5.2.4. Thermodynamics of Carbon Reduction	127
5.2.5. Formation Energy of Copper Incorporation in PCN.....	128
5.2.6. Charge Density Difference.....	128
5.3. Results and Discussion	129
5.3.1. Structures and Stability	129

5.3.2. Reaction Path to C ₁ product on Single Cu	131
5.3.3. Reaction path to C ₂ product on geminal Cu.....	134
5.3.5. Electronic Structures Analysis	143
5.3.6. Cu-poor Conditions.....	148
5.5. Conclusions.....	152
References:.....	154
Chapter 6. Conclusions and Future Works	156
6.1 Conclusions.....	156
6.2 Future works	158

List of Figures

FIGURE 1.1 SCHEMATIC ILLUSTRATION OF APPLICATIONS OF ELECTROCATALYSTS.	3
FIGURE 1.2 THE TRENDS IN THE ADSORPTION ENERGIES OF OXYGEN- AND HYDROGEN-CONTAINING ADSORBATES ON VARIOUS PLATINUM NANOPARTICLES AND EXTENDED SURFACES ARE ANALYZED ^[15] . (REPRODUCED WITH PERMISSION FROM DAVID LOFFREDA, PHILIPPE SAUTET, JUAN M. GARCÍA-LASTRA, ET AL., ANGEWANDTE CHEMIE INTERNATIONAL EDITION, 2014. 53(32): P. 8316-8319. COPYRIGHT 2025, JOHN WILEY AND SONS).....	5
FIGURE 1.3 (TOP) EXPERIMENTALLY MEASURED EXCHANGE CURRENT, $\log i_0$, FOR HER ON VARIOUS METAL SURFACES, PLOTTED AS A FUNCTION OF THE CALCULATED HYDROGEN CHEMISORPTION ENERGY PER ATOM, ΔE_H (TOP AXIS). DATA FOR SINGLE-CRYSTAL SURFACES ARE INDICATED BY HOLLOW SYMBOLS. (BOTTOM) RESULT FROM A SIMPLE KINETIC MODEL NOW PLOTTED AS A FUNCTION OF THE FREE ENERGY OF HYDROGEN ADSORPTION, $\Delta G_H^* = \Delta E_H + 0.24 \text{ eV}$ ^[27] . (REPRINTED WITH PERMISSION FROM NØRSKOV, J.K., ET AL., JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 2005. 152(3): P. J23. COPYRIGHT 2025, THE ELECTROCHEMICAL SOCIETY.)	8
FIGURE 1.4 CO ₂ RR ACTIVITY AND SELECTIVITY ON POLYCRYSTALLINE COPPER IN CO ₂ -SATURATED 0.1 M KHCO ₃ (pH 6.8). PRODUCT FARADAIC EFFICIENCIES ARE SHOWN, WITH DATA ADAPTED FROM HORI ET AL. ^[43] (HOLLOW SYMBOLS) AND KUHLE ET AL. ^[8] (FILLED SYMBOLS). ^[1] (OPEN ACCESS).....	10
FIGURE 1.5 THE POSSIBLE REACTION ROADMAP OF CO ₂ ^[53] . (REPRODUCED FROM ^[53] WITH PERMISSION FROM THE ROYAL SOCIETY OF CHEMISTRY. COPYRIGHT 2025.).....	13
FIGURE 1.6 THEORETICAL CALCULATIONS FOR THE EFFECTS OF S-VACANCIES AND STRAIN ON THE HER ACTIVITY OF MoS ₂ . (A) ΔG_H VERSUS %X-STRAIN FOR VARIOUS %S-VACANCY, RANGING FROM 0.0% (PRISTINE) TO 18.75%. (B) COLOURED CONTOUR PLOT OF SURFACE ENERGY PER UNIT CELL Γ (WITH RESPECT TO THE BULK MoS ₂) AS A FUNCTION OF S-VACANCY AND UNIAXIAL STRAIN. COLOUR BAR REPRESENTS THE VALUE OF Γ . THE BLACK LINES IN A AND B INDICATE COMBINATIONS OF S-VACANCY AND STRAIN THAT YIELD $\Delta G_H = 0 \text{ eV}$, THE OPTIMAL THERMODYNAMIC REQUIREMENT FOR HER ACTIVITY ^[74] .	

(REPRODUCED WITH PERMISSION FROM HONG LI ET AL NAT MATER, 2016. 15(1): P. 48-53. COPYRIGHT 2025, SPRINGER NATURE).....	17
FIGURE 1.7 THE CONTENT HISTOGRAM OF ISOLATED PT MONOMERS, NEIGHBORING PT MONOMERS, AND PATCHES OF PT MONOMERS FOR ATOMICALLY DISPERSED PT/MoS ₂ WITH DIFFERENT PT LOADINGS ^[84] . (REPRODUCED WITH PERMISSION FROM DINGSHENG WANG, RUNZE LI. ADVANCED ENERGY MATERIALS, 2022. 12(9): P. 2103564. COPYRIGHT 2025, JOHN WILEY AND SONS)	20
FIGURE 1.8 ILLUSTRATION OF THE PROPOSED 2E-ORR MECHANISM ON CoIN-N-C ^[92] . (.....	22
FIGURE 3.1 (A) TOP AND (B) SIDE VIEW OF 180-PRI MoS ₂ WITH A CURVATURE OF $K = 0.14 \text{ \AA}^{-1}$	65
FIGURE 3.2 FORMATION ENERGY PER ATOM OF PRISTINE MoS ₂ ARCS.	66
FIGURE 3.3 FORMATION ENERGY OF SULFUR VACANCY ON MoS ₂ ARCS.....	67
FIGURE 3.4 PDOS FOR THE SULFUR- <i>P</i> ORBITAL: 0-PRI MoS ₂ ARCS (BLACK LINE), MONOLAYER FLAT MoS ₂ SLAB (GREEN SHADED AREA), 240-PRI MoS ₂ ARCS (RED LINE) AND (6,6) ARMCHAIR NANOTUBE (PURPLE SHADED AREA). THE VACUUM LEVEL IS SET AS THE REFERENCE AT 0 eV.	69
FIGURE 3.5 GIBBS FREE ENERGY PROFILES FOR HER ON PRISTINE (BLUE) AND VACANCY-CONTAINING (RED) MoS ₂ ARC MODELS.	71
FIGURE 3.6 PDOS OF THE S- <i>P</i> ORBITALS BEFORE ADSORPTION FOR X-PRI (SOLID LINES) AND X-VAC (SHADED AREAS) MoS ₂ ARC MODELS, WHERE $X = 0, 60, 120, 180$, AND 240 FROM TOP TO BOTTOM. THE VACUUM LEVEL IS SET AS THE REFERENCE AT 0 eV.....	72
FIGURE 3.7 PDOS OF THE S- <i>P</i> (SOLID LINES) AND H- <i>S</i> (SHADED AREAS) ORBITALS AT THE ADSORPTION SITES FOR X-VAC MoS ₂ ARC MODELS, WHERE $X = 0, 60, 120, 180$, AND 240 FROM TOP TO BOTTOM. THE VACUUM LEVEL IS SET AS THE REFERENCE AT 0 eV.....	74
FIGURE 3.8 TOP VIEW OF HYDROGEN ADSORBED ON (A) 0-VAC MoS ₂ , (B) 120-VAC MoS ₂ AND (C) 240-VAC MoS ₂ WITH A CURVATURE OF $K = 0 \text{ \AA}^{-1}$, $0.10 \text{ \AA}^{-1}$ AND $0.19 \text{ \AA}^{-1}$, RESPECTIVELY.	75
FIGURE 3.9 GIBBS FREE ENERGY PROFILES FOR HER ON MoS ₂ ARC MODELS WITH SULFUR VACANCIES AND HYDROGEN ADSORPTION LOCATED ON THE SAME SIDE.	76

FIGURE 3.10 PDOS OF THE Mo- <i>D</i> ORBITALS BEFORE (SOLID LINES) AND AFTER (SHADED AREAS) ADSORPTION FOR X-VAC MoS ₂ ARC MODELS, WHERE X = 0, 60, 120, 180, AND 240 FROM TOP TO BOTTOM. THE VACUUM LEVEL IS SET AS THE REFERENCE AT 0 eV.....	77
FIGURE 3.11 PDOS OF THE Mo- <i>D</i> (SOLID LINES) AND H- <i>s</i> (SHADED AREAS) ORBITALS AT THE ADSORPTION SITES FOR X-VAC MoS ₂ ARC MODELS, WHERE X = 0, 60, 120, 180, AND 240 FROM TOP TO BOTTOM. THE VACUUM LEVEL IS SET AS THE REFERENCE AT 0 eV.....	78
FIGURE 4.1 THE TOP (TOP ROW) AND SIDE VIEW (BOTTOM ROW) OF (A) TM _{CEN} -TM _{COR} @N×N-I AND (B) TM _{CEN} -TM _{COR} @N×N-II AT N = 7 WITH THE TM LOADING OF 9.1 WT%.	89
FIGURE 4.2 THE AVERAGE DISTANCE BETWEEN Fe _{CEN} AND Co _{COR} (DSITE) AND THE RELATIVE ENERGETIC STABILITY BETWEEN Fe _{CEN} -Co _{COR} @N×N-I AND Fe _{CEN} -Co _{COR} @N×N-II, E(N×N-I)-E(N×N-II), AS FUNCTIONS OF THE SUPERCELL SIZE (TM LOADING).	90
FIGURE 4.3 THE FORMATION ENERGY AND THE DISSOLUTION POTENTIAL OF Fe _{CEN} AND Co _{COR} AS FUNCTIONS OF THE SUPERCELL SIZE (TM LOADING).....	91
FIGURE 4.4 THE Fe _{CEN} -N AND Co _{COR} -N BOND LENGTHS AS FUNCTIONS OF (TOP X AXIS) THE TM LOADING AND (BOTTOM X AXIS) THE CORRESPONDING SIMULATION SUPERCELL SIZE.	92
FIGURE 4.5 THE GIBBS FREE ENERGY DIAGRAM FOR ORR ON THE (A) Fe SITE OF Fe@9×9-S AND THE (B) Co SITE OF Co@9×9-S.....	93
FIGURE 4.6 GIBBS FREE ENERGY DIAGRAMS FOR THE OXYGEN REDUCTION REACTION (ORR) AT THE Fe AND Co SITES OF (A) Fe _{CEN} -Co _{COR} @9×9-II, (B) Fe _{CEN} -Co _{COR} @7×7-II, AND (C) Fe _{CEN} -Co _{COR} @5×5-II. THE CORRESPONDING TRANSITION METAL (TM) LOADING FOR EACH SYSTEM IS INDICATED.	95
FIGURE 4.7 THE GIBBS FREE ENERGY OF (A) *OH ADSORPTION (G(*OH)) AND (B) *OOH ADSORPTION (G(*OOH)), THE ORR LIMITING POTENTIAL (UL) AND THE PROJECTED MAGNETIC MOMENT (M) ON (A) Fe _{CEN} @N×N AND (B) Co _{COR} @N×N, RESPECTIVELY. THE LIMITING POTENTIAL OF THE Fe _{CEN} SITE PRE-OCCUPIED BY *OH (UL*OH) IS MARKED BY THE EMPTY PURPLE STAR. THE PROTRUSION HEIGHT OF TM (h _{TM}) IN THE PRESENCE OF (C) THE *OH ADSORBATE ON Fe _{CEN} @N×N (TM=Fe) AND (D) THE *OOH ADSORBATE ON	

Co_{COR}@N×N (TM=Co), RESPECTIVELY. THE INSETS ARE THE SIDE VIEW OF (C) *OH ADSORPTION ON Fe_{CEN}@N×N AND (D) *OOH ADSORPTION ON Co_{COR}@N×N.....99

FIGURE 4.8 THE PROJECTED DENSITY OF STATES (PDOS) ONTO THE FE SITE OF (A) Fe_{CEN}-Co_{COR}@7×7-II, (B) Fe_{CEN}-Co_{COR}@8×8-II, (C) Fe_{CEN}-Co_{COR}@9×9-II AND (D) Fe@9×9-S. THE FERMI LEVEL HAS BEEN SET TO 0 eV..... 103

FIGURE 4.9 THE PDOS ONTO THE FE SITE AND THE *OH ADSORBATE. (A-B) PDOS OF Fe_{CEN}-Co_{COR}@5×5-II AT 16.8 WT% TM (A) WITHOUT AND (B) WITH *OH ADSORBED ON THE FE SITE. (C) PDOS OF Fe_{CEN}-Co_{COR}@9×9-II AT 5.7 WT% TM WITH *OH ADSORBED ON THE FE SITE. (D) PDOS OF THE CONSTRAINED Fe_{CEN}-Co_{COR}@5×5-II WITH *OH ADSORBED ON THE FE SITE AND THE PROTRUSION HEIGHT OF THE FE SITE CONSTRAINED TO THAT OF *OH-ADSORBED Fe_{CEN}-Co_{COR}@9×9-II. THE FERMI LEVEL HAS BEEN SET TO 0 eV. 105

FIGURE 4.10 THE ENERGY CENTRE OF THE PROJECTED OCCUPIED STATES OF THE *OH ADSORBATE ON THE FE SITE (TOP X AXIS) AND THE *OOH ADSORBATE ON THE Co SITE (BOTTOM X AXIS) OF Fe_{CEN}Co_{COR}@N×N-II, Fe@9×9-S AND Co@9×9-S. THE RED SQUARES ENCLOSED BY THE DASH ELLIPSE DENOTE THE ENERGY CENTRE UNDER THE CONSTRAINED LOW-PROTRUSION RELAXATION. 107

FIGURE 4.11 PDOS ONTO THE Co SITE OF (A) Fe_{CEN}-Co_{COR}@7×7-II, (B) Fe_{CEN}-Co_{COR}@9×9-II, AND (C) Co@9×9-S. THE FERMI LEVEL HAS BEEN SET TO 0 eV. 108

FIGURE 4.12 PDOS ONTO THE Co SITE AND THE *OOH ADSORBATE. (A-B) PDOS OF Fe_{CEN}-Co_{COR}@5×5-II AT 16.8 WT% TM (A) WITHOUT AND (B) WITH *OOH ADSORBED ON THE Co SITE. THE FERMI LEVEL HAS BEEN SET TO 0 eV..... 109

FIGURE 4.13 THE SPIN-RESOLVED OCCUPATION OF (A) THE Fe-DZ₂ ORBITAL AND Fe-DXZ, DY_Z ORBITALS AFTER *OH ADSORPTION ON THE FE SITE OF Fe_{CEN}-Co_{COR}@N×N-II AND Fe@9×9-S, AND (C) THE TOTAL OCCUPATION. THE SPIN-RESOLVED OCCUPATION OF (B) THE Co-DZ₂ ORBITAL AND Co-DXZ, DY_Z ORBITALS AFTER *OOH ADSORPTION ON THE Co SITE OF Fe_{CEN}-Co_{COR}@N×N-II AND Co@9×9-S AND (D) THE TOTAL OCCUPATION..... 111

FIGURE 4.14 OXYGEN REDUCTION REACTION ON THE FE SITE PRE-OCCUPIED BY *OH IN Fe_{CEN}-Co_{COR}@7×7-II AND Fe_{CEN}-Co_{COR}@5×5-II, AND ON THE Co SITE IN Fe_{CEN}-

CO _{COR} @3×3 (TM LOADING: 38.4 WT%) WHERE ALL FE SITES AND ¾ OF THE CO SITES ARE COVERED BY *OH.	112
FIGURE 4.15 THE TOP AND SIDE VIEW OF FE _{CEN} -CO _{COR} @3×3. THE DISTANCES BETWEEN A CO SITE AND ITS THREE NEIGHBOURING FE SITES ARE MARKED.	113
FIGURE 4.16 AIMD SIMULATION OF FE _{CEN} -CO _{COR} @3×3 AT 300 K. THE OSCILLATORY LINES ARE THE BOND LENGTHS BETWEEN FE OR CO AND ITS FOUR NEIGHBORING N SITES AS FUNCTIONS OF TIME. THE SMOOTH LINES ARE THE AVERAGED BOND LENGTHS OVER A PERIOD OF 1.2 PS. THE BOTTOM PANEL VISUALIZES THE INITIAL AND FINAL STRUCTURES OF THE AIMD SIMULATION.	114
FIGURE 4.17 THE SURFACE POURBAIX DIAGRAM OF FE _{CEN} -CO _{COR} @3×3, AND THE TOP AND SIDE VIEW OF THE RELEVANT STATES. THE 2 × 2 SUPERCELL WAS ADOPTED.....	116
FIGURE 4.18 THE ESTIMATED ORR LIMITING POTENTIAL OF THE CO SITE AND THE TM LOADING OF TM _{CEN} -CO _{COR} @5×5-II (TM _{CEN} = MN, FE, CO, NI, CU, IR AND PT).	118
FIGURE 5.1 (A) TOP VIEW AND (B) SIDE VIEW OF THE CU/PCN STRUCTURE. COPPER ATOMS ARE SHOWN IN BLUE, CARBON IN BROWN, NITROGEN IN GREY, AND HYDROGEN IN PINK. THE UPPER COPPER ATOM (Cu ¹) AND THE LOWER COPPER ATOM (Cu ²) ARE INDICATED IN THE FIGURE.	130
FIGURE 5.2 PDOS OF THE CU 3D ORBITAL IN THE CU/PCN SYSTEM, FERMI LEVEL WAS SET TO BE 0 EV.	131
FIGURE 5.3 INTERMEDIATE STATES OF THE CU/PCN SYSTEM DURING THE CO REDUCTION REACTION TO C ₁ PRODUCT: (A) *CO, (B) *CHO, (C) *OCH ₂ AND (D) *OCH ₃	132
FIGURE 5.4 GIBBS FREE ENERGY DIAGRAMS FOR THE CORR TO C ₁ PRODUCTS.....	134
FIGURE 5.5 INTERMEDIATE STATES OF THE CU/PCN SYSTEM DURING THE CO REDUCTION REACTION TO C ₂ PRODUCT: (A) *CO + *CO, (B) AND (C) TWO DIFFERENT CONFIGURATIONS OF *CHO + *CO, AND (D) *CO + *COH.....	136
FIGURE 5.6 INTERMEDIATE STATES OF THE CU/PCN SYSTEM DURING THE CO REDUCTION REACTION TO C ₂ PRODUCT: (A) *CHO + *CHO, (B) *CHOCOH, (C) AND (D) TWO DIFFERENT CONFIGURATIONS OF *HOCCOH.....	137

FIGURE 5.7 INTERMEDIATE STATES OF THE CU/PCN SYSTEM DURING THE CO REDUCTION REACTION TO C ₂ PRODUCT: (A) *HOCCHOH, (B) TRANS *HOCHCHOH, (C) CIS *HOCHCHOH AND (D) *HOCCH ₂ OH.	139
FIGURE 5.8 INTERMEDIATE STATES OF THE CU/PCN SYSTEM DURING THE CO REDUCTION REACTION TO C ₂ PRODUCT: (A-D) DIFFERENT STATES OF *HOCHCH ₂ OH.....	140
FIGURE 5.9 GIBBS FREE ENERGY DIAGRAMS FOR THE CORR TO C ₂ PRODUCTS.....	141
FIGURE 5.10 PDOS OF THE *CHO + *CHO INTERMEDIATE ON CU ₁ , WITH THE FERMI LEVEL SET TO 0 eV	144
FIGURE 5.11 (A) TOP AND (B) SIDE VIEW OF DIFFERENCE CHARGE DENSITY FOR *CHO + *CHO. YELLOW AND BLUE REGIONS REPRESENT CHARGE ACCUMULATION AND DEPLETION, RESPECTIVELY. ISOSURFACE VALUE IS SET TO 0.001 e/Å ³	145
FIGURE 5.12 PDOS OF THE *HOCCOH INTERMEDIATE ON CU ₁ , WITH THE FERMI LEVEL SET TO 0 eV.....	146
FIGURE 5.13 (A) TOP AND (B) SIDE VIEW OF DIFFERENCE CHARGE DENSITY FOR *HOCCOH. YELLOW AND BLUE REGIONS REPRESENT CHARGE ACCUMULATION AND DEPLETION, RESPECTIVELY. ISOSURFACE VALUE IS SET TO 0.001 e/Å ³	147
FIGURE 5.14 (A) TOP VIEW AND (B) SIDE VIEW OF THE CU-POOR SITUATION. COPPER ATOMS ARE SHOWN IN BLUE, CARBON IN BROWN, NITROGEN IN GREY, AND HYDROGEN IN PINK.	149
FIGURE 5.15 INTERMEDIATE STATES OF THE CU-POOR SITUATION DURING THE CO REDUCTION REACTION TO C ₂ PRODUCT: (A) *HOCCOH AND (B) *CHO + *CHO.....	150
FIGURE 5.16 GIBBS FREE ENERGY DIAGRAMS FOR THE CORR TO C ₂ PRODUCTS IN CU-POOR SITUATION.....	151

List of Tables

TABLE 5.1 GIBBS FREE ENERGY OF CORR TO C ₁ PRODUCTS, THE EXPERIMENTAL VALUES ARE GIVEN IN BRACKETS[19].....	133
TABLE 5.2 GIBBS FREE ENERGY OF CORR TO C ₂ PRODUCTS.	142
TABLE 5.3 BADER CHARGE ANALYSIS OF ADSORBED SPECIES AND CU ATOM. .	143
TABLE 5.4 GIBBS FREE ENERGY OF CORR TO C ₂ PRODUCTS ON CU-POOR SITUATION.	152

Chapter 1. Introduction

Global energy demand is continues growing, and the related environment problems are exacerbated. Under this background, it is urgent to develop efficient and robust methods for energy conversion and storage. Central to this work is the field of electrocatalysis, which includes water splitting, fuel cell operation and carbon dioxide reduction, etc. It is the fundamental to many solutions in the sustainable energy^[1, 2].

1.1 Background

This section first provides an overview of the significance of sustainable energy technologies. Then, we highlight the critical role of electrocatalysis. After that, we discuss the limitation of conventional electrocatalysts. Finally, we introduce the atomic-scale engineering for next-generation electrocatalysts.

1.1.1 The Urgency of Sustainable Energy Conversion and Storage

The increasing demand for energy, coupling with various environment problems, has made clean energy conversion and storage technologies increasingly important. Fossil fuel remains the dominant on global energy; however, the extraction and use of them are associated with environmental drawbacks, including greenhouse gas emissions, air pollutions and water pollutions, etc. These consequences have led to an urgent call for a transition toward cleaner and more sustainable energy systems to reduce pollutions and climate change^[3].

Under this background, the usage of renewable energy sources (such as solar, wind, and hydropower) has increased gradually, but these sources are discontinuous in time and limited in space. Thus, it is crucial for the modern society to find methods of efficient conversion, storage, and utilization of renewable energy ^[4]. Electrochemical energy conversion and storage technologies, including water electrolysis, fuel cells, and metal-air batteries, play an important role in this transition by enabling the direct transformation of renewable electricity into chemical fuels ^[2]. These technologies can help human realize an environment-friendly future.

1.1.2. Electrocatalysis in Energy Technologies

Electrocatalysis is the core of numerous energy conversion and storage applications; because it governs the kinetics and thermodynamics of reactions. Prominent examples include the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water splitting, the oxygen reduction reaction (ORR) in fuel cells, and the carbon dioxide reduction reaction (CO₂RR) in electrochemical CO₂ conversion devices ^[5-8]. The efficiency, selectivity, and operational stability of these systems are intimately linked to the properties and performance of the electrocatalysts employed at their electrodes ^[9].

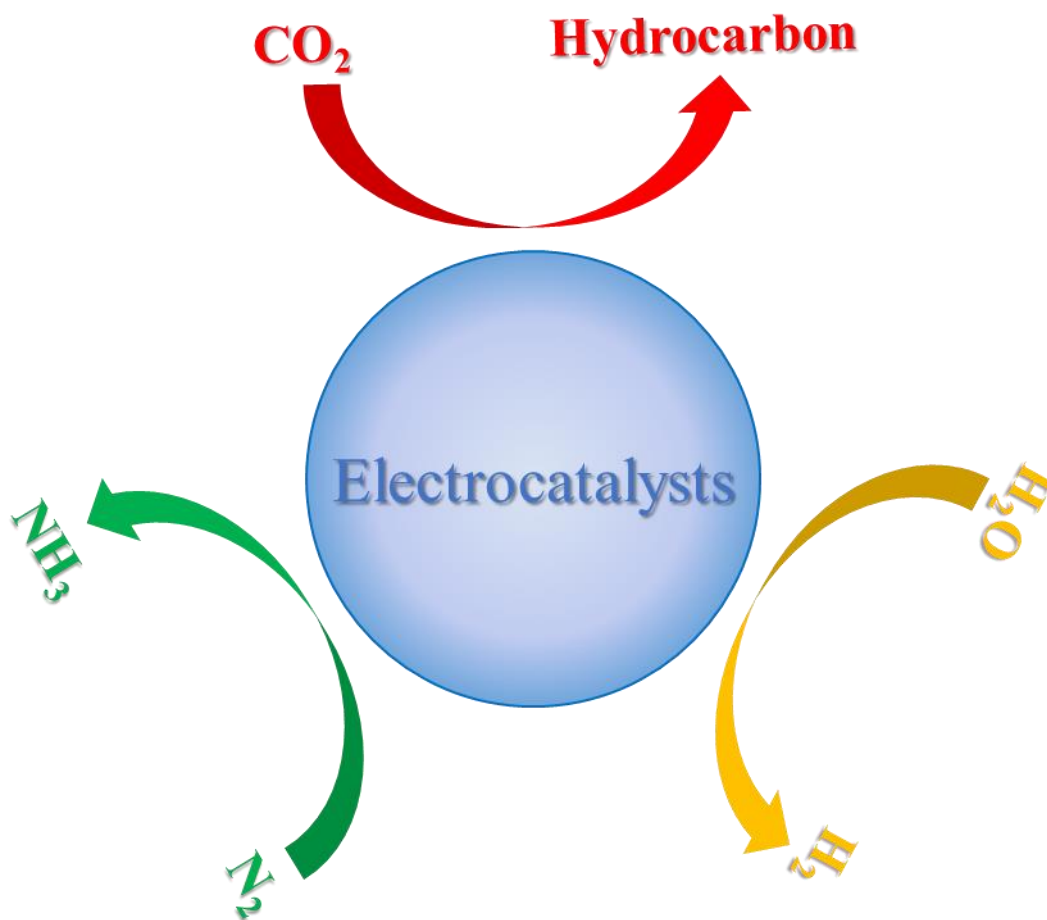


Figure 1.1 Schematic illustration of applications of electrocatalysts.

For instance, in the context of water electrolysis, the HER and OER are critical for the sustainable production of hydrogen—a clean energy carrier with high gravimetric energy density ^[10]. Achieving low overpotentials and high current densities in these reactions necessitates the use of highly active electrocatalysts ^[2]. Similarly, in fuel cells, the slow kinetics of the ORR at the cathode limit the overall efficiency of the device, prompting extensive research into catalysts that can enhance ORR activity ^[11]. The electrochemical reduction of CO_2 to value-added chemicals and fuels presents another grand challenge, where catalyst design decides selectivity, efficiency and stability ^[1].

1.1.3. Limitations of Conventional Bulk Catalysts

Traditional bulk catalysts, typically noble metals, have served as the workhorses of electrocatalysis for decades ^[9, 12]. However, their performance is fundamentally constrained by several intrinsic and extrinsic factors.

Firstly, only a small fraction of the atoms in bulk catalysts are exposed at the surface and accessible as active sites, leading to low atom utilization efficiency ^[13]. This issue is particularly acute for precious metals because of the cost ^[11].

Secondly, the electronic and geometric structures of bulk catalysts are often fixed and difficult to tune, limiting the extent to which their surface properties can be optimized for specific reactions ^[14]. The strong metal-support interactions and coordination environments present in bulk materials can hinder the binding and transformation of reactants and intermediates, restricting catalytic efficiency ^[15]. Furthermore, the lack of precise control over the spatial distribution and chemical identity of active sites impedes the rational design of catalysts with tailored activity and selectivity ^[13].

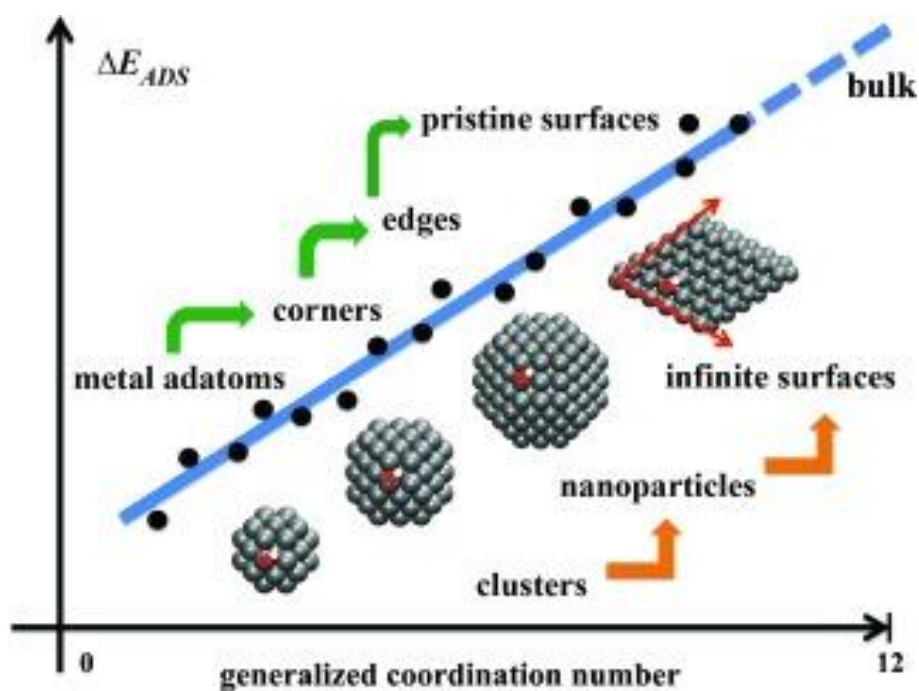


Figure 1.2 The trends in the adsorption energies of oxygen- and hydrogen-containing adsorbates on various platinum nanoparticles and extended surfaces are analyzed ^[15].

(Reproduced with permission from David Loffreda, Philippe Sautet, Juan M. García-Lastra, et al., *Angewandte Chemie International Edition*, 2014, 53(32): p. 8316-8319. Copyright 2025, John Wiley and Sons)

Another major limitation of conventional bulk catalysts is that they tend to undergo structure and composition changes under electrochemical conditions ^[16]. These changes (including dissolution, aggregation, phase transitions, and poisoning by reaction byproducts, etc.) can lead to rapid decline of catalytic performance and shorten device lifetimes ^[17]. For example, platinum-based catalysts in fuel cells are susceptible to sintering and dissolution in acidic environments, while transition metal sulfides may suffer from leaching and oxidation during water splitting ^[18].

Therefore, it is necessary to explore next-generation electrocatalyst to overcome these drawbacks.

1.1.4. Potential of Atomic-Scale Engineering

Recent progress in material science and nanotechnology have enabled the design and synthesis of electrocatalysts in atomic-scale^[2]. Among these, two-dimensional (2D) materials—such as graphene, transition metal dichalcogenides (TMDs), and 2D carbon framework anchored single-atom catalysts—have garnered a lot attention due to their unique structural, electronic, and surface properties^[14, 19, 20]. The atomic thickness and high surface-to-volume ratio of 2D materials facilitate the exposure of a large number of active sites, while their tunable electronic structures allow for precise modulation of catalytic activity^[21].

Atomic-scale engineering encompasses a range of strategies, including the introduction of structural defects, heteroatom doping, strain engineering, and the stability of isolated metal atoms or clusters on suitable supports^[14, 22-25]. These approaches can change the coordination environment, electron's structure and chemical reactivity of electrocatalyst. Thereby, to enhance the activity, selectivity, and durability of electrocatalysts. For example, the creation of edge sites, vacancies, and strain in TMDs such as MoS₂ has been shown to significantly improve HER performance by lowering the hydrogen adsorption free energy^[26]. Similarly, single-atom catalysts—where individual metal atoms are dispersed on 2D supports—exhibit exceptional atom utilization efficiency and can be used for specific reactions through control of the metal-support interaction^[24].

The potential of atomic-scale engineering is beyond simply activity enhance. By selectively tuning the binding energies of key intermediates and optimizing charge transfer processes, it is possible to break traditional scaling relationships and achieve unprecedented catalytic performance ^[27]. Moreover, the integration of multiple functionalities—such as bifunctional or tandem active sites—can enable complex multi-step reactions and improve product selectivity ^[28].

1.2. Key Challenges and Knowledge Gaps

Advancements in atomic-scale catalyst engineering have yielded remarkable progress in the design of materials with enhanced activity, selectivity, and stability for energy conversion reactions such as HER, ORR, and CO₂RR ^[29]. Nonetheless, several challenges block the theory into practice. This section describes three principal challenges: (1) catalytic efficiency constraints, (2) durability and selectivity limitations, and (3) insufficient control of active sites at the atomic scale.

1.2.1. Catalytic Efficiency Constraints

Catalytic efficiency remains a central challenge in the development of advanced electrocatalysts, particularly when the goal is to enable multi-electron transformations under ambient conditions ^[30, 31]. The efficiency of a catalyst is typically quantified in terms of activity metrics such as turnover frequency (TOF), current density at a given overpotential, and Faradaic efficiency for the desired product ^[32]. Despite substantial advances, many state-of-the-art catalysts still require high overpotentials to achieve

practical current densities, especially for reactions involving complex bond rearrangements and the formation of C-C bonds ^[1, 2].

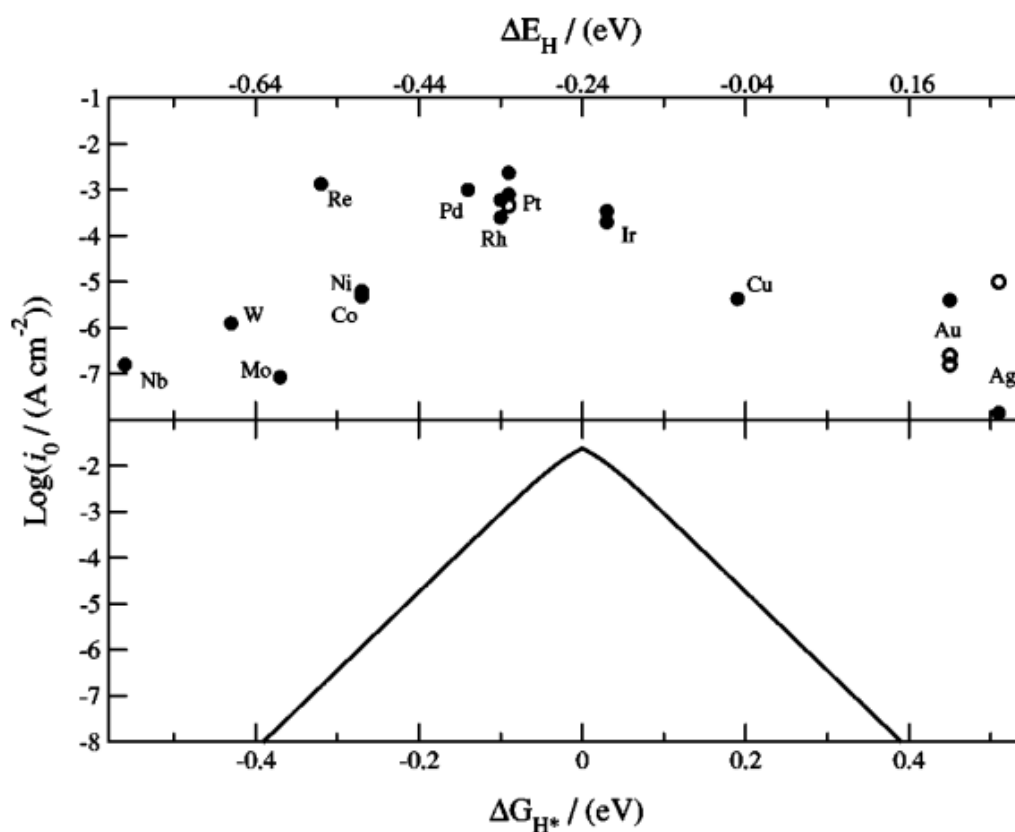


Figure 1.3 (top) Experimentally measured exchange current, $\log(i_0)$, for HER on various metal surfaces, plotted as a function of the calculated hydrogen chemisorption energy per atom, ΔE_H (top axis). Data for single-crystal surfaces are indicated by hollow symbols. (bottom) Result from a simple kinetic model now plotted as a function of the free energy of hydrogen adsorption, $\Delta G_{H^*} = \Delta E_H + 0.24 \text{ eV}$ ^[27]. (Reprinted with permission from Nørskov, J.K., et al., Journal of The Electrochemical Society, 2005. 152(3): p. J23. Copyright 2025, The Electrochemical Society.)

One major source of catalytic inefficiency is the scaling relationship between the adsorption energies of key reaction intermediates on catalyst surfaces ^[33]. For example,

in the case of the ORR and CO₂RR, the Sabatier principle dictates that the binding energies of intermediates must be neither too strong nor too weak to facilitate optimal reaction rates ^[9]. However, for most catalysts, the energetics of different intermediates are correlated, making it difficult to independently tune the binding strength and break the so-called "volcano plot" limitations ^[27, 34]. This results in a trade-off between activity and selectivity, as strong binding may favor certain steps but hinder product desorption, while weak binding may result in poor activation of reactants ^[35].

Furthermore, for multi-carbon product formation, as in the reduction of CO₂ to ethylene or ethanol, the kinetic and thermodynamic requirements are even more strict. Copper-based electrocatalysts remain the only known materials capable of catalyzing the formation of C₂+ products with reasonable efficiency ^[1]. Yet, even with copper, the overall efficiency is affected by high overpotentials, low selectivity, and competitive side reactions (leading to hydrogen evolution or the formation of undesired C₁ products.)^[36, 37].

The challenge of achieving high catalytic efficiency is further compounded by mass transport limitations, especially at high current densities relevant to industrial applications ^[38]. The local concentration of reactants, pH gradients, and bubble formation can all impact the effective availability of active sites and alter reaction pathways ^[39-41]. In addition, catalyst layers must balance electronic conductivity, ionic transport, and mechanical stability, further complicating the optimization of overall device performance ^[42].

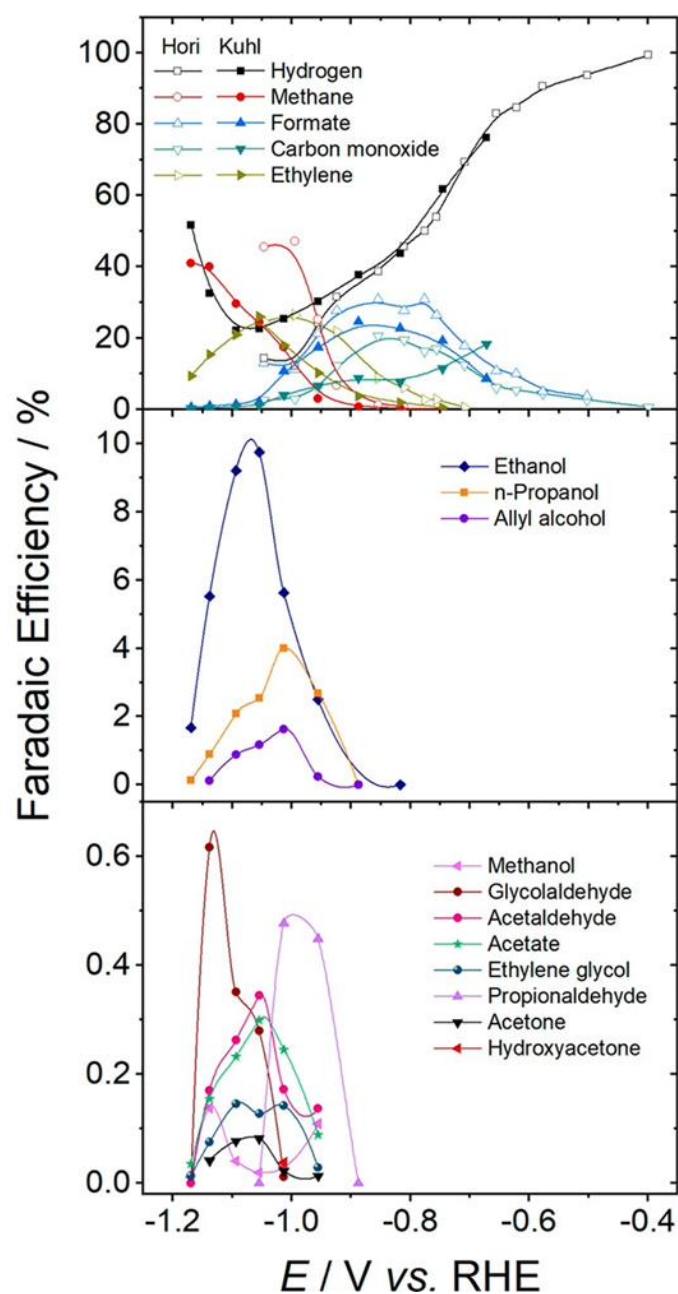


Figure 1.4 CO₂RR activity and selectivity on polycrystalline copper in CO₂-saturated 0.1 M KHCO₃ (pH 6.8). Product Faradaic efficiencies are shown, with data adapted from Hori et al.

^[43] (hollow symbols) and Kuhl et al. ^[8] (filled symbols).^[1] (Open Access)

1.2.2. Durability and Selectivity Limitations

Durability and selectivity are equally critical for the practical deployment of advanced catalysts in electrochemical devices. The operational lifetime of a catalyst is

determined by its resistance to structural degradation, poisoning, sintering, and other deactivation mechanisms under working conditions ^[11, 44, 45]. Selectivity, on the other hand, refers to the ability of a catalyst to preferentially produce the target product over undesired side products, which is particularly important for multi-pathway reactions such as CO₂RR and ORR ^[46, 47].

Durability Challenges

One of the primary durability challenges arises from the dynamic nature of catalyst surfaces under electrochemical conditions ^[48]. Many catalysts, especially those with high surface area or abundant defects, are prone to surface reconstruction, dissolution, or aggregation during operation ^[49]. For example, SACs, while offering exceptional atom utilization and unique electronic properties, can suffer from atom migration and aggregation, especially under high current densities or in the presence of aggressive adsorbates ^[29]. This leads to a loss of active sites and a gradual decline in catalytic performance over time.

In the case of copper-based catalysts, which are widely studied for CO₂RR, the surface can undergo significant restructuring, resulting in the formation of new active sites or the loss of previously engineered ensembles ^[50]. Moreover, the accumulation of reaction intermediates or products can result in poisoning or blockage of active sites, further reducing durability ^[51]. The stability of supports, especially for 2D materials or carbon-based substrates, is also a concern, as oxidation or hydrogenation can degrade their structural integrity and disrupt the metal-support interaction critical for maintaining atomic dispersion ^[52].

Selectivity Limitations

Selectivity is a challenge with many aspects, especially for reactions where multiple products are thermodynamically or kinetically accessible. For instance, in CO₂RR, the formation of C₁ products such as CO, CH₄, or formate often competes with the formation of C₂⁺ products like ethylene (C₂H₄) or ethanol (C₂H₅OH) [53]. The simultaneous thermodynamic feasibility and kinetic accessibility of these various reaction pathways result in intense competition at the catalyst surface, making high selectivity toward a single desirable product extremely difficult to achieve [1, 8, 43].

Several interrelated factors govern the selectivity of CO₂RR. The atomic structure and composition of active sites play a fundamental role in determining the binding strength of key reaction intermediates, which in turn influence the reaction pathways that are favored under given conditions [54, 55]. In addition, the local reaction environment further modulates selectivity; parameters such as pH, electrolyte identity, and concentration can affect the stability of intermediates and the migration of ions at the electrochemical interface [53].

Moreover, selectivity is highly sensitive to the applied potential, with different products favored at different electrode potentials due to the varying energetics of competing elementary steps^[1]. Finally, surface reconstruction, adsorption of spectator species, or changes in oxidation state can all lead to fluctuations in the nature and distribution of active sites [56, 57].

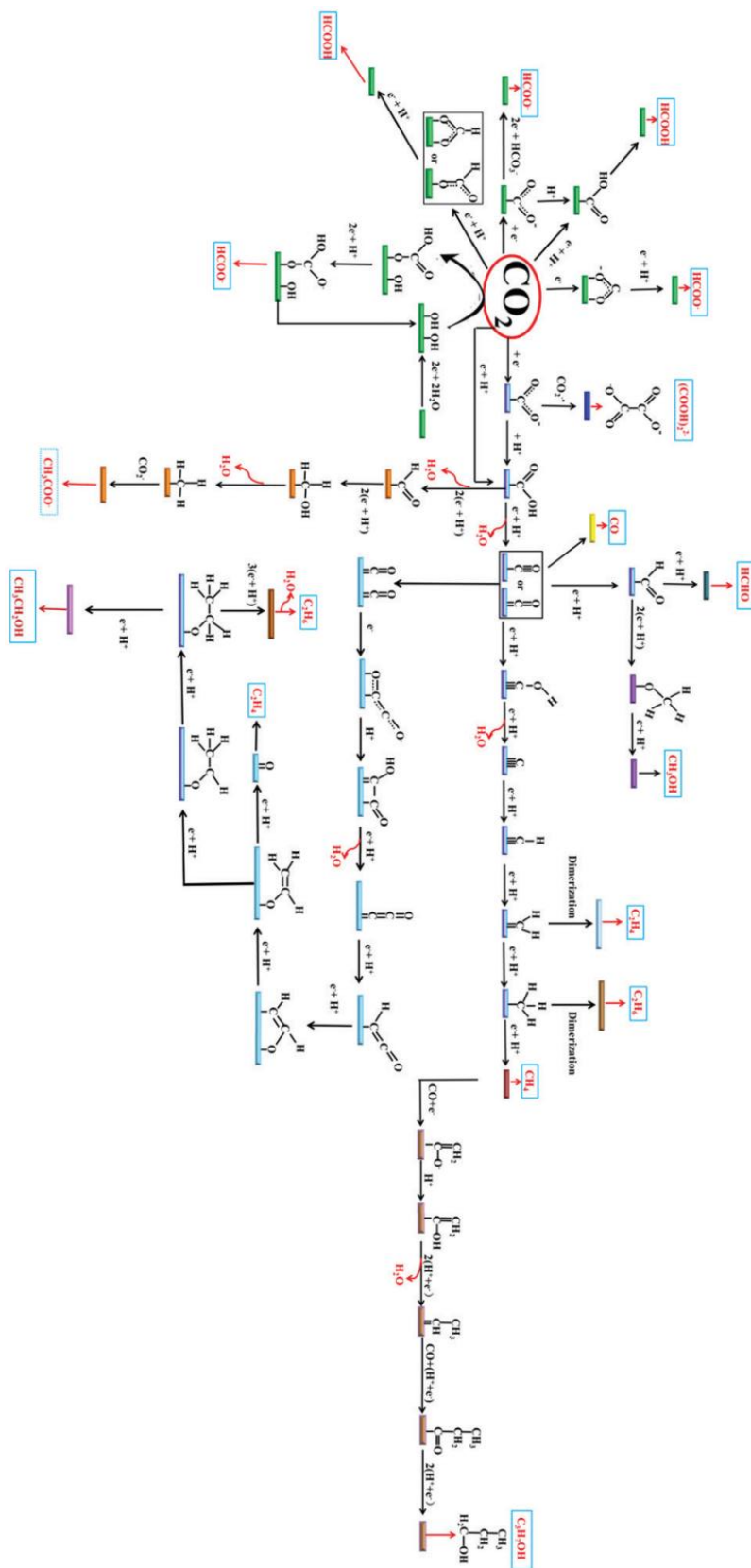


Figure 1.5 The possible reaction roadmap of CO₂ ^[53]. (Reproduced from ^[53] with permission

from the Royal Society of Chemistry. Copyright 2025.)

1.2.3. Insufficient Control of Active Sites at the Atomic Scale

Another fundamental challenge in the field of catalyst development is the insufficient control over the active sites (such as property, distribution, and dynamics of at the atomic scale). The concept of the “active site” has evolved from simple notions of exposed metal atoms to encompass a rich diversity of atomic ensembles, coordination environments, and interface structures, particularly in heterogeneous and nanostructured catalysts [58, 59].

Identifying and quantifying the true active sites responsible for catalytic activity is a persistent challenge. Many catalysts, especially those based on nanoparticles, possess a distribution of surface atoms, steps, edges, and defects, each with distinct catalytic properties [60-62]. Even in seemingly uniform systems such as SACs or atomically dispersed metal catalysts on 2D supports, it is often difficult to confirm the atomic configuration and coordination environment of active sites under actual reaction conditions [63]. In situ and operando spectroscopies, such as X-ray absorption or Raman spectroscopy, have provided valuable insights into the nature of active sites and their evolution during catalysis, but a comprehensive understanding of the structure–function relationship is still lacking [64, 65]. Moreover, scaling up selective catalysts from model systems to practical devices often results in reduced performance due to mass transport limitations, electrode architecture, or catalyst inhomogeneity [42].

1.3. Recent Advances in Material Engineering

In the past decade, with the help of atomic-level characterization and computational modeling, the design of catalytic materials has undergone a major change. Material engineering strategies now enable the deliberate manipulation of structure, composition, and local environment at the atomic or molecular level, yielding catalysts with unprecedented activity, selectivity, and stability for diverse energy conversion reactions. Among the most impactful approaches are (1) structural modifications of catalyst surfaces, (2) species-specific loading engineering, and (3) geminal atom site engineering.

1.3.1. Structural Modifications

Structural modifications include a broad range of strategies: tailoring the atomic arrangement, surface morphology, defect landscape and electron's structure of catalysts, etc. They can be applied at different scales, and confirmed to have great impact on catalytic performance.

(1) Atomic and Nanoscale Defects

One of the most effective ways to enhance catalytic activity is through the deliberate introduction of defects, such as vacancies, dislocations, grain boundaries, and edge sites. Defects can serve as active sites by altering the local coordination environment, modulating electronic structure, and facilitating the adsorption and activation of reactants ^[66]. For instance, in TMDs such as MoS₂, creation of sulfur vacancies and edge sites dramatically increases HER activity by exposing catalytically

active motifs that are otherwise inert in the basal plane^[20]. Similarly, oxygen vacancies in metal oxides and chalcogenides are known to improve both HER and OER performance by tuning adsorption energies and enhancing charge transfer^[2].

(2) Facet and Morphology Engineering

The exposure of specific crystallographic facets is another powerful approach for tuning catalytic properties. Different facets exhibit distinct atomic arrangements and electron's structures, which influence the binding strength of intermediates. For example, on copper catalysts for CO₂RR, the (100) facet is more selective for C₂⁺ products due to its ability to stabilize key intermediates involved in C–C coupling, whereas the (111) facet favors the formation of methane^[1, 43, 67]. Rossi et al. tailored the morphology of nanoparticles to reveal how precise control of Cu catalyst shape and size enhances CO₂ reduction selectivity^[68]. Nanostructuring at the mesoscale, including the fabrication of hollow structures, nanoframes, or porous architectures, can further enhance performance by increasing the density of active sites, facilitating mass transport, and improving catalyst durability^[69]. Wang et al. crafted cage-in-cage hollow porous carbon codoped with Co and N via ZIF-triggered polydopamine polymerization, yielding highly efficient bifunctional electrocatalysts for ORR and OER applications^[70].

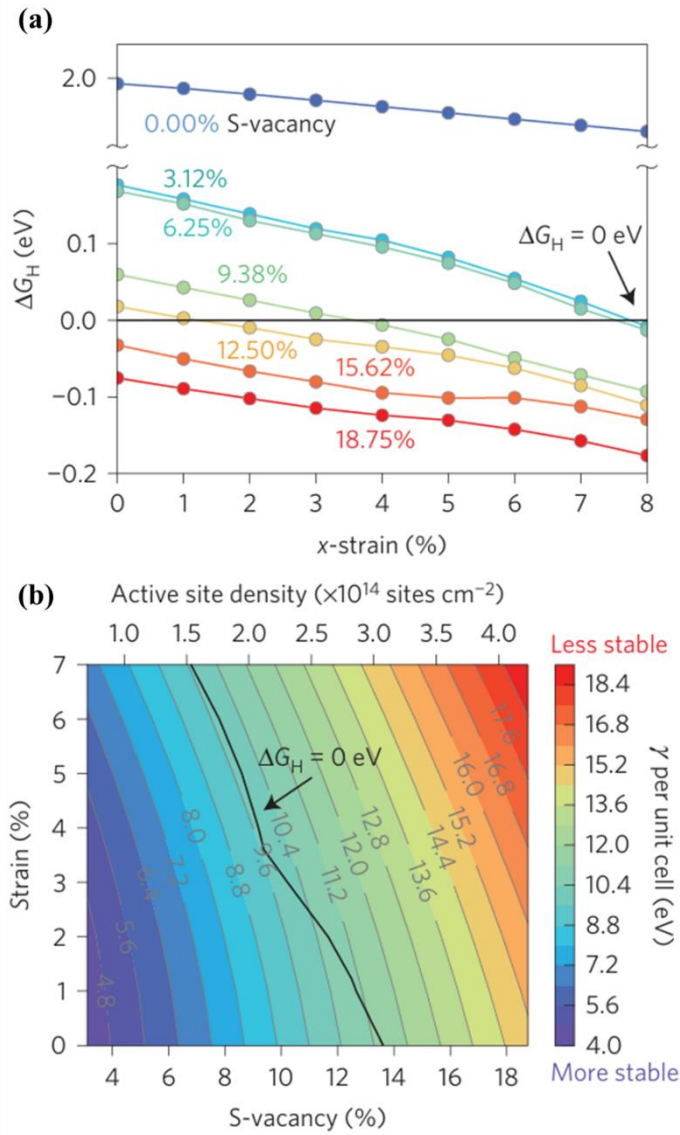


Figure 1.6 Theoretical calculations for the effects of S-vacancies and strain on the HER activity of MoS₂. (a) ΔG_H versus %x-strain for various %S-vacancy, ranging from 0.0% (pristine) to 18.75%. (b) Coloured contour plot of surface energy per unit cell γ (with respect to the bulk MoS₂) as a function of S-vacancy and uniaxial strain. Colour bar represents the value of γ . The black lines in a and b indicate combinations of S-vacancy and strain that yield $\Delta G_H = 0$ eV, the optimal thermodynamic requirement for HER activity^[74]. (Reproduced with permission from Hong Li et al Nat Mater, 2016. 15(1): p. 48-53. Copyright 2025, Springer

Nature)

(3) Strain Engineering

Applying lattice strain to catalytic materials provides a means of modulating their electronic properties without altering chemical composition. Strain alters the *d*-band center, thereby tuning the adsorption energies of key intermediates ^[71]. For example, compressive strain in Pt-based catalysts has been shown to enhance ORR activity by weakening the binding of oxygenated species, reducing overpotential and improving durability ^[72]. Guo et al. synthesized curved ultrathin PtPd with long-range compressive strain, demonstrating that such strain modulates active sites, lowers *d*-band centers, and boosts HER and methanol oxidation reaction activities ^[73]. In TMDs, local strain fields generated by curvature or heterointerfaces can activate otherwise inert basal planes for HER ^[74, 75]. Owing to strain effects, Gao et al. achieved enhanced HER activity in Co, Ni-co-doped MoTe₂ nanofilms with stabilized metallic 1T' phase ^[76].

(4) Heterostructure and Interface Engineering

Creating heterostructures by combining two or more materials at the nanoscale can give rise to synergistic effects, such as charge transfer across interfaces and formation of new active sites ^[77]. For instance, integrating metal nanoparticles with conductive carbon supports or 2D materials can facilitate electron transfer and prevent catalyst agglomeration ^[78, 79]. The interface between catalytically active and inactive phases can also serve as a unique site for reactant activation or product desorption. Li et al. designed molecule–metal catalyst interfaces on copper to create a CO-rich environment, promoting C-C coupling and enhancing the efficiency of CO₂-to-ethanol conversion. ^[80]

1.3.2. Species-Specific Loading Engineering

Species-specific loading engineering refers to the deliberate incorporation and spatial arrangement of distinct atomic or molecular species—typically metal atoms or dopants—onto a catalytic support. This strategy enables to create of well-defined, isolated active sites with tailored coordination environments, electron's structures, and functions.

A prime example of this strategy is found in SACs, which are consisted of individual metal atoms dispersed on substrates such as graphene, metal oxides, or other 2D materials. In SACs, each atom acts as an isolated active site, offering high atomic efficiency and unique opportunities for tuning catalytic properties ^[29]. A key advantage of SACs lies in their tunable local environment. For example, Fe-N₄ and Co-N₄ sites embedded in graphene or carbon nanotubes have demonstrated outstanding performance in ORR and HER, attributed to the optimal binding of reaction intermediates and the suppression of side reactions ^[81, 82]. Recent advances have extended the concept of SACs to dual-atom and multi-atom ensembles, where two or more distinct metal atoms are co-anchored in close position ^[83, 84]. These SACs exhibit synergistic effects among anchored atoms; for instance, dual-atom sites have been shown to promote C-C coupling in CO₂RR, enabling the formation of C₂⁺ products with higher selectivity compared to single-metal sites ^[85, 86].

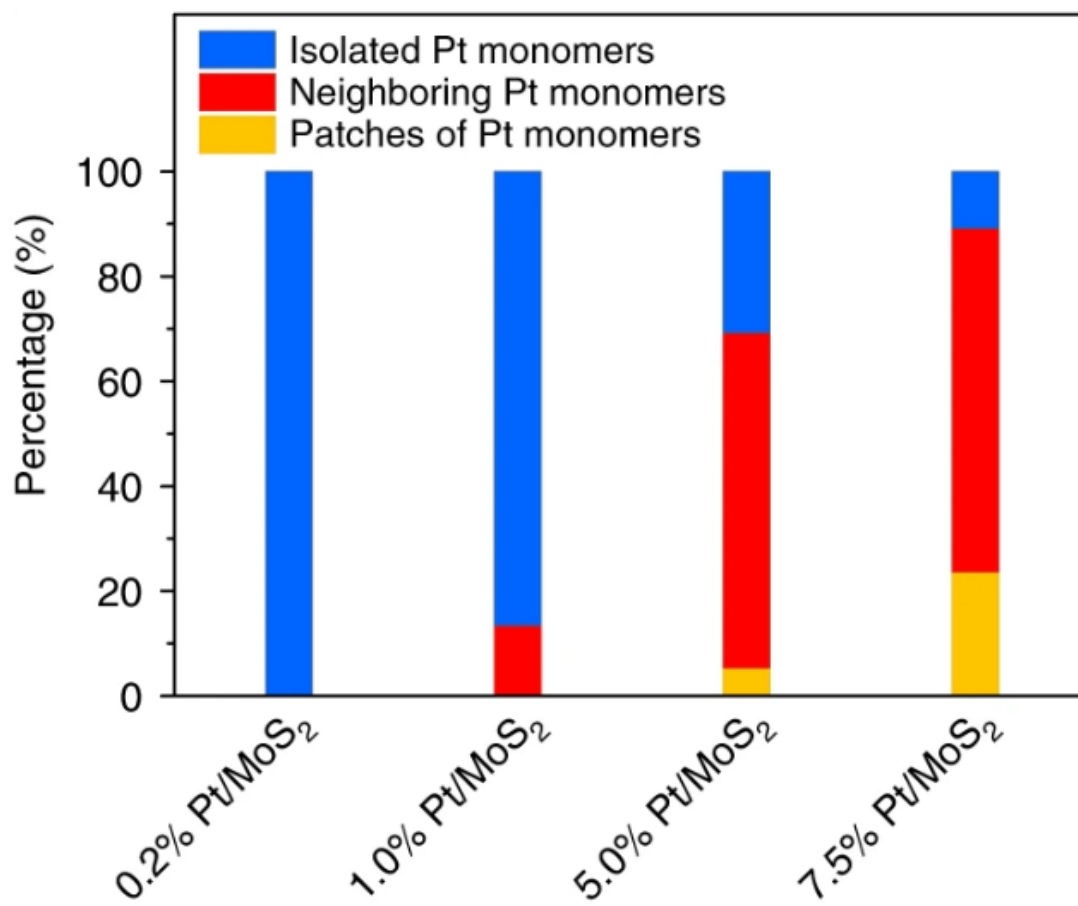


Figure 1.7 The content histogram of isolated Pt monomers, neighboring Pt monomers, and patches of Pt monomers for atomically dispersed Pt/MoS₂ with different Pt loadings^[84].

(Reproduced with permission from Dingsheng Wang, Runze Li. *Advanced Energy Materials*, 2022. 12(9): p. 2103564. Copyright 2025, John Wiley and Sons)

The loading density and spatial arrangement of active species critically determine catalyst performance. Too high a loading can lead to aggregation and loss of atomic dispersion, while too low a loading may result in insufficient active site density^[87]. Strategies to control loading include the use of anchoring sites, confinement within porous supports, and surface functionalization to direct metal precursor binding^[78].

1.3.3. Geminal Atom Site Engineering

Geminal atom site engineering refers to the construction of catalyst architectures featuring two adjacent atomic sites—commonly termed “dual-atom” or “dimer” catalysts—anchored on a support. These geminal sites can be homonuclear (same element) or heteronuclear (different elements), and their proximity enables cooperative effects that are inaccessible to isolated single-atom sites.

The rationale behind geminal atom site engineering stems from the recognition that many important catalytic transformations, such as C-C or C-N bond formation, require the simultaneous activation of multiple reactants or the stability of key multidentate intermediates [83, 88]. Dual-atom sites provide adjacent active sites with different electronic properties, which can enable cooperative catalyze and facilitate multi-step reaction mechanisms. Yang et al. developed a MOF with less-coordinated copper dimers, achieving high efficiency for C₂ products by stabilizing key intermediates and promoting efficient C-C coupling in CO₂RR [89].

Recent studies show that both homonuclear and heteronuclear geminal atom sites can promote catalyst's performance. Homonuclear dimers often exhibit enhanced activity for transformations involving the activation of two identical reactants or the formation of symmetric intermediates: Hai et al. developed heterogeneous geminal-atom catalysts with paired Cu sites on polymeric carbon nitride (PCN), enabling dynamic cooperative Cu-Cu bonding for efficient, selective C-C cross-couplings in organic synthesis, overcoming limitations of single-atom catalysts [90]; Zhang et al. systematically investigated homonuclear dual-atom catalysts for nitric oxide reduction,

identifying $\text{Ti}_2\text{-N}_6$ as a highly selective, low-voltage catalyst that delivers enhanced catalytic performance and stability compared to single-atom catalysts ^[91]. In contrast, heteronuclear dimers can introduce asymmetric electronic environments, enabling selective activation of complex substrates and multi-step reaction pathways: Du et al. designed a dimer Co-In catalyst, where O-affinitive In optimizes OOH adsorption on Co, promoting efficient two-electron oxygen reduction to H_2O_2 in acid ^[92]; Wang et al. designed selenium-based heteronuclear dimmer catalysts, notably SeFe sites, which enhance charge polarization and lower energy barriers, achieving superior alkaline ORR activity through synergistic interactions and co-adsorption mechanisms ^[93].

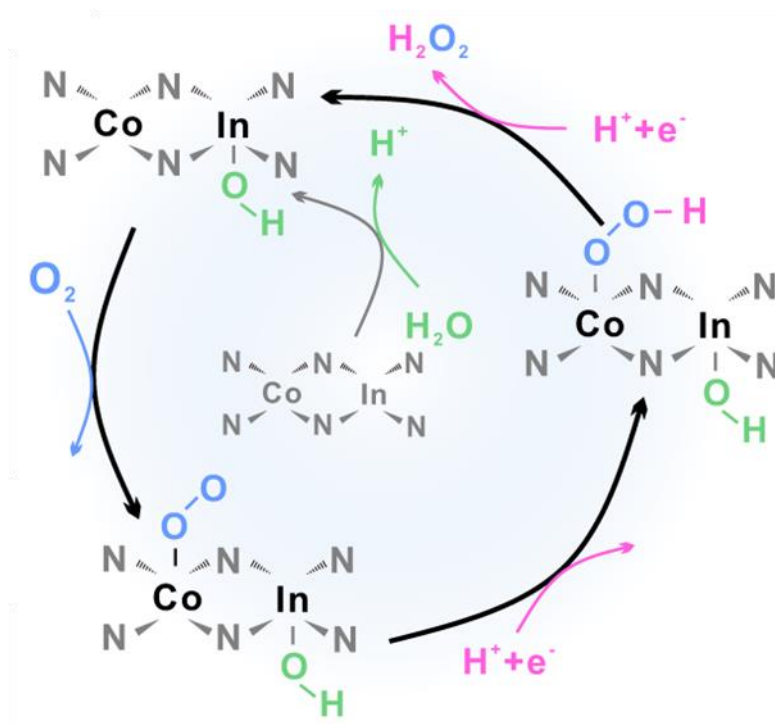


Figure 1.8 Illustration of the proposed 2e-ORR mechanism on CoIn-N-C ^[92]. (Open access)

1.4. Motivation and Research Objectives of This Thesis

Motivated by the urgent need for cost-effective, efficient, and durable electrocatalysts for sustainable energy technologies, this thesis aims to advance the understanding and application of atomic-scale engineering in two-dimensional materials for enhanced electrocatalytic reactions. The previous sections have discussed both the limitations of conventional catalysts and the potential of atomic-scale engineered catalysts. However, there are still several important research gaps—how structure features, the environments of active sites, and the cooperation between geminal atoms affect catalytic performance.

In order to fill these gaps, the following research objectives are proposed:

(1) Investigating Curvature Effects on Hydrogen Evolution Performance in Two-Dimensional Curved MoS₂

While pristine, planar MoS₂ is generally considered catalytically inert toward HER, it is well-established that the introduction of structural defects and strain can activate its basal planes and enhance catalytic performance ^[74]. More recently, both theoretical and experimental studies have demonstrated that imparting curvature to MoS₂ nanosheets can further modulate their electronic structure, alter carrier mobility, and potentially generate new active sites ^[94]. Similar curvature-induced enhancements in HER activity have also been observed in other 2D materials, such as waved graphene ^[95]. Despite these promising findings, a systematic understanding of how controlled curvature affects the HER activity of MoS₂ remains lacking. This thesis systematically

studies the relationship between curvature and HER performance in MoS₂ nanosheets, and identifies strategies for optimizing HER performance.

(2) Assessing Species-Specific Loading Effects on Oxygen Reduction Activity in Heteronuclear Single-Atom Catalysts

SACs have emerged as a new class of materials with unparalleled atom efficiency and tunable catalytic properties ^[14]. In particular, the incorporation of heteronuclear single atoms into 2D supports offers a platform for synergistic interactions and multi-site catalysis, such as FeN₄-C and CoN₄-C systems ^[81, 96]. Despite significant progress in the synthesis and characterization of these materials, the effect of species-specific loading on ORR activity remains inadequately understood ^[82, 97, 98]. This thesis calculates the heteronuclear SACs on graphene substrates, and establishes correlations between loading effect and catalytic performance.

(3) Enhancing Carbon Reduction via Twin Copper Sites in Diatomic Two-Dimensional Materials

The electrochemical reduction of CO to valuable products, such as hydrocarbons and alcohols, is a promising route for carbon recycling and energy storage ^[99]. Copper-based catalysts are among the few materials capable of catalyzing the formation of multi-carbon products, but their selectivity and efficiency remain suboptimal ^[43]. Recent studies have indicated that introducing well-defined atomic ensembles, such as twin copper sites on 2D materials can dramatically influence product distribution by C-C coupling ^[90]. This thesis explores carbon reduction reaction on geminal copper sites

embedded in PCN, and focus on understanding how coordination environment affects the selectivity of C₂ products.

Through these objectives, this thesis endeavors to provide mechanistic insights for the atomic-scale engineering electrocatalysts.

1.5. Thesis Structure

This thesis is organized into six chapters, each systematically addressing key aspects of atomic-scale engineering and mechanistic insights for next-generation electrocatalysts. The overall structure is designed to build logically: first is background and research gaps; second is computational methodology; then is results and discussion; and final is conclusion and future works.

Chapter 1 provides the background and motivation for this work. We summarize the current state of research in electrocatalysis, identify key challenges and knowledge gaps, and outline recent progress on engineering in the atomic-scale. The objectives and the outline of the thesis are stated.

Chapter 2 provides introduction to the density functional theory (DFT) framework in detail. We illustrate both theory and application.

Chapter 3 investigates the impact of structural modifications—especial curvature engineering—on the HER performance of representative 2D MoS₂. Relationships between structure and activity are explored by DFT calculations.

Chapter 4 focuses on the design and computational characterization of species-specific loaded catalysts, especial Fe-Co single-atom sites on graphene supports.

Systematically explored the influence of atomic identity, coordination environment, and loading density on ORR activity.

Chapter 5 analyzes geminal atom site engineering in 2D materials, exploring the cooperative effects of geminal Cu on PCN and its contribution to enhanced CORR activity and selectivity to C₂ products.

Chapter 6 summarized the main conclusions and provided an outlook for future work.

References

1. Nitopi, S., et al., *Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte*. Chemical Reviews, 2019. **119**(12): p. 7610-7672.
2. Seh, Z.W., et al., *Combining theory and experiment in electrocatalysis: Insights into materials design*. Science, 2017. **355**(6321): p. eaad4998.
3. Lewis, N.S. and D.G. Nocera, *Powering the planet: Chemical challenges in solar energy utilization*. Proceedings of the National Academy of Sciences, 2006. **103**(43): p. 15729-15735.
4. Chu, S. and A. Majumdar, *Opportunities and challenges for a sustainable energy future*. nature, 2012. **488**(7411): p. 294-303.
5. McCrory, C.C., et al., *Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction*. Journal of the American Chemical Society, 2013. **135**(45): p. 16977-16987.
6. Jiao, Y., et al., *Design of electrocatalysts for oxygen-and hydrogen-involving energy conversion reactions*. Chemical Society Reviews, 2015. **44**(8): p. 2060-2086.
7. Nørskov, J.K., et al., *Origin of the overpotential for oxygen reduction at a fuel-cell cathode*. The Journal of Physical Chemistry B, 2004. **108**(46): p. 17886-17892.
8. Kuhl, K.P., et al., *New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces*. Energy & Environmental Science, 2012. **5**(5): p. 7050-7059.
9. Bard, A.J., L.R. Faulkner, and H.S. White, *Electrochemical methods: fundamentals and applications*. 2022: John Wiley & Sons.
10. Turner, J.A., *Sustainable hydrogen production*. Science, 2004. **305**(5686): p. 972-974.
11. Gasteiger, H.A., et al., *Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs*. Applied Catalysis B: Environmental, 2005. **56**(1-2): p. 9-35.
12. Trasatti, S., *Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions*. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1972. **39**(1): p. 163-184.
13. Liu, J., *Catalysis by supported single metal atoms*. Acs Catalysis, 2017. **7**(1): p. 34-59.
14. Yang, X.-F., et al., *Single-atom catalysts: a new frontier in heterogeneous catalysis*. Accounts of chemical research, 2013. **46**(8): p. 1740-1748.

15. Calle-Vallejo, F., et al., *Fast prediction of adsorption properties for platinum nanocatalysts with generalized coordination numbers*. *Angewandte Chemie International Edition*, 2014. **53**(32): p. 8316-8319.
16. Debe, M.K., *Electrocatalyst approaches and challenges for automotive fuel cells*. *Nature*, 2012. **486**(7401): p. 43-51.
17. Borup, R., et al., *Scientific aspects of polymer electrolyte fuel cell durability and degradation*. *Chemical reviews*, 2007. **107**(10): p. 3904-3951.
18. Cherevko, S., N. Kulyk, and K.J. Mayrhofer, *Durability of platinum-based fuel cell electrocatalysts: Dissolution of bulk and nanoscale platinum*. *Nano energy*, 2016. **29**: p. 275-298.
19. Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. *science*, 2004. **306**(5696): p. 666-669.
20. Chhowalla, M., et al., *The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets*. *Nature chemistry*, 2013. **5**(4): p. 263-275.
21. Voiry, D., A. Mohite, and M. Chhowalla, *Phase engineering of transition metal dichalcogenides*. *Chemical Society Reviews*, 2015. **44**(9): p. 2702-2712.
22. Jia, Y., et al., *The role of defect sites in nanomaterials for electrocatalytic energy conversion*. *Chem*, 2019. **5**(6): p. 1371-1397.
23. Zhang, J. and L. Dai, *Heteroatom-doped graphitic carbon catalysts for efficient electrocatalysis of oxygen reduction reaction*. *Acs Catalysis*, 2015. **5**(12): p. 7244-7253.
24. Qiao, B., et al., *Single-atom catalysis of CO oxidation using Pt1/FeO x*. *Nature chemistry*, 2011. **3**(8): p. 634-641.
25. Feng, J., et al., *Strain-engineered artificial atom as a broad-spectrum solar energy funnel*. *Nature Photonics*, 2012. **6**(12): p. 866-872.
26. Jaramillo, T.F., et al., *Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts*. *science*, 2007. **317**(5834): p. 100-102.
27. Nørskov, J.K., et al., *Trends in the exchange current for hydrogen evolution*. *Journal of The Electrochemical Society*, 2005. **152**(3): p. J23.
28. Quan, L., et al., *Bifunctional electrocatalysts for overall and hybrid water splitting*. *Chemical Reviews*, 2024. **124**(7): p. 3694-3812.
29. Liu, M., et al., *Atomically dispersed metal catalysts for the oxygen reduction reaction: synthesis, characterization, reaction mechanisms and electrochemical energy applications*. *Energy & Environmental Science*, 2019. **12**(10): p. 2890-2923.

30. Wang, J., et al., *Non-noble metal-based carbon composites in hydrogen evolution reaction: fundamentals to applications*. Advanced materials, 2017. **29**(14): p. 1605838.
31. Zheng, Y., et al., *The hydrogen evolution reaction in alkaline solution: from theory, single crystal models, to practical electrocatalysts*. Angewandte Chemie International Edition, 2018. **57**(26): p. 7568-7579.
32. Zhang, B., et al., *Homogeneously dispersed multimetal oxygen-evolving catalysts*. Science, 2016. **352**(6283): p. 333-337.
33. Cuenya, B.R. and F. Behafarid, *Nanocatalysis: size-and shape-dependent chemisorption and catalytic reactivity*. Surface Science Reports, 2015. **70**(2): p. 135-187.
34. Bligaard, T., et al., *The Brønsted–Evans–Polanyi relation and the volcano curve in heterogeneous catalysis*. Journal of catalysis, 2004. **224**(1): p. 206-217.
35. Peterson, A.A., et al., *How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels*. Energy & Environmental Science, 2010. **3**(9).
36. Jouny, M., W. Luc, and F. Jiao, *General techno-economic analysis of CO₂ electrolysis systems*. Industrial & Engineering Chemistry Research, 2018. **57**(6): p. 2165-2177.
37. Li, C.W. and M.W. Kanan, *CO₂ reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films*. Journal of the American Chemical Society, 2012. **134**(17): p. 7231-7234.
38. Clark, E.L., et al., *Standards and protocols for data acquisition and reporting for studies of the electrochemical reduction of carbon dioxide*. Acs Catalysis, 2018. **8**(7): p. 6560-6570.
39. Subbaraman, R., et al., *Enhancing hydrogen evolution activity in water splitting by tailoring Li⁺-Ni (OH) 2-Pt interfaces*. Science, 2011. **334**(6060): p. 1256-1260.
40. Sheng, W., H.A. Gasteiger, and Y. Shao-Horn, *Hydrogen oxidation and evolution reaction kinetics on platinum: acid vs alkaline electrolytes*. Journal of The Electrochemical Society, 2010. **157**(11): p. B1529.
41. Raciti, D., M. Mao, and C. Wang, *Mass transport modelling for the electroreduction of CO₂ on Cu nanowires*. Nanotechnology, 2017. **29**(4): p. 044001.
42. Burdyny, T. and W.A. Smith, *CO₂ reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions*. Energy & Environmental Science, 2019. **12**(5): p. 1442-1453.
43. Hori, Y., *Electrochemical CO₂ reduction on metal electrodes*. Modern aspects of electrochemistry, 2008: p. 89-189.

44. Rabis, A., P. Rodriguez, and T.J. Schmidt, *Electrocatalysis for polymer electrolyte fuel cells: recent achievements and future challenges*. *Acs Catalysis*, 2012. **2**(5): p. 864-890.
45. De Luna, P., et al., *What would it take for renewably powered electrosynthesis to displace petrochemical processes?* *Science*, 2019. **364**(6438): p. eaav3506.
46. Chen, Y., C.W. Li, and M.W. Kanan, *Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles*. *Journal of the American Chemical Society*, 2012. **134**(49): p. 19969-19972.
47. Kulkarni, A., et al., *Understanding catalytic activity trends in the oxygen reduction reaction*. *Chemical reviews*, 2018. **118**(5): p. 2302-2312.
48. Rao, R.R., et al., *Operando identification of site-dependent water oxidation activity on ruthenium dioxide single-crystal surfaces*. *Nature Catalysis*, 2020. **3**(6): p. 516-525.
49. Zhang, L., et al., *Direct observation of dynamic bond evolution in single-atom Pt/C₃N₄ catalysts*. *Angewandte Chemie*, 2020. **132**(15): p. 6283-6288.
50. Favaro, M., et al., *Subsurface oxide plays a critical role in CO₂ activation by Cu (111) surfaces to form chemisorbed CO₂, the first step in reduction of CO₂*. *Proceedings of the National Academy of Sciences*, 2017. **114**(26): p. 6706-6711.
51. Resasco, J., et al., *Promoter effects of alkali metal cations on the electrochemical reduction of carbon dioxide*. *Journal of the American Chemical Society*, 2017. **139**(32): p. 11277-11287.
52. Voiry, D., et al., *Low-dimensional catalysts for hydrogen evolution and CO₂ reduction*. *Nature Reviews Chemistry*, 2018. **2**(1): p. 0105.
53. Wang, G., et al., *Electrocatalysis for CO₂ conversion: from fundamentals to value-added products*. *Chemical Society Reviews*, 2021. **50**(8): p. 4993-5061.
54. Wang, L., et al., *Electrochemical carbon monoxide reduction on polycrystalline copper: effects of potential, pressure, and pH on selectivity toward multicarbon and oxygenated products*. *Acs Catalysis*, 2018. **8**(8): p. 7445-7454.
55. Koper, M.T., *Theory of multiple proton–electron transfer reactions and its implications for electrocatalysis*. *Chemical science*, 2013. **4**(7): p. 2710-2723.
56. Kou, Z., et al., *Dynamic surface chemistry of catalysts in oxygen evolution reaction*. *Small Science*, 2021. **1**(7): p. 2100011.
57. Lai, W., et al., *Dynamic evolution of active sites in electrocatalytic CO₂ reduction reaction: fundamental understanding and recent progress*. *Advanced Functional Materials*, 2022. **32**(16): p. 2111193.
58. Shao, M., et al., *Recent advances in electrocatalysts for oxygen reduction reaction*. *Chemical reviews*, 2016. **116**(6): p. 3594-3657.

59. Christopher, P., H. Xin, and S. Linic, *Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures*. Nature chemistry, 2011. **3**(6): p. 467-472.
60. Zambelli, T., et al., *Identification of the "active sites" of a surface-catalyzed reaction*. Science, 1996. **273**(5282): p. 1688-1690.
61. Li, Y. and G.A. Somorjai, *Nanoscale advances in catalysis and energy applications*. Nano letters, 2010. **10**(7): p. 2289-2295.
62. Stamenkovic, V.R., et al., *Improved oxygen reduction activity on Pt₃Ni (111) via increased surface site availability*. science, 2007. **315**(5811): p. 493-497.
63. Wang, Y., et al., *Advanced electrocatalysts with single-metal-atom active sites*. Chemical reviews, 2020. **120**(21): p. 12217-12314.
64. Li, X., et al., *In situ/operando characterization techniques to probe the electrochemical reactions for energy conversion*. Small Methods, 2018. **2**(6): p. 1700395.
65. Timoshenko, J. and B. Roldan Cuenya, *In situ/operando electrocatalyst characterization by X-ray absorption spectroscopy*. Chemical reviews, 2020. **121**(2): p. 882-961.
66. Wu, X., et al., *Recent advances on transition metal dichalcogenides for electrochemical energy conversion*. Advanced Materials, 2021. **33**(38): p. 2008376.
67. Jiang, K., et al., *Metal ion cycling of Cu foil for selective C–C coupling in electrochemical CO₂ reduction*. Nature Catalysis, 2018. **1**(2): p. 111-119.
68. Rossi, K. and R. Buonsanti, *Shaping copper nanocatalysts to steer selectivity in the electrochemical CO₂ reduction reaction*. Accounts of Chemical Research, 2022. **55**(5): p. 629-637.
69. Li, X., et al., *Nanostructured catalysts for electrochemical water splitting: current state and prospects*. Journal of Materials Chemistry A, 2016. **4**(31): p. 11973-12000.
70. Wang, T., et al., *A ZIF-triggered rapid polymerization of dopamine renders Co/N-codoped cage-in-cage porous carbon for highly efficient oxygen reduction and evolution*. Nano Energy, 2021. **79**: p. 105487.
71. Strasser, P., et al., *Lattice-strain control of the activity in dealloyed core–shell fuel cell catalysts*. Nature chemistry, 2010. **2**(6): p. 454-460.
72. Huang, X., et al., *A rational design of carbon-supported dispersive Pt-based octahedra as efficient oxygen reduction reaction catalysts*. Energy & Environmental Science, 2014. **7**(9): p. 2957-2962.

73. Guo, K., et al., *Functional surfactant-induced long-range compressive strain in curved ultrathin nanodendrites boosts electrocatalysis*. Nano Letters, 2023. **23**(3): p. 1085-1092.
74. Li, H., et al., *Activating and optimizing MoS₂ basal planes for hydrogen evolution through the formation of strained sulphur vacancies*. Nat Mater, 2016. **15**(1): p. 48-53.
75. Tan, Y., et al., *Monolayer MoS₂ films supported by 3D nanoporous metals for high-efficiency electrocatalytic hydrogen production*. Advanced Materials (Deerfield Beach, Fla.), 2014. **26**(47): p. 8023-8028.
76. Gao, B., et al., *Electron strain-driven phase transformation in transition-metal-co doped MoTe₂ for electrocatalytic hydrogen evolution*. Chemical Engineering Journal, 2022. **433**: p. 133768.
77. Zhang, Z., et al., *Heterostructure engineering of 2D superlattice materials for electrocatalysis*. Advanced science, 2022. **9**(35): p. 2204297.
78. Peng, Y., B. Lu, and S. Chen, *Carbon-supported single atom catalysts for electrochemical energy conversion and storage*. Advanced Materials, 2018. **30**(48): p. 1801995.
79. Liu, A., et al., *Recent progress in MXene-based materials: potential high-performance electrocatalysts*. Advanced Functional Materials, 2020. **30**(38): p. 2003437.
80. Li, F., et al., *Cooperative CO₂-to-ethanol conversion via enriched intermediates at molecule–metal catalyst interfaces*. Nature Catalysis, 2020. **3**(1): p. 75-82.
81. Chung, H.T., et al., *Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst*. Science, 2017. **357**(6350): p. 479-483.
82. Wan, X., et al., *Fe-N-C electrocatalyst with dense active sites and efficient mass transport for high-performance proton exchange membrane fuel cells*. Nature Catalysis, 2019. **2**(3): p. 259-268.
83. Li, Y., et al., *Atomically dispersed dual-metal site catalysts for enhanced CO₂ reduction: mechanistic insight into active site structures*. Angewandte Chemie, 2022. **134**(28): p. e202205632.
84. Li, R. and D. Wang, *Superiority of dual-atom catalysts in electrocatalysis: one step further than single-atom catalysts*. Advanced Energy Materials, 2022. **12**(9): p. 2103564.
85. Han, X., et al., *Atomically dispersed binary Co-Ni sites in nitrogen-doped hollow carbon nanocubes for reversible oxygen reduction and evolution*. Advanced Materials, 2019. **31**(49): p. 1905622.
86. Hao, Q., et al., *Nickel dual-atom sites for electrochemical carbon dioxide reduction*. Nature Synthesis, 2022. **1**(9): p. 719-728.

87. Wu, J., et al., *Densely populated single atom catalysts*. Small Methods, 2020. **4**(2): p. 1900540.
88. Pu, T., et al., *Dual atom catalysts for energy and environmental applications*. Angewandte Chemie International Edition, 2023. **62**(40): p. e202305964.
89. Yang, K., et al., *Less-Coordinated Atomic Copper-Dimer Boosted Carbon–Carbon Coupling During Electrochemical CO₂ Reduction*. Small, 2023. **19**(36): p. 2301536.
90. Hai, X., et al., *Geminal-atom catalysis for cross-coupling*. Nature, 2023. **622**(7984): p. 754-760.
91. Zhang, X., et al., *Comparative study and screening of Single-Atom and homonuclear Dual-Atom catalysts for NO reduction via electrocatalysis*. Fuel, 2024. **366**: p. 131432.
92. Du, J., et al., *CoIn dual-atom catalyst for hydrogen peroxide production via oxygen reduction reaction in acid*. Nature Communications, 2023. **14**(1): p. 4766.
93. Wang, X., et al., *Precisely designing asymmetrical selenium-based dual-atom sites for efficient oxygen reduction*. Nature Communications, 2025. **16**(1): p. 470.
94. Ng, H.K., et al., *Improving carrier mobility in two-dimensional semiconductors with rippled materials*. Nature Electronics, 2022. **5**(8): p. 489-496.
95. Qu, Y., et al., *Effect of curvature on the hydrogen evolution reaction of graphene*. The Journal of Physical Chemistry C, 2018. **122**(44): p. 25331-25338.
96. Wang, X.X., et al., *Nitrogen-Coordinated Single Cobalt Atom Catalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells*. Advanced Materials, 2018. **30**(11).
97. Mehmood, A., et al., *High loading of single atomic iron sites in Fe–NC oxygen reduction catalysts for proton exchange membrane fuel cells*. Nature Catalysis, 2022. **5**(4): p. 311-323.
98. Hai, X., et al., *Scalable two-step annealing method for preparing ultra-high-density single-atom catalyst libraries*. Nature nanotechnology, 2022. **17**(2): p. 174-181.
99. Peterson, A.A. and J.K. Nørskov, *Activity descriptors for CO₂ electroreduction to methane on transition-metal catalysts*. The Journal of Physical Chemistry Letters, 2012. **3**(2): p. 251-258.

Chapter 2. Methodology

This thesis employs in-depth first-principles calculations to investigate electronic and catalytic properties of two-dimensional materials based electrocatalysts, aiming to understand their reaction mechanism. This chapter outlines the theoretical foundation of density functional theory (DFT) used in the first-principles calculations, as well as the methods and tools applied in practical implementations.

2.1. Schrödinger Equation

The Schrödinger equation serves as the foundation of quantum mechanics. It is a linear partial differential equation that governs the evolution of the wave function in a quantum mechanical system. Named after Erwin Schrödinger, it represents a cornerstone of quantum mechanics and marked a milestone in the discipline's development. Schrödinger proposed the equation in 1925 and published it in 1926, establishing a framework for future research and earning the Nobel Prize in Physics in 1933 ^[1].

Conceptually, the Schrödinger equation serves as the quantum analogue of Newton's second law, governing the time evolution of a system's wave function, $\Psi(x, t)$. For a particle of mass m in potential $V(x, t)$, it is given by:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right] \Psi(x, t) \quad \dots (2.1)$$

Here, i is the imaginary unit, $\hbar$ is the reduced Planck's constant, m represents the mass of the particle. This equation determines how the quantum state evolves over

time. In modern quantum mechanics, the state is represented as a vector in Hilbert space, and the equation can be written in operator form as ^[2]:

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad \dots (2.2)$$

In this expression: $\hat{H}$ is the Hamiltonian operator, representing the total energy of the system. $|\Psi(t)\rangle$ is the time-dependent quantum state vector in the Hilbert space. The Hamiltonian operator $\hat{H}$ plays a central role in determining the dynamics of the system. The time-dependent Schrödinger equation predicts that the wave function can form a standing wave, referred to as a *steady state*. The steady-state Schrödinger equation is given by:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad \dots (2.3)$$

Here, E is the energy eigenvalue of the system; $|\psi\rangle$ is the corresponding eigenfunction of the Hamiltonian operator. This formulation applies when the Hamiltonian $\hat{H}$ is independent of time. While the steady-state wave function $|\psi\rangle$ does not explicitly depend on time, the total wave function can still depend on time through a phase factor.

From the perspective of linear algebra, the steady-state Schrödinger equation (Equation 2.3) is an eigenvalue equation. In this context, the wave function $|\psi\rangle$ is the eigenfunction of the Hamiltonian operator $\hat{H}$, with the eigenvalue E representing the energy of the quantum system. The connection between the quantum mechanics and linear algebra is built by this formula.

The Schrödinger equation is the cornerstone of modern quantum mechanics and serves as the foundation of computational materials science. In principle, fundamental properties of matter—such as force, heat, light, electricity, and magnetism—can be studied by solving the Schrödinger equation. However, solving the multi-body Schrödinger equation exactly is nearly impossible due to its complexity. As a result, approximate methods are essential for simplifying its solution.

The following sections will introduce several widely used approximate methods that enable practical applications of the Schrödinger equation in computational materials science.

2.2. Born-Oppenheimer Approximation

In quantum chemistry and molecular physics, the Born-Oppenheimer approximation (BO approximation) is one of the most important mathematical simplifications in molecular dynamics ^[3]. Proposed in the early days of quantum mechanics by Max Born and J. Robert Oppenheimer, it is also referred to as the adiabatic approximation. The BO approximation is based on the significant mass difference between electrons and atomic nuclei, which allows for a separation of their motion. This approximation is widely applied in quantum mechanics to accelerate the calculation of molecular wave functions and physical properties.

The basis of this approximation lies in the relationship between mass and velocity, as described by the kinetic energy formula:

$$E = \frac{1}{2}mv^2 \quad \dots (2.4)$$

Here, E is the kinetic energy, m is the mass, and v is the velocity of the particle. Since the mass of the nucleus is much larger than that of the electron, a nucleus moves much more slowly than an electron under the same kinetic energy. This allows the wave functions of electrons and nuclei to be treated as approximately independent of each other. Mathematically, the molecular wave function Ψ can be expressed as:

$$\Psi = \Psi_e \Psi_n \quad \dots (2.5)$$

In this expression, Ψ_e represents the electronic wave function, and Ψ_n represents the nuclear wave function. This separation allows the Hamiltonian operator to be divided into two parts: one for electrons and the other for nuclei. Cross terms between electronic and nuclear motion are neglected, simplifying the solution process significantly.

For a molecule with m electrons and n atoms, each with three spatial degrees of freedom, the total degrees of freedom in the system are $3(m + n)$. Solving the full Schrödinger equation for such a system involves finding the eigenvalues of partial differential equations in three-dimensional space for both electrons and nuclei. The computational complexity of solving this system grows faster than the square of $3(m + n)$ as m and n increase. Using the BO approximation, the solution process can be divided into two steps:

(1) Solve the electronic Schrödinger equation

In this step, the nuclei are assumed to be stationary relative to the electrons. By fixing the positions of the nuclei, the Schrödinger equation is solved for the electronic

wave function. This reduces the degrees of freedom to $3m$, as only the electrons are considered.

(2) Solve the nuclear motion

The electronic results from step one provides the potential energy surface for the nuclei. The Schrödinger equation is then solved for the nuclear motion, which depends only on the positions of the nuclei. The complexity of solving the nuclear motion equation is simplified to a constant factor N , which depends on the specific methods used.

As a result, the total computational complexity is reduced to approximately $9m^2N$. This reduction in complexity is particularly significant for larger systems, where the numbers of electrons (m) and nuclei (n) are huge. The separation of electronic and nuclear makes it feasible to perform practical calculations for complex molecular systems. Without this approximation, solving the full Schrödinger equation for such systems would be computationally intractable.

2.3. Hartree-Fock theory

Another important approximation is Hartree-Fock theory. It is used to determine the wave function and total energy of a steady-state quantum many-body system. This theory was built upon the earlier self-consistent field (SCF) method, first proposed by Douglas R. Hartree in 1927 ^[4, 5]. Hartree's goal was to eliminate empirical parameters and solve the many-body Schrödinger equation from fundamental physical principles. This method became one of the first *ab initio* approaches in quantum chemistry. In 1930,

Slater and V. A. Fock independently pointed out that Hartree's approach did not satisfy the antisymmetric principle of wave functions^[6]. This principle, which arises from the Pauli exclusion principle, requires that the wave function of a system of fermions (e.g., electrons) change sign when any two particles are exchanged. To address this, Slater and Fock introduced the Slater determinant, a mathematical representation of the wave function for a multi-fermion system that inherently satisfies both the wave function's antisymmetric and the Pauli exclusion principle. The Slater determinant is expressed as:

$$\Psi(X_1, X_2, \dots, X_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \varphi_1(X_1) & \varphi_2(X_1) & \cdots & \varphi_N(X_1) \\ \varphi_1(X_2) & \varphi_2(X_2) & \cdots & \varphi_N(X_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(X_N) & \varphi_2(X_N) & \cdots & \varphi_N(X_N) \end{bmatrix} \quad \dots (2.6)$$

Here, $\Psi(X_1, X_2, \dots, X_N)$ is the wave function of the system, $\varphi(X)$ represents the single-particle spin-orbital wave function, X represents the position and spin of a single particle, $N!$ normalizes the determinant to satisfy the normalization condition for wave functions. The determinant satisfies the antisymmetric property, meaning that exchanging two particles flips the sign of the wave function, and it inherently enforces the Pauli exclusion principle, which prevents two electrons from occupying the same quantum state. Hartree optimized the method to make it more suitable for calculations^[7], and the resulting approach became known as Hartree-Fock theory, combining Hartree's SCF method with the antisymmetric considerations introduced by Fock.

Over the next decade, Hartree-Fock theory underwent significant refinements and became one of the most accurate methods for describing quantum systems at the time. Initially, it was applied almost exclusively to atoms, as their spherical symmetry greatly simplified the problem. Despite this simplification, manually solving the Hartree-Fock

equations for medium-sized atoms was extremely challenging, and applying the method to molecules was practically impossible using the computational tools available at the time. The computational complexity of Hartree-Fock arises from the need to iteratively solve the many-electron Schrödinger equation while enforcing self-consistency in the electron-electron interactions. Even for small systems, the computational cost was substantial, underscoring the limitations of the available technology. These challenges lead to the development of alternative methods, most notably density functional theory, which emerged as a more computationally efficient approach to solving many-body quantum systems.

2.4. Density Functional Theory

The origins of Density Functional Theory (DFT) can be traced back to the Thomas-Fermi model. Compared with the Hartree-Fock method, DFT significantly reduces workload of calculation. Since the 1970s, DFT has become a commonly used method for studying solid materials. However, in its early stages, the accuracy of DFT was often questioned. This issue was largely resolved in the 1990s with the development of improved exchange-correlation functionals. Up to now, DFT has become one of the most widely used methods in computational science.

2.4.1. Thomas-Fermi Model

The Thomas-Fermi model, named after Llewellyn Thomas and Enrico Fermi, is one of the earliest quantum mechanical models used to describe the distribution of electrons in atoms ^[8]. In 1927, both scientists independently developed a statistical

approach to estimate the electron distribution within atoms. The model assumes that the electron distribution is not uniform but can be approximated by dividing the space around the atom into small spatial units, denoted as ΔV . Within and between these units, the electron density is assumed to be continuous, simplifying the calculations compared to wave function-based methods.

In the Thomas-Fermi model, for each spatial unit of a ground-state atom, a spherical momentum space with radius determined by the Fermi momentum p_F filled. This is expressed by the volume of momentum space as:

$$V_F = \frac{4}{3}\pi p_F^3(\mathbf{r}) \quad \dots (2.7)$$

Here, $\mathbf{r}$ is the position vector corresponding to the small spatial unit ΔV . The phase space volume ΔV_{ph} for this unit is then given by:

$$\Delta V_{ph} = V_F \Delta V = \frac{4}{3}\pi p_F^3(\mathbf{r}) \Delta V \quad \dots (2.8)$$

Electrons in this phase space obey a fundamental distribution rule: Two electrons can occupy each unit of phase space with volume $\hbar^3$. Using this, the number of electrons ΔN_{ph} in the phase space ΔV_{ph} is given by:

$$\Delta N_{ph} = \frac{2}{\hbar^3} \Delta V_{ph} = \frac{8\pi}{3\hbar^3} p_F^3(\mathbf{r}) \Delta V \quad \dots (2.9)$$

The relationship between the number of electrons ΔN and the electron density $n(\mathbf{r})$ in the spatial unit ΔV is expressed as:

$$\Delta N = n(\mathbf{r}) \Delta V \quad \dots (2.10)$$

Substituting ΔN from equation (2.10) into equation (2.9) gives an expression for the electron density $n(\mathbf{r})$:

$$n(\mathbf{r}) = \frac{8\pi}{3\hbar^3} p_F^3(\mathbf{r}) \quad \dots (2.11)$$

The momentum distribution of electrons in a unit is expressed as:

$$F_r(p)dp = \begin{cases} \frac{4\pi p^2 dp}{3} & p \leq p_F(\mathbf{r}) \\ 0 & p > p_F(\mathbf{r}) \end{cases} \quad \dots (2.12)$$

Using this, the kinetic energy of the electrons in a unit volume ΔV is given by:

$$t(\mathbf{r}) = \int \frac{p^2}{2m_e} n(\mathbf{r}) F_r(p) dp = C_F [n(\mathbf{r})]^{5/3} \quad \dots (2.13)$$

Here, C_F is a constant derived from the model. Integrating over all space, the total kinetic energy of the electrons in the system is:

$$T = C_F \int [n(\mathbf{r})]^{5/3} d^3\mathbf{r} \quad \dots (2.14)$$

The constant C_F is expressed as:

$$C_F = \frac{3\hbar^2}{40m_e} \left(\frac{3}{\pi}\right)^{2/3} \quad \dots (2.15)$$

From equation (2.15), it is evident that the Thomas-Fermi model departs significantly from Schrödinger's wave function theory by describing the total kinetic energy of electrons based solely on the spatial electron density rather than the wave function. This approach simplifies calculations drastically, as it avoids solving complex differential equations for electron wave functions. However, the model's simplicity comes at the cost of accuracy due to its strict approximations. Nevertheless, the model

laid the groundwork for later developments in quantum mechanics simulation, including DFT, which incorporates electron density as the primary variable while addressing the limitations of the Thomas-Fermi model through the use of improved functionals [9].

2.4.2. Hohenberg-Kohn Theorems

The Hohenberg-Kohn theorem (HK theorem), proposed by Walter Kohn and Pierre Hohenberg, forms the theoretical foundation of DFT [10]. The theorem is divided into two parts, which collectively demonstrate how electron density can be used to solve the quantum many-body problem efficiently. This breakthrough simplified quantum mechanical calculations and made DFT a practical tool for studying multi-electron systems.

(1) First Hohenberg-Kohn Theorem

The first HK theorem states that the ground-state properties of a multi-electron system are uniquely determined by its electron density. This means that the degrees of freedom in the system can be greatly reduced, which significantly simplifies the problem and lowers the computational complexity.

(2) Second Hohenberg-Kohn Theorem

The second HK theorem defines the energy functional of a system and proves that this functional reaches its minimum value when and only when the electron density corresponds to the ground state of the system. It provides a practical route to solve the ground-state properties of a system by optimizing the electron density.

2.4.3. Kohn-Sham Equations

The Kohn-Sham equation (KS equation), proposed by Walter Kohn and Lu Jeu Sham in 1965, is the cornerstone of DFT. This equation simplifying the many-body problem for a system of interacting electrons into a problem involving non-interacting electrons with the same electron density ^[11].

From a physical and quantum chemical perspective, the KS equation is a reformulation of the Schrödinger equation, where the complex system of interacting particles is replaced by a system of non-interacting particles moving in an effective potential. This potential, called the Kohn-Sham potential (denoted as $V_{eff}(\mathbf{r})$), is defined to reproduce the same electron density as the original interacting system.

The KS equation for this non-interacting system can be written as:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad \dots (2.16)$$

Here, $\varphi_i(\mathbf{r})$ is the i -th single-electron orbital in the Kohn-Sham system, ε_i is the corresponding orbital energy, and $V_{eff}(\mathbf{r})$ is the effective potential felt by the non-interacting electrons, which incorporates all interactions implicitly.

The electron density $n(\mathbf{r})$ of the system can be obtained by summing the square of the absolute values of these orbitals:

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2 \quad \dots (2.17)$$

In the Kohn-Sham framework, the total energy functional of the system, $E[n]$, is expressed as a functional of the electron density $n(\mathbf{r})$. A functional is a “function of a

function” meaning the total energy is determined by the spatial electron density. The functional dependent total energy is given by:

$$E[n] = T_s[n] + \int d\mathbf{r} v_{ext}(\mathbf{r})n(\mathbf{r}) + E_H[n] + E_{xc}[n] \quad \dots (2.18)$$

where $T_s[n]$ is kinetic energy term of non-interacting electrons, expressed as:

$$T_s[n] = \sum_{i=1}^N \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_i(\mathbf{r}) \quad \dots (2.19)$$

$E[n]$ is Hartree energy (Coulomb energy), representing the classical electron-electron repulsion:

$$E_H[n] = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad \dots (2.20)$$

and $v_{ext}(\mathbf{r})$ is external potential, which describes the influence of external fields.

$E_{xc}[n]$ is exchange-correlation energy, which accounts for all quantum mechanical effects not captured by the other terms.

The Kohn-Sham potential, $V_{eff}(\mathbf{r})$, is the effective external potential, in which the non-interacting electrons move. It is derived from the total energy functional and consists of three components:

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta \rho(\mathbf{r})} \quad \dots (2.21)$$

Where $V_{ext}(\mathbf{r})$ is external potential from nuclei or external fields; $e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$ is Hartree potential, accounting for the classical electrostatic repulsion between electrons; $\frac{\delta E_{xc}[n]}{\delta \rho(\mathbf{r})}$ is exchange-correlation potential, denoted as $V_{xc}(\mathbf{r})$. The exchange-correlation term, $E_{xc}(\mathbf{r})$, is the only unknown term in the KS equation. It encapsulates

all the complex many-body interactions that are not explicitly accounted for by the kinetic, external, and Hartree energy terms.

The KS equation simplified the nearly unsolvable many-body Schrödinger equation into a set of single-electron Schrödinger equations with the same ground-state density.

2.4.4. Exchange-correlation Functional

From the previous discussion, we know that the exchange-correlation energy term, $E_{xc}(\mathbf{r})$, is the only unknown in the KS equation. Once this term is accurately determined as a functional of the electron density $n(\mathbf{r})$, the KS equation becomes complete and solvable. Although $E_{xc}(\mathbf{r})$ does not have a precise physical interpretation, it is a general term that accounts for the quantum mechanical interactions between electrons, including exchange and correlation effects.

Since deriving $E_{xc}(\mathbf{r})$ analytically is infeasible, mathematical approximations are used to model it. The most widely used approximations are the local-density approximation (LDA) ^[12] and the generalized gradient approximation (GGA) ^[13].

(1) Local-Density Approximation

LDA is the simplest and most used exchange-correlation functional. It assumes that the exchange-correlation energy at a given point depends only on the electron density at that point, similar to a uniform electron gas. If the electron spin is not considered, the LDA exchange-correlation energy is written as:

$$E_{xc}^{LDA}[n] = \int \varepsilon_{xc}(n)n(\mathbf{r})d^3\mathbf{r} \quad \dots (2.22)$$

If the electron spin is considered, the spin-resolved LDA exchange-correlation energy is written as:

$$E_{xc}^{LDA}[n_{\uparrow}, n_{\downarrow}] = \int \varepsilon_{xc}(n_{\uparrow}, n_{\downarrow})n(\mathbf{r})d^3\mathbf{r} \quad \dots (2.23)$$

Here, $n(\mathbf{r})$ represents the electron density at position $\mathbf{r}$ and ε_{xc} is the exchange-correlation energy per particle in a uniform electron gas at density $n(\mathbf{r})$.

In the LDA, the exchange-correlation energy ε_{xc} is divided linearly into exchange energy ε_x and correlation energy ε_c :

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c \quad \dots (2.24)$$

Thus, the total exchange-correlation energy can also be separated into exchange and correlation contributions. For example, the LDA exchange energy is given by:

$$E_x^{LDA}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int n(\mathbf{r})^{4/3}d\mathbf{r} \quad \dots (2.25)$$

The LDA functional is simple, effective, and widely used, particularly for systems with relatively uniform electron densities, such as metals and simple solids. However, the main limitation of LDA is its assumption of a uniform electron gas, which is a constrained approximation. In real systems, electron densities are rarely uniform, especially near atomic nuclei or in molecular systems. As a result, LDA can

underestimate or overestimate interaction energies, leading to inaccuracies in bond strength, band gaps, and other properties.

(2) Generalized Gradient Approximation

To address the limitations of LDA, GGA was introduced. Unlike LDA, GGA incorporates information about the gradient of the electron density to improve accuracy.

The GGA exchange-correlation energy is expressed as:

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int \varepsilon_{xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) n(\mathbf{r}) d^3\mathbf{r} \quad \dots (2.26)$$

By incorporating the gradient of the density ∇n , GGA provides a more realistic description of electron distributions, especially in systems with rapidly varying densities, such as molecules and surfaces. One of the most widely used GGA functionals is PBE (Perdew-Burke-Ernzerhof), developed by John P. Perdew, K. Burke, and M. Ernzerhof. The PBE functional improves upon LDA by providing more accurate descriptions of molecular geometries and ground-state energies.

(3) Dispersion Correction

Despite their successes, both LDA and GGA face challenges that neither LDA nor GGA can accurately describe long-range van der Waals (vdW) forces, which are critical for molecular interactions, adsorption, and soft materials. To improve the treatment of long-range interactions, modifications are developed to the PBE functional, such as PBE+D3 ^[14]. This approach incorporates dispersion corrections to describe vdW interactions. The D3 correction adds an empirical term to account for long-range vdW

forces, improving the accuracy of calculations for molecular systems and weakly bound complexes ^[15, 16]. In this thesis, the catalytic properties of two-dimensional materials are primarily investigated through calculations. Since vdW forces play a significant role, the PBE+D3 computational method is employed to account for these interactions.

2.4.5. Bloch Theorem

Bloch theorem describes the behavior of electrons in a periodic potential (such as the potential created by the nuclei in a crystal lattice). In this situation, the solution of the Schrödinger equation can be written as the product of a plane wave function and a periodic function. This is expressed as:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad \dots (2.27)$$

where $\psi(\mathbf{r})$ is the Schrödinger wave function at position vector $\mathbf{r}$, which describes the quantum state of an electron; $u_{\mathbf{k}}(\mathbf{r})$ is a periodic function with the same periodicity as the crystal lattice. This function captures the influence of the periodic potential; $\mathbf{k}$ represents the wave vector, which describes the electron's momentum and is defined in the reciprocal space of the lattice.

Bloch theorem reveals that the wave function $\psi(\mathbf{r})$ for an electron in a crystal can be split into two parts: a plane wave component $e^{i\mathbf{k}\cdot\mathbf{r}}$, which accounts for the translational symmetry of the crystal; and a periodic component $u_{\mathbf{k}}(\mathbf{r})$, which reflects the periodicity of the potential. As the wave vector $\mathbf{k}$ varies continuously within the reciprocal lattice, both the wave function and the energy also vary continuously. Also,

Bloch theorem concludes that the wave vector $\mathbf{k}$ can always be confined to the first Brillouin zone, the fundamental domain of the reciprocal lattice. This is because the wave functions outside the first Brillouin zone are equivalent to those inside, due to the periodicity of the reciprocal lattice.

Modern computational tools, such as DFT software, use periodic boundary conditions to simulate infinite crystals by defining a small, repeating unit cell. Bloch theorem provides the theoretical foundation for these boundary conditions, as it ensures that the wave functions and physical properties are periodic. In electronic structure calculations, the wave vector $\mathbf{k}$ is sampled within the first Brillouin zone to determine the electronic structure of the system. These discrete sampling points are referred to as K points. Generally, increasing the density of K points in the first Brillouin zone improves the precision of calculations, ensuring a more accurate representation of the system's properties ^[17].

2.4.6. Plane-Waves and Pseudopotentials

From the previous section, we have established that the Schrödinger wave function in a periodic potential can be expressed as the product of a plane wave function and a periodic function in the first Brillouin zone. Since the periodic function $u_{\mathbf{k}}(\mathbf{r})$ has the same periodicity as the crystal lattice, it can be expanded into a Fourier series. From mathematical knowledge, any periodic function that is continuous within two periods has a convergent Fourier series. Thus, the wave function $\psi(\mathbf{r})$ can be expressed in the form of a plane wave expansion:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{G}}^{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad \dots (2.28)$$

Here, $\mathbf{G}$ represents the reciprocal lattice vector in Fourier space, and the wave vector $\mathbf{k}$ and $\mathbf{G}$ combine to form the total wave vector $\mathbf{k} + \mathbf{G}$, which determines the oscillatory behavior of the plane wave. The product of $\mathbf{k}$ and $\mathbf{G}$ with the lattice vector is always an integer multiple of 2π due to the periodicity of the lattice. The index n is used to label the electronic energy bands, which arise from the quantized states of electrons in a periodic potential. The coefficients $c_{n,\mathbf{G}}^{\mathbf{k}}$ are the unknown quantities to be solved in the expansion. These coefficients describe the contribution of each plane wave to the total wave function.

The plane wave expansion is one of the most concise and effective methods for solving the KS equation in DFT ^[18]. Its simplicity and efficiency make it well-suited for computational implementations. In practical calculations, the plane wave expansion is truncated by introducing a cutoff energy. The cutoff energy, E_{cut} , determines the maximum kinetic energy of the plane waves included in the expansion:

$$E_{cut} = \frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} \quad \dots (2.29)$$

A larger E_{cut} includes more plane wave basis functions, improving the accuracy of the wave function representation, however, it increases computational cost and time. When the cutoff energy is sufficiently large, adding more plane wave basis functions does not change the total energy of the system. At this point, the calculation is said to

have converged. To balance efficiency and precision, the cutoff energy is chosen based on the system being studied, with convergence tests often performed to ensure accuracy.

To further reduce the calculation workload of solving the KS equation, the pseudopotential method is employed. In this method, the complex interactions between the nucleus and core electrons are replaced with an effective potential. This allows us to focus on the valence electrons, which play the most significant role in chemical bonding and material properties. Here are some types of pseudopotentials:

Norm-Conserving Pseudopotentials (NCPP): Developed in the early days of DFT, these pseudopotentials preserve the norm of the all-electron wave function outside a certain core radius, which require a relatively large number of plane waves, especially for transition metals and heavier elements ^[19].

Ultrasoft Pseudopotentials (USPP): Introduced to reduce the number of required plane waves by allowing the wave function norm to vary within the core region. USPPs are more computationally efficient than NCPPs but can introduce slight inaccuracies in some cases ^[20].

Projector Augmented Wave (PAW) Method: The PAW method combines pseudopotential methods with the linear augmented plane wave (LAPW) method. It reconstructs the all-electron wave function from the pseudo-wave function by using projector functions. PAW offers both high accuracy and efficiency, making it the most widely used approach in modern DFT calculations ^[21, 22].

2.5. Software Utilized in This Thesis

2.5.1. VASP

The Vienna Ab initio Simulation Package (VASP) is a widely used software for DFT calculations ^[18, 20, 23, 24]. Originating from Mike Payne's code and further developed by Georg Kresse and Jürgen Furthmüller at the University of Vienna, VASP has become a powerful tool for studying material properties.

VASP implements advanced theoretical methods, such as plane wave expansion and the PAW method, making it efficient for solving the Kohn-Sham equations. It is capable of calculating lattice parameters, electronic structures, optical properties, molecular dynamics, and thermodynamic properties. Written in Fortran, VASP is optimized for parallel computing, enabling efficient simulations of complex systems.

To complement VASP, software tools like VASPKIT ^[25] and QVASP ^[26] are often used for data analysis and structural manipulation. All of the calculations in this thesis are based on VASP.

2.5.2. VESTA

VESTA (Visualization for Electronic and Structural Analysis) is a widely used software for visualizing crystal structures ^[27]. In this thesis, VESTA is used to build and display the model of electrocatalysts.

2.6. General Concept of Electrocatalysis Calculation

2.6.1. Thermodynamics Determines the Reactivity

The Gibbs energy change (ΔG) is a fundamental thermodynamic descriptor for describing the electrocatalytic properties of materials in DFT calculations^[28, 29]. During the electrocatalytic process, the clean catalytic slab is denoted as (*), while the intermediate state of an adsorbed product (e.g., X) on the slab is represented as (X* or *X). The Gibbs energy change associated with this adsorption, denoted as ΔG_{X*} , can be expressed as:

$$\Delta G_{X*} = G(X *) - G(X) - G(*) \quad \dots (2.30)$$

Here, the $G(X *)$, the Gibbs energy of the adsorbed intermediate state, can be calculated using the following equation:

$$G(X *) = E_{DFT}(X *) + E_{ZPE} - TS \quad \dots (2.31)$$

Where $E_{DFT}(X *)$ is the total energy of the system with the adsorbed intermediate, calculated using DFT. E_{ZPE} is the zero-point energy correction, which accounts for the quantum mechanical vibrational energy of the adsorbed intermediate. This can be computed using VASP. T is temperature in Kelvin, and ΔS is the entropy change.

The Gibbs energy of gaseous intermediate, $G(X)$, can be calculated as:

$$G(X) = E_{DFT}(X) + E_{ZPE} - TS \quad \dots (2.32)$$

Finally, the Gibbs energy of the clean catalytic slab, $G(*)$, can typically be approximated as:

$$G(*) \approx E_{DFT}(*) \quad \dots (2.33)$$

Further analysis of $G(X*)$, including its role in determining electrocatalytic properties, will be discussed in detail in the following three chapters.

2.6.2. Kinetics Determines the Selectivity

While thermodynamic parameters like ΔG indicate the feasibility and driving force of a reaction, kinetic factors dictate the selectivity between different possible reaction pathways ^[30]. The key kinetic descriptor is the reaction barrier (or activation energy E_a), which represents the energy difference between the reactant (or intermediate) and the transition state:

$$E_a = E_{TS} - E_{IS} \quad \dots (2.34)$$

where E_{TS} and E_{IS} are the DFT-calculated energies of the transition state and initial state, respectively. The corresponding Gibbs energy barrier is:

$$\Delta G_a = G_{TS} - G_{IS} \quad \dots (2.35)$$

These barriers are typically determined using transition state search methods such as the Nudged Elastic Band (NEB) in DFT calculations ^[31, 32]. The magnitude of the activation energy dictates the rate at which a reaction proceeds via the Arrhenius equation:

$$k = A \exp\left(-\frac{\Delta G_a}{k_B T}\right) \quad \dots (2.36)$$

where k is the reaction rate constant, A is the pre-exponential factor, k_B is the Boltzmann constant, and T is the temperature. During electrocatalytic reactions, multiple reaction pathways may compete, each with distinct intermediates and transition states. Even if a pathway is thermodynamically favorable, a high kinetic barrier can make it inactive. Conversely, a pathway with a lower barrier but less favorable thermodynamics might dominate, thereby affect the selectivity.

Therefore, a comprehensive understanding of both thermodynamic and kinetic factors is essential for rational catalyst design. Thermodynamics establishes whether a reaction is feasible, while kinetics determines the rate and selectivity of product formation.

2.6.3. Band Center Theory

The concept of the band center is extensively used in surface science and catalysis, particularly for understanding and optimizing the activity of electrocatalysts. It provides a quantitative description of the average energy position of electrons within a specific electronic band (e.g., the d-band for transition metals or the p-band for oxides). The band center plays a critical role in determining the bonding interaction between the catalyst surface and adsorbates ^[33, 34]. By analyzing the position of the band center relative to the Fermi level, it is possible to predict and tune the catalytic activity of materials. The d -band center ε_d is mathematically defined as:

$$\varepsilon_d = \frac{\int \varepsilon \rho_d(\varepsilon) d\varepsilon}{\int \rho_d(\varepsilon) d\varepsilon} \quad \dots (2.37)$$

Where ε represents energy relative to the Fermi level; and $\rho_d(\varepsilon)$ is the density of states of d -electrons at energy ε . Similarly, the p -band center ε_p is defined analogously as:

$$\varepsilon_p = \frac{\int \varepsilon \rho_p(\varepsilon) d\varepsilon}{\int \rho_p(\varepsilon) d\varepsilon} \quad \dots (2.38)$$

Where $\rho_p(\varepsilon)$ represents the density of states of p -electrons at energy ε .

The position of the band center relative to the Fermi level has a direct impact on the adsorption properties of the catalyst. Attributed to enhanced orbital overlap between the catalyst surface and the adsorbate, a higher band center (closer to the Fermi level) indicates stronger adsorption. Conversely, a lower band center (farther from the Fermi level) results in weaker adsorption due to diminished overlap. The application of band center theory in the context of electrocatalysis will be further elaborated in subsequent chapters.

References

1. Schrödinger, E., *An Undulatory Theory of the Mechanics of Atoms and Molecules*. Physical Review, 1926. **28**(6): p. 1049-1070.
2. Isham, C.J. and N. Linden, *Continuous histories and the history group in generalized quantum theory*. Journal of Mathematical Physics, 1995. **36**: p. 5392-5408.
3. Born, M. and R. Oppenheimer, *Zur Quantentheorie der Molekeln*. Annalen der Physik, 1927. **389**(20): p. 457-484.
4. Slater, J.C., *The Self Consistent Field and the Structure of Atoms*. Physical Review, 1928. **32**(3): p. 339-348.
5. Hartree, D.R., *The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods*. Mathematical Proceedings of the Cambridge Philosophical Society, 1928. **24**(1): p. 89-110.
6. Slater, J.C., *Note on Hartree's Method*. Physical Review, 1930. **35**(2): p. 210-211.
7. Hartree, D.R. and W. Hartree, *Self-consistent field, with exchange, for beryllium*. Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences, 1935. **150**(869): p. 9-33.
8. Thomas, L.H., *The calculation of atomic fields*. Mathematical Proceedings of the Cambridge Philosophical Society, 1927. **23**(5): p. 542-548.
9. Dirac, P.A.M., *Note on Exchange Phenomena in the Thomas Atom*. Mathematical Proceedings of the Cambridge Philosophical Society, 1930. **26**(3): p. 376-385.
10. Hohenberg, P. and W. Kohn, *Inhomogeneous Electron Gas*. Physical Review, 1964. **136**(3B): p. B864-B871.
11. Kohn, W. and L.J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects*. Physical Review, 1965. **140**(4A): p. A1133-A1138.
12. Perdew, J.P. and A. Zunger, *Self-interaction correction to density-functional approximations for many-electron systems*. Physical Review B, 1981. **23**(10): p. 5048-5079.
13. Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*. Physical review letters, 1996. **77**(18): p. 3865.
14. Thanthiriwatte, K.S., et al., *Assessment of the Performance of DFT and DFT-D Methods for Describing Distance Dependence of Hydrogen-Bonded Interactions*. J Chem Theory Comput, 2011. **7**(1): p. 88-96.
15. Grimme, S., et al., *A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu*. J Chem Phys, 2010. **132**(15): p. 154104.
16. Grimme, S., *Semiempirical GGA-type density functional constructed with a long-range dispersion correction*. Journal of Computational Chemistry, 2006. **27**(15): p. 1787-1799.

17. Monkhorst, H.J. and J.D. Pack, *Special points for Brillouin-zone integrations*. Physical Review B, 1976. **13**(12): p. 5188-5192.
18. Kresse, G. and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*. Physical review B, 1996. **54**(16): p. 11169.
19. Bachelet, G.B., D.R. Hamann, and M. Schlüter, *Pseudopotentials that work: From H to Pu*. Physical Review B, 1982. **26**(8): p. 4199-4228.
20. Kresse, G. and D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method*. Physical Review B, 1999. **59**(3): p. 1758-1775.
21. Blochl, P.E., *Projector augmented-wave method*. Phys Rev B Condens Matter, 1994. **50**(24): p. 17953-17979.
22. Kleinman, L. and D.M. Bylander, *Efficacious Form for Model Pseudopotentials*. Physical Review Letters, 1982. **48**(20): p. 1425-1428.
23. Kresse, G. and J. Furthmüller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*. Computational Materials Science, 1996. **6**(1): p. 15-50.
24. Kresse, G. and J. Hafner, *Ab initio molecular dynamics for liquid metals*. Phys Rev B Condens Matter, 1993. **47**(1): p. 558-561.
25. Wang, V., et al., *VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code*. Computer Physics Communications, 2021. **267**.
26. Yi, W., et al., *qvasp: A flexible toolkit for VASP users in materials simulations*. Computer Physics Communications, 2020. **257**.
27. Momma, K. and F. Izumi, *VESTA: a three-dimensional visualization system for electronic and structural analysis*. Journal of Applied Crystallography, 2008. **41**(3): p. 653-658.
28. Asthagiri, A. and M. Janik, *Computational catalysis*. Vol. 48. 2024: Royal Society of Chemistry.
29. Chorkendorff, I. and J.W. Niemantsverdriet, *Concepts of modern catalysis and kinetics*. 2017: John Wiley & Sons.
30. Nørskov, J.K., et al., *Origin of the overpotential for oxygen reduction at a fuel-cell cathode*. The Journal of Physical Chemistry B, 2004. **108**(46): p. 17886-17892.
31. Henkelman, G., B.P. Uberuaga, and H. Jónsson, *A climbing image nudged elastic band method for finding saddle points and minimum energy paths*. The Journal of chemical physics, 2000. **113**(22): p. 9901-9904.
32. Henkelman, G. and H. Jónsson, *Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points*. The Journal of chemical physics, 2000. **113**(22): p. 9978-9985.
33. Nørskov, J.K., et al., *Density functional theory in surface chemistry and catalysis*. Proceedings of the National Academy of Sciences, 2011. **108**(3): p. 937-943.

34. Hong, W.T., et al., *Toward the rational design of non-precious transition metal oxides for oxygen electrocatalysis*. Energy & Environmental Science, 2015. **8**(5): p. 1404-1427.

Chapter 3. Curvature Effects on Hydrogen Evolution

Performance in Two-Dimensional Curved MoS₂

3.1. Introduction

MoS₂, as a prototypical member of the family of two-dimensional transition metal dichalcogenides (TMDs), has garnered significant attention in recent years for its potential in functional materials and device applications ^[1-3]. In addition to the electronic device applications, 2D MoS₂ has shown promising performance to catalyze water splitting. However, it turns out the basal plane of 2D MoS₂ is inert to hydrogen evolution process and its catalytic activity is largely limited to its edge sites ^[4, 5]. To overcome this inherent limitation and fully realize the catalytic capabilities of MoS₂, recent research has focused on structural modification. Approaches such as defect and strain engineering have proven effective in substantially altering the electronic structure and surface reactivity of MoS₂, thereby enhancing its hydrogen evolution reaction (HER) performance ^[6-9].

More recently, curvature engineering has been proposed as another effective strategy to tailor the local structure and electronic properties of 2D materials ^[10-13]. Theoretical studies and experimental observations have shown that imparting curvature to MoS₂ nanosheets can induce local strain, modulate carrier distribution, and improve the catalytic activity of MoS₂-based SACs ^[14-17]. Similar curvature-induced enhancements in HER activity have also been reported in other two-dimensional systems, such as waved graphene ^[18]. Nonetheless, despite these promising results, a

comprehensive and atomistic understanding of how controlled curvature modulates the HER performance of MoS₂ remains lacking.

To address this gap, this chapter employs DFT calculations, to systematically investigate the impact of curvature on the HER activity of 2D MoS₂. By constructing a series of curved MoS₂ models and analyzing their structure, electronic properties, and catalytic properties, we aim to explain the underlying structure–activity relationships that govern curvature-enhanced HER performance.

3.2. Computational Methods

3.2.1. Computational Parameters

All DFT calculations in this study were carried out using VASP. The exchange–correlation interactions were treated within the GGA-PBE functional, while the PAW method was employed to describe the core–electron interaction. To accurately account for van der Waals interactions, the DFT-D3 dispersion correction scheme was applied. The plane-wave cutoff energy was set to 450 eV. Brillouin zone sampling was performed using a Γ -centered k-point mesh, with a product of ~ 40 with the in-plane lattice constant and vacuum layers of over 20 Å in the out-of-plane direction. The electronic and ionic convergence criteria were set to 1×10^{-6} eV and 0.02 eV/Å, respectively.

3.2.2. System Design and Curvature Define

In differential geometry, the curvature K of a curve $f(x)$ is defined as ^[19]:

$$K = \frac{|f''(x)|}{(1 + f'(x)^2)^{3/2}} \quad \dots (3.1)$$

To systematically quantify the effects of curvature in this study, a single-layer MoS₂ sheet is modeled as being bent into MoS₂ arcs of varying radii. In this construction, the curvature K is simply given by the inverse of the arc's radius $1/R$. Considering the theoretically achievable minimum radius (i.e., maximum curvature) for a single-layer MoS₂ nanotube, all MoS₂ arcs developed in this chapter are constructed by bending along the armchair direction^[20].

3.2.3. Catalytic Path and Thermodynamics of HER in Calculation

Catalytic path of HER can be shown as ^[21]:



Where “*” represents slab, and “* H” represents the intermediate state.

Gibbs energy change of step1 ΔG_{H*} indicates the HER activity ^[22], which can be defined as:

$$\Delta G_{H*} = G(H *) - \frac{1}{2} G(H_2) - G(*) \quad \dots (3.2)$$

where the calculation process of each Gibbs energy is shown in **Chapter 2.6.1**.

3.2.4. Formation energy

The formation energy of MoS₂ arcs E_f^{arc} , can be expressed as:

$$E_f^{arc} = E_{DFT}^{arc} - E_{DFT}^{flat} \quad \dots (3.3)$$

where E_{DFT}^{arc} and E_{DFT}^{flat} are the total energies of the curved and flat MoS₂ structures, respectively.

Similarly, the formation energy of sulfur vacancy, $E_f^{S_{vac}}$ is given by:

$$E_f^{S_{vac}} = E_{DFT}^{defect} - E_{DFT}^{pristine} + \mu_S \quad \dots (3.4)$$

where E_{DFT}^{defect} is the total energy of the curved MoS₂ with a sulfur vacancy, and μ_S represents the chemical potential of sulfur in its most stable phase.

3.3. Results and Discussion

3.3.1. Structures and Reasonableness

To assess the validity of the computational model, a 3×4 MoS₂ supercell was constructed and bent along the armchair direction to form arc-shaped structures of equal length but varying radii of curvature. In this configuration, the zigzag edge spans 3 unit cells, corresponding to a length of 9.50 Å, while the armchair edge covers 4 unit cells, with a length of 21.93 Å. Vacuum layers exceeding 15 Å were introduced to the MoS₂ arc to minimize interactions between periodic images. Owing to the use of periodic boundary conditions, the two ends of the arc remain disconnected. To preserve the desired arc geometry during structural optimization, the atoms at both ends were fixed (corresponding to the exposed zigzag edges). It is noteworthy that these zigzag edges have been reported to exhibit metallic characteristics and enhance the catalytic activity toward the HER [23-25]. To ensure an unbiased investigation of intrinsic properties, both the sulfur vacancy and hydrogen adsorption sites were modeled at the central region of the arc, specifically along the axis of symmetry and maximally distant from the fixed

ends. This approach guarantees that the local electronic and structural environment at the defect or adsorption site is representative of the curved MoS₂ surface, minimally influenced by the boundary conditions or fixed edge atoms.

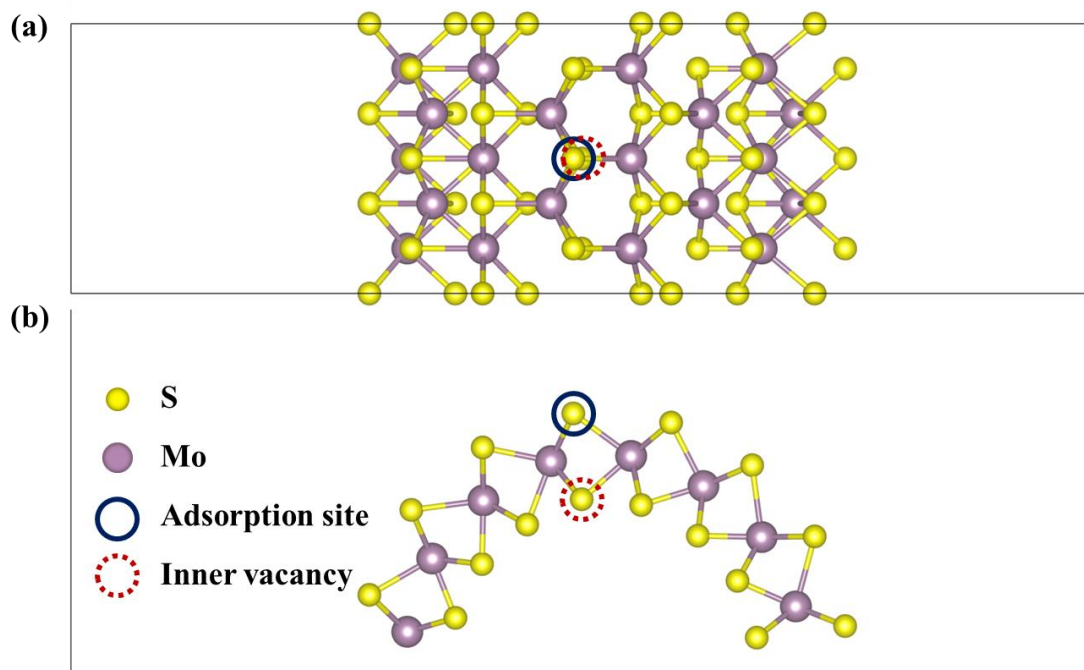


Figure 3.1 (a) Top and (b) side view of 180-pri MoS₂ with a curvature of $K = 0.14 \text{ \AA}^{-1}$.

Building upon this framework, a series of MoS₂ arc structures with bending angles of 0°, 60°, 120°, 180°, and 240° were systematically constructed, corresponding to curvature $K = 0 \text{ \AA}^{-1}$, $0.05 \text{ \AA}^{-1}$, $0.10 \text{ \AA}^{-1}$, $0.14 \text{ \AA}^{-1}$, $0.19 \text{ \AA}^{-1}$, respectively. In this model, the maximum curvature is equivalent to that of a single-layer MoS₂ nanotube with the smallest theoretically stable radius, specifically the (6,6) armchair configuration^[20]. Nanotubes with radii smaller than this are generally unstable due to the significant strain energy associated with increased curvature^[20].

Since the convex (outer) surface of curved MoS₂ in the experiment is more likely to be exposed, this model defines the top surface as the outside of the arc^[23]. Hydrogen

adsorption is simulated on the top site of a sulfur atom on this convex surface, as indicated by the blue solid circle in **Figure 3.1**. To control variables and ensure that hydrogen atoms are adsorbed on sulfur sites, sulfur vacancies are consistently introduced on the concave (inner) surface of the arc, as depicted by the red dashed line in Figure 3.1. For clarity, the pristine arc model is designated as x -pri MoS₂, where x denotes the bending angle. Models with sulfur vacancy positioned on the inner surface of the arc is referred to as x -vac MoS₂.

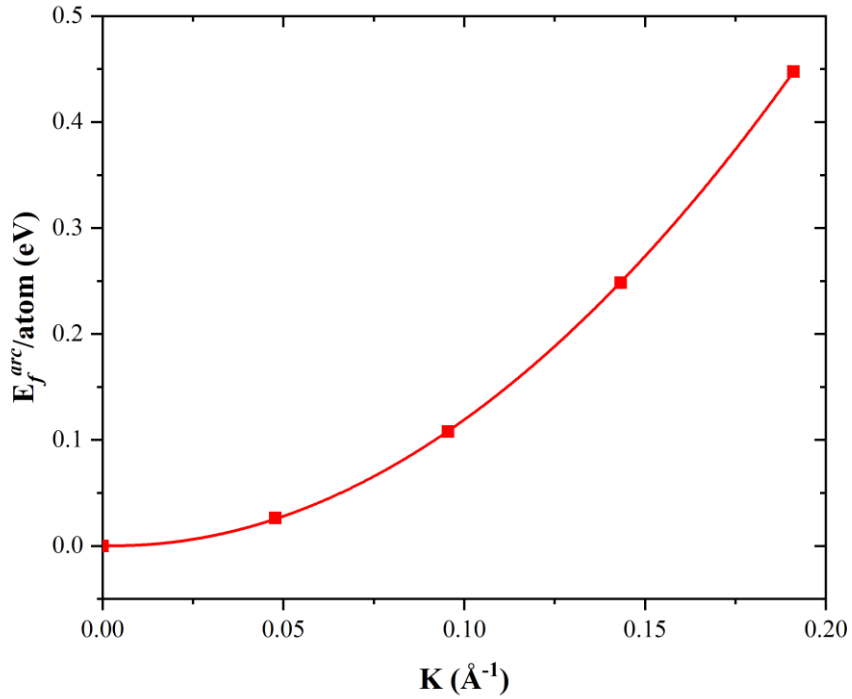


Figure 3.2 Formation energy per atom of pristine MoS₂ arcs.

As shown in **Figure 3.2**, the formation energy of MoS₂ arcs (E_f^{arc}) exhibits a quadratic dependence on curvature. This trend aligns with previous reports, which indicate that the formation energy of a nanotube is inversely proportional to the square of its radius, given that curvature is defined as the inverse of the radius [26, 27].

For comparison, (6,6) armchair MoS₂ nanotube was also constructed and analyzed. In this nanotube, the Mo-S bond lengths on the outer surface range from 2.44 Å to 2.61 Å, while those on the inner surface range from 2.35 Å to 2.37 Å. At the same curvature, the corresponding Mo-S bond lengths in the 240-pri MoS₂ arc model range from 2.42 Å to 2.62 Å on the outer surface, and from 2.31 Å to 2.35 Å on the inner surface.

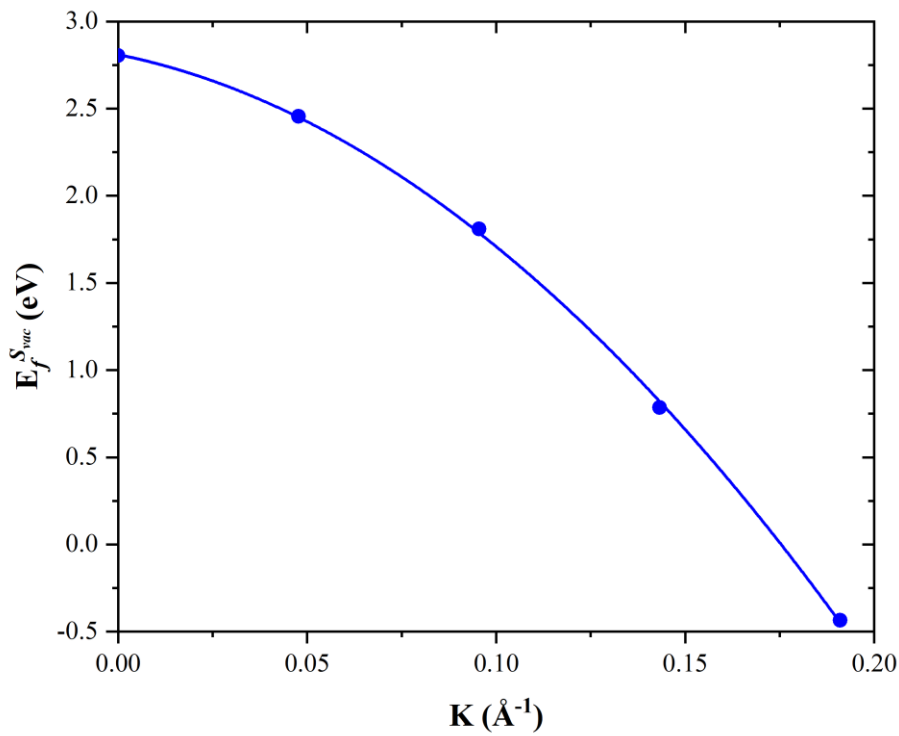


Figure 3.3 Formation energy of sulfur vacancy on MoS₂ arcs.

According to the literature, the formation energy for a sulfur vacancy ($E_f^{S_{vac}}$) in monolayer MoS₂ is reported as 2.54 eV for curved structures and 2.73 eV for flat sheets^[28]. In our model, the formation energy for a sulfur vacancy in flat MoS₂ is 2.80 eV and decreases with the increase of curvature, exhibiting a quadratic relationship similar to that observed for E_f^{arc} . At the maximum curvature investigated (i.e., the 240-

vac model), $E_f^{S_{vac}}$ indicating that sulfur vacancy formation becomes energetically favorable and may occur spontaneously. This also means that the stability of this highly curved structure is fragile. Consistent with this, for the (6,6) armchair MoS₂ nanotube, our calculations show that each sulfur vacancy (inner) or hydrogen adsorption (outer) leads to structural instability, resulting in the breakdown of the nanotube.

To further compare the electronic environment at the adsorption site, we calculated the PDOS of the sulfur atoms indicated in **Figure 3.1**. Specifically, we compared the 0-pri model with a monolayer of infinite planar MoS₂, and the 240-pri model with the (6,6) armchair MoS₂ nanotube. As shown in **Figure 3.4**, the results demonstrate that our model preserves similar electronic characteristics at the adsorption site under both extremes of curvature.

In summary, MoS₂ arc models with varying curvature were constructed and validated by comparing bond lengths, formation energies, and PDOS with reference structures. Results show consistent structural and electronic properties across models, confirming their reasonableness and suitability for further adsorption and electronic studies under different curvature conditions.

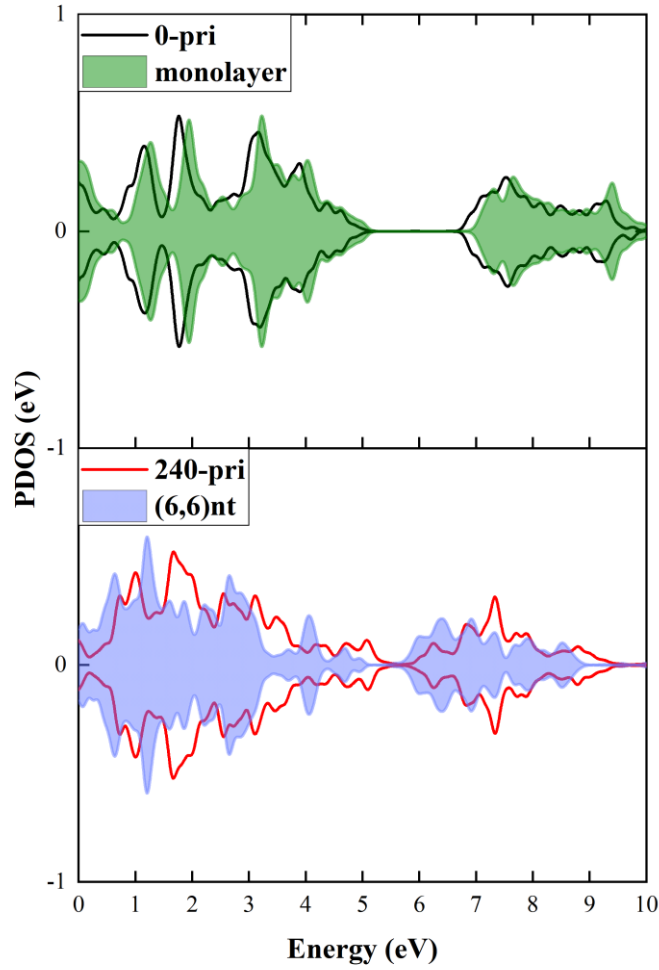


Figure 3.4 PDOS for the Sulfur-*p* orbital: 0-pri MoS₂ arcs (black line), monolayer flat MoS₂ slab (green shaded area), 240-pri MoS₂ arcs (red line) and (6,6) armchair nanotube (purple shaded area). The vacuum level is set as the reference at 0 eV.

3.3.2. HER Activity of MoS₂ Arcs

Figure 3.5 presents the calculated Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) as a function of curvature (K) for both pristine and sulfur-vacancy MoS₂ arc models. HER is highly sensitive to the electronic and geometric structure of the catalytic surface, with ΔG_{H^*} widely regarded as a key descriptor of HER activity [22].

Ideally, ΔG_{H^*} should be close to zero, facilitating optimal hydrogen adsorption and desorption [22]. In the present study, the pristine MoS₂ arc models (blue squares) exhibit relatively high ΔG_{H^*} values (1.22 eV), which decrease monotonically as curvature increases. This trend suggests that introducing curvature can effectively tune the hydrogen binding strength, making the surface more HER-active.

In contrast, the sulfur-vacancy models (red circles) consistently display lower ΔG_{H^*} values compared to their pristine counterparts at corresponding curvatures. The presence of sulfur vacancies thus significantly promotes hydrogen adsorption, in line with previous reports that highlight the role of defects in enhancing HER activity on MoS₂. [6, 29]. Notably, the reduction in ΔG_{H^*} with increasing curvature is also observed in the vacancy models, indicating a synergistic effect between curvature and defect engineering.

At the highest curvature examined, the ΔG_{H^*} value of the 240-pri MoS₂ arc model is even lower than that of the 240-vac model. This anomaly may be attributed to the significant strain present at such high curvature, which the fixed model is unable to fully relax. Unable to reflect the real situation, the instability of (6,6) armchair nanotube model, discussed in **Section 3.3.1**.

Interestingly, as the curvature K increases by 0.14 from the 0-pristine to the 180-pristine model, the ΔG_{H^*} decreases by 0.20 eV. In contrast, for the models with sulfur vacancies, the same increase in curvature results in only a 0.10 eV decrease in ΔG_{H^*} . This indicates that the introduction of sulfur vacancies diminishes the ability of curvature to modulate HER activity.

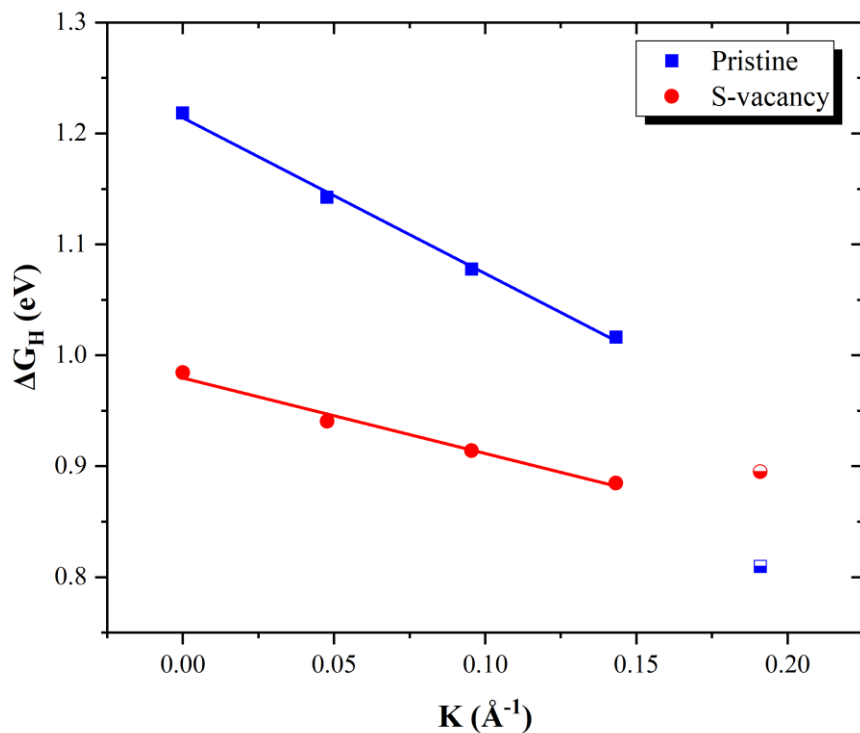


Figure 3.5 Gibbs free energy profiles for HER on pristine (blue) and vacancy-containing (red) MoS₂ arc models.

3.3.3. Electronic Structures Analysis

Figure 3.5 displays the PDOS of the S-*p* orbitals at the hydrogen adsorption sites for both pristine (solid lines) and sulfur-vacancy (shaded areas) MoS₂ arc models, with curvature parameters $x = 0, 60, 120, 180,$ and 240 (top to bottom). Notably, the energy scale is referenced to the vacuum level, set at 0 eV, ensuring a uniform basis for interpreting electronic structure variations due to both curvature and defect introduction. The Fermi level for each model is indicated by values of approximately 5.41, 5.36, 5.39, 5.44 and 5.51 eV for $x = 0, 60, 120, 180,$ and 240 , respectively.

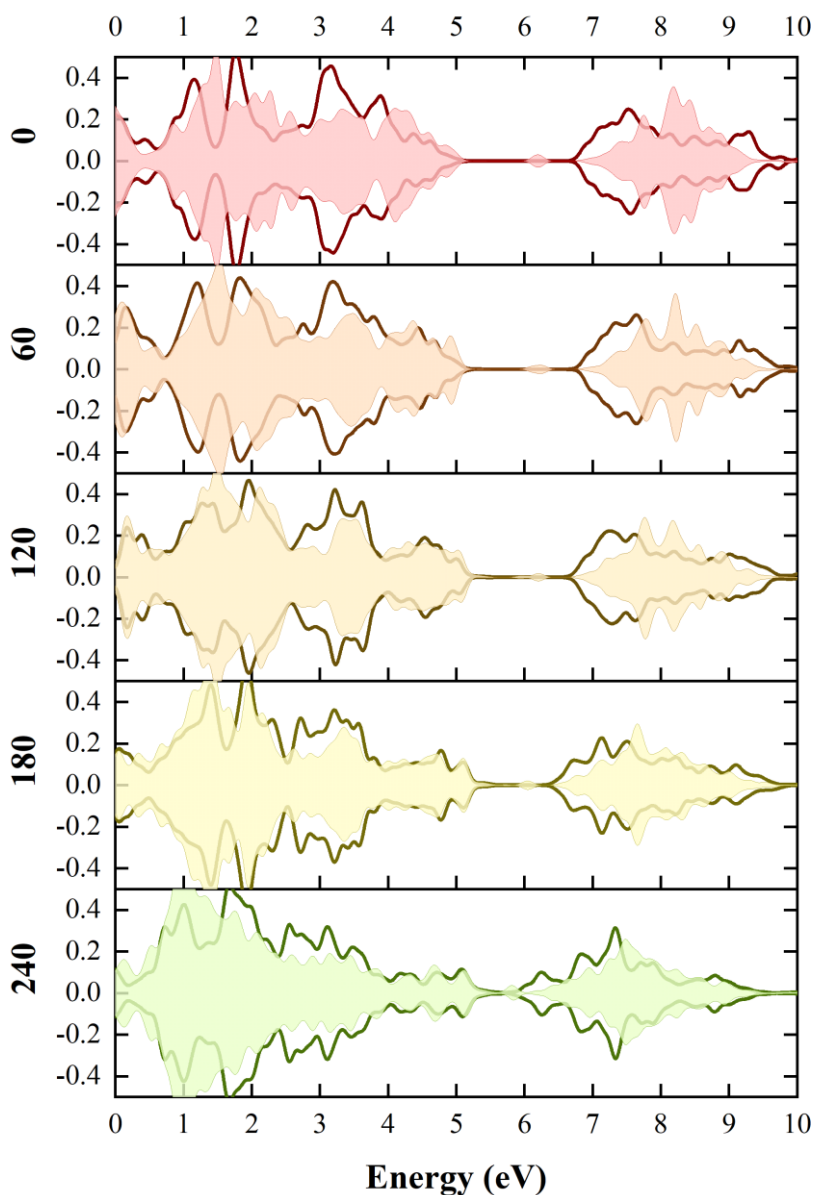


Figure 3.6 PDOS of the S-*p* orbitals before adsorption for x-pri (solid lines) and x-vac (shaded areas) MoS₂ arc models, where x = 0, 60, 120, 180, and 240 from top to bottom. The vacuum level is set as the reference at 0 eV.

Across all curvatures, the sulfur-vacancy (-vac) models display a noticeably higher and broader PDOS near their respective Fermi levels compared to the pristine (-pri) models. This enhancement in the electronic states around the Fermi level is crucial for

catalytic activity, as it increases the availability of electrons for hydrogen adsorption and subsequent evolution. Furthermore, the band gap associated with the S-*p* orbitals decreases as curvature increases, which aligns with literature findings that strain induces band gap narrowing [6].

Figure 3.6 presents the projected density of states (PDOS) for the S-*p* (solid lines) and H-*s* (shaded areas) orbitals at the hydrogen adsorption sites for x-vac MoS₂ arc models, with curvature parameters $x = 0, 60, 120, 180,$ and 240 (from top to bottom). The energy scale is referenced to the vacuum level, set at 0 eV.

Across all curvatures, the PDOS reveals significant hybridization between the S-*p* and H-*s* orbitals, as evidenced by the overlapping features in the vicinity of the adsorption sites. This hybridization is crucial for effective hydrogen adsorption and subsequent catalytic activity. As curvature increases from $0 \text{ \AA}^{-1}$ to $0.19 \text{ \AA}^{-1}$ (0-vac to 240-vac), several trends become apparent. First, the intensity and distribution of the S-*p* states near the Fermi level (approximately 5.13~5.22 eV, as noted for similar models) gradually broaden and shift, indicating a modification of the local electronic environment due to both curvature and the presence of sulfur vacancies.

On the other hand, the H-*s* orbital contributions (shaded regions) closely follow these changes, suggesting that the electronic structure of the adsorbed hydrogen atom is strongly influenced by the curvature-induced modifications in the S-*p* orbitals. It is noteworthy that the antibonding states formed between the S-*p* and H-*s* orbitals (located above the Fermi level) gradually diminish in intensity as the curvature increases. This reduction indicates a strengthening of the S-H bond, which correlates with the enhanced

hydrogen adsorption capacity observed in the x-vac models. Consequently, this trend provides a clear explanation for the improved HER performance with increasing curvature.

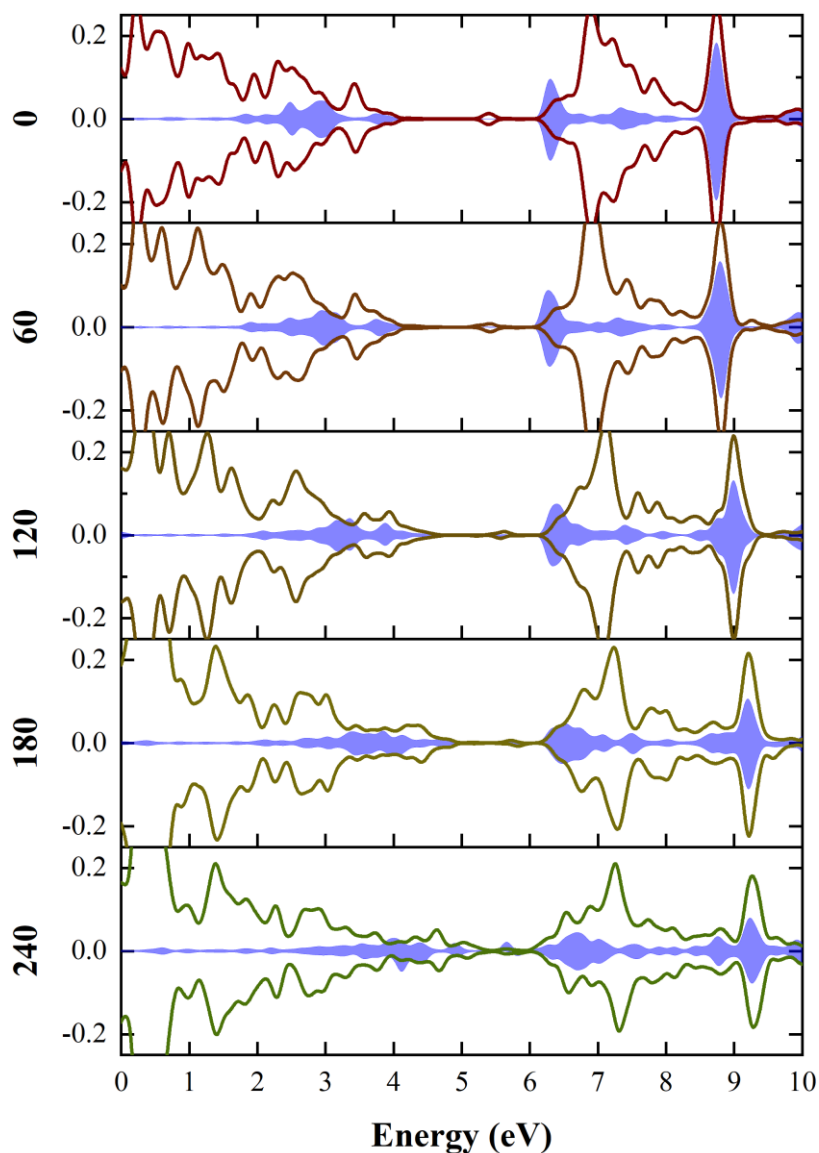


Figure 3.7 PDOS of the S-*p* (solid lines) and H-*s* (shaded areas) orbitals at the adsorption sites for x-vac MoS₂ arc models, where x = 0, 60, 120, 180, and 240 from top to bottom. The vacuum level is set as the reference at 0 eV.

3.3.4. Adsorption and Vacancy Located on the Same Side

Sections 3.3.2 and Sections 3.3.3 examined situations on which hydrogen adsorption and sulfur vacancies are situated on opposite sides of the MoS₂ arc models. The results indicate that, even under conditions of pronounced curvature, the HER performance remains poor. To address this limitation, we next consider the case where both hydrogen adsorption and sulfur vacancies are located on the same side of the structure (i.e., the top surface). As illustrated in **Figure 3.7**, our results reveal that hydrogen atoms preferentially adsorb at sulfur vacancy sites.

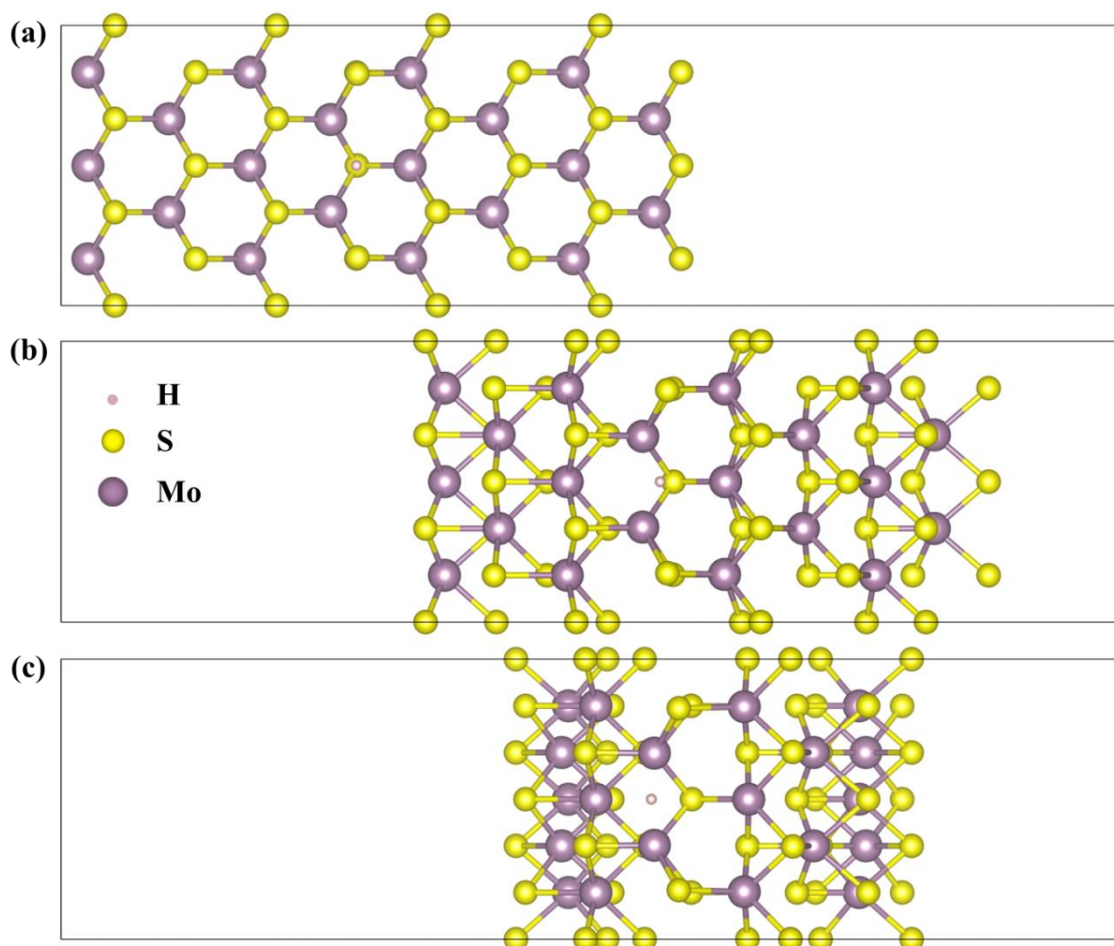


Figure 3.8 Top view of hydrogen adsorbed on (a) 0-vac MoS₂, (b) 120-vac MoS₂ and (c) 240-vac MoS₂ with a curvature of $K = 0 \text{ \AA}^{-1}$, $0.10 \text{ \AA}^{-1}$ and $0.19 \text{ \AA}^{-1}$, respectively.

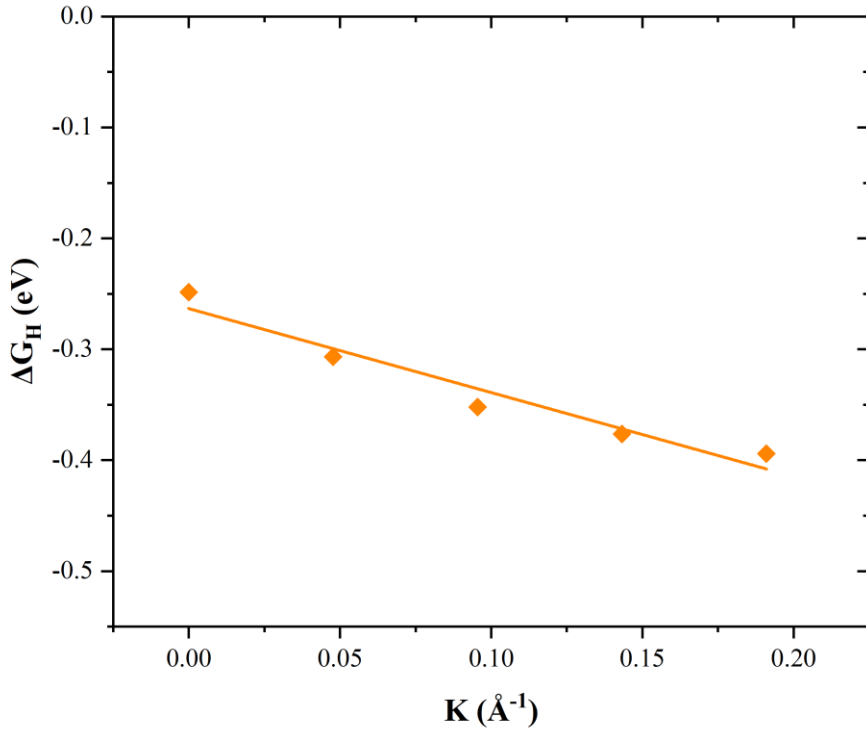


Figure 3.9 Gibbs free energy profiles for HER on MoS₂ arc models with sulfur vacancies and hydrogen adsorption located on the same side.

Moreover, The Mo-H bond lengths presented in **Figure 3.7** are 2.03, 1.97, and 1.94 Å, respectively. As the curvature increases, the preferred adsorption site for hydrogen progressively shifts from hollow to bridge sites. This transition in active sites reflects a corresponding change in Mo-H bond strength, which accounts for the observed decrease in the ΔG_{H^*} (**Figure 3.8**) as curvature increases, indicative of enhanced hydrogen adsorption capacity. Notably, at the maximum curvature considered, the ΔG_{H^*} reaches 0.39 eV, approaching the value characteristic of a pure metallic Mo surface [23]. This phenomenon is further corroborated by the PDOS analysis shown in **Figure 3.9**. As curvature increases, the band gap progressively narrows and ultimately

closes at the highest curvature, at which point the Mo atoms exhibit metallic characteristics.

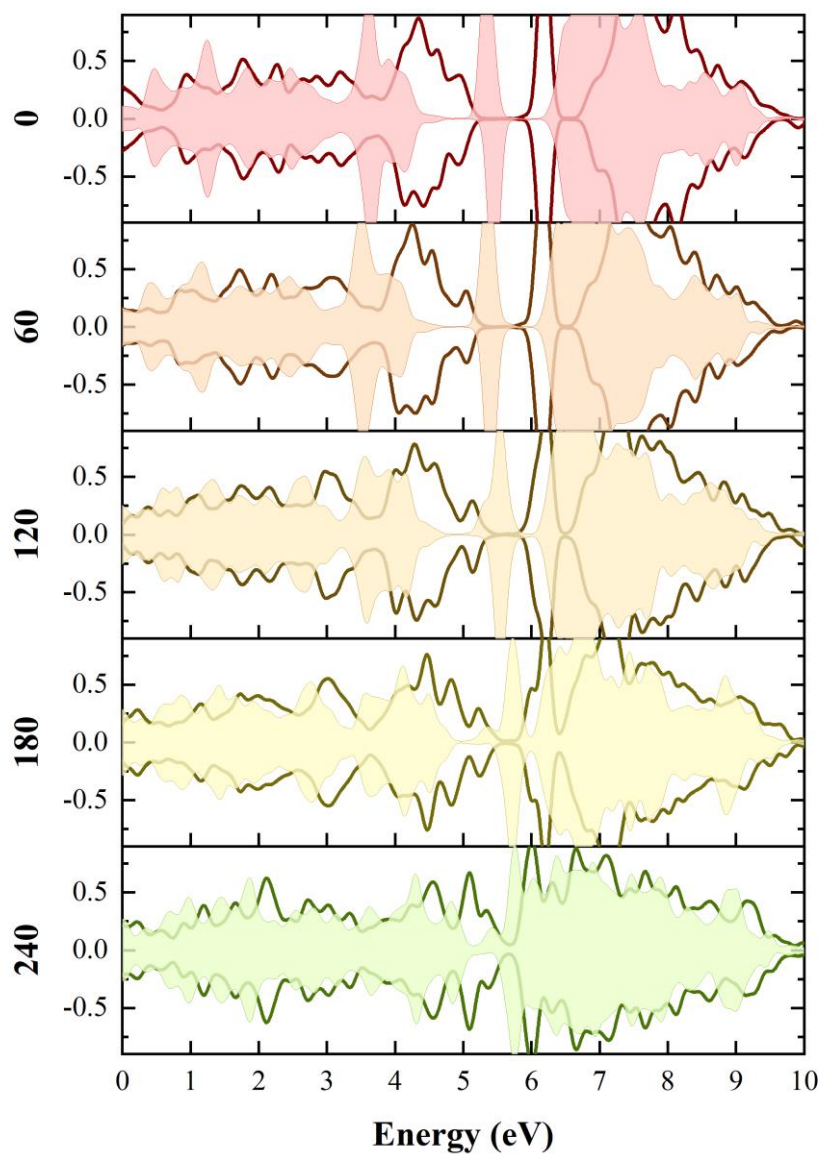


Figure 3.10 PDOS of the Mo-*d* orbitals before (solid lines) and after (shaded areas)

adsorption for x-vac MoS₂ arc models, where x = 0, 60, 120, 180, and 240 from top to

bottom. The vacuum level is set as the reference at 0 eV.

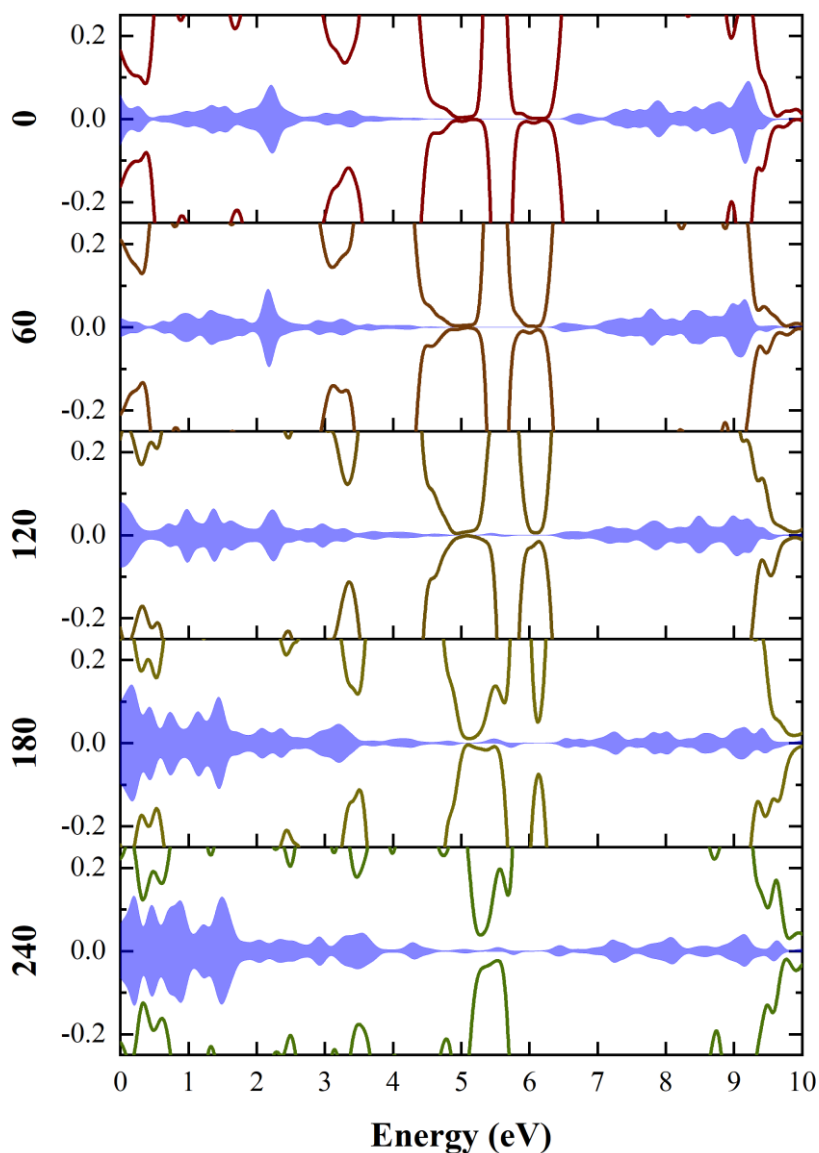


Figure 3.11 PDOS of the Mo-*d* (solid lines) and H-*s* (shaded areas) orbitals at the adsorption sites for x-vac MoS₂ arc models, where x = 0, 60, 120, 180, and 240 from top to bottom. The vacuum level is set as the reference at 0 eV.

The PDOS calculations presented in **Figures 3.9** and **Figure 3.10** are both based on Mo atoms at the bridge adsorption sites, as these sites make the greatest contribution to hydrogen adsorption. As illustrated in **Figure 3.10**, the antibonding states associated

with hydrogen atoms weaken with increasing curvature, indicating enhanced bonding strength. This trend accounts for the observed decrease in ΔG_{H^*} with increasing curvature. Notably, this behavior is consistent with the hydrogen adsorption characteristics at sulfur sites discussed in **Section 3.3.3**.

3.4. Conclusions

In this chapter, we systematically investigated the electronic structure and catalytic properties of MoS₂ arc models with varying curvature and engineered sulfur vacancies. We focus on their impacts on the HER. By employing PDOS analysis, we revealed how both curvature and defect engineering modulate the local environment at the adsorption sites.

Our findings demonstrate that curvature of MoS₂ can narrow the band gap, which is similar with previous literature on strain-induced band gap modulation [6]. More importantly, the sulfur vacancy significantly enhances the S-*p* states near the Fermi level. This makes electron transfer more efficient and promotes hydrogen adsorption. The PDOS analysis further shows pronounced hybridization between S-*p* orbitals of MoS₂ and H-*s* orbitals from the adsorbed hydrogen, with clear signatures of bonding and antibonding states. A key observation is that the antibonding states above the Fermi level weaken as curvature increases, indicating stronger S-H or Mo-H bonds and improved hydrogen adsorption capacity in the models with vacancy. This directly contributes to lower ΔG_{H^*} , which is critical for HER activity.

Although the ΔG_{H^*} for the 0-pri model is lower than the theoretically calculated value (~ 2.0 eV), likely due to the exposure of zigzag edges at both ends^[6, 24, 25]. This chapter primarily focuses on the relationship between curvature and HER activity trends qualitatively. Therefore, this deviation can be reasonably disregarded.

Overall, by manipulating curvature and defect concentration, this chapter underscores the catalytic properties of MoS₂ can be tuned by microstructures, offering valuable insights for the rational design of advanced HER electrocatalysts.

References

1. Chhowalla, M., et al., *The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets*. Nature chemistry, 2013. **5**(4): p. 263-275.
2. Zeng, H., et al., *Valley polarization in MoS₂ monolayers by optical pumping*. Nature nanotechnology, 2012. **7**(8): p. 490-493.
3. Samy, O., et al., *A review on MoS₂ properties, synthesis, sensing applications and challenges*. Crystals, 2021. **11**(4): p. 355.
4. Laursen, A.B., et al., *Molybdenum sulfides—efficient and viable materials for electro - and photoelectrocatalytic hydrogen evolution*. Energy & Environmental Science, 2012. **5**(2).
5. Voiry, D., et al., *The role of electronic coupling between substrate and 2D MoS₂ nanosheets in electrocatalytic production of hydrogen*. Nature materials, 2016. **15**(9): p. 1003-1009.
6. Li, H., et al., *Corrigendum: Activating and optimizing MoS₂ basal planes for hydrogen evolution through the formation of strained sulphur vacancies*. Nat Mater, 2016. **15**(3): p. 364.
7. Li, L., et al., *Role of Sulfur Vacancies and Undercoordinated Mo Regions in MoS₂ Nanosheets toward the Evolution of Hydrogen*. ACS Nano, 2019. **13**(6): p. 6824-6834.
8. Tan, Y., et al., *Monolayer MoS₂ films supported by 3D nanoporous metals for high-efficiency electrocatalytic hydrogen production*. Adv Mater, 2014. **26**(47): p. 8023-8.
9. Li, G., et al., *Engineering Substrate Interaction To Improve Hydrogen Evolution Catalysis of Monolayer MoS₂ Films beyond Pt*. ACS Nano, 2020. **14**(2): p. 1707-1714.
10. Cepitis, R., et al., *Surface Curvature Effect on Dual-Atom Site Oxygen Electrocatalysis*. ACS Energy Letters, 2023. **8**(3): p. 1330-1335.
11. Wang, X., et al., *Highly Curved Defect Sites: How Curvature Effect Influences Metal-Free Defective Carbon Electrocatalysts*. Small, 2024. **20**(36): p. 2401447.
12. Zhu, G., et al., *Curvature-Dependent Selectivity of CO₂ Electrocatalytic Reduction on Cobalt Porphyrin Nanotubes*. ACS Catalysis, 2016. **6**(9): p. 6294-6301.
13. Ma, N., et al., *Curvature effects regulate the catalytic activity of Co@ N₄-doped carbon nanotubes as bifunctional ORR/OER catalysts*. Journal of Colloid and Interface Science, 2024. **654**: p. 1458-1468.

14. Li, J., et al., *Eggshell-like MoS₂ Nanostructures with Negative Curvature and Stepped Faces for Efficient Hydrogen Evolution Reactions*. ACS Applied Nano Materials, 2021. **4**(12): p. 14086-14093.
15. Ng, H.K., et al., *Improving carrier mobility in two-dimensional semiconductors with rippled materials*. Nature Electronics, 2022. **5**(8): p. 489-496.
16. Liu, Y., et al., *Curved structure regulated single metal sites for advanced electrocatalytic reactions*. Small, 2024. **20**(47): p. 2404758.
17. Hong, J., et al., *Exploring atomic defects in molybdenum disulphide monolayers*. Nat Commun, 2015. **6**: p. 6293.
18. Qu, Y., et al., *Effect of curvature on the hydrogen evolution reaction of graphene*. The Journal of Physical Chemistry C, 2018. **122**(44): p. 25331-25338.
19. Villarreal, E., et al., *Nanoscale Surface Curvature Effects on Ligand–Nanoparticle Interactions: A Plasmon-Enhanced Spectroscopic Study of Thiolated Ligand Adsorption, Desorption, and Exchange on Gold Nanoparticles*. Nano Letters, 2017. **17**(7): p. 4443-4452.
20. Ansari, R., et al., *An ab initio investigation into the elastic, structural and electronic properties of MoS₂ nanotubes*. Superlattices and Microstructures, 2015. **82**: p. 188-200.
21. Tafel, J., *Über die Polarisation bei kathodischer Wasserstoffentwicklung*. Zeitschrift für physikalische Chemie, 1905. **50**(1): p. 641-712.
22. Nørskov, J.K., et al., *Trends in the exchange current for hydrogen evolution*. Journal of The Electrochemical Society, 2005. **152**(3): p. J23.
23. Jaramillo, T.F., et al., *Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nanocatalysts*. Science, 2007. **317**(5834): p. 100-102.
24. Liu, L., et al., *Effect of edge structure on the activity for hydrogen evolution reaction in MoS₂ nanoribbons*. Applied Surface Science, 2017. **396**: p. 138-143.
25. Lazar, P. and M. Otyepka, *Role of the Edge Properties in the Hydrogen Evolution Reaction on MoS₂*. Chemistry, 2017. **23**(20): p. 4863-4869.
26. Hao, J., Z. Wang, and Q. Jin, *DFT study of structural, elastic, electronic and dielectric properties of blue phosphorus nanotubes*. Sci Rep, 2019. **9**(1): p. 11264.
27. Gülseren, O., T. Yildirim, and S. Ciraci, *Systematic ab initio study of curvature effects in carbon nanotubes*. Physical Review B, 2002. **65**(15): p. 153405.
28. Zhang, H., et al., *In-plane defect engineering on MoS₂ through a novel two-phase hydrothermal synthesis*. Catalysis Today, 2022. **404**: p. 269-278.

29. Jiao, S., et al., *Pt Atom on the Wall of Atomic Layer Deposition (ALD)-Made MoS(2) Nanotubes for Efficient Hydrogen Evolution*. *Small*, 2022. **18**(16): p. e2105129.

Chapter 4. Loading Effects on the Oxygen Reduction Reaction

Activity of Heteronuclear Fe-Co Single-Atom Catalysts

4.1. Introduction

Single-atom catalysts (SACs) have emerged as a transformative class of materials for catalytic applications due to their maximized atom utilization, high catalytic activity, and unique selectivity ^[1-3]. Among SACs, FeN₄-C and CoN₄-C systems have demonstrated excellent catalytic performance for the oxygen reduction reaction (ORR), a key process in energy conversion technologies such as fuel cells and metal-air batteries ^[4, 5]. However, achieving high SAC loadings while preserving site-specific activity remains a significant challenge ^[6-8].

The loading of SACs is critical for improving the overall catalytic performance but introduces complex inter-site interactions that can alter intrinsic activity. For example, homonuclear SACs such as FeN₄-C show a non-linear relationship between loading concentration and ORR performance, where site-specific activity peaks at intermediate loadings and declines at higher loadings due to excessive inter-site coupling. In contrast, heteronuclear SACs, which integrate two or more distinct atomic species, provide an additional degree of freedom for tuning catalytic properties and exhibit synergistic effects that enhance performance beyond their homonuclear counterparts. Despite their promise, the loading effects on the site-specific activity of heteronuclear SACs remain poorly understood.

This chapter investigates the loading-dependent catalytic behavior of heteronuclear Fe_{cen}-Co_{cor} SACs, where Fe and Co atoms are co-supported on a nitrogen-doped graphene substrate. Using DFT calculations, this study explained the interplay between loading, electronic structure, spin state, and catalytic activity. The findings provide a comprehensive understanding of species-specific loading effects in heteronuclear SACs and establish design principles for optimizing their performance.

4.2. Computational methods

4.2.1. Computational Parameters

All DFT calculations were performed using the VASP. The PBE parametrized GGA was employed for exchange-correlation interactions, while the PAW method was used for core-electron interactions. To account for van der Waals interactions, the DFT-D3 dispersion correction was applied. Key computational parameters include: plane wave cutoff energy is 500 eV; Γ -centered grid with a product of ~ 60 with the in-plane lattice constant; a vacuum layer of ~ 20 Å in the out-of-plane direction; the energy and force convergence thresholds were set to 1×10^{-5} eV and 0.01 eV/Å, respectively. Localized 3d-electron interactions for transition metals were described using a Hubbard U correction with values of 3.06 eV, 3.29 eV, 3.42 eV, 3.4 eV, and 3.87 eV for Mn, Fe, Co, Ni, and Cu, respectively [9, 10]. The *ab initio* molecular dynamics (AIMD) simulation was conducted at 300 K using the Nosé-Hoover thermostat with a time step of 1 fs. [5, 11]

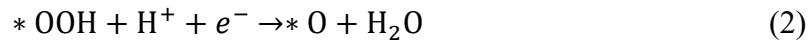
4.2.2. System Design and Metal Loading

Heteronuclear Fe_{cen}-Co_{cor} SACs were modeled by embedding Fe and Co atoms into a nitrogen-doped graphene substrate. The metal loading concentration was varied by adjusting the size of the simulation supercell, with values ranging from 2.8 wt% to 16.8 wt%. An ultra-high loading of 38.4 wt% was also simulated to explore extreme strong inter-site coupling effects. The metal loading was calculated using the following equation:

$$\text{TM Loading} = \frac{\sum_{i=\text{Fe,Co}} n_i \times m_i}{\sum_{i=\text{Fe,Co,N,C}} n_i \times m_i} \times 100\% \quad \dots (4.1)$$

where n_i is the number of atoms of species i , and m_i the mass of the atom of species i .

4.2.3. Catalytic Path of ORR in Calculation



Where “*” represents slab, and “* X” represents intermediates in catalysis.

4.2.4. Thermodynamics of ORR

The Gibbs free energy (ΔG) for each elementary ORR step can be calculated under the Computational Hydrogen Electrode (CHE) framework ^[4, 12]:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} \quad \dots (4.2)$$

where ΔE is the reaction energy. ΔE_{ZPE} and ΔS are the change in the zero-point energy and the vibrational entropy at temperature $T = 298.15$ K, respectively. ΔG_U is the free energy correction from the applied potential. ΔG_{pH} is the correction from the proton concentration (pH) in the following formula:

$$\Delta G_{\text{pH}} = 2.303 \times k_{\text{B}} T \times \text{pH} \quad \dots (4.3)$$

where k_{B} is the Boltzmann constant and pH is set to 0. The limiting potential (U_{L}) can be obtained according to the below equation:

$$U_{\text{L}} = - \frac{\max_i \{\Delta G_i\}}{e} \quad \dots (4.4)$$

where ΔG_i stands for the Gibbs free energy change of the i -th elementary step of ORR.

4.2.5. Energy Center of the Occupied States

The energy center of the occupied states of the *OH on the Fe site is calculated as:

$$\langle E(*\text{OH}) \rangle = \frac{\int_{-\infty}^{E_{\text{f}}} \rho_{*\text{OH}}(E) \times E dE}{\int_{-\infty}^{E_{\text{f}}} \rho_{*\text{OH}}(E) dE} \quad \dots (4.5)$$

where $\rho_{*\text{OH}}(E)$ is the projected density of states onto the *OH adsorbate and the Fermi level E_{f} is set to zero. For the real numerical integration, the lower limit is set to ~ 10 eV below the Fermi level where there are very little projected states. The energy center of the occupied states of the *OOH adsorbate on the Co site can be calculated by substituting $\rho_{*\text{OOH}}(E)$ for $\rho_{*\text{OH}}(E)$. Analogously, the energy center of the occupied 3d orbitals of the Fe and Co site can be calculated.

4.3. Results and Discussion

4.3.1. Structures and Stability

To investigate the structural stability of heteronuclear SACs, a pair of TMN₄ moieties (TM = Fe, Co) was embedded into a nitrogen-doped graphene substrate. The total metal loading was systematically varied from approximately ~3 wt% to ~38.4 wt% by adjusting the graphene supercell size ($n \times n$). A recent study indicates that at a high metal loading of 14.3 wt%, increasing the distance between Fe and Co single atoms enhances the energetic stability of the heteronuclear SACs [13]. Therefore, two configurations with nearly identical maximum inter-site distances ($\langle d_{\text{site}} \rangle$) were considered for a given TM loading. As illustrated in **Figure 4.1a-b**, at a metal loading of 9.1 wt% ($n=7$), one TMN₄ moiety (TM_{cen}N₄) was positioned near the center of the supercell, while the other moiety (TM_{cor}N₄) was placed near a corner. Two configurations were considered based on the relative alignment of TM_{cen}-TM_{cor}: in **Configuration I**, the line connecting the Fe_{cen} and Co_{cor} moieties was parallel to the diagonal of the supercell, whereas in **Configuration II**, the line slightly deviated from the diagonal. These configurations are referred to as TM_{cen}-TM_{cor}@ $n \times n$ -I and TM_{cen}-TM_{cor}@ $n \times n$ -II, respectively. The average inter-site distance ($\langle d_{\text{site}} \rangle$) between Fe_{cen} and Co_{cor} was found to vary from ~3 Å to ~16 Å across the loading ranges.

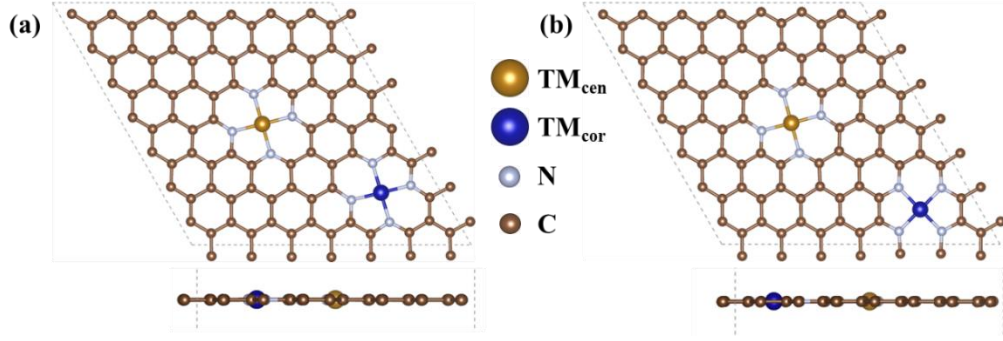


Figure 4.1 The top (top row) and side view (bottom row) of (a) $\text{TM}_{\text{cen}}\text{-TM}_{\text{cor}}@n\times n\text{-I}$ and (b)

$\text{TM}_{\text{cen}}\text{-TM}_{\text{cor}}@n\times n\text{-II}$ at $n = 7$ with the TM loading of 9.1 wt%.

To simulate isolated $\text{TMN}_4\text{-C}$ systems, a 9×9 graphene supercell was used, containing only one TMN_4 moiety ($\langle d_{\text{site}} \rangle = 22.21 \text{ \AA}$). This configuration was denoted as $\text{TM}@9\times 9\text{-S}$. It is worth noting that the simulation models employed may overestimate the experimental metal loadings, as real-world samples typically contain pores and nitrogen dopants that are not occupied by transition metal atoms. For instance, experimental studies have reported $\text{FeN}_4\text{-C}$ systems with average inter-site distances of 5 $\text{\AA}$, 7 $\text{\AA}$, and 12 $\text{\AA}$, corresponding to metal loadings of 8.02 wt%, 5.41 wt%, and 1.82 wt%, respectively. These experimentally estimated loadings, based on inductively coupled plasma mass spectrometry (ICP-MS), are approximately one-third of the theoretical values derived from inter-site distances ^[14].

The structural stability of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n\times n$ was first evaluated by comparing the total energies of Configurations I and II. As shown in **Figure 4.2**, Configuration II was consistently more energetically stable than Configuration I across the loading range. The energy difference, $E(n\times n\text{-I}) - E(n\times n\text{-II})$, reached a maximum at $n=7$ (9.1 wt% loading), beyond which it decreased rapidly. This suggests that the inter-site

interactions between Fe_{cen} and Co_{cor} weaken significantly at lower loadings (below 3.8 wt%) or when the average inter-site distance exceeds (above ~ 16 Å).

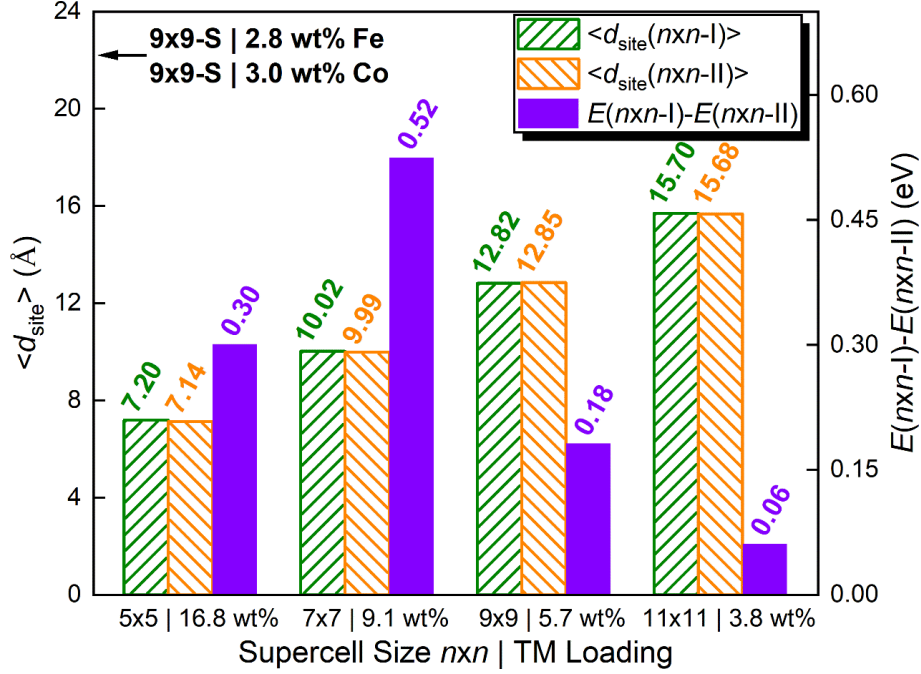


Figure 4.2 The average distance between Fe_{cen} and Co_{cor} ($\langle d_{\text{site}} \rangle$) and the relative energetic stability between $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n \times n\text{-I}$ and $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n \times n\text{-II}$, $E(n \times n\text{-I}) - E(n \times n\text{-II})$, as functions of the supercell size (TM loading).

The thermodynamic and electrochemical stabilities of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n \times n$ were further assessed using the formation energy (E_f) calculated as follows:

$$E_f(\text{TM}) = E(\text{tot}) - E(V_{\text{TM}}) - E(\text{TM}_{\text{bulk}}) \quad \dots (4.6)$$

and the dissolution potential (U_d),

$$U_d(\text{TM}) = U_d^0(\text{TM}_{\text{bulk}}) - \frac{E_f(\text{TM})}{Ne} \quad \dots (4.7)$$

Here, $E(\text{tot})$ and $E(V_{\text{TM}})$ represent the total energy of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n \times n$ without and with a TM vacancy (TM = Fe_{cen} or Co_{cor}), respectively. $E(\text{TM}_{\text{bulk}})$ is the energy per

atom of bulk-phase TM, $U_d^0(\text{TM}_{\text{bulk}})$ is the standard dissolution potential of bulk-phase TM, and Ne is the number of electrons involved in dissolution. According to the established stability criteria ($E_f(\text{TM}) < 0$ eV and $U_d(\text{TM}) > 0$ V [15]), all $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n\times n\text{-II}$ configurations considered in this study were found to be stable (**Figure 4.3**), even at the ultra-high loading of 38.4 wt% ($n=3$).

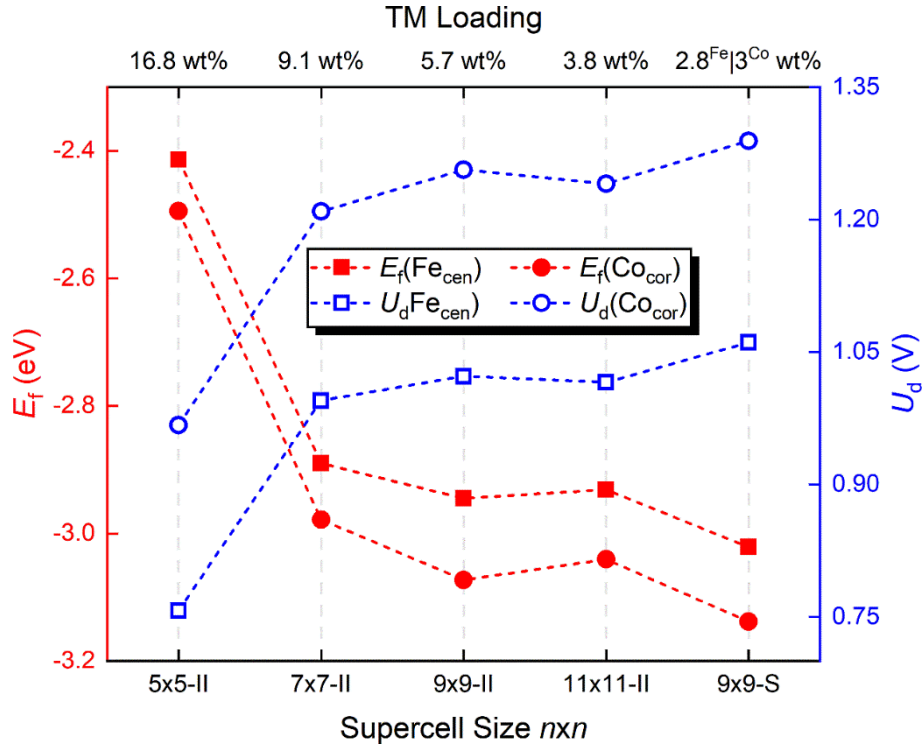


Figure 4.3 The formation energy and the dissolution potential of Fe_{cen} and Co_{cor} as functions of the supercell size (TM loading).

Interestingly, the formation energy (E_f) increases, and the dissolution potential (U_d) decreases with increasing metal loading, indicating reduced stability as Fe and Co sites approach each other. These trends align with experimental observations that synthesizing high-density SACs poses significant challenges. Moreover, the formation energy of Co_{cor} is consistently lower than that of Fe_{cen} , suggesting that Co_{cor} forms

stronger chemical bonds with neighboring nitrogen atoms. This is corroborated by the shorter $\text{Co}_{\text{cor}}\text{-N}$ bond lengths observed in **Figure 4.4**.

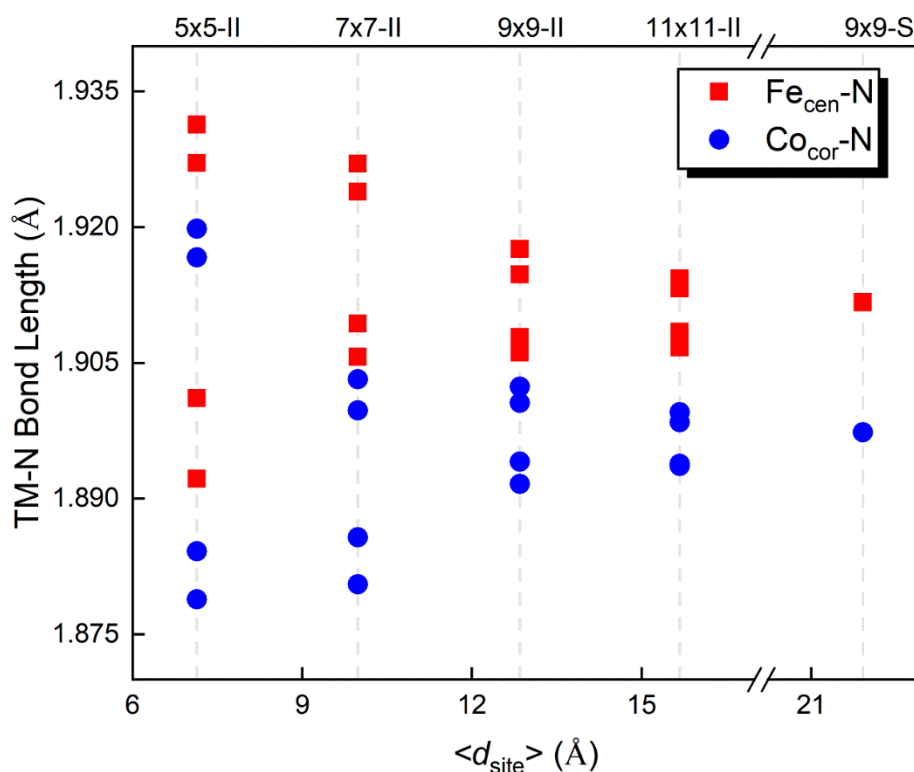


Figure 4.4 The $\text{Fe}_{\text{cen}}\text{-N}$ and $\text{Co}_{\text{cor}}\text{-N}$ bond lengths as functions of (top x axis) the TM loading and (bottom x axis) the corresponding simulation supercell size.

In summary, $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n \times n\text{-II}$ (with $n=9,7,5$) was identified as the most stable configuration. These models, along with the isolated $\text{TM}@9 \times 9\text{-S}$, were selected for subsequent analyses to explain the interplay between metal loading, inter-site distance, and catalytic activity.

4.3.2. ORR Activity of Isolated Fe and Co Sites

Before investigating the loading-dependent site-specific ORR activity, the catalytic performance of nearly isolated $\text{FeN}_4\text{-C}$ and $\text{CoN}_4\text{-C}$ was explored using $\text{Fe}@9 \times 9\text{-S}$ (2.8 wt% Fe) and $\text{Co}@9 \times 9\text{-S}$ (3.0 wt% Co), respectively. In these

configurations, the inter-site distance exceeds 20 Å (**Figure 4.2**), ensuring minimal interaction between the single-atom sites. The Gibbs free energy diagrams along the 4-electron ORR pathway for the isolated Fe and Co sites are presented in **Figure 4.5a-b**.

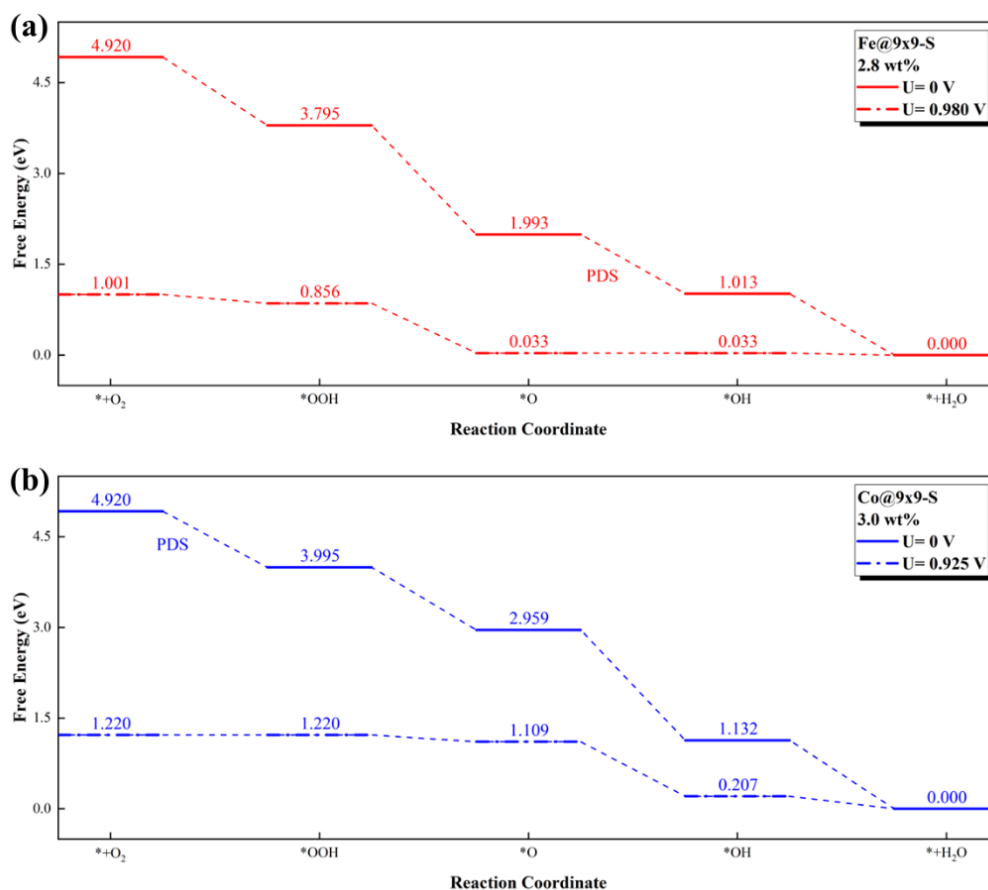


Figure 4.5 The Gibbs free energy diagram for ORR on the (a) Fe site of Fe@9×9-S and the (b) Co site of Co@9×9-S.

The calculated Gibbs free energies reveal that the Fe site binds all intermediate adsorbates more strongly than the Co site, especially the *O adsorbate. This behavior can be attributed to the relatively stronger binding of the Co site with the substrate (**Figure 4.3**). For the isolated Fe site, the hydrogenation of *O to *OH is identified as the potential-determining step (PDS), whereas for the isolated Co site, the PDS is the first hydrogenation step to form *OOH. Using the Gibbs free energy values, the limiting

potential (U_L) was calculated to be 0.980 V for the Fe site and 0.925 V for the Co site.

These results indicate that both isolated Fe and Co sites exhibit high catalytic activity for the ORR; and in thermodynamic, the Fe site is more favorable than that of Co.

Notably, the superior ORR catalytic activity of Fe and Co SACs, as well as the relative trend of Fe SACs > Co SACs, has been widely observed in experimental studies [4, 5, 8, 16-18]. The consistency between our theoretical findings and experimental observations underscores the reliability of the computational approach adopted in this study. Furthermore, it is worth mentioning that Fe@9×9-S corresponds to an Fe loading of 2.8 wt%, which closely matches the reported loading of 2.78 wt% for concave-shaped FeN₄-C. Experimental studies on the latter have demonstrated superior ORR performance, corroborating the high catalytic activity predicted for the isolated Fe site [8].

4.3.3. Loading-Dependent Catalytic Behavior

The effect of metal loading on the Fe site of Fe_{cen}-Co_{cor}@ $n \times n$ was systematically investigated. For clarity, the TM_{cen} and TM_{cor} sites in TM_{cen}-TM_{cor}@ $n \times n$ is hereafter referred to as TM_{cen}@ $n \times n$ and TM_{cor}@ $n \times n$, respectively. **Figure 4.6a-c** depict the calculated Gibbs free energy diagrams along the 4-electron ORR pathway for Fe_{cen}@ $n \times n$ -II at metal loadings of 5.7 wt%, 9.1 wt%, and 16.8 wt%, respectively.

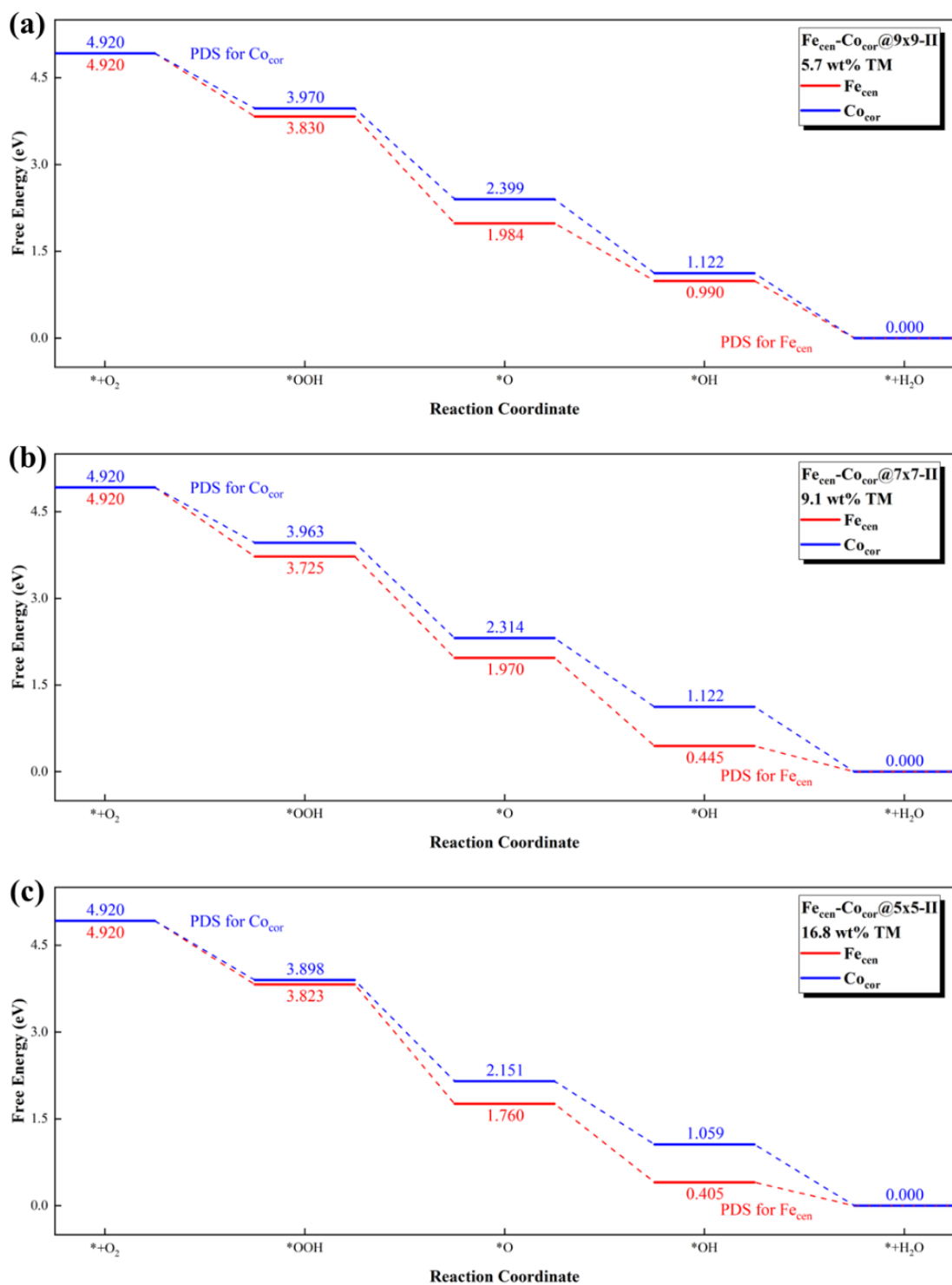


Figure 4.6 Gibbs free energy diagrams for the oxygen reduction reaction (ORR) at the Fe and Co sites of (a) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@9\times9\text{-II}$, (b) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@7\times7\text{-II}$, and (c) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@5\times5\text{-II}$. The corresponding transition metal (TM) loading for each system is indicated.

As the metal loading increases from 2.8 wt% (Fe@9×9-S) to 5.7 wt%, the energetics of ORR intermediate states undergo slight modulation. At this loading, the PDS shifts from the hydrogenation of *O₂ to *OH to the hydrogenation of *OH to H₂O (**Figure 4.6a**). However, the calculated limiting potential ($U_L = 0.990$ V) for Fe_{cen}@9×9-II is nearly identical to that of the isolated Fe@9×9-S ($U_L = 0.980$ V), indicating that the ORR catalytic performance remains largely unaffected. This is attributed to the relatively large inter-site distance (~13 Å) between neighboring Co sites and the Fe site, which minimizes their interaction.

When the metal loading increases to 9.1 wt% (Fe_{cen}-Co_{cor}@7×7-II), a significant change is observed. The binding strength of *OH on the Fe site increases dramatically, reaching 0.445 eV (**Figure 4.6b**). In this case, the PDS remains the hydrogenation of *OH; however, the enhanced *OH adsorption significantly lowers the limiting potential from 0.990 V to 0.445 V, leading to a substantial decline in ORR catalytic activity. At an even higher loading of 16.8 wt%, the Fe site exhibits further deterioration in catalytic performance due to even stronger *OH adsorption (**Figure 4.6c**).

The abrupt decline in ORR catalytic activity between 5.7 wt% and 9.1 wt% is further corroborated by calculations for the Fe site at an intermediate loading of 7.1 wt% (Fe_{cen}-Co_{cor}@8×8-II). At this loading, the Fe site exhibits binding energetics for ORR intermediates that are highly similar to those at 5.7 wt% and 2.8 wt%. The PDS remains the hydrogenation of *OH, with a calculated limiting potential of $U_L = 0.975$ V, further confirming that the significant degradation in catalytic performance occurs at loadings of 9.1 wt% and above.

In contrast, the Co site demonstrates a markedly different behavior. Across the entire loading range investigated (3.0 wt% to 16.8 wt%), the PDS for the 4-electron ORR pathway remains unchanged, corresponding to the hydrogenation of O_2 to $*OOH$. Interestingly, the adsorption strength of $*OOH$ on the Co site is progressively optimized as the metal loading increases, resulting in a monotonic increase in the limiting potential (**Figure 4.7**). This suggests that the intrinsic ORR activity of the Co site is slightly but continuously enhanced with increasing loading.

At the highest loading of 16.8 wt%, the Co site achieves a limiting potential of $U_L = 1.022$ V, which is higher than that of both the nearly isolated $Fe@9\times9-S$ ($U_L = 0.980$ V) and $Fe_{cen}@9\times9-II$ ($U_L = 0.990$ V). This stands in stark contrast to the Fe site, where increased loading negatively impacts intrinsic ORR activity at 9.1 wt% and above. These findings highlight the distinct loading-dependent catalytic behaviors of Fe and Co sites in heteronuclear SACs, with the Co site demonstrating a more robust response to increased metal loading.

4.3.4. Magnetism and Spin State Evolution

Both Fe and Co are magnetic elements, and previous studies have demonstrated that the spin states of SACs can significantly influence their catalytic performance.^[19-24] Accordingly, we investigated the spin states of Fe_{cen} and Co_{cor} sites in $Fe_{cen}-Co_{cor}@n\times n-II$, with particular attention to configurations where the potential-determining ORR intermediate is adsorbed. Prior to the onset of the ORR, our calculations reveal that $Fe_{cen}@n\times n-II$ and $Co_{cor}@n\times n-II$ exhibit nearly constant magnetic moments of approximately $2 \mu_B$ and $1 \mu_B$, respectively, irrespective of the

metal loading. These values are comparable to those of isolated Fe and Co atoms in Fe@9×9-S and Co@9×9-S, respectively. Notably, the Fe site with a magnetic moment of 2 μ_B has recently been identified as the most stable spin state. [25, 26]

For Fe_{cen}@n×n-II, *OH serves as the potential-determining intermediate adsorbate across all n values from 9 to 5, corresponding to metal loadings ranging from 5.7 wt% to 16.8 wt% (see **Figure 4.6**). Accordingly, the spin state of Fe_{cen} with *OH adsorbed was systematically investigated, with the results summarized in **Figure 4.7a**. At a lower metal loading of 2.8 wt% (Fe@9×9-S), *OH adsorption reduces the magnetic moment of the Fe site from 2 μ_B to approximately 1.3 μ_B , resulting in a stabilized low-spin state. This low-spin configuration persists as the metal loading increases, until a threshold is reached at 9.1 wt% (Fe_{cen}-Co_{cor}@7×7-II), above which Fe_{cen} energetically favors a high-spin state (~4 μ_B). Notably, this stepwise spin-state transition coincides with an abrupt and substantial increase in the *OH adsorption free energy ($G(*OH)$), which is accompanied by a marked decline in the ORR activity of Fe_{cen}.

For the Co site, adsorption of *OOH (the relevant potential-determining intermediate) also leads to a substantial reduction in the magnetic moment of Co@9×9-S (3.0 wt%) compared to its pristine state, as illustrated in **Figure 4.7b**. As the metal loading increases from 3.0 wt% to 5.7 wt%, the magnetic moment of the Co site rises modestly by approximately 0.3 μ_B , a change notably smaller than that observed for the *OH-adsorbed Fe site (~1.7 μ_B). Beyond this range, the magnetic moment of Co_{cor} continues to increase gradually with further increases in metal loading. Overall, this

relatively minor enhancement in the magnetic moment of the Co site closely parallels the loading-dependence of its ORR activity, as presented in **Figure 4.7b**.

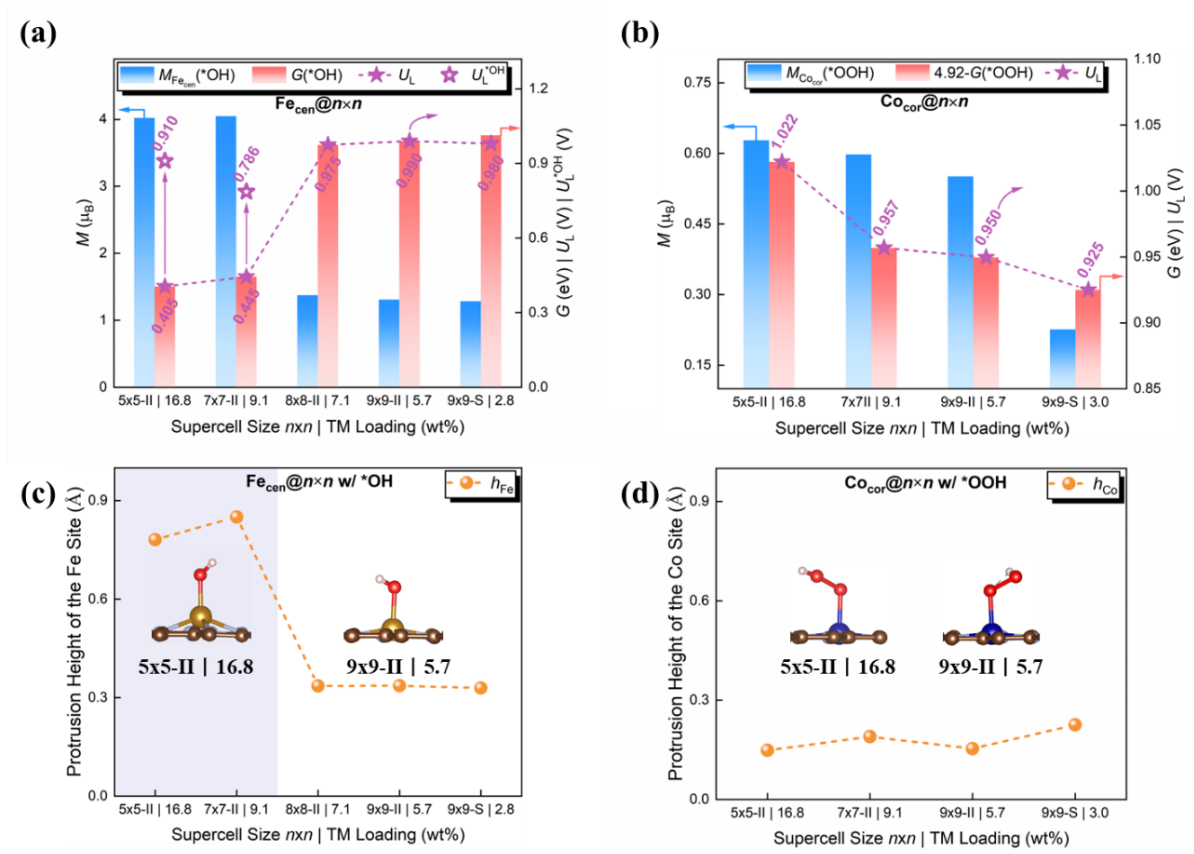


Figure 4.7 The Gibbs free energy of (a) *OH adsorption ($G(*OH)$) and (b) *OOH adsorption ($G(*OOH)$), the ORR limiting potential (U_L) and the projected magnetic moment (M) on (a) Fe_{cen}@n×n and (b) Co_{cor}@n×n, respectively. The limiting potential of the Fe_{cen} site pre-occupied by *OH (U_L^{*OH}) is marked by the empty purple star. The protrusion height of TM (h_{TM}) in the presence of (c) the *OH adsorbate on Fe_{cen}@n×n (TM=Fe) and (d) the *OOH adsorbate on Co_{cor}@n×n (TM=Co), respectively. The insets are the side view of (c) *OH adsorption on Fe_{cen}@n×n and (d) *OOH adsorption on Co_{cor}@n×n.

4.3.5 Local Coordination Environment

The distinct loading dependence of the spin state and magnetic moment at the Fe and Co sites can be attributed to differences in their local structural responses upon adsorption of the potential-determining intermediate. Prior to adsorption, both pristine Fe and Co sites reside within the plane of the graphene substrate, which underlies the observed loading-independent spin states discussed previously.

Upon adsorption of *OH (*OOH), however, the Fe (Co) atom is likely displaced out of the graphene substrate plane, thereby disrupting the previously observed loading-independent behavior. This structural change can be quantitatively described by the protrusion height of the Fe (Co) atom relative to the substrate, denoted as h_{Fe} (h_{Co}), as summarized in **Figure 4.7**. For *OH adsorption on the Fe site of Fe@9×9-S, the Fe atom is elevated by approximately 0.33 Å. This low-protrusion configuration remains energetically favorable until the metal loading reaches 9.1 wt% (Fe_{cen}-Co_{cor}@7×7-II), at which point the Fe site abruptly adopts a high-protrusion configuration ($h_{\text{Fe}} > 0.75$ Å). If the highly protruded Fe site at 9.1 wt% or 16.8 wt% is artificially constrained to the low protrusion height characteristic of 5.7 wt% (Fe_{cen}-Co_{cor}@9×9-II), the total energy increases by 0.420 eV and 0.363 eV, respectively. This indicates a pronounced energetic preference for the high-protrusion configuration at elevated metal loadings, which correlates with a marked strengthening of the interaction between the Fe site and the *OH adsorbate. Consequently, the intrinsic ORR activity of the Fe site deteriorates significantly at 9.1 wt% and higher loadings (see **Figures 4.6** and **4.7a, c**).

The preference for a high-protrusion configuration at metal loadings of 9.1 wt% and above also alters the local coordination environment of the Fe site, transforming it from a nearly square planar geometry to a tetrahedral one. This structural transition is accompanied by a switch from an intermediate-spin ($2 \mu_B$) state to a high-spin state, consistent with previously reported findings.^[23] Notably, such an *OH-induced transition—from a $2 \mu_B$ intermediate-spin, square-planar configuration to a high-spin, highly-protruded tetrahedral configuration—has also been observed in recent studies of FeN₄-C catalysts.^[25, 26] In those investigations, the Fe sites were separated by less than 10 Å, closely matching the inter-site distances in Fe_{cen}-Co_{cor}@7×7-II and falling within the range associated with the high-spin, high-protrusion transition observed in this work.

In contrast to the behavior observed at the Fe site, **Figure 4.7b** and **d** demonstrates that *OOH adsorption induces only a minor and nearly constant protrusion of the Co site from the substrate plane across the entire range of metal loadings considered. Consequently, the Co site consistently maintains a nearly square planar coordination environment and remains in the low-spin state throughout this loading range. This structural stability is also reflected in the relatively modest variation in *OOH adsorption strength at the Co site as the metal loading increases.

4.3.6. Electronic Structures Analysis

The electronic structure of the Fe and Co sites was systematically investigated to provide deeper insight into the loading-dependent intrinsic ORR activity and the associated spin state evolution. Prior to adsorption, the calculated projected density of states (PDOS) reveal that the Fe site exhibits a consistent electronic structure across the

relevant loading range (**Figure 4.8**), attributable to its similar square planar coordination environment. The constant magnetic moment of $2 \mu_B$ observed for the pristine Fe site arises from partial occupation of the Fe- d_{xz}, d_{yz} orbitals in the spin-down channel, as well as half occupation of the Fe- d_{z^2} orbital. Notably, significant broadening of the Fe- d_{xz}, d_{yz} orbitals indicate strong coupling with neighboring N- p_z orbitals, which plays a key role in stabilizing the Fe site within the substrate.

Upon $^*OH$ adsorption at the Fe site, our calculations reveal a pronounced difference in the PDOS depending on whether the Fe atom adopts a low- or high-protruded configuration. The low-protruded configuration is energetically favored below 9.1 wt% loading (e.g., Fe_{cen}-Co_{cor}@7×7-II), while the high-protruded configuration becomes energetically preferred at 9.1 wt% and above, as illustrated in **Figure 4.9**. Since the electronic structures of low- and high-protruded configurations are respectively similar across different loadings, we selected low-protruded Fe_{cen}-Co_{cor}@9×9-II and high-protruded Fe_{cen}-Co_{cor}@5×5-II as representative systems for detailed analysis, as presented in **Figures 4.9b** and **c**.

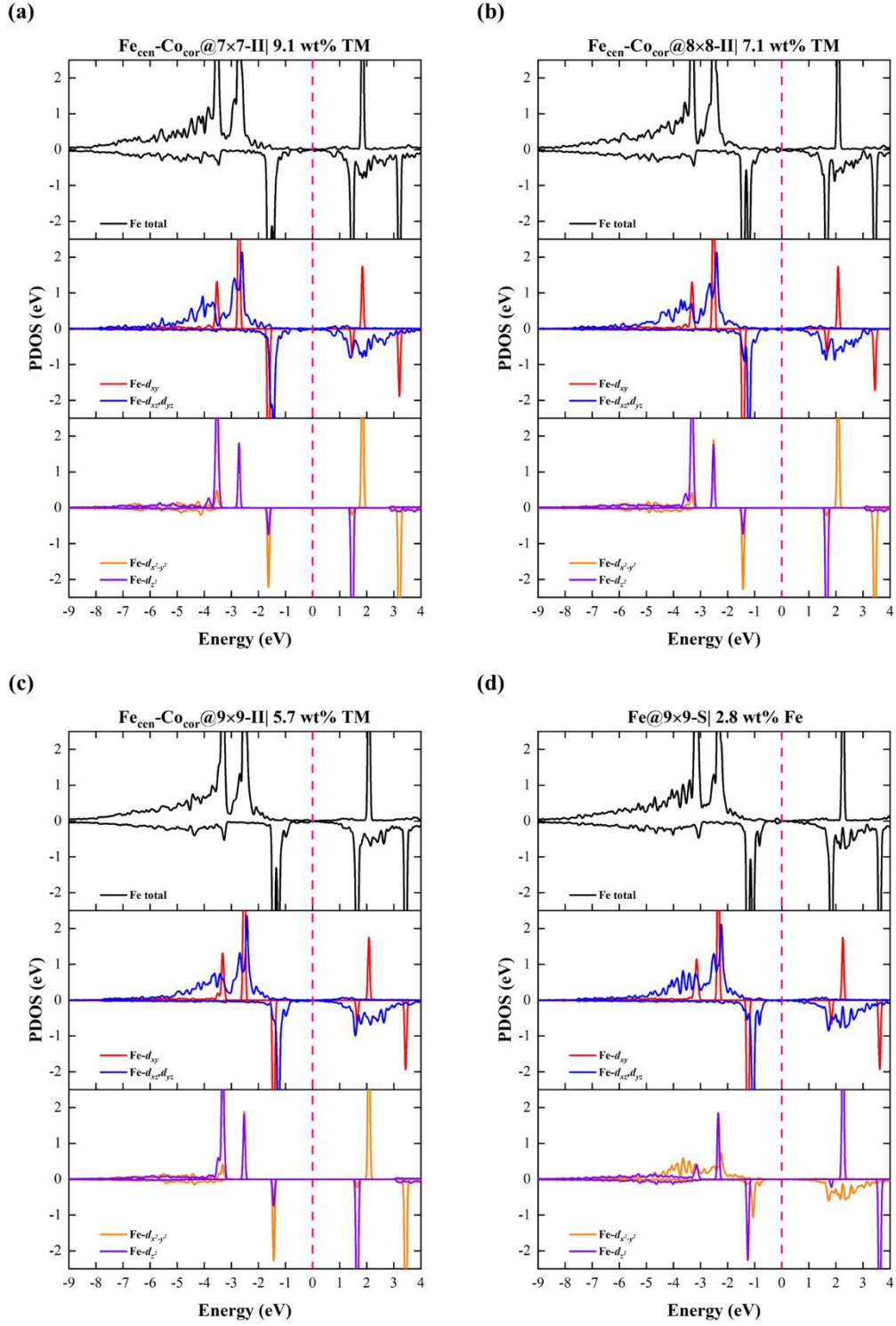


Figure 4.8 The projected density of states (PDOS) onto the Fe site of (a) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@7\times7\text{-II}$, (b) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@8\times8\text{-II}$, (c) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@9\times9\text{-II}$ and (d) $\text{Fe}@9\times9\text{-S}$. The Fermi level has been set to 0 eV.

For Fe_{cen}-Co_{cor}@5×5-II (16.8 wt%), *OH adsorption causes the Fe site to protrude significantly from the substrate, adopting a high-protruded tetrahedral coordination and resulting in a high spin-polarized state. In this configuration, the *OH adsorbate primarily interacts with the spin-up Fe- d_{z^2} orbital, with minor contribution from the Fe- d_{xz}, d_{yz} orbitals. Simultaneously, the spin-down Fe- d_{xz}, d_{yz} orbitals become nearly unoccupied, indicating a reduced role in in-plane interactions with the substrate N- p_z orbitals. This weakened in-plane Fe-substrate binding, together with the dominance of Fe- d_{z^2} —*OH interactions, stabilizes the high-protrusion configuration of the Fe site.

Conversely, for *OH adsorption on the Fe site of Fe_{cen}-Co_{cor}@9×9-II (5.7 wt%), **Figures 4.9c and 4.13a** show that the low-protruded Fe site exhibits reduced occupation of the Fe- d_{z^2} orbital. In this case, Fe- d_{xz}, d_{yz} —O- p_x, p_y interactions are likely to dominate over Fe- d_{z^2} —O- p_z interactions during *OH adsorption. Moreover, the retained occupation of the Fe- d_{xz}, d_{yz} orbitals in the spin-down channel helps to maintain strong in-plane Fe-substrate binding. As a result, the low-protrusion configuration is more favorable for the Fe site in Fe_{cen}-Co_{cor}@9×9-II, and the decrease in magnetic moment upon *OH adsorption can be attributed to the reduced occupation of the Fe- d_{z^2} orbital in the spin-up channel.

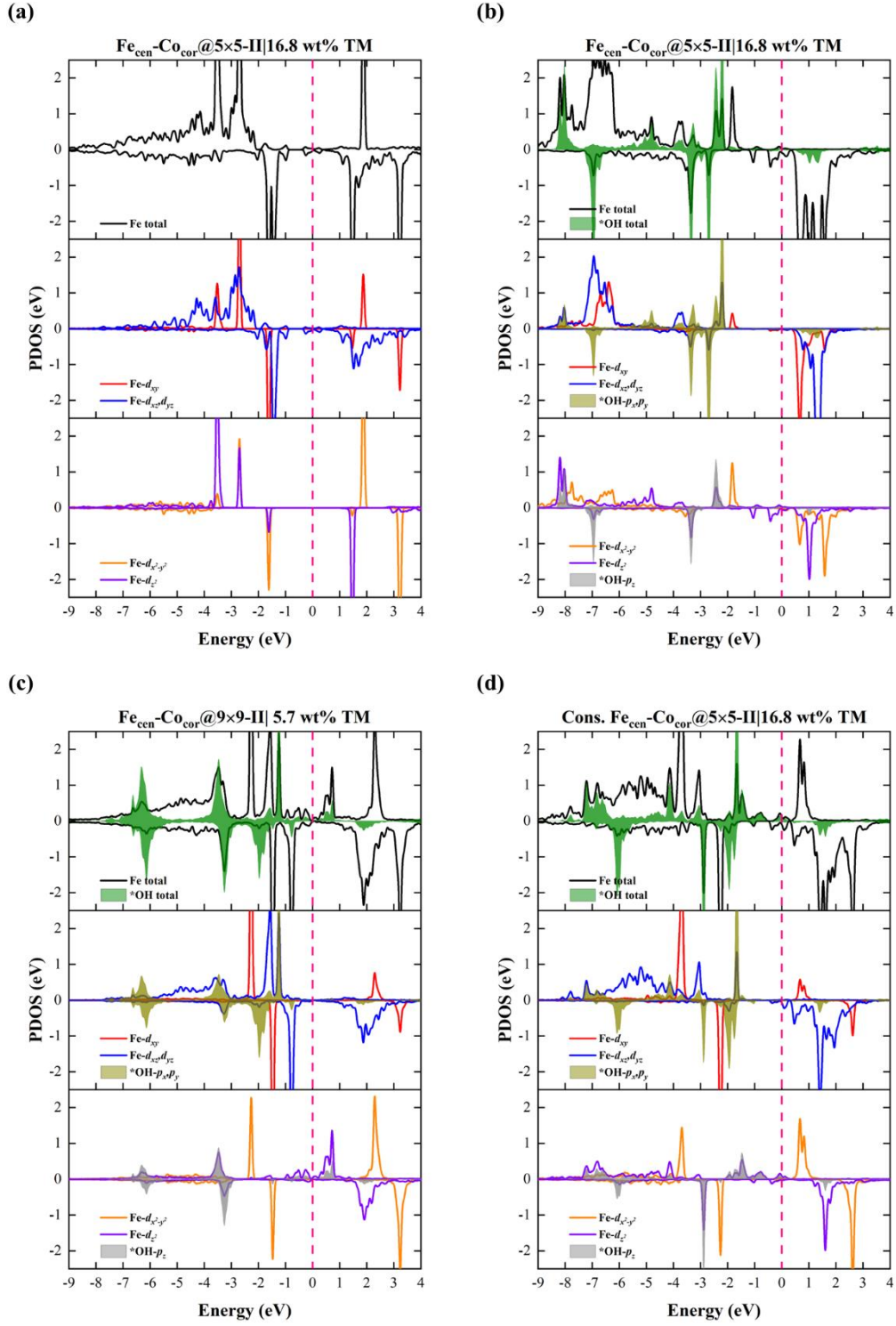


Figure 4.9 The PDOS onto the Fe site and the *OH adsorbate. (a-b) PDOS of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@5\times5\text{-II}$ at 16.8 wt% TM (a) without and (b) with *OH adsorbed on the Fe site. (c) PDOS of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@9\times9\text{-II}$ at 5.7 wt% TM with *OH adsorbed on the Fe site. (d) PDOS of the constrained $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@5\times5\text{-II}$ with *OH adsorbed on the Fe site and the protrusion

height of the Fe site constrained to that of *OH-adsorbed Fe_{cen}-Co_{cor}@9×9-II. The Fermi level has been set to 0 eV.

The PDOS for *OH adsorption on the constrained Fe site of Fe_{cen}-Co_{cor}@5×5-II (16.8 wt%) was also calculated as shown in **Figure 4.9d**. In this calculation, the energetically preferred high-protrusion configuration of the Fe site was artificially constrained to the same low protrusion height as that in Fe_{cen}-Co_{cor}@9×9-II (5.7 wt%). Despite sharing the same low protrusion height as Fe_{cen}-Co_{cor}@9×9-II (**Figure 4.9c**), the constrained Fe site in Fe_{cen}-Co_{cor}@5×5-II exhibits nearly empty Fe- d_{xz} , d_{yz} orbitals in the spin-down channel and a higher occupation of the Fe- d_{z^2} orbital in both spin channels (**Figures 4.9d** and **4.13a, c**). This configuration implies a weaker in-plane Fe–substrate interaction and a stronger Fe- d_{z^2} —O- p_z interaction. If the low-protrusion constraint is removed, the Fe site in Fe_{cen}-Co_{cor}@5×5-II spontaneously adopts the high protrusion configuration. Indeed, the substantial spin polarization associated with the high protrusion state in Fe_{cen}-Co_{cor}@5×5-II drives both the occupied Fe 3d orbitals and the occupied *OH states to lower energies compared to the low protrusion configuration (**Figures 4.9b, d** and **4.10**), resulting in a significant reduction in total energy. These observations are also applicable to the constrained low-protruded Fe site in Fe_{cen}-Co_{cor}@7×7-II (9.1 wt%).

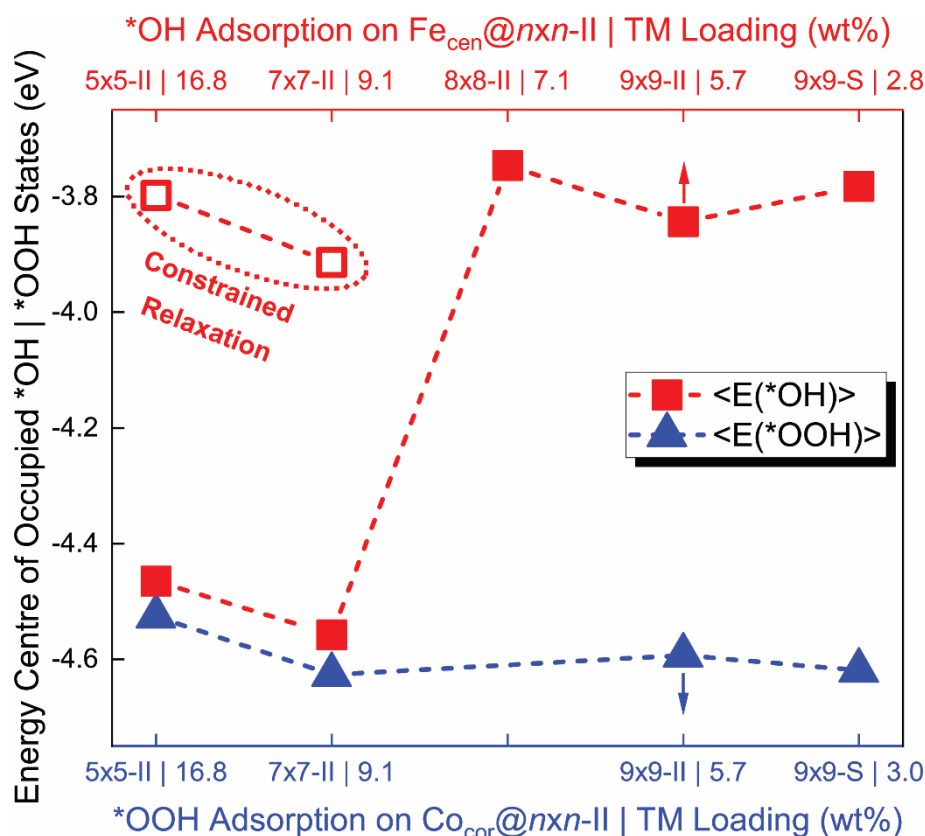


Figure 4.10 The energy centre of the projected occupied states of the $\ast\text{OH}$ adsorbate on the Fe site (top x axis) and the $\ast\text{OOH}$ adsorbate on the Co site (bottom x axis) of $\text{Fe}_{\text{cen}}\text{Co}_{\text{cor}}@n \times n$ -II, $\text{Fe}@9 \times 9$ -S and $\text{Co}@9 \times 9$ -S. The red squares enclosed by the dash ellipse denote the energy centre under the constrained low-protrusion relaxation.

For the pristine Co site, **Figure 4.11** demonstrate that its electronic structure remains nearly unchanged across the entire loading range. Compared to Fe, Co possesses one additional valence electron, which leads to the complete occupation of the spin-down $\text{Co-}d_{xz}, d_{yz}$ orbitals. This leaves only the d_{z^2} orbital half-filled, resulting in a loading-independent magnetic moment of $1 \mu_{\text{B}}$ for the pristine Co site. Upon $\ast\text{OOH}$ adsorption (**Figure 4.13b, d**), the $\text{Co-}d_{xz}, d_{yz}$ orbitals remain fully occupied across all considered loadings.

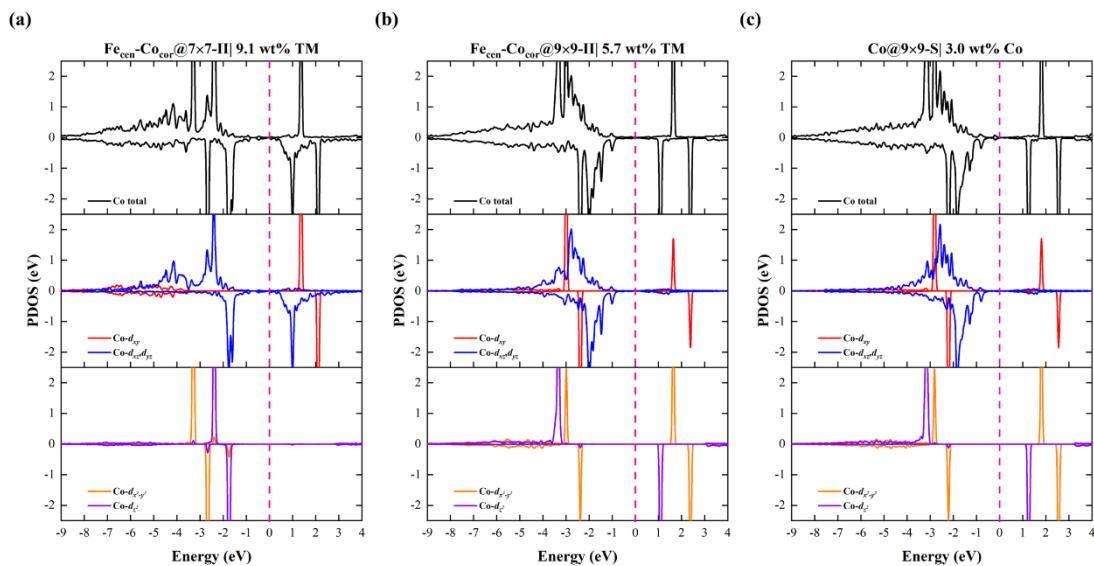


Figure 4.11 PDOS onto the Co site of (a) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@7\times7\text{-II}$, (b) $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@9\times9\text{-II}$, and (c) $\text{Co}@9\times9\text{-S}$. The Fermi level has been set to 0 eV.

Consequently, the Co site has sufficient d_{xz}, d_{yz} states to (i) maintain strong in-plane coupling with the substrate N- p_z orbitals and (ii) predominantly hybridize with the p_x, p_y orbitals of the *OOH adsorbate. While the Co- d_{z^2} orbital also interacts with *OOH p_z , this hybridization is relatively weak due to the lower occupation of Co- d_{z^2} compared to Co- d_{xz}, d_{yz} (**Figures 4.12b** and **4.13**). As a result, *OOH adsorption does not induce significant protrusion of the Co site from the substrate, and a high-protruded configuration is not favored. These electronic characteristics persist throughout the entire loading range studied here. Consequently, both the loading and inter-site coupling have only minor and gradual effects on *OOH adsorption—the potential-determining intermediate—at the Co site, and thus on the intrinsic ORR activity of Co. Slight optimization of *OOH adsorption can be observed with increasing loading; this can be attributed to a subtle increase in the occupation of the Co- d_{z^2} orbital and a minor decrease in the occupation of the Co- d_{xz}, d_{yz} orbitals (**Figure**

4.13b, d). Additionally, the gradual increase in the magnetic moment of the *OOH-adsorbed Co site results from enhanced spin polarization of the Co- d_{z^2} orbital, as shown in **Figure 4.13b, d**.

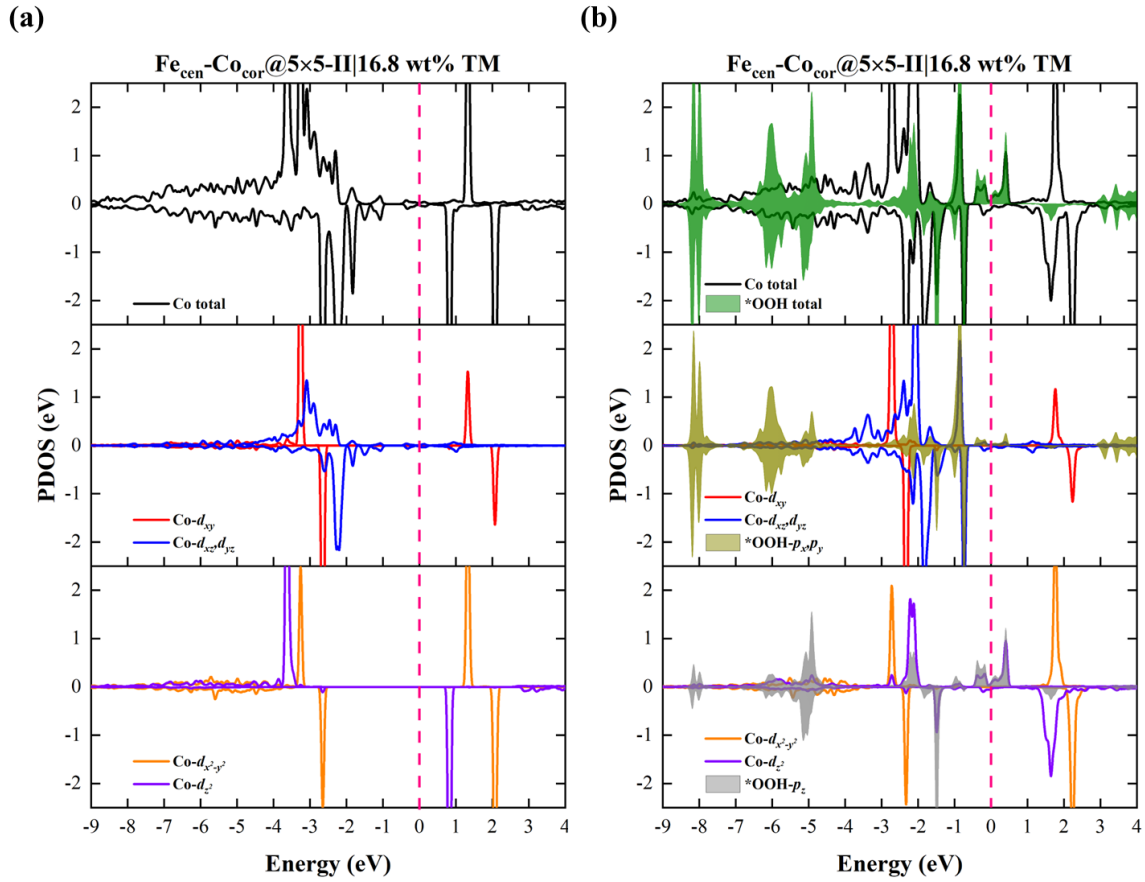


Figure 4.12 PDOS onto the Co site and the *OOH adsorbate. (a-b) PDOS of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@5\times5\text{-II}$ at 16.8 wt% TM

(a) without and (b) with *OOH adsorbed on the Co site. The

Fermi level has been set to 0 eV.

As discussed above, *OH adsorption on the Fe site exhibits an abrupt change in local structure, magnetism, and electronic configuration at a metal loading of 9.1 wt% ($\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@7\times7\text{-II}$). In contrast, such a transition is not observed for *OOH adsorption on the Co site. This difference can be attributed to the higher occupation of the Co- d_{xz}, d_{yz} orbitals compared to their Fe counterparts. Calculated formation

energies (**Figure 4.3**) indicate that increasing metal loading reduces the binding strength of both Fe and Co sites to the substrate, making it easier for these sites to protrude upon adsorbate binding at higher loadings. For Fe, this weakening substrate interaction is reflected in a transition of the dominant Fe—*OH interaction: from Fe- d_{xz} , d_{yz} —*OH- p_x, p_y coupling to Fe- d_{z^2} —*OH- p_z coupling at 9.1 wt% and above (Fe_{cen}-Co_{cor}@7×7-II), even when the Fe site is geometrically constrained to a low protrusion height (**Figures 4.9d** and **4.13a, c**). In contrast, for the Co site, the greater availability of d_{xz}, d_{yz} states not only result in stronger binding to the substrate than Fe, but also ensures that Co- d_{xz}, d_{yz} —*OOH- p_x, p_y hybridization remains the dominant interaction. Together, these factors prevent significant protrusion of the Co site upon *OOH adsorption at both 9.1 wt% (Fe_{cen}-Co_{cor}@7×7-II) and 16.8 wt% (Fe_{cen}-Co_{cor}@5×5-II). However, if the metal loading is further increased—or the Co-substrate binding further weakened—the Co site may also transition to a high-protrusion configuration after *OOH adsorption, as discussed in the next section.

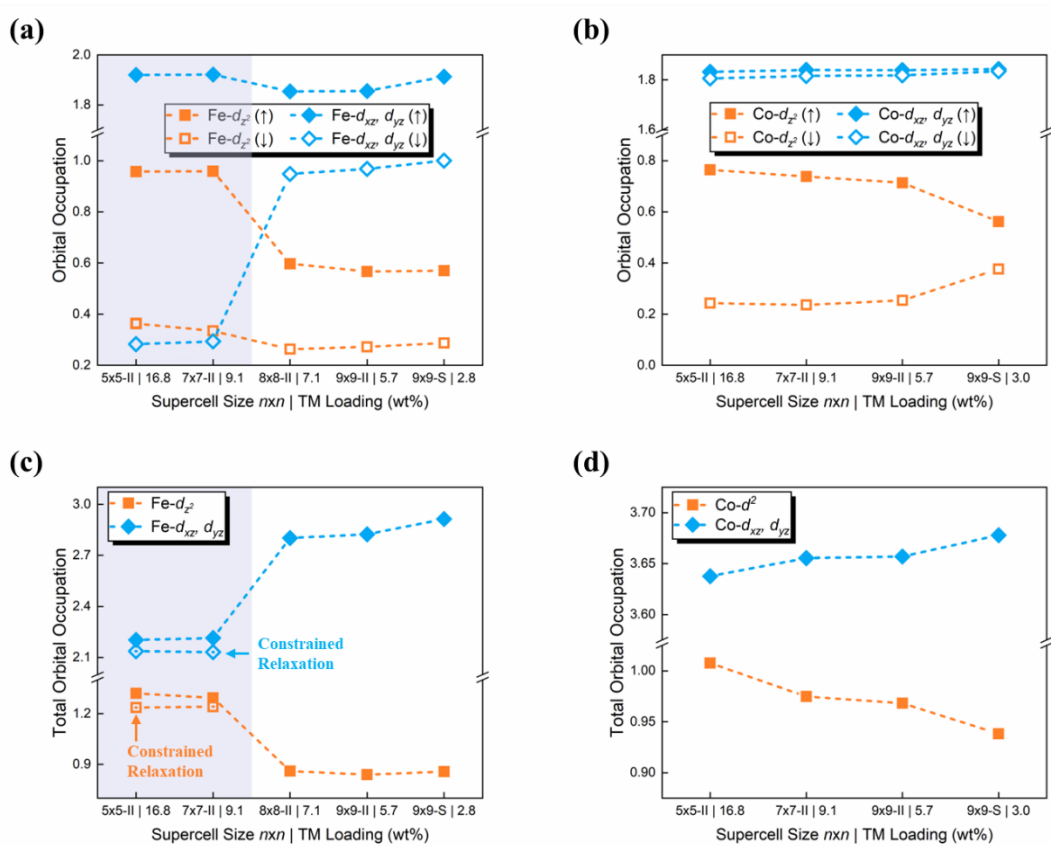


Figure 4.13 The spin-resolved occupation of (a) the Fe- d_{z^2} orbital and Fe- d_{xz}, d_{yz} orbitals after *OH adsorption on the Fe site of Fe_{cen}-Co_{cor}@ $n \times n$ -II and Fe@9×9-S, and (c) the total occupation. The spin-resolved occupation of (b) the Co- d_{z^2} orbital and Co- d_{xz}, d_{yz} orbitals after *OOH adsorption on the Co site of Fe_{cen}-Co_{cor}@ $n \times n$ -II and Co@9×9-S and (d) the total occupation.

4.3.7 Ultra-High Loading and Preoccupation Effects

At metal loadings of 9.1 wt% and 16.8 wt%, as discussed above, the Fe site binds *OH excessively strongly (**Figures 4.6b-c**). Under ORR conditions, this strong adsorption suggests that the first *OH molecule is likely pre-adsorbed as an axial ligand, resulting in a five-coordinated Fe site during the actual ORR process. [20, 23, 26] Following hydroxyl passivation, adsorption of ORR intermediates on the Fe site,

particularly *O and *OH, is significantly weakened (**Figure 4.14**). Consequently, the potential-determining step shifts to the first hydrogenation step, and the calculated limiting potential increases from 0.445 V to 0.786 V at 9.1 wt%, and from 0.405 V to 0.910 V at 16.8 wt% (**Figures 4.14** and **4.7a**). These results indicate that at metal loadings of 9.1 wt% or higher, the ORR active site transitions from the pristine Fe site to the one pre-occupied by *OH.

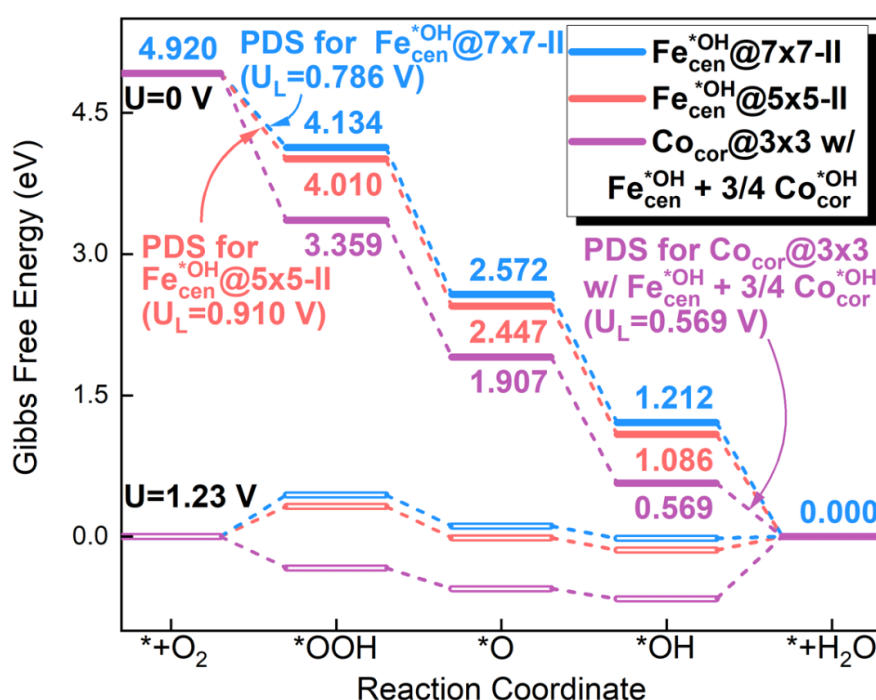


Figure 4.14 Oxygen reduction reaction on the Fe site pre-occupied by *OH in Fe_{cen}-

Co_{cor}@7×7-II and Fe_{cen}-Co_{cor}@5×5-II, and on the Co site in Fe_{cen}-Co_{cor}@3×3 (TM loading:

38.4 wt%) where all Fe sites and ¾ of the Co sites are covered by *OH.

With a further increase in metal loading, pre-adsorbed species play an increasingly significant role in determining the ORR activity. To investigate this effect at ultra-high loading, a system with a metal loading of 38.4 wt% was modeled using the Fe_{cen}-Co_{cor}@3×3 structure, as depicted in **Figure 4.15**. The calculated formation energies for

the Fe and Co sites are -1.663 eV and -1.779 eV, respectively, while the corresponding dissolution potentials are 0.381 V for Fe and 0.610 V for Co. These values are consistent with the observed trend of decreasing site stability as metal loading increases (**Figure 4.3**). Nevertheless, both transition metal sites satisfy the previously established stability criteria and are thus resistant to aggregation and dissolution under operating conditions. The structural integrity of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@3\times3$ is further corroborated by *ab initio* molecular dynamics (AIMD) simulations conducted at 300 K (**Figure 4.16**). For Gibbs free energy calculations, the simulation cell was doubled in the in-plane direction to accommodate surface intermediate coverage.

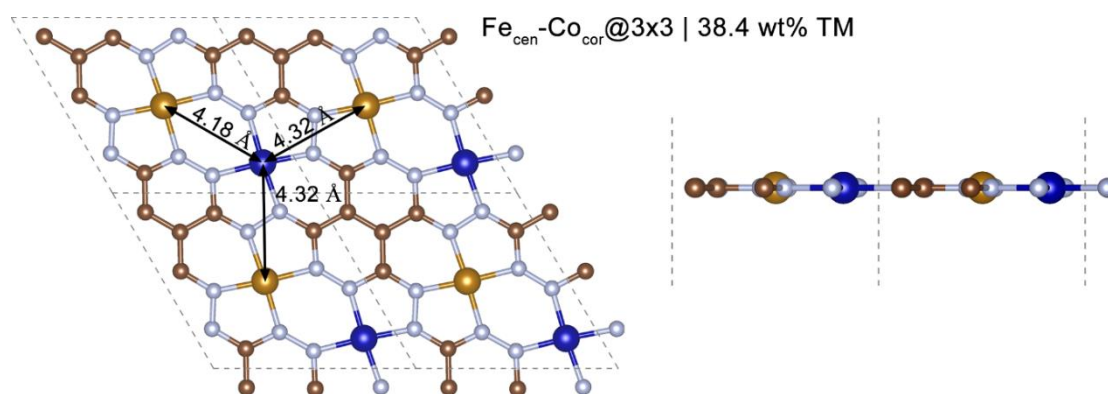


Figure 4.15 The top and side view of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@3\times3$. The distances between a Co site and its three neighbouring Fe sites are marked.

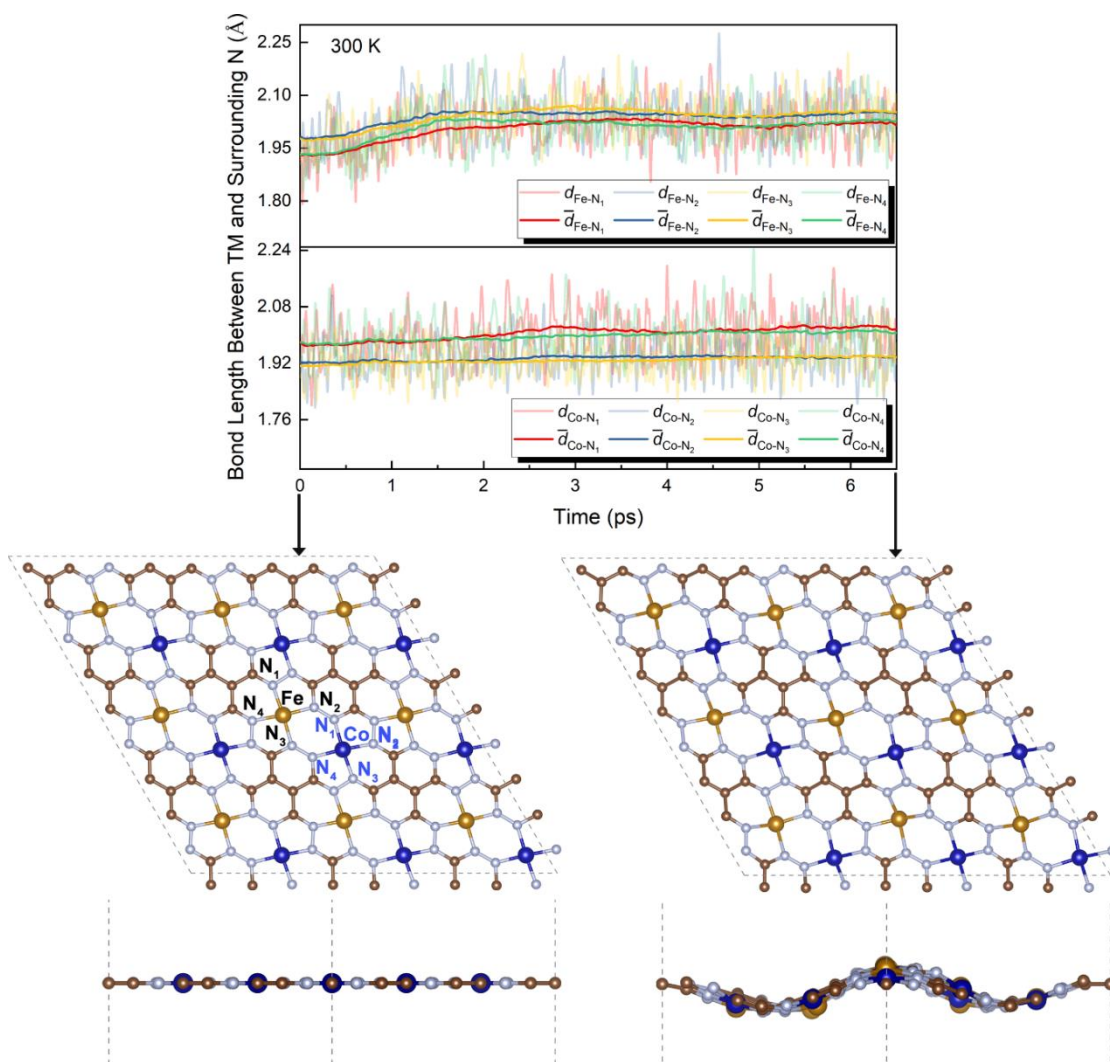


Figure 4.16 AIMD simulation of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@3\times 3$ at 300 K. The oscillatory lines are the bond lengths between Fe or Co and its four neighboring N sites as functions of time. The smooth lines are the averaged bond lengths over a period of 1.2 ps. The bottom panel visualizes the initial and final structures of the AIMD simulation.

According to the constructed surface Pourbaix diagram and the illustration (**Figure 4.17**), under ORR-relevant conditions, *OH is predicted to pre-occupy all Fe sites and either three-quarters or the entirety of the Co sites. These configurations are denoted as $\text{Fe}_{\text{cen}}^{\text{*OH}} + 3/4 \text{Co}_{\text{cor}}^{\text{*OH}}$ and $\text{Fe}_{\text{cen}}^{\text{*OH}} + \text{Co}_{\text{cor}}^{\text{*OH}}$. Subsequent calculations suggest that, under $\text{Fe}_{\text{cen}}^{\text{*OH}} + 3/4 \text{Co}_{\text{cor}}^{\text{*OH}}$ coverage, the remaining unoccupied Co_{cor} site serves

as the self-consistent ORR active site. For this configuration, the PDS is the hydrogenation of *OH to H₂O, with a calculated limiting potential of 0.569 V (**Figure 4.14**). This relatively low limiting potential indicates a marked decrease in ORR activity as the metal loading increases to 38.4 wt%. Furthermore, analysis of the surface Pourbaix diagram suggests that, at such high loading, the Fe site transitions to a spectator role and no longer acts as an active center for the ORR.

It is also noteworthy that, at this elevated metal loading, the Co site adopts a high-protrusion configuration (0.56 Å) upon *OOH adsorption, in contrast to the lower-protrusion states observed at or below 16.8 wt% (**Figure 4.7b**). This structural change is primarily attributed to the further weakened interaction between the Co site and the substrate at high loading. Similarly, the Fe site exhibits a high protrusion of 0.70 Å upon *OH adsorption, consistent with the values observed at 16.8 wt% and 9.1 wt% (**Figure 4.7a**).

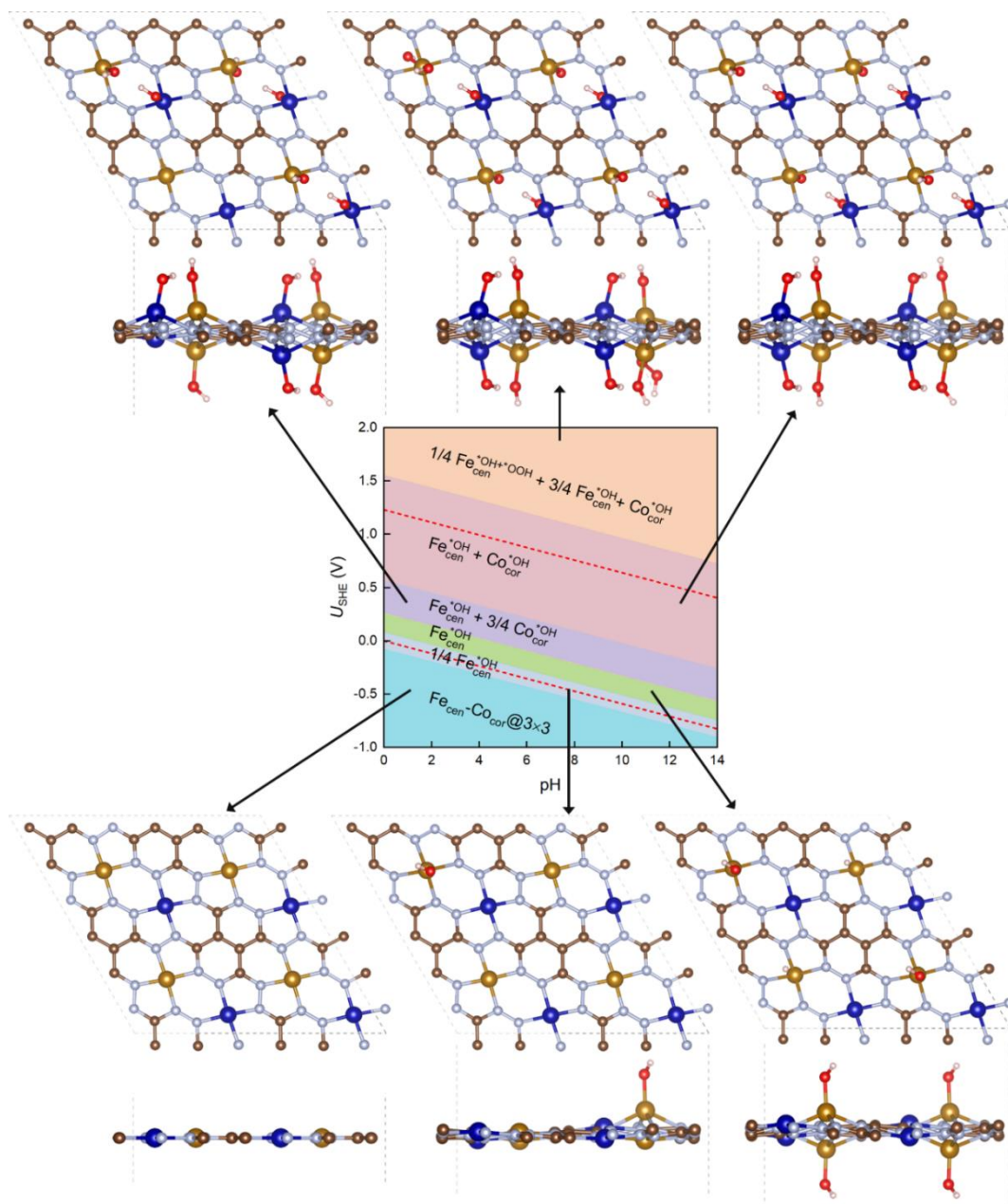


Figure 4.17 The surface Pourbaix diagram of $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@3\times3$, and the top and side view of the relevant states. The 2×2 supercell was adopted.

Based on the above analyses, the ORR activity of the Fe and Co sites in heteronuclear $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@n\times n$ systems exhibit markedly different dependencies on metal loading. For the Co site, its intrinsic ORR activity is expected to increase initially, reaching a maximum at a metal loading of approximately 16.8 wt%, beyond which it

declines significantly (**Figures 4.7b** and **4.14**). In contrast, the intrinsic ORR activity of the Fe site decreases in an oscillatory fashion as the metal loading increases, ultimately becoming spectator-like at the ultra-high loading of 38.4 wt% (**Figures 4.7a** and **4.17**). This oscillatory decrease in Fe site activity commences between 7.1 wt% ($d_{\text{site}} > \sim 11.4 \text{ \AA}$) and 9.1 wt% ($d_{\text{site}} > \sim 10.0 \text{ \AA}$), which is comparable to the onset inter-site distance of approximately 12 $\text{\AA}$ observed for homonuclear Fe SACs. ^[14] However, it should be noted that the site-specific ORR activity dependence on loading for the Fe site in the homonuclear case is substantially different. Specifically, in homonuclear Fe SACs, the intrinsic activity of the Fe site begins to increase at an inter-site distance of $\sim 12 \text{ \AA}$, peaks at $\sim 7 \text{ \AA}$, and then slightly decreases with further reduction in distance. ^[14]

These observations indicate that the effect of loading on the site-specific intrinsic activity of heteronuclear SACs is fundamentally species-specific, depending critically on the atomic identity of the co-supported single atoms. This conclusion is further substantiated by the following calculations. Among all the sites investigated above, the Co site in $\text{Fe}_{\text{cen}}\text{-Co}_{\text{cor}}@5\times 5\text{-II}$ is identified as the most active (**Figure 4.7**). To further explore the influence of the co-supported species, Fe_{cen} in this configuration was substituted with Mn, Co, Ni, Cu, Ir, and Pt, and the catalytic activity of the Co_{cor} site was evaluated. Notably, these single-atom elements have all been experimentally synthesized and demonstrated to be stable under ORR conditions. ^[27-31] The corresponding limiting potential for these systems are summarized in **Figure 4.18**. These results reveal that substitution with Pt_{cen} further enhances the catalytic activity of

the Co_{cen} site, while replacement with Mn_{cen}, Co_{cen}, or Ir_{cen} leads to a slight decrease in activity.

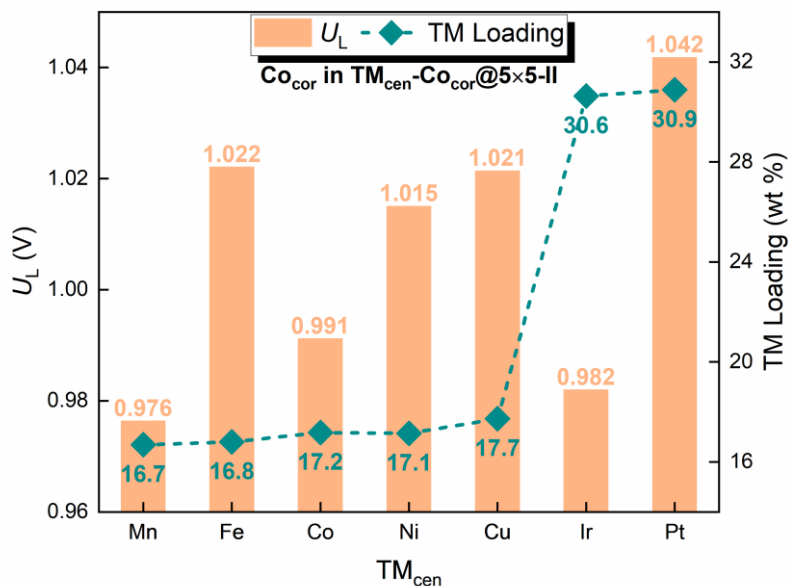


Figure 4.18 The estimated ORR limiting potential of the Co site and the TM loading of

TM_{cen}-Co_{cor}@5×5-II (TM_{cen} = Mn, Fe, Co, Ni, Cu, Ir and Pt).

4.4. Conclusions

In this chapter, we systematically investigated the loading effect on the stability and site-specific ORR activity of heteronuclear Fe and Co SACs co-supported on nitrogen-doped graphene. Our findings reveal that the Fe_{cen}-Co_{cor} configurations remain stable against aggregation and dissolution, even at high metal loadings. This stability is attributed to the robust binding between the transition metal sites and the nitrogen-doped substrate.

The analysis of intrinsic ORR activity highlights distinct loading-dependent trends for the Fe and Co sites. The Co site exhibits a volcano-like dependence on loading,

achieving peak activity at 16.8 wt% ($\langle d_{\text{site}} \rangle \approx 7 \text{ \AA}$). This optimal performance arises from the synergistic balance between Co- d_{xz}, d_{yz} orbital occupation, substrate binding strength, and moderate adsorption of ORR intermediates. In contrast, the Fe site demonstrates an oscillatory decrease in intrinsic activity with increasing loading, primarily due to hydroxyl passivation and a transition to a high-spin state at higher loadings. When the loading is pushed to ultra-high levels (e.g., 38.4 wt%, $\langle d_{\text{site}} \rangle \approx 4 \text{ \AA}$), the Fe site becomes a spectator, while the Co site serves as the primary active site for ORR.

The distinct loading effects observed for the Fe and Co sites can be attributed to differences in TM-substrate binding strength and d_{xz}, d_{yz} orbital occupation. The Co site benefits from stronger substrate binding and richer d_{xz}, d_{yz} orbital states, which delay the transition to excessive adsorption of intermediates and prevent catalytic activity degradation. Conversely, the Fe site, with weaker substrate binding and more pronounced d_{z^2} -dominated interactions, is more susceptible to overbinding of *OH species, leading to diminished ORR activity at higher loadings.

These findings underscore the importance of controlling inter-site distance and metal loading to optimize the performance of heteronuclear SACs. Specifically, an inter-site distance of approximately 7 Å provides the best balance between Fe and Co activity, maximizing overall ORR performance. Furthermore, this study demonstrates that loading effects in heteronuclear SACs are not only site-specific but also influenced by the properties of the co-supported species. These results may stimulate further

investigations into other heteronuclear SACs, including high-entropy SACs or concentration-complex systems, to unlock their full catalytic potential.

References

1. Wang, Y., D.S. Wang, and Y.D. Li, *Rational Design of Single-Atom Site Electrocatalysts: From Theoretical Understandings to Practical Applications*. Advanced Materials, 2021. **33**(34): p. 38.
2. Wang, Y.X., et al., *Advanced Electrocatalysts with Single-Metal-Atom Active Sites*. Chemical Reviews, 2020. **120**(21): p. 12217-12314.
3. Qin, R.X., et al., *Surface Coordination Chemistry of Atomically Dispersed Metal Catalysts*. Chemical Reviews, 2020. **120**(21): p. 11810-11899.
4. Wang, X.X., et al., *Nitrogen-Coordinated Single Cobalt Atom Catalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells*. Advanced Materials, 2018. **30**(11).
5. Chung, H.T., et al., *Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst*. Science, 2017. **357**(6350): p. 479-483.
6. Mehmood, A., et al., *High loading of single atomic iron sites in Fe-NC oxygen reduction catalysts for proton exchange membrane fuel cells*. Nature Catalysis, 2022. **5**(4): p. 311-323.
7. Hai, X., et al., *Scalable two-step annealing method for preparing ultra-high-density single-atom catalyst libraries*. Nature nanotechnology, 2022. **17**(2): p. 174-181.
8. Wan, X., et al., *Fe-N-C electrocatalyst with dense active sites and efficient mass transport for high-performance proton exchange membrane fuel cells*. Nature Catalysis, 2019. **2**(3): p. 259-268.
9. Cao, L.L., et al., *Identification of single-atom active sites in carbon-based cobalt catalysts during electrocatalytic hydrogen evolution*. Nature Catalysis, 2019. **2**(2): p. 134-141.
10. Fang, S., et al., *Uncovering near-free platinum single-atom dynamics during electrochemical hydrogen evolution reaction*. Nature Communications, 2020. **11**(1).
11. Shi, Y., et al., *Site-specific electrodeposition enables self-terminating growth of atomically dispersed metal catalysts*. Nature Communications, 2020. **11**(1).
12. Zhang, H.B., et al., *Unveiling the Activity Origin of Electrocatalytic Oxygen Evolution over Isolated Ni Atoms Supported on a N-Doped Carbon Matrix*. Advanced Materials, 2019. **31**(48).
13. Hu, R., et al., *Role of active sites in N-coordinated Fe-Co dual-metal doped graphene for oxygen reduction and evolution reactions: A theoretical insight*. Applied Surface Science, 2020. **525**: p. 146588.

14. Jin, Z.Y., et al., *Understanding the inter-site distance effect in single-atom catalysts for oxygen electroreduction*. Nature Catalysis, 2021. **4**(7): p. 615-622.
15. Guo, X.Y., et al., *Simultaneously Achieving High Activity and Selectivity toward Two-Electron O₂ Electroreduction: The Power of Single-Atom Catalysts*. Acs Catalysis, 2019. **9**(12): p. 11042-11054.
16. Wang, J., et al., *Design of N-Coordinated Dual-Metal Sites: A Stable and Active Pt-Free Catalyst for Acidic Oxygen Reduction Reaction*. Journal of the American Chemical Society, 2017. **139**(48): p. 17281-17284.
17. Peng, H.L., et al., *Effect of Transition Metals on the Structure and Performance of the Doped Carbon Catalysts Derived From Polyaniline and Melamine for ORR Application*. Acs Catalysis, 2014. **4**(10): p. 3797-3805.
18. Wang, J., et al., *Synergistic effect of well-defined dual sites boosting the oxygen reduction reaction*. Energy & Environmental Science, 2018. **11**(12): p. 3375-3379.
19. Li, X.F., et al., *Conversion of Dinitrogen to Ammonia by FeN₃-Embedded Graphene*. Journal of the American Chemical Society, 2016. **138**(28): p. 8706-8709.
20. Kramm, U.I., et al., *Correlations between Mass Activity and Physicochemical Properties of Fe/N/C Catalysts for the ORR in PEM Fuel Cell via ⁵⁷Fe Mossbauer Spectroscopy and Other Techniques*. Journal of the American Chemical Society, 2014. **136**(3): p. 978-985.
21. Zhong, W.H., et al., *Electronic Spin Moment As a Catalytic Descriptor for Fe Single-Atom Catalysts Supported on C₂N*. Journal of the American Chemical Society, 2021. **143**(11): p. 4405-4413.
22. Li, F.F., et al., *An enhanced oxygen evolution reaction on 2D CoOOH via strain engineering: an insightful view from spin state transition*. Journal of Materials Chemistry A, 2021. **9**(33): p. 17749-17759.
23. Li, X.N., et al., *Identification of the Electronic and Structural Dynamics of Catalytic Centers in Single-Fe-Atom Material*. Chem, 2020. **6**(12): p. 3440-3454.
24. Hwang, J., et al., *Perovskites in catalysis and electrocatalysis*. Science, 2017. **358**(6364): p. 751-756.
25. Zheng, T., et al., *Spin-dependent active centers in Fe-N-C oxygen reduction catalysts revealed by constant-potential density functional theory*. Journal of Materials Chemistry A, 2023. **11**(36): p. 19360-19373.
26. Yu, M.Y., et al., *Substantial Impact of Spin State Evolution in OER/ORR Catalyzed by Fe-N-C*. Acs Catalysis, 2024. **14**(9): p. 6816-6826.
27. Han, A., et al., *An Adjacent Atomic Platinum Site Enables Single-Atom Iron with High Oxygen Reduction Reaction Performance*. Angewandte Chemie-International Edition, 2021. **60**(35): p. 19262-19271.

28. Hu, B.T., et al., *Atomic Co/Ni dual sites with N/P-coordination as bifunctional oxygen electrocatalyst for rechargeable zinc-air batteries*. Nano Research, 2021. **14**(10): p. 3482-3488.
29. Li, F., et al., *Boosting oxygen reduction catalysis with abundant copper single atom active sites*. Energy & Environmental Science, 2018. **11**(8): p. 2263-2269.
30. Yang, G.G., et al., *Regulating Fe-spin state by atomically dispersed Mn-N in Fe-N-C catalysts with high oxygen reduction activity*. Nature Communications, 2021. **12**(1).
31. Xiao, M.L., et al., *A Single-Atom Iridium Heterogeneous Catalyst in Oxygen Reduction Reaction*. Angewandte Chemie-International Edition, 2019. **58**(28): p. 9640-9645.

Chapter 5. Geminal copper atoms catalyzed CO Reduction

5.1. Introduction

The selective formation of C₂ products, such as ethylene (C₂H₄) and ethanol (C₂H₅OH), via CO or CO₂ reduction represents a critical research field in the sustainable production of value-added chemicals from renewable energy sources [1-4]. Copper-based catalysts remain the benchmark materials for this transformation; however, achieving high selectivity toward C₂ products, as opposed to C₁ products like methane, remains a significant challenge [5-8].

Geminal-atom catalysis (GAC) represents an emerging paradigm in heterogeneous catalysis, wherein pairs of single-atom active sites are deliberately positioned in close proximity on a support material to enable efficient cross-coupling reactions [9, 10]. In particular, systems comprising copper atom pairs anchored on polymeric carbon nitride (PCN) have demonstrated notable efficacy in facilitating C-C bond formation [11]. Such geminal configurations offer unique opportunities to engineer reaction pathways and improve selectivity, providing access to products and mechanisms inaccessible to isolated single-atom or conventional nanoparticle catalysts. However, the effect of Cu-based geminal single atoms on the C-C coupling towards CO reduction has not been well studied.

In this chapter, we present a detailed computational study of the electrochemical reduction of CO to the C₂ oxygenate ethylene glycol over dual-copper atom catalysts supported on PCN. Using DFT calculations, we systematically examine the adsorption

properties, reaction intermediates, and elementary steps involved in the transformation of CO to ethylene glycol. Our results provide atomistic insights into the unique advantages of dual-copper/PCN catalysts for enabling efficient C₂ product formation and offer guidance for the rational design of advanced electrocatalysts tailored for ethylene glycol synthesis from CO reduction.

5.2. Computational Methods

5.2.1. Computational Parameters

All DFT calculations in this study were performed using VASP. Exchange-correlation effects were described using the GGA functional with the PBE parameters, and the PAW method was employed to approximate the core-electron interaction. To accurately capture van der Waals interactions, the DFT-D3 dispersion correction scheme was applied. A plane-wave cutoff energy of 500 eV was used throughout. Brillouin zone sampling was conducted with a Γ -centered k-point mesh corresponding to a product of approximately 30 with the in-plane lattice constant, and a vacuum layer exceeding 15 Å was introduced in the out-of-plane direction to minimize spurious interactions. Electronic and ionic convergence criteria were set to 1×10^{-5} eV and 0.02 eV/Å, respectively. Spin polarization was included in all calculations to account for the presence of transition metal atoms.

5.2.2. System Design

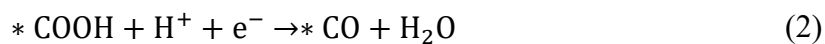
Geminal copper structures were modeled by embedding copper atoms into the PCN substrate. Four copper atoms, arranged as two pairs, were introduced to substitute

hydrogen atoms within a PCN unit cell. In each pair, the distance between the copper atoms was set to $\sim 4 \text{ \AA}$, consistent with previous studies ^[11].

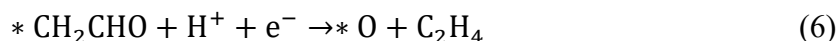
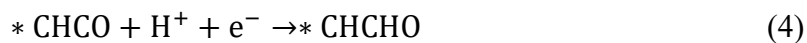
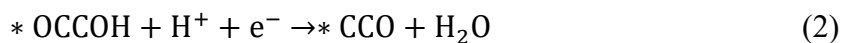
5.2.3. Catalytic Path of Carbon reduction

The reaction pathways for carbon reduction are highly diverse, with various possible intermediates and products. Here, representative pathways leading to typical C₁ and C₂ products are illustrated ^[1, 12].

1. Reduction of CO₂ to methane (CH₄)



2. Reduction of CO to ethylene (C₂H₄)



Here, “*” denotes the catalyst surface, and “* X” corresponds to adsorbed reaction intermediates.

5.2.4. Thermodynamics of Carbon Reduction

The theoretical framework employed in this study is based on the Nørskov model[1], which streamlines the calculation of free energy changes for proton-coupled electron transfer steps by equating the chemical potential of a proton–electron pair ($H^+ + e^-$) in solution to that of half a molecule of gaseous hydrogen ($\frac{1}{2}H_2$) under standard conditions (0 V vs. the standard hydrogen electrode, SHE). This approach enables the calculation of free energy changes at different electrode potentials (U) using the following equation[1]:

$$\Delta G_n(U) = \Delta G_n^0 + neU \quad \dots (5.1)$$

where ΔG_n^0 is the free energy change at 0 V vs. SHE and e is the elementary charge, n is the number of proton-electron pairs transferred in the carbon reduction process.

Within this model, the limiting potential serves as a critical thermodynamic descriptor, representing the minimum applied potential necessary to render all elementary steps in a reaction pathway exergonic (downhill in free energy)^[13, 14]. The limiting potential is dictated by the most energetically demanding step, referred to as the potential-determining step (PDS). It can be calculated as follows^[14]:

$$\Delta U_L = -\frac{\Delta G_{max}}{e} \quad \dots (5.2)$$

where ΔG_{max} is the largest free energy difference between two consecutive intermediates in the reaction pathway at $U = 0$ V, and e is the elementary charge.

5.2.5. Formation Energy of Copper Incorporation in PCN

The formation energy of copper atoms inserted into the PCN slab, E_f^{Cu} , is calculated as follows:

$$E_f^{Cu} = E_{DFT}^{Cu/PCN} - E_{DFT}^{PCN} - n \times (\mu_{Cu} - \mu_H) \quad \dots (5.3)$$

Here, $E_{DFT}^{Cu/PCN}$ is the total energy of the Cu/PCN system, E_{DFT}^{PCN} is the total energy of the pristine PCN slab, n is the number of hydrogen atoms substituted by copper, μ_{Cu} is the chemical potential of copper in bulk face-centered cubic (FCC) copper, and μ_H is the chemical potential of hydrogen, taken as half the total energy of an H_2 molecule.

5.2.6. Charge Density Difference

To gain insight into the electronic interactions between Cu/PCN substrate and adsorbed reaction intermediates, charge density difference analyses were performed. This approach allows for visualization of charge redistribution upon the formation of the catalyst or upon adsorption of reactants and intermediates^[15-17].

The difference charge density, $\Delta\rho(\mathbf{r})$, is defined as:

$$\Delta\rho(\mathbf{r}) = \Delta\rho_{total}(\mathbf{r}) - \Delta\rho_{Cu/PCN}(\mathbf{r}) - \Delta\rho_{adsorbate}(\mathbf{r}) \quad \dots (5.4)$$

where $\Delta\rho_{total}(\mathbf{r})$ is the charge density of the entire system (i.e., Cu/PCN with the adsorbate), $\Delta\rho_{Cu/PCN}(\mathbf{r})$ is the charge density of the clean Cu/PCN substrate, and $\Delta\rho_{adsorbate}(\mathbf{r})$ is the charge density of the isolated adsorbate in the same configuration

as in the combined system. All charge densities are calculated with the atomic positions fixed to those in the fully relaxed combined system to ensure consistency.

5.3. Results and Discussion

5.3.1. Structures and Stability

Two pairs of geminal Cu atoms were introduced to replace hydrogen atoms in the PCN cell. After structural relaxation, the distance between the Cu atoms was found to be 4.25 Å, which is in close agreement with the reported value of 4.28 Å in the literature (see **Figure 5.1**) [11]. Adsorption studies were performed on the central Cu pair in the model, with the upper and lower Cu atoms designated as Cu¹ and Cu², respectively, for clarity. The calculated formation energy for Cu incorporation is 0.80 eV per atom, which is slightly higher than the reported values of 0.75 ~ 0.72 eV per atom in previous studies [18]. Our calculations indicate that the adsorption energies of the same adsorbate on Cu¹ and Cu² are identical, which can be attribute to the symmetry of the structure. As shown in **Figure 5.2**, the projected density of states (PDOS) for the 3*d* orbitals of Cu¹ and Cu² are also identical, further confirming their equivalence.

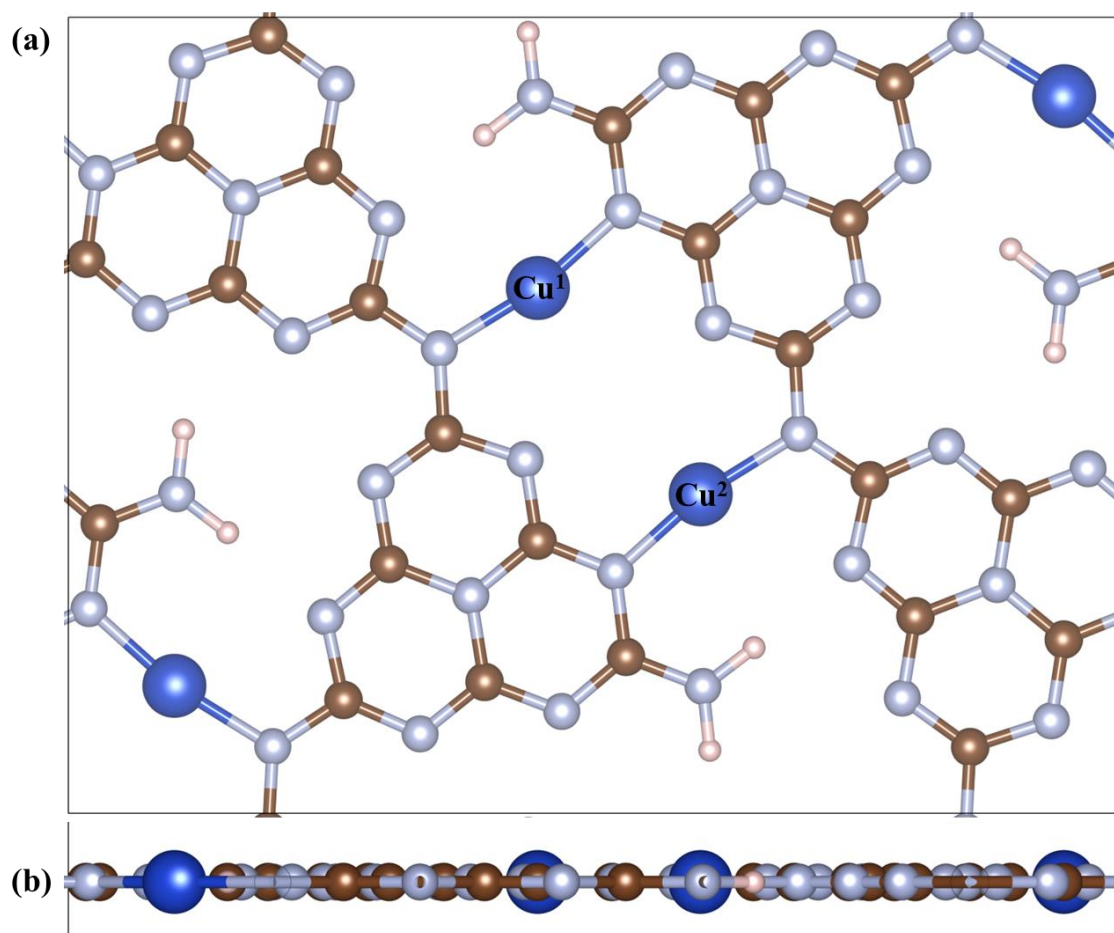


Figure 5.1 (a) Top view and (b) side view of the Cu/PCN structure. Copper atoms are shown in blue, carbon in brown, nitrogen in grey, and hydrogen in pink. The upper copper atom (Cu^1) and the lower copper atom (Cu^2) are indicated in the figure.

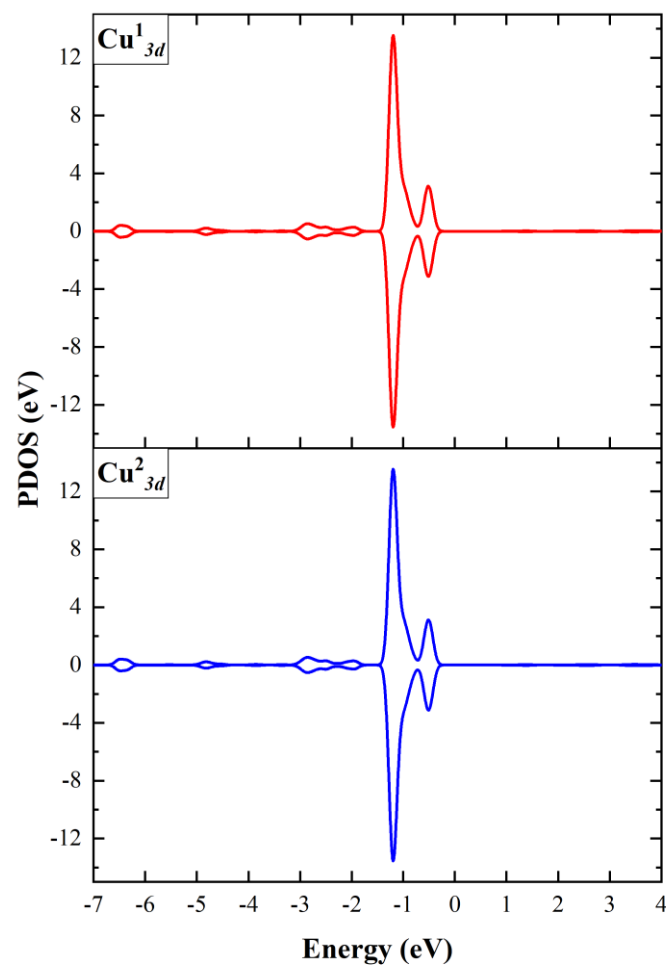


Figure 5.2 PDOS of the Cu 3d orbital in the Cu/PCN system, Fermi level was set to be 0 eV.

5.3.2. Reaction Path to C₁ product on Single Cu

We first investigated the carbon reduction reaction on a single Cu atom. The calculated adsorption energy of CO is -0.79 eV, and CO₂ cannot form a chemical bond with Cu atoms. This result aligns with previous literature, which reports a CO adsorption energy of -0.60 eV, and CO₂ can only be physically adsorbed on Cu/PCN^[18]. Therefore, CO was chosen as the starting reactant for subsequent studies.

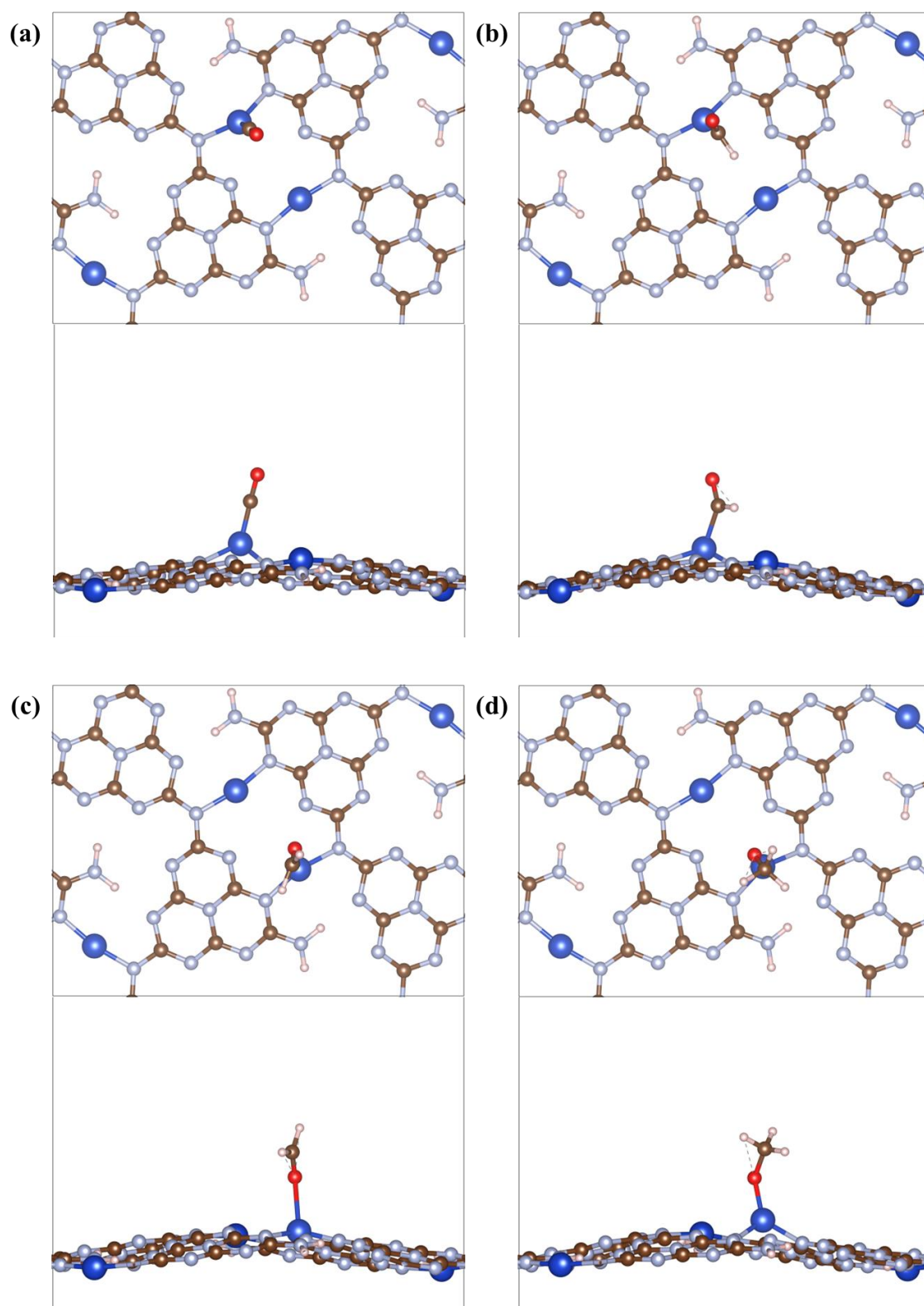


Figure 5.3 Intermediate states of the Cu/PCN system during the CO reduction reaction to C₁

product: (a) *CO, (b) *CHO, (c) *OCH₂ and (d) *OCH₃.

The key intermediates involved in the carbon monoxide reduction reaction are shown in **Figure 5.3**. The calculated Gibbs free energy is shown in **Table 5.1**.

Table 5.1 Gibbs free energy of CORR to C₁ products, the experimental values are given in brackets^[19].

Reaction	ΔG (eV)
$* + CO(g) \rightarrow * CO$	-0.27
$* CO + \frac{1}{2} H_2(g) \rightarrow * CHO$	1.11
$* CHO + \frac{1}{2} H_2(g) \rightarrow * OCH_2$	-0.42
$* OCH_2 + \frac{1}{2} H_2(g) \rightarrow * OCH_3$	0.40
$* OCH_3 + \frac{1}{2} H_2(g) \rightarrow * O + CH_4(g)$	1.07
$* O + \frac{1}{2} H_2(g) \rightarrow * OH$	-2.00
$* OH + \frac{1}{2} H_2(g) \rightarrow H_2O(g)$	-1.50
$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$	-1.61 (-1.47)
$* OCH_3 + \frac{1}{2} H_2(g) \rightarrow CH_3OH(g)$	-1.36
$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$	-0.54 (-0.26)

The table shows that the PDS for the C₁ product pathway—the first hydrogenation step—has a Gibbs free energy of 1.11 eV, which is higher than the 0.74 eV reported in the literature^[1]. This suggests that the formation of C₁ products is less favorable in this system. However, at the *OCH₃ addition step, a distinction arises: the Gibbs free energy for methane (CH₄) formation is 1.07 eV, while for methanol (CH₃OH) it is -1.36 eV.

This indicates that, within the C_1 pathway, methanol is the preferred final product.

Gibbs free energy diagrams are shown in **Figure 5.4**.

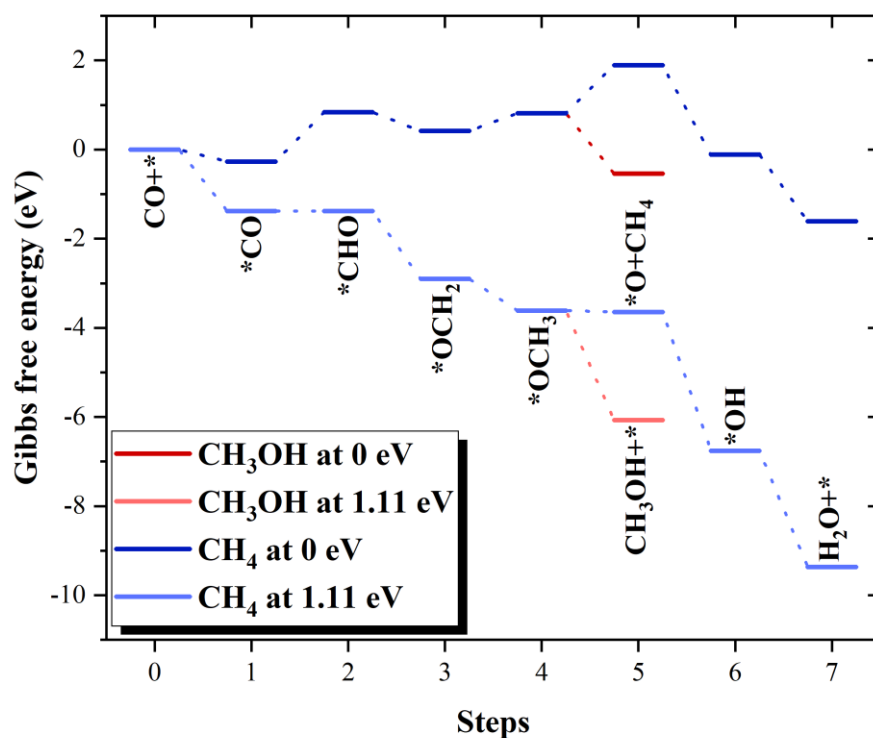


Figure 5.4 Gibbs free energy diagrams for the CORR to C_1 products.

5.3.3. Reaction path to C_2 product on geminal Cu

Since both the adsorption energy and ΔG of CO on Cu/PCN are negative, CO can spontaneously adsorb onto the Cu atoms even in the absence of an applied voltage. As shown in **Figure 5.5(a)**, the initial step of the C_2 reaction is modeled as the adsorption of two CO molecules—one on Cu^1 and the other on Cu^2 .

The next step involves the addition of the first hydrogen atom, similar to the process observed for the intermediate state on a single Cu atom, resulting in the formation of either $*CHO$ or $*COH$ species. As illustrated in **Figures 5.5(b)** and (c),

two distinct configurations can be obtained. In **Figure 5.5(b)**, the hydrogen atom adsorbed on Cu¹ is positioned away from Cu², whereas in **Figure 5.5(c)**, the situation is reversed. The adsorption energy of the configuration shown in Figure 5.4(b) is nearly identical to that in **Figure 5.5(c)**, being only 0.01 eV lower. In contrast, the energy of the *CO + *COH configuration depicted in **Figure 5.5(d)** is significantly higher—1.41 eV above that of *CO + *CHO. Exchanging the adsorbates between Cu¹ and Cu² yields the same results.

With the addition of a second hydrogen atom, four possible configurations arise, as shown in **Figure 5.6**. Among these, the configuration in **Figure 5.6(d)** is the most stable, featuring a Cu-Cu distance of 3.17 Å and a C-C bond length of 1.39 Å. **Figure 5.6(c)** presents a configuration with an energy 0.25 eV higher than the most stable state, a Cu-Cu distance of 3.23 Å, and a C-C bond length of 1.40 Å. In **Figure 5.6(a)**, two *CHO groups are adsorbed separately on the Cu atoms; this configuration is 0.05 eV higher in energy, with a Cu-Cu distance of 4.15 Å. Finally, the configuration in **Figure 5.6(b)**, which features a C-O-C linkage, has the highest energy, being 0.30 eV above the most stable configuration.

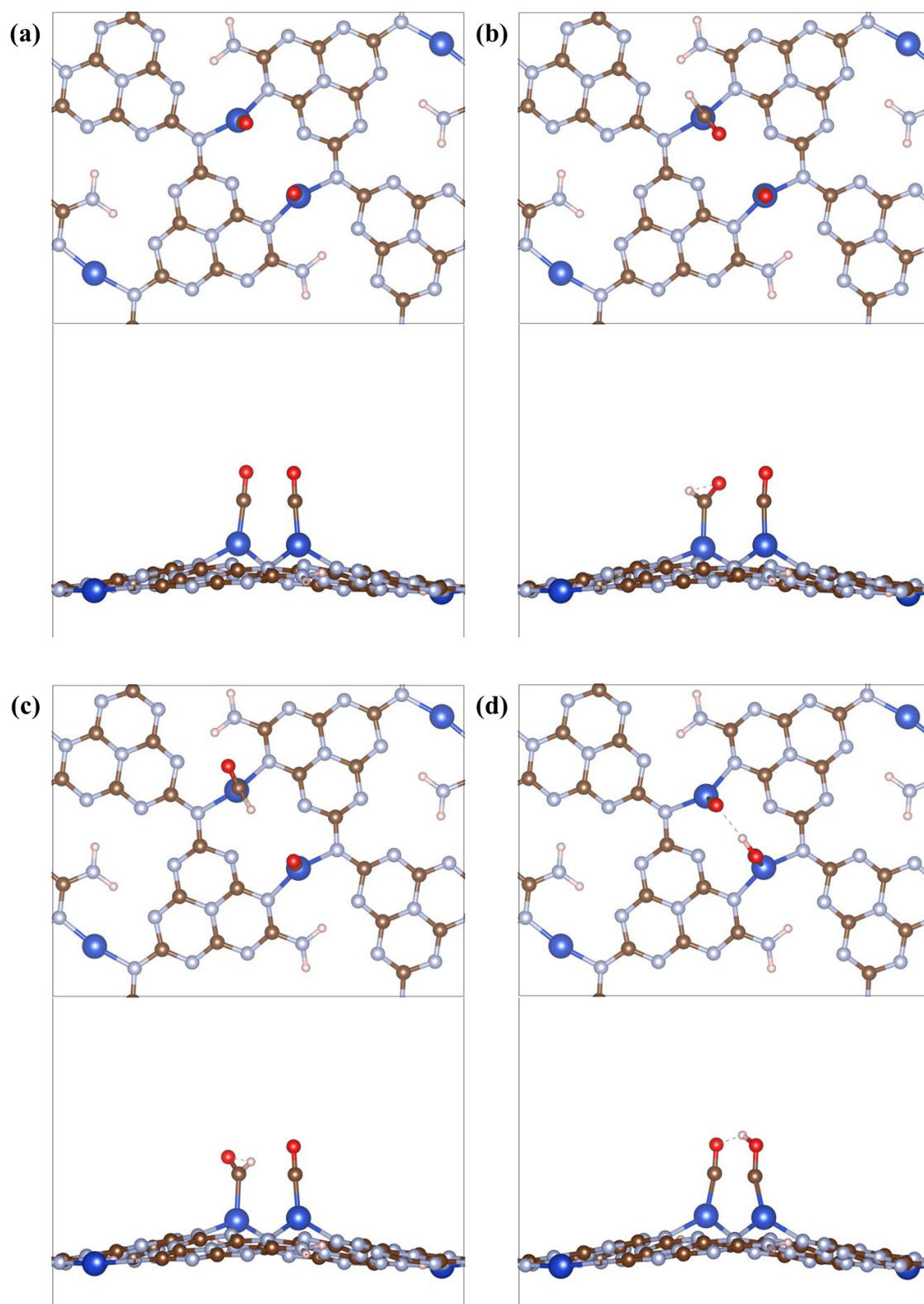


Figure 5.5 Intermediate states of the Cu/PCN system during the CO reduction reaction to C₂

product: (a) $\ast\text{CO} + \ast\text{CO}$, (b) and (c) two different configurations of $\ast\text{CHO} + \ast\text{CO}$, and (d)

$\ast\text{CO} + \ast\text{COH}$.

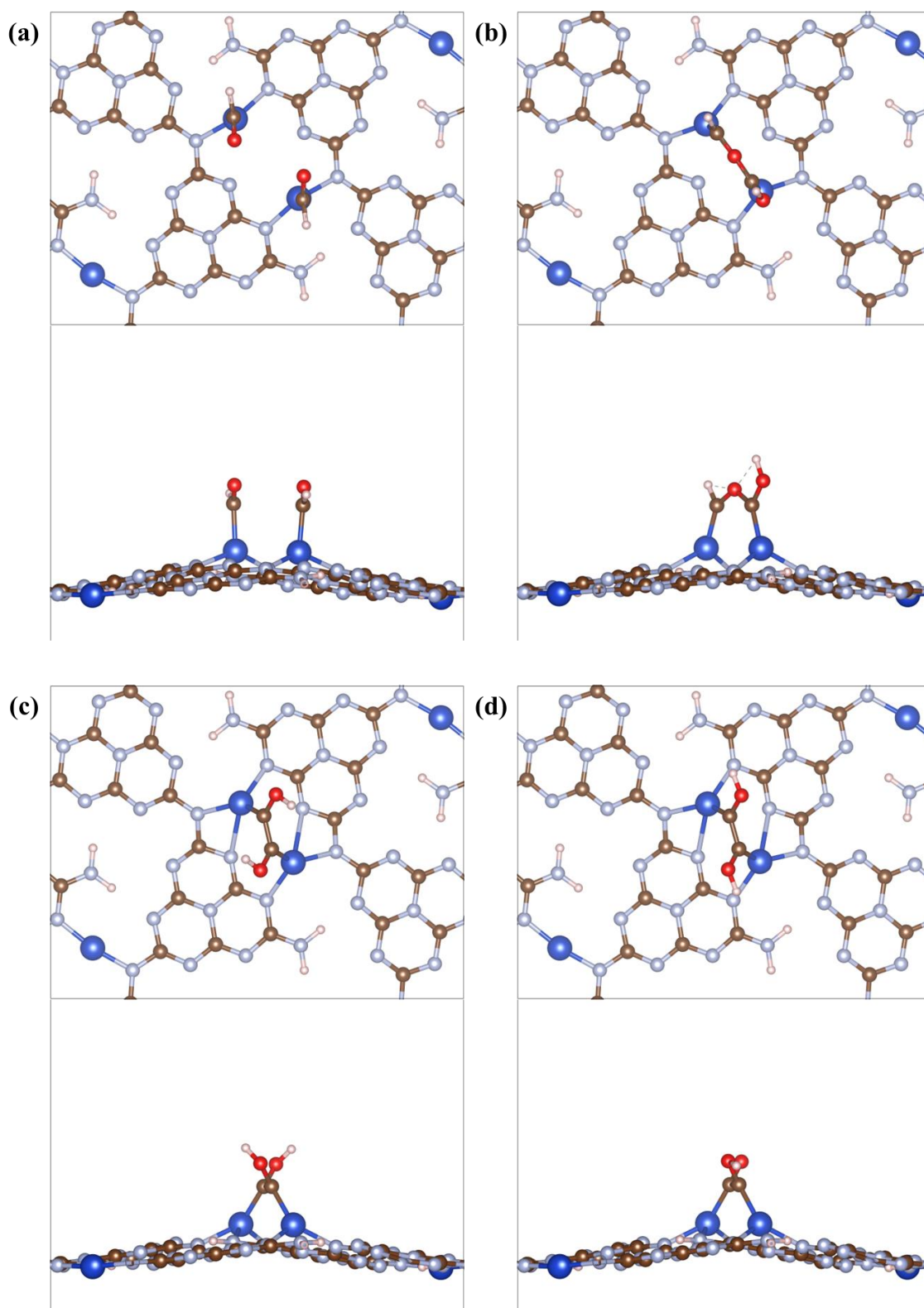


Figure 5.6 Intermediate states of the Cu/PCN system during the CO reduction reaction to C₂

product: (a) $^*CHO + ^*CHO$, (b) $^*CHOCOH$, (c) and (d) two different configurations of

$^*HOCCOH$.

After the addition of a third hydrogen atom, and considering symmetry, the resulting configuration is shown in **Figure 5.7(a)**. At this stage, the C-C bond length is 1.41 Å, and the Cu-Cu distance is 3.25 Å. Upon addition of the fourth hydrogen atom, three distinct configurations are observed. The most stable configuration occurs when each carbon atom is bonded to one hydrogen atom (**Figure 5.7(b)**), with the two OH groups in the trans position. In **Figure 5.7(c)**, the two OH groups are in the cis position. The energies of these two configurations are very similar, differing by only 0.05 eV. Both exhibit a C-C bond length of 1.37 Å and a Cu-Cu distance of 4.28 Å. In contrast, if one carbon atom is bonded to two hydrogen atoms while the other carbon atom are not hydrogenated (**Figure 5.7(d)**), the energy increases significantly by 0.79 eV. In this case, the C-C bond length extends to 1.49 Å, approaching that of a typical C–C single bond (1.54 Å), and the Cu-Cu distance is 4.15 Å.

After the addition of the fifth hydrogen atom, all intermediate states convert to *HOCHCH₂OH, each exhibiting slightly different configurations on the Cu surface, as shown in **Figure 5.8**. The configuration in **Figure 5.8(a)** is the most stable, with a C-C bond length of 1.51 Å—very close to that of the final product, ethylene glycol (1.518 Å ^[20])—and a Cu-Cu distance of 4.30 Å, which is slightly longer than that at the beginning of the reaction. The configuration **Figure 5.8(b)** shows 0.12 eV higher in energy, with a C-C bond length of 1.50 Å and a Cu-Cu distance of 4.25 Å. **Figure 5.8(c)** is 0.17 eV above the minimum energy, with a C-C bond length of 1.50 Å and a Cu-Cu distance of 4.22 Å. In **Figure 5.8(d)**, the energy is 0.07 eV higher than the most stable configuration, with a C-C bond length of 1.51 Å and a Cu-Cu distance of 4.20 Å.

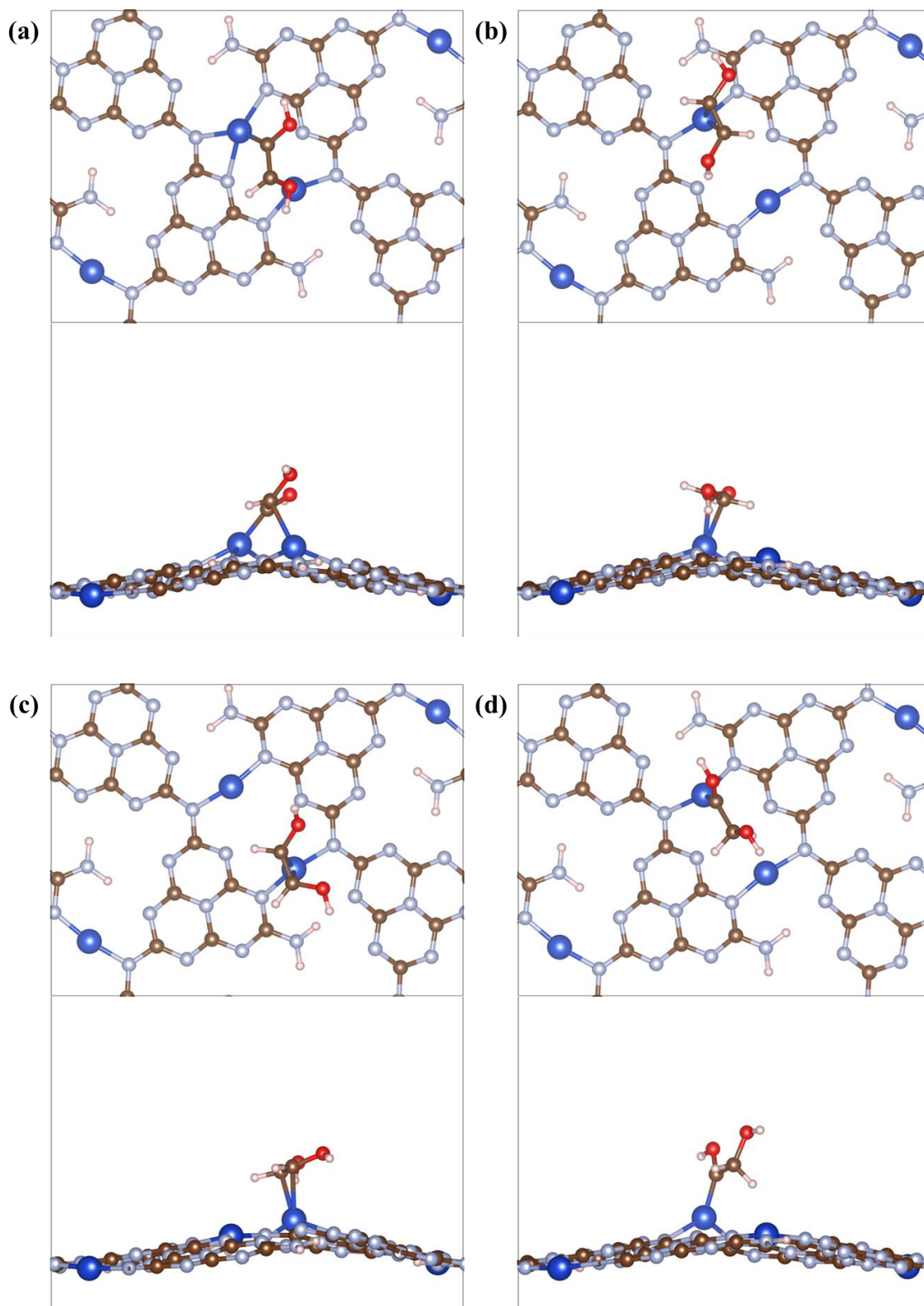


Figure 5.7 Intermediate states of the Cu/PCN system during the CO reduction reaction to C₂

product: (a) *HOCCHOH, (b) trans *HOCHCHOH, (c) cis *HOCHCHOH and (d)

*HOCCH₂OH.

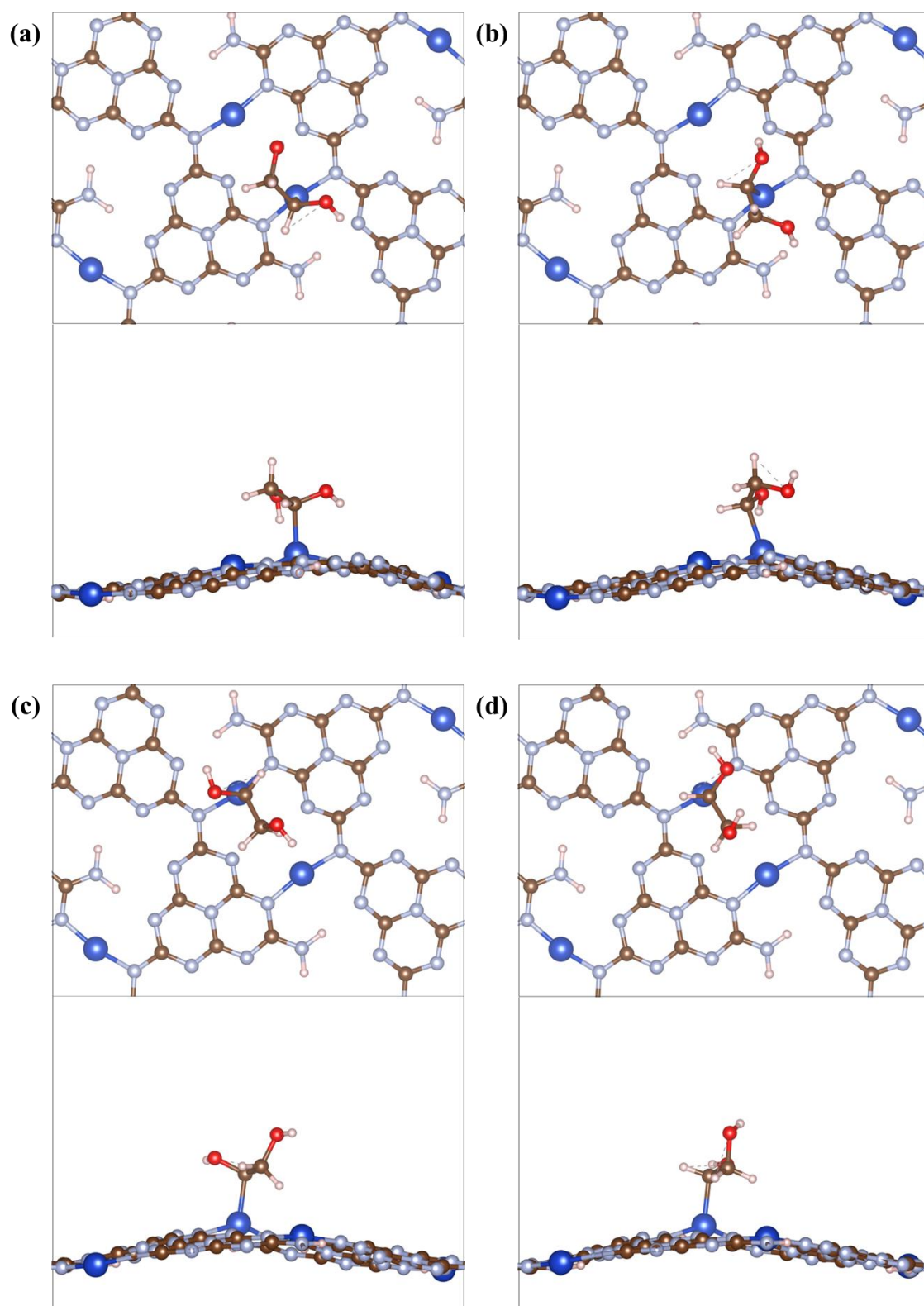


Figure 5.8 Intermediate states of the Cu/PCN system during the CO reduction reaction to C₂

product: (a-d) different states of *HOCHCH₂OH.

It is worth noting that, in typical carbon reduction reactions, the intermediate states usually involve direct contact between the oxygen atom and the catalyst atom, making it necessary to consider whether the O-C bond will break during the formation of the final product. However, in this study, the oxygen atom does not directly interact with the catalyst, eliminating the need to consider O-C bond cleavage. As a result, ethylene glycol is identified as the final product.

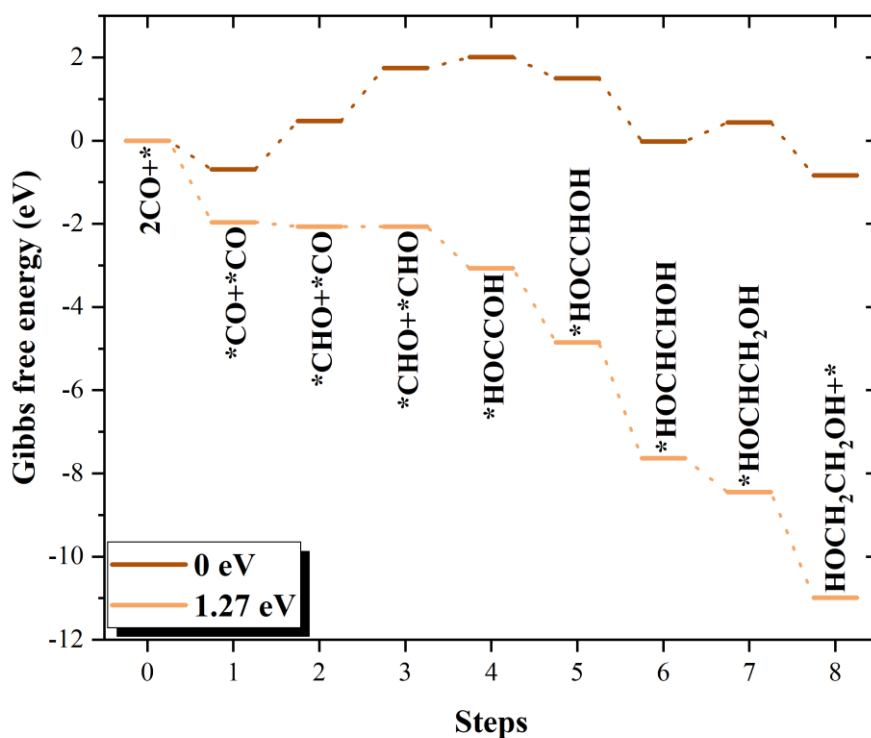


Figure 5.9 Gibbs free energy diagrams for the CORR to C₂ products.

Furthermore, upon addition of the second hydrogen atom, the $\text{*CHO} + \text{*CHO}$ configuration (**Figure 5.6a**) has an energy that is 0.05 eV higher than that of *HOCCOH (**Figure 5.6d**), but 0.26 eV lower than the Gibbs free energy of the preceding step (see **Table 5.2**). This indicates that second hydrogen addition is more

favorable than C-C bond formation at this stage. However, as the reaction progresses, the intermediate *HOCCOC, which is lower in energy and more stable, will form. As shown in **Table 5.2**, the PDS for the C₂ pathway is the adsorption of the second hydrogen atom, with a barrier of 1.27 eV—slightly higher than the 1.17 eV required for the first hydrogen adsorption. This is consistent with the general trend that C₂ product formation is more difficult than C₁ product formation. Compared with reported PDS values for different Cu surfaces and ion concentrations (ranging from 0.763 eV to 1.668 eV), our results are relatively moderate^[21]. The Gibbs free energy diagram for the entire catalytic reaction is presented in **Figure 5.9**.

Table 5.2 Gibbs free energy of CORR to C₂ products.

Reaction	ΔG (eV)
$* + 2CO(g) \rightarrow *CO + *CO$	-0.69
$*CO + *CO + \frac{1}{2}H_2(g) \rightarrow *CHO + *CO$	1.17
$*CHO + *CO + \frac{1}{2}H_2(g) \rightarrow *CHO + *CHO$	1.27
$*CHO + *CHO \rightarrow *HOCCOH$	0.26
$*HOCCOH + \frac{1}{2}H_2(g) \rightarrow *HOCCHOH$	-0.51
$*HOCCHOH + \frac{1}{2}H_2(g) \rightarrow *HOCHCHOH$	-1.52
$*HOCHCHOH + \frac{1}{2}H_2(g) \rightarrow *HOCHCH_2OH$	0.45
$*HOCHCH_2OH + \frac{1}{2}H_2(g) \rightarrow HOCH_2CH_2OH(g)$	-1.27
$2CO(g) + 3H_2(g) \rightarrow HOCH_2CH_2OH(g)$	-0.83

5.3.5. Electronic Structures Analysis

To investigate the C–C bonding mechanism, we first performed a Bader charge analysis on the *CHO + *CHO and *HOCCOH configurations. Since the results for Cu₁ and Cu₂ were highly similar, we present only the data for Cu₁. **Table 5.3** summarizes the Bader charges of the Cu₁ atom and its adsorbed C, H, and O atoms. Overall, the Cu-CHO structure exhibits minimal electron transfer. Compared to the *CHO + *CHO structure, the H atom in *HOCCOH loses 0.55 electrons, indicating strong positive associated with C-H bond breaking and O-H bond formation. The C atom gains 0.41 electrons, reducing its positivity. Notably, the number of electrons contributed by the catalytic Cu atom to the adsorbate remains nearly unchanged.

Table 5.3 Bader Charge Analysis of Adsorbed Species and Cu Atom.

Bader charge (e)	*CHO	*HOCCOH
H	+0.08	+0.63
O	-0.99	-1.09
C	+0.78	+0.37
Cu	+0.73	+0.72
Total	+0.60	+0.62

Figure 5.10 presents the PDOS of *CHO adsorbed on a Cu₁ atom. Strong, overlapping peaks for the C-2*p* (brown) and O-2*p* (red) orbitals are observed in the deep energy region (-7 eV to -5 eV), indicating significant hybridization and strong covalent

bonding within the formyl group. In the Cu d-band region (-4.0 eV to -1.5 eV), there is clear overlap between the tails of the C-2*p* and O-2*p* states and the main Cu-3*d* band. This pronounced hybridization between the adsorbate (C-2*p*, O-2*p*) and substrate (Cu-3*d*) orbitals is direct evidence of chemisorption and strong interfacial bonding. Notably, spin-splitting is especially evident in the unoccupied peak near +0.7 eV, suggesting that the system's magnetism is primarily associated with these frontier orbitals.

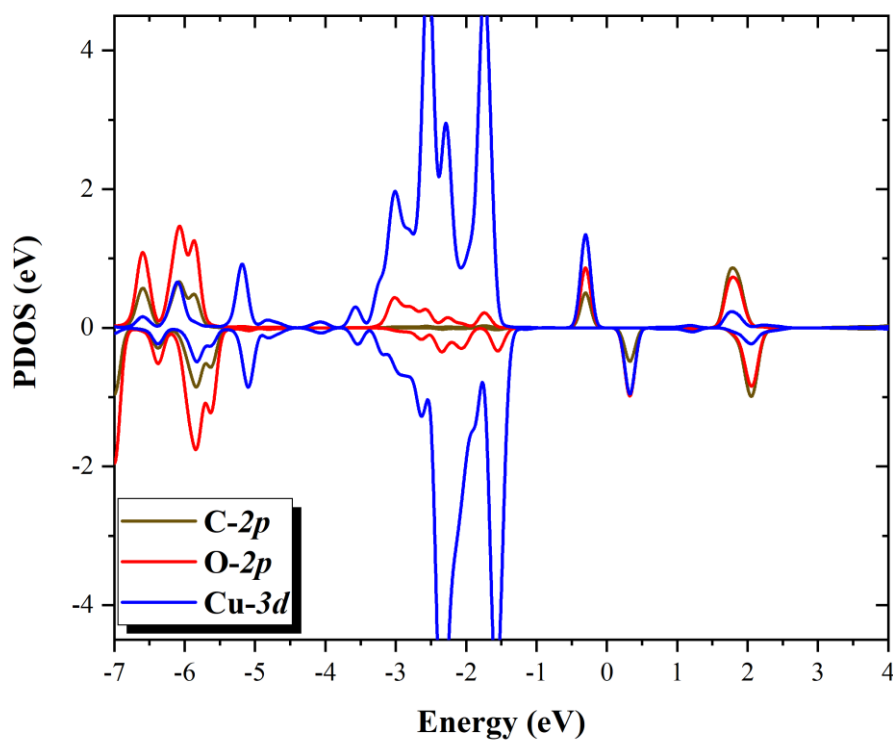


Figure 5.10 PDOS of the *CHO + *CHO intermediate on Cu₁, with the Fermi level set to 0

eV

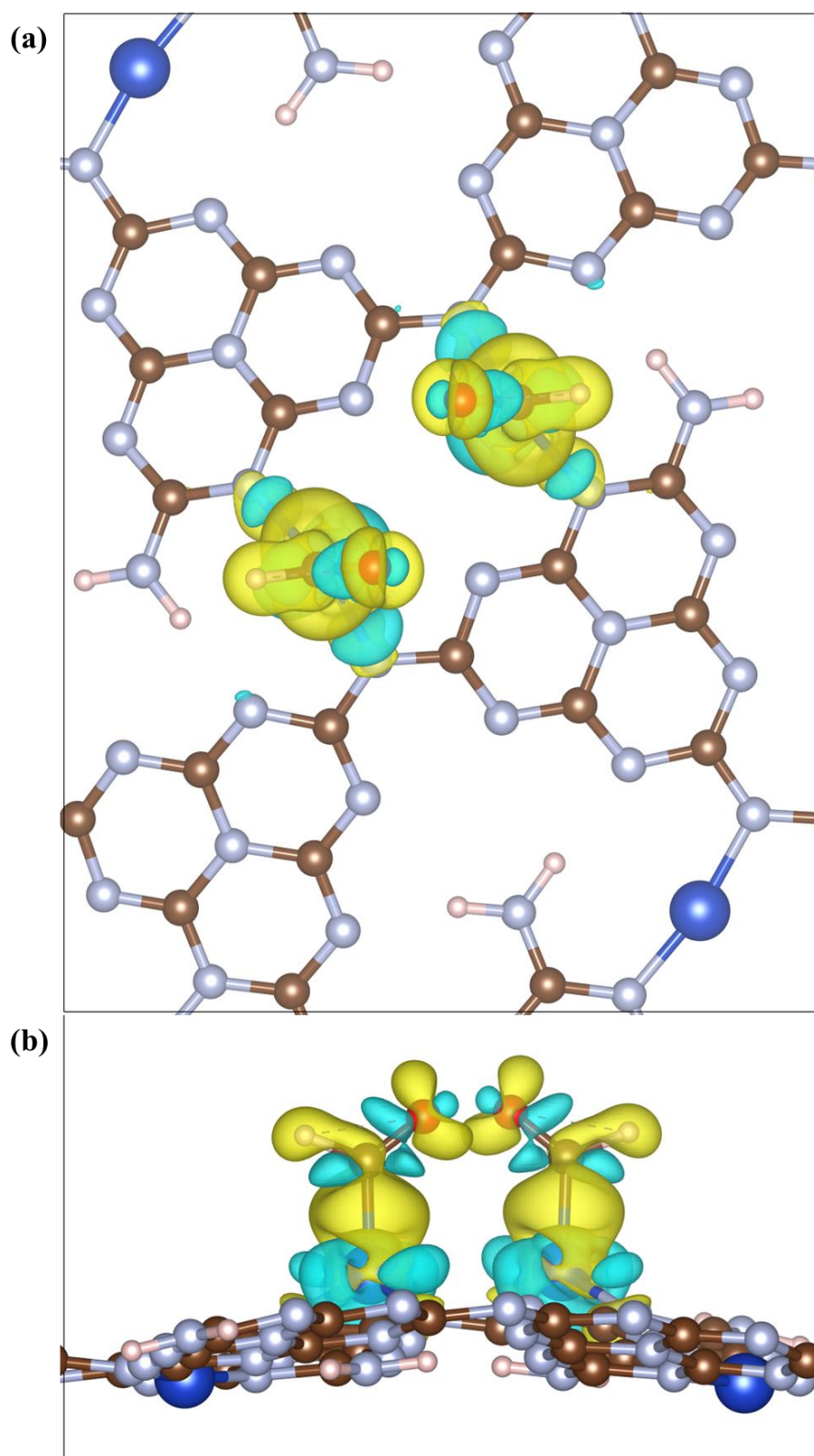


Figure 5.11 (a) Top and (b) side view of difference charge density for $*CHO + *CHO$.

Yellow and blue regions represent charge accumulation and depletion, respectively.

Isosurface value is set to $0.001 \text{ e}/\text{\AA}^3$.

The difference charge density for $*\text{CHO} + *\text{CHO}$ is shown in **Figure 5.11**. A prominent yellow region, indicating charge accumulation, is observed directly between the carbon atom and the copper surface, highlighting the formation of a strong covalent bond between the adsorbate and the substrate.

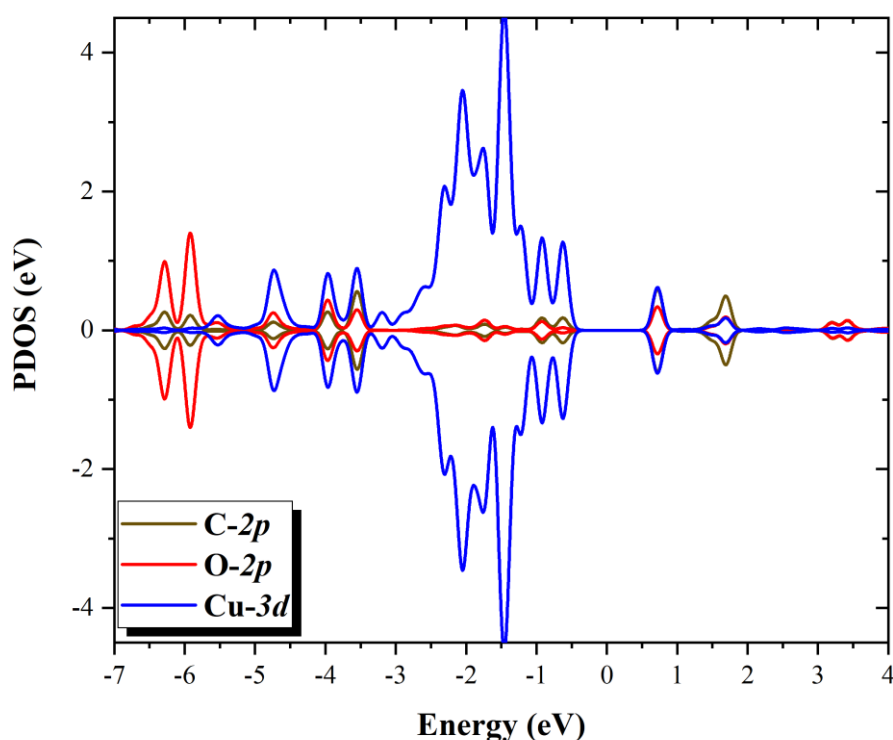


Figure 5.12 PDOS of the $*\text{HOCCOH}$ intermediate on Cu_1 , with the Fermi level set to 0 eV

Figure 5.12 presents the PDOS of $*\text{HOCCOH}$ adsorbed on a Cu_1 atom. Compared to the PDOS for $*\text{CHO}$, the most notable difference is the much broader and more complex distribution of the C-2p and O-2p states. This complexity is a clear electronic signature of new C-C bond formation and the transition from a C_1 to a C_2 species.

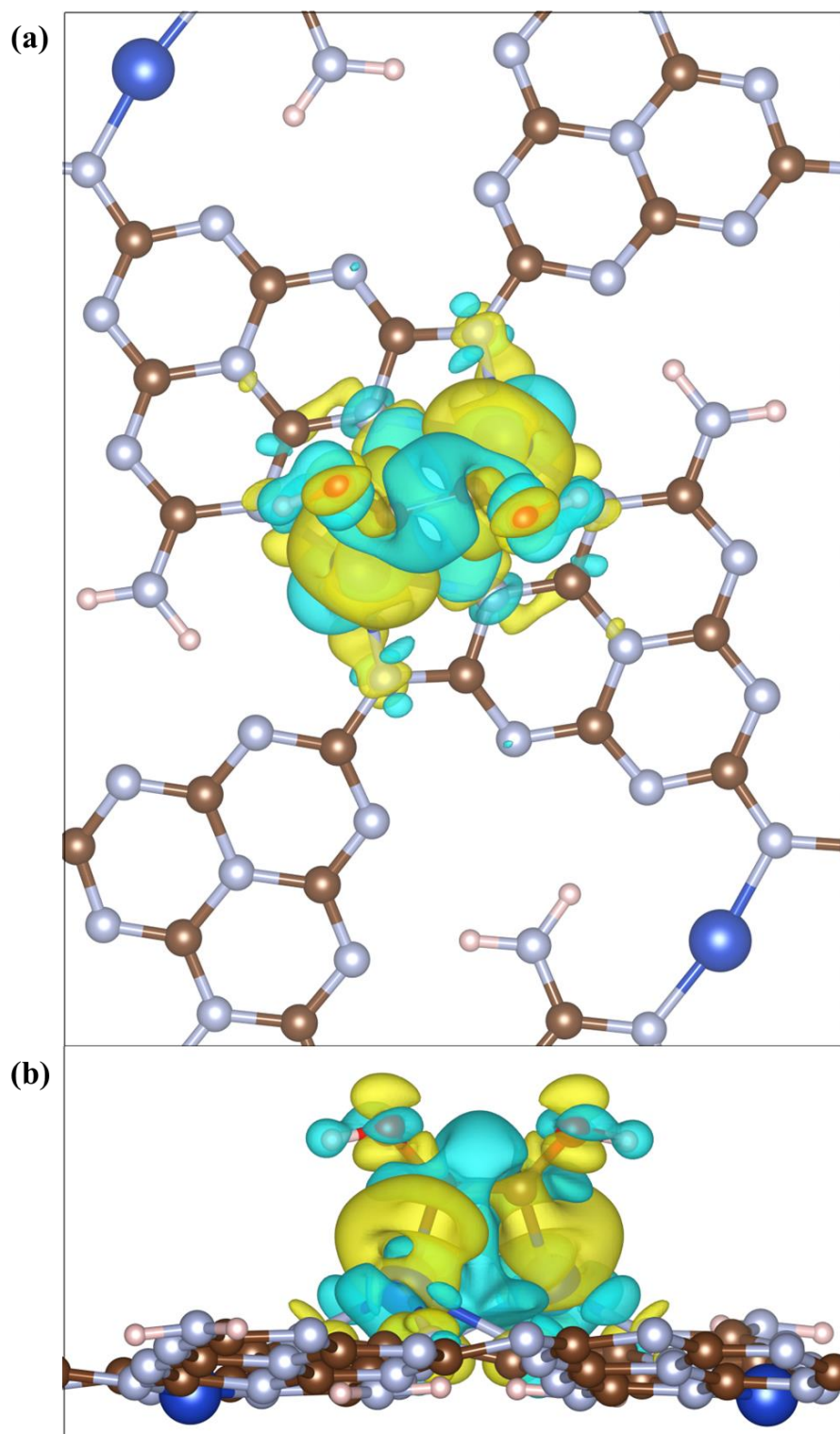


Figure 5.13 (a) Top and (b) side view of difference charge density for $^*\text{HOCCOH}$. Yellow and blue regions represent charge accumulation and depletion, respectively. Isosurface value is set to $0.001 \text{ e}/\text{\AA}^3$.

A series of sharp, intense peaks resulting from strong overlap between the O-2*p* (red) and C-2*p* (brown) orbitals is observed around -6.0 eV, representing the highly stable C-O bond orbitals within the *HOCCOH molecule. In the Cu-3*d* band region (-4.0 eV to -1.0 eV), significant overlap of the C-2*p* and O-2*p* states with the Cu-3*d* band indicates strong electronic mixing between the molecule and the copper surface, forming stable C-Cu and O-Cu bonds that firmly anchor the molecule to the catalyst. This conclusion is further supported by the differential charge density shown in **Figure 5.13**: **Figure 5.13(a)** reveals substantial charge accumulation (yellow regions) between the substrate Cu atoms and the C atoms, covering part of the C-C bond region. Additionally, the disappearance of magnetism is observed, which may also contribute to the system's lower energy.

5.3.6. Cu-poor Conditions

To investigate the effect of minor copper doping, we removed a pair of Cu atoms from the Cu-rich model (**Figure 5.1b**) and performed calculations on the modified structure ^[11]. The slab is shown in **Figure 5.14**. The calculated formation energy for Cu incorporation is 0.81 eV per atom, slightly larger than that (0.80 eV) in Cu-rich model. Similar to the results calculated by the Cu-rich model, the two Cu species are also equivalent in the reaction.

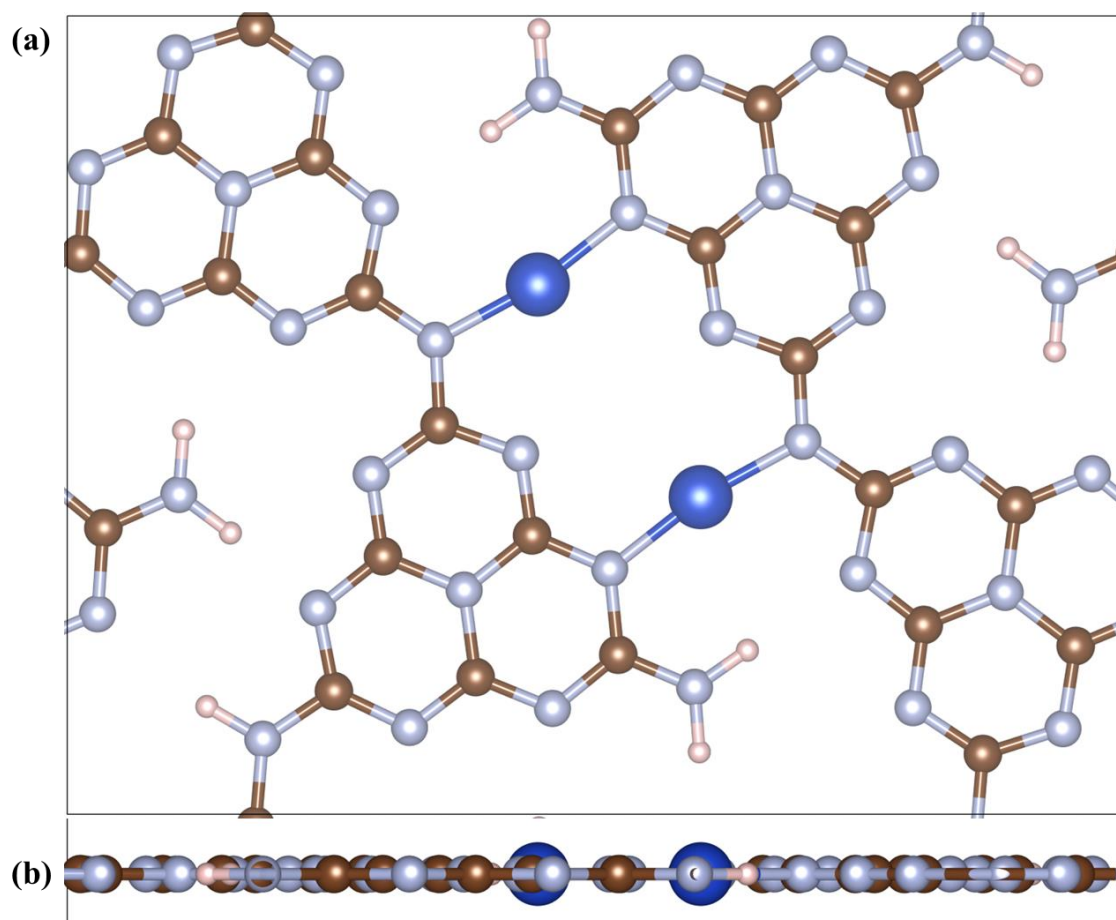


Figure 5.14 (a) Top view and (b) side view of the Cu-poor situation. Copper atoms are shown in blue, carbon in brown, nitrogen in grey, and hydrogen in pink.

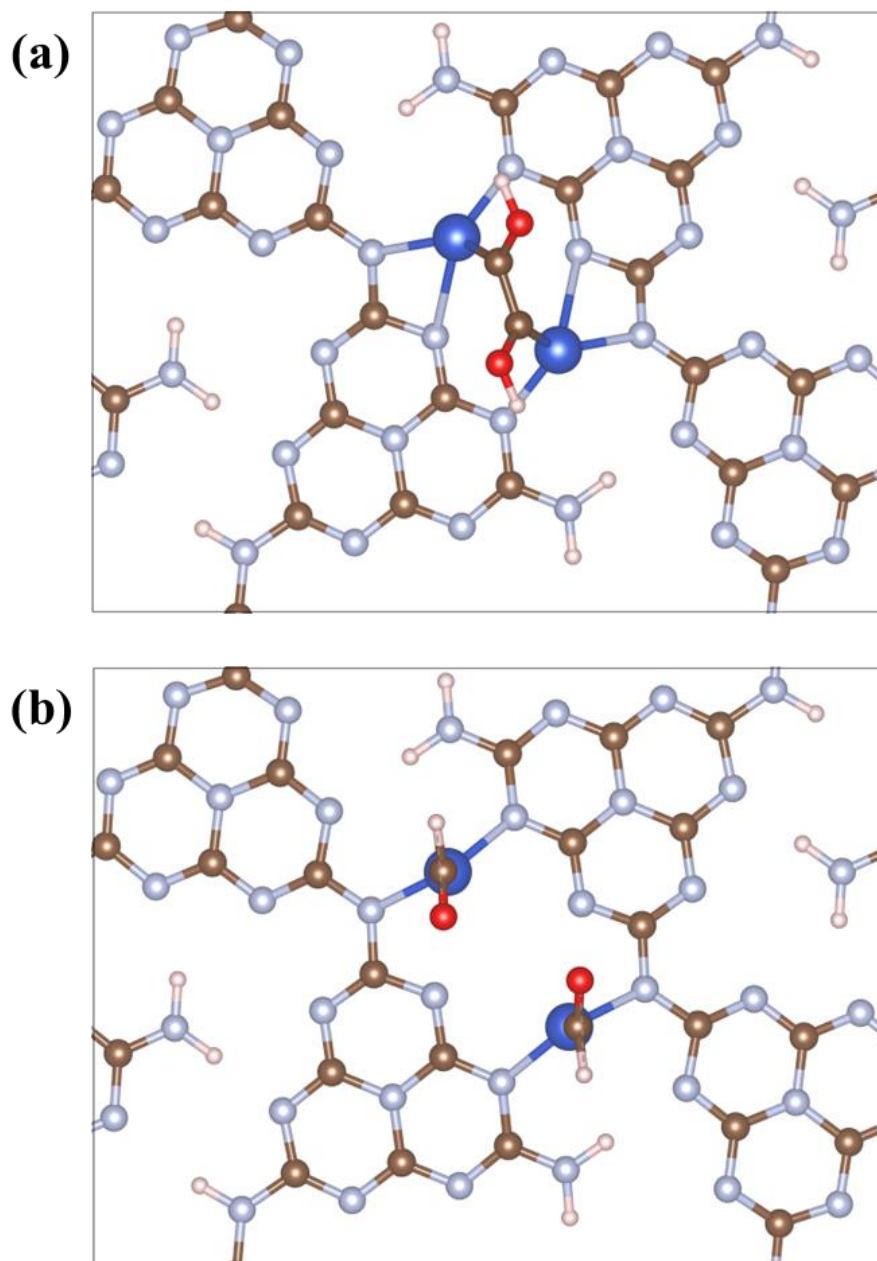


Figure 5.15 Intermediate states of the Cu-poor situation during the CO reduction reaction to

C₂ product: (a) *HOCCOH and (b) *CHO + *CHO.

In the C₂ pathway calculations, we obtained results and configurations similar to those of the Cu-rich model. As shown in **Figure 5.15**, these remain the two most stable configurations following the second hydrogenation. Notably, the energy difference between these two configurations is only 0.01 eV, indicating that the thermodynamic

advantage of the $\ast\text{HOCCOH}$ configuration has nearly disappeared. Additionally, the Gibbs free energy is 0.30 eV higher than that of $\ast\text{CHO} + \ast\text{CHO}$. This suggests that, in the Cu-poor case, the $\ast\text{CHO} + \ast\text{CHO}$ intermediate struggles to form a C-C bond and directly competes with $\ast\text{HOCCOH}$. The calculated Gibbs free energies are presented in **Table 5.4**. At this stage of the PDS, hydrogen adsorption and C-C bond formation occur simultaneously, yielding a value of 1.53 eV. The corresponding reaction pathway is illustrated in **Figure 5.16**. Compared to the Cu-rich case, the C_2 energy barrier in the Cu-poor system is significantly higher, indicating that a Cu-rich environment is more favorable for the C_2 pathway in CORR.

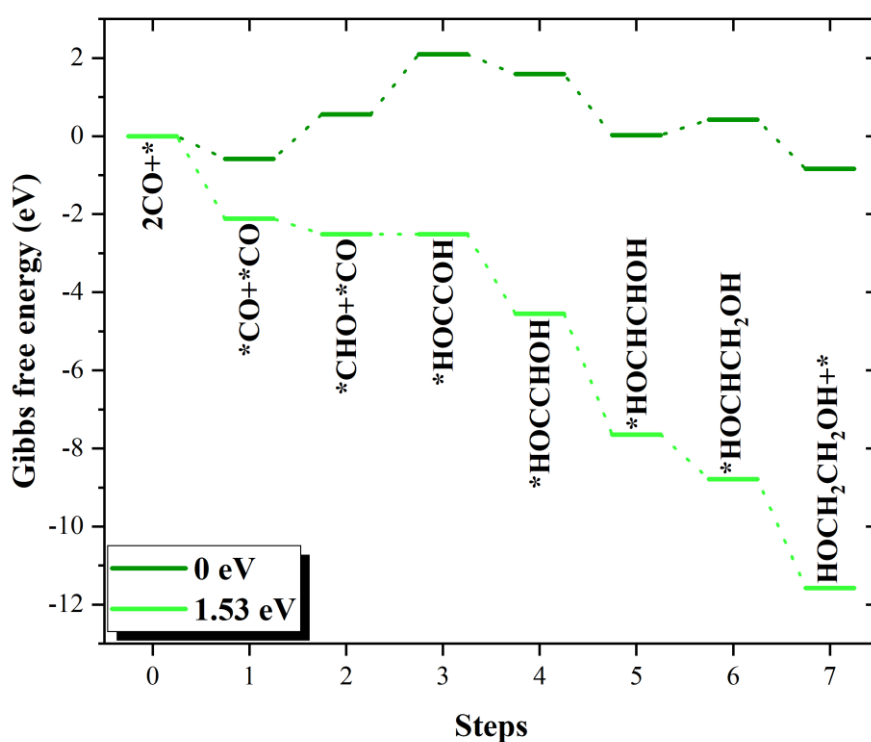


Figure 5.16 Gibbs free energy diagrams for the CORR to C_2 products in Cu-poor situation.

Table 5.4 Gibbs free energy of CORR to C₂ products on Cu-poor situation.

Reaction	ΔG (eV)
$* + 2CO(g) \rightarrow *CO + *CO$	-0.58
$*CO + *CO + \frac{1}{2}H_2(g) \rightarrow *CHO + *CO$	1.14
$*CHO + *CO + \frac{1}{2}H_2(g) \rightarrow *HOCCOH$	1.53
$*HOCCOH + \frac{1}{2}H_2(g) \rightarrow *HOCCHOH$	-0.51
$*HOCCHOH + \frac{1}{2}H_2(g) \rightarrow *HOCHCHOH$	-1.56
$*HOCHCHOH + \frac{1}{2}H_2(g) \rightarrow *HOCHCH_2OH$	0.39
$*HOCHCH_2OH + \frac{1}{2}H_2(g) \rightarrow HOCH_2CH_2OH(g)$	-1.26
$2CO(g) + 3H_2(g) \rightarrow HOCH_2CH_2OH(g)$	-0.83

5.5. Conclusions

We established a catalytic model for geminal Cu atoms on a PCN substrate, demonstrating its potential to produce both C₁ and C₂ products using CO as a precursor. Gibbs free energy calculations indicate that methanol is the most likely final product for the C₁ pathway, while ethylene glycol is favored for the C₂ pathway. The potential-determining step (PDS) for the C₁ reaction is 1.11 eV, compared to 1.27 eV for the C₂ pathway, highlighting the strong competitiveness of C₂ product formation.

Using projected density of states (PDOS) and differential charge density analyses, we investigated the electronic structure and bonding characteristics of key intermediates on the copper catalyst surface. These analyses illustrate why the *HOCCOH intermediate is more stable than *CHO+*CHO. The transition from the C₁

(*CHO) intermediate to the C₂ (*HOCCOH) intermediate is accompanied by increased complexity and broadening of the C-2*p* and O-2*p* states, with copper playing a significant role in C-C bond formation.

We also examined a Cu-poor situation and found that *HOCCOH and *CHO+*CHO intermediates compete, resulting in a higher PDS of 1.53 eV, which is unfavorable for the C₂ reaction. Our findings suggest that high concentrations of geminal Cu doping and abundant CO at catalytic sites favor the selective production of ethylene glycol from CO. Collectively, these results deepen our understanding of the interaction between intermediates and geminal Cu catalysts, providing valuable guidance for the rational design of more efficient electrocatalysts.

References:

1. Peterson, A.A., et al., *How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels*. Energy & Environmental Science, 2010. **3**(9).
2. Durand, W.J., et al., *Structure effects on the energetics of the electrochemical reduction of CO₂ by copper surfaces*. Surface Science, 2011. **605**(15-16): p. 1354-1359.
3. Shi, X.-D., et al., *Electrocatalytic reduction of CO₂ to produce the C₂+ products: from selectivity to rational catalyst design*. Nanoscale, 2025. **17**(8): p. 4338-4364.
4. Mi, Y., et al., *Selective formation of C₂ products from electrochemical CO₂ reduction over CuI. 8Se nanowires*. ACS Applied Energy Materials, 2018. **1**(10): p. 5119-5123.
5. Ren, D., B.S.-H. Ang, and B.S. Yeo, *Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu_xZn catalysts*. Acs Catalysis, 2016. **6**(12): p. 8239-8247.
6. Zhi, X., et al., *Directing the selectivity of CO₂ electroreduction to target C₂ products via non-metal doping on Cu surfaces*. Journal of materials chemistry A, 2021. **9**(10): p. 6345-6351.
7. Li, M., et al., *How to enhance the C₂ products selectivity of copper-based catalysts towards electrochemical CO₂ reduction?—a review*. Materials Today, 2023. **67**: p. 320-343.
8. Li, L., et al., *New paradigm of in situ characterization for next-generation CO₂ electroreduction towards multi-carbon products over Cu-based catalysts*. Next Energy, 2023. **1**(3): p. 100027.
9. Li, X., et al., *Engineering Local Coordination and Electronic Structures of Dual-Atom Catalysts*. ACS Nano, 2025. **19**(18): p. 17114-17139.
10. Hai, X., et al., *Scalable two-step annealing method for preparing ultra-high-density single-atom catalyst libraries*. Nature nanotechnology, 2022. **17**(2): p. 174-181.
11. Hai, X., et al., *Geminal-atom catalysis for cross-coupling*. Nature, 2023. **622**(7984): p. 754-760.
12. Calle-Vallejo, F. and M.T. Koper, *Theoretical considerations on the electroreduction of CO to C₂ species on Cu(100) electrodes*. Angew Chem Int Ed Engl, 2013. **52**(28): p. 7282-5.
13. Sun, X., *Achieving Selective and Efficient Electrocatalytic Activity for CO(2) Reduction on N-Doped Graphene*. Front Chem, 2021. **9**: p. 734460.

14. Peterson, A.A. and J.K. Nørskov, *Activity Descriptors for CO₂ Electroreduction to Methane on Transition-Metal Catalysts*. The Journal of Physical Chemistry Letters, 2012. **3**(2): p. 251-258.
15. Chen, B.W.J., L. Xu, and M. Mavrikakis, *Computational Methods in Heterogeneous Catalysis*. Chemical Reviews, 2021. **121**(2): p. 1007-1048.
16. Liao, X., et al., *Density functional theory for electrocatalysis*. Energy & Environmental Materials, 2022. **5**(1): p. 157-185.
17. Sameera, W. and F. Maseras, *Transition metal catalysis by density functional theory and density functional theory/molecular mechanics*. Wiley Interdisciplinary Reviews: Computational Molecular Science, 2012. **2**(3): p. 375-385.
18. Gouveia, J.D. and J.R.B. Gomes, *Cu-doped polymeric carbon nitrides: structural and electronic properties and sensitivity to flue gas*. Surfaces and Interfaces, 2024. **46**.
19. Johnson, R., *Computational Chemistry Comparison and Benchmark Database* <http://cccbdb.nist.gov/> DOI:10.18434/T47C7Z. 2018.
20. Kazerouni, M.R., *Conformational analysis, ethylene glycol and ethylenediamine: an electron diffraction investigation of the molecular structures, compositions, anti-gauche energy differences and entropy differences*. 1987.
21. Ahmad, T., et al., *Electrochemical CO₂ reduction to C₂+products using Cu-based electrocatalysts: A review*. Nano Research Energy, 2022. **1**.

Chapter 6. Conclusions and Future Works

6.1 Conclusions

Through in-depth DFT calculation, we aim to deepen our understanding of how atomic-level design can create more efficient and selective electrocatalysts for energy conversion. By systematically exploring a diverse set of catalytic systems—ranging from transition metal dichalcogenides to single-atom and geminal-atom catalysts—this thesis explained the core principles that govern catalytic activity, stability, and selectivity at the atom level.

In **Chapter 3**, we systematically investigated the electronic structure and catalytic properties of MoS₂ arc models with varying curvatures and engineered sulfur vacancies, focusing on their implications for the hydrogen evolution reaction (HER). Our findings reveal that the interplay between curvature and sulfur vacancy concentration profoundly modulates the local electronic environment. As evidenced by projected density of states (PDOS) analyses, introducing curvature into MoS₂ narrows the band gap, while sulfur vacancies enhance the density of S-*p* states near the Fermi level, both of which synergistically facilitate electron transfer and hydrogen adsorption. The resulting changes in electronic structure leads to strengthened S-H or Mo-H bonds and improved HER activity in curved models. These results underscore the potential of microstructural tailoring, specifically the control of curvature, as a powerful strategy for optimizing HER electrocatalysts.

In **Chapter 4**, we systematically explored the loading effect on the stability and site-specific oxygen reduction reaction (ORR) activity of heteronuclear Fe and Co single-atom catalysts (SACs) co-supported on nitrogen-doped graphene. Through detailed analysis of metal loading and inter-site distance, we identified a volcano-like dependence of Co site activity on loading, achieving optimal ORR performance at intermediate values. In contrast, Fe site activity was found to decrease with increasing loading due to hydroxyl passivation and spin-state transitions, leading to its spectator role at ultra-high loadings. The observed differences between Fe and Co sites are attributed to variations in metal-substrate binding strength and *d*-orbital occupation, which govern the adsorption energetics of key ORR intermediates. These results offer valuable insights into the electrocatalytic behavior of heteronuclear SACs, establishing a framework for designing high-performance catalysts through precise control of metal loading and inter-site interactions.

In **Chapter 5**, we established a catalytic model for geminal copper atoms on a polymeric carbon nitride (PCN) substrate, demonstrating their potential for selective CO electroreduction to both C₁ and C₂ products. Gibbs free energy calculations indicate that methanol and ethylene glycol are the most favored products for the respective pathways, with ethylene glycol formation being particularly competitive at high geminal Cu concentrations and abundant CO availability. Electronic structure analyses, including PDOS and differential charge density, revealed the key role of copper in stabilizing C-C bond-forming intermediates and steering product selectivity. We further showed that under Cu-poor conditions, the competition between intermediates leads to

higher reaction barriers and diminished C₂ selectivity, indicating the importance of precise control over catalyst local environment.

Over all, these three chapters build a coherent framework for understanding and guiding the rational design of advanced electrocatalysts. The results demonstrate that atomic-scale engineering—whether through morphological modulation, control of atomic site distribution, or tuning of catalyst environment—can be systematically harnessed to optimize catalytic properties for hydrogen evolution, oxygen reduction, and carbon reduction. This thesis not only provides mechanistic insights into the structure–activity relationships of cutting-edge catalysts but also lays a solid foundation for future research aimed at developing next-generation materials for sustainable energy conversion.

6.2 Future works

Building on the insights gained throughout this thesis, several promising directions can be pursued to further advance the development of efficient and selective electrocatalysts:

1. Examining a broader range of transition metals, non-metal dopants, and support materials could further enhance catalytic activity and selectivity. For example, extending the study to other dichalcogenides, multi-metallic SACs, or alternative carbon-based substrates may reveal new structure–activity relationships.

2. Going beyond thermodynamic analyses, future work could systematically investigate reaction kinetics by identifying transition states and calculating activation barriers (e.g., via Nudged Elastic Band), thus offering a more complete understanding of catalytic mechanisms.
3. Integrating machine learning approaches with DFT can enable rapid screening of vast compositional and structural spaces, identifying promising catalyst candidates and key descriptors for activity and stability.

By pursuing these DFT-focused research directions, future studies can deliver deeper, more predictive insights into the structure–function relationships that govern electrocatalyst behavior, thereby accelerating the rational design of next-generation catalytic materials.