

Mechanisms and microkinetic modeling of CO<sub>2</sub> conversions on multi-functional catalysts

by

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B.S., Isfahan University of Technology, 2009

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DOCTOR OF PHILOSOPHY

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## Abstract

Our heavy dependence on fossil fuels allows a large amount of CO<sub>2</sub> to be directly emitted into the atmosphere. There is strong evidence that the rise of atmospheric CO<sub>2</sub> level causes a cascade of severe environmental issues such as ocean acidification, sea level rises, long drought, and intense heat waves. This thesis explores relevant catalysis technologies that will transform CO<sub>2</sub> into a building block species for chemicals production. Catalytic CO<sub>2</sub> utilization faces major limitations because of the chemical stability of this molecule. Multiple technologies such as dry reforming of methane (DRM) and CO<sub>2</sub> hydrogenation have demonstrated their technological and economical potentials to overcome CO<sub>2</sub> conversion's limitations.

Yet, the catalysis science and technology for CO<sub>2</sub> utilization is far from mature. Effective and affordable catalysts suitable for industrial-scale applications are not readily available. Fundamentally, the catalytic reactivities of simple mono-functional catalysts are limited by the so-called Sabatier principle. Moreover, the best performing catalysts often rely on expensive noble metals. Catalyst discovery and design have shifted focus toward composite, bifunctional materials manufactured from earth-abundant elements. Breakthroughs have already been made in ammonia synthesis, CO oxidation, water-gas-shift reaction, and hydrogen production reactions.

DRM converts CO<sub>2</sub> and CH<sub>4</sub> (both are potent greenhouse gases) into syngas, a versatile industrial mixture. Currently, DRM catalysts are challenged by inadequate reactivity and short lifetime. In this thesis, systematic investigations were carried out to understand the mechanistic origin of DRM on the dual-site models representative of real-life bifunctional catalysts. An unconventional material, Co<sub>3</sub>Mo<sub>3</sub>N (a ternary nitride), was the focus in this study. Earlier experimental studies indicated that Co<sub>3</sub>Mo<sub>3</sub>N is active and durable, but the source of its reactivity and stability remain unclear. The adsorptions, desorption, and surface reactions of DRM

intermediates on the  $\text{Co}_3\text{Mo}_3\text{N}$  (111) facet were investigated using the quantum mechanical density functional theory (DFT) method. The site preferences and DRM pathways on  $\text{Co}_3\text{Mo}_3\text{N}$  are revealed for the first time regarding this catalytic material. My work yielded clear evidence that  $\text{Co}_3\text{Mo}_3\text{N}$  promotes  $\text{CH}_4$  activation and the oxidations of surface carbonaceous species at its Co site and Co-Mo<sub>2</sub>N boundary site, respectively. DFT calculations further showed that, due to the presence of two distinct sites, the OH and CHO intermediates that appear during DRM do not obey the linear scaling relationships, resulting in the oxidation reactions occurring at higher than usual rates. The analyses based on DFT calculations are then corroborated by the mean-field microkinetic modeling (MKM) designed especially for dual-site catalytic systems. My work concluded that bifunctional catalysts containing sites with O affinities are desirable for DRM. The MKM results further clarify that cross-site diffusions of DRM intermediates, i.e., C, O, OH, CO, and CH, play the most prominent role in mitigating coke formation.

In addition, solid and liquid Ga containing well-dispersed Ni, Pd, and Ru atoms were modeled for DRM. It was found that Ru trimer embedded in Ga solid solutions yields one of the best  $\text{H}_2$  production rates. Then, the topological cluster classification (TCC) analyses on *ab initio* molecular dynamics (AIMD) simulations suggested that the transition metal solutes (e.g., Ni, Pd) dissolved in liquid Ga prefer the liquid-gas interface at low or moderate temperatures.

This thesis also considered indium oxide ( $\text{In}_2\text{O}_3$ ) catalysts supported on Zr, Ce, and Pr oxides for methanol production via  $\text{CO}_2$  hydrogenation. Experimentally, the highest  $\text{CO}_2$  conversion and  $\text{CH}_3\text{OH}$  selectivity were observed on  $\text{ZrO}_2$ -supported  $\text{In}_2\text{O}_3$  (Zr- $\text{In}_2\text{O}_3$ ). DFT calculations revealed that a unique bent configuration of  $\text{CO}_2$  adsorption at the oxygen vacancy site ( $\text{O}_\text{v}$ ) in Zr- $\text{In}_2\text{O}_3$  stabilizes the formate ( $\text{HCOO}$ ) intermediate. Subsequent hydrogenations of  $\text{HCOO}$  to  $\text{CH}_2\text{O}$ , and then  $\text{CH}_3\text{O}$  are also thermodynamically more favorable over Zr- $\text{In}_2\text{O}_3$  than

on other oxide catalysts. DFT modeling also showed that the product selectivity depends on the relative activation energies between hydrogenation (for  $\text{CH}_3\text{OH}$  formation) and the C–O bond cleavage (for CO formation) of  $\text{HCOO}$ .

This thesis demonstrated the predictive power of DFT in elucidating the complex surface chemistries on bifunctional catalytic materials. Based on the case studies, DFT, coupled with the microkinetic modeling and molecular dynamics simulation techniques, produced highly valuable knowledge that can be elusive for other research tools. More importantly, the theoretical knowledge will allow researchers to continue the pursuit of more efficient and stable catalysts for  $\text{CO}_2$  utilizations so that we will be better equipped to solve some of the most urgent societal issues.



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## Abstract

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In addition, solid and liquid Ga containing well dispersed Ni, Pd, and Ru atoms were modeled for the development DRM technology. It is also found that trimer clustering of Ru is the key that guarantees sufficient reactivities of alloyed Ga. Also, TCC analysis obtained from AIMD simulation results suggested that the active Ni and Pd configurations will more likely appear at the liquid-gas interface at low or moderate temperatures.

This thesis also considered indium oxide ( $\text{In}_2\text{O}_3$ ) catalysts supported on Zr, Ce, and Pr oxides for methanol production via  $\text{CO}_2$  hydrogenation. Experimentally, the highest  $\text{CO}_2$  conversion and  $\text{CH}_3\text{OH}$  selectivity were observed on  $\text{ZrO}_2$ -supported  $\text{In}_2\text{O}_3$  (Zr- $\text{In}_2\text{O}_3$ ). DFT calculations revealed that the unique bent configuration of  $\text{CO}_2$  adsorption at the oxygen vacancy site ( $\text{O}_v$ ) in Zr- $\text{In}_2\text{O}_3$  stabilizes of the formate ( $\text{HCOO}$ ) intermediate. The subsequent hydrogenations of  $\text{HCOO}$  to  $\text{CH}_2\text{O}$ , and then  $\text{CH}_3\text{O}$  are also thermodynamically favorable than on

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# Table of Contents

|                                                                          |       |
|--------------------------------------------------------------------------|-------|
| List of Figures .....                                                    | xv    |
| List of Tables .....                                                     | xxii  |
| Acknowledgements .....                                                   | xxiii |
| Dedication .....                                                         | xxiv  |
| 1 Introduction.....                                                      | 1     |
| 1.1 Grand Challenge for Catalyst Design and the Sabatier Principle ..... | 1     |
| 1.2 Bifunctional Catalysts .....                                         | 3     |
| 1.3 Rational Catalyst Design Using Molecular Mechanisms .....            | 6     |
| 1.4 Case Studies .....                                                   | 9     |
| 1.4.1 Dry Reforming of Methane.....                                      | 9     |
| 1.4.2 Methanol Formation via CO <sub>2</sub> Hydrogenation.....          | 12    |
| 1.5 Thesis Outline .....                                                 | 14    |
| 2 Computational Methods and Theory .....                                 | 15    |
| 2.1 Density Functional Theory (DFT) .....                                | 15    |
| 2.1.1 Kohn-Sham Formulation .....                                        | 15    |
| 2.1.2 Electron Exchange-Correlation Functional.....                      | 16    |
| 2.1.3 Self-Interaction Errors (SIE).....                                 | 17    |
| 2.1.4 Plane Wave Basis Set and Pseudopotential .....                     | 18    |
| 2.1.5 Bader Charge Analysis .....                                        | 19    |
| 2.2 Reaction Thermodynamics .....                                        | 20    |
| 2.3 Climbing Image-Nudged Elastic Band (CI-NEB) .....                    | 20    |
| 2.4 Dimer Method.....                                                    | 21    |

|         |                                                                                                                    |    |
|---------|--------------------------------------------------------------------------------------------------------------------|----|
| 2.5     | <i>d</i> -Band Theory .....                                                                                        | 22 |
| 2.5.1   | Rate Theory for Elementary Steps.....                                                                              | 24 |
| 2.5.2   | Linear Scaling Relationship.....                                                                                   | 25 |
| 2.5.3   | Brønsted–Evans–Polanyi (BEP) Relationship.....                                                                     | 27 |
| 2.6     | Microkinetic Modeling .....                                                                                        | 29 |
| 2.7     | <i>Ab initio</i> Molecular Dynamics (AIMD).....                                                                    | 30 |
| 2.8     | Topological Cluster Classification (TCC) .....                                                                     | 31 |
| 3       | Molecular Mechanisms of Methane Dry Reforming on Dual-Site Co <sub>3</sub> Mo <sub>3</sub> N Catalysts .....       | 34 |
| 3.1     | Introduction.....                                                                                                  | 34 |
| 3.2     | Methods.....                                                                                                       | 38 |
| 3.2.1   | Catalyst Models .....                                                                                              | 38 |
| 3.2.2   | Density Functional Theory .....                                                                                    | 40 |
| 3.3     | Results and Discussion .....                                                                                       | 42 |
| 3.3.1   | DRM Intermediates on Co <sub>3</sub> Mo <sub>3</sub> N(111) and Site Preference .....                              | 42 |
| 3.3.2   | Elementary DRM Steps on Co <sub>3</sub> Mo <sub>3</sub> N(111).....                                                | 47 |
| 3.3.2.1 | CH <sub>4</sub> Activation.....                                                                                    | 48 |
| 3.3.2.2 | CO <sub>2</sub> Activation.....                                                                                    | 51 |
| 3.3.2.3 | Coke Formation .....                                                                                               | 53 |
| 3.3.2.4 | DRM Pathways on Co <sub>3</sub> Mo <sub>3</sub> N(111).....                                                        | 55 |
| 3.3.3   | Microkinetic Modeling of DRM on Co <sub>3</sub> Mo <sub>3</sub> N .....                                            | 58 |
| 3.4     | Conclusions.....                                                                                                   | 64 |
| 4       | Mitigating Coke Formations for Dry Reforming of Methane on Dual-Site Catalysts: A Microkinetic Modeling Study..... | 67 |

|       |                                                                   |     |
|-------|-------------------------------------------------------------------|-----|
| 4.1   | Introduction.....                                                 | 67  |
| 4.2   | Methods.....                                                      | 70  |
| 4.2.1 | Catalyst Models .....                                             | 70  |
| 4.2.2 | Density Functional Theory .....                                   | 72  |
| 4.2.3 | Linear Scaling Relationships .....                                | 73  |
| 4.2.4 | Microkinetic Modeling .....                                       | 74  |
| 4.3   | Results and Discussion .....                                      | 75  |
| 4.3.1 | Binding Site Preference of DRM Intermediates .....                | 75  |
| 4.3.2 | Coke Formation .....                                              | 82  |
| 4.3.3 | Catalytic Trends in DRM Reactivity .....                          | 82  |
| 4.3.4 | Bifunctionality and Coke Mitigation .....                         | 86  |
| 4.3.5 | Mechanisms Responsible for Coke Mitigation.....                   | 88  |
| 4.3.6 | Rational Design of Bifunctional Catalysts for DRM.....            | 90  |
| 4.4   | Conclusions.....                                                  | 91  |
| 5     | Liquid Metal Gallium Catalysts for Dry Reforming of Methane ..... | 93  |
| 5.1   | Introduction.....                                                 | 93  |
| 5.2   | Computational Details .....                                       | 95  |
| 5.2.1 | Solid-State Catalyst Models.....                                  | 95  |
| 5.2.2 | Liquid State Catalysts Models .....                               | 96  |
| 5.2.3 | Microkinetic Modeling .....                                       | 97  |
| 5.3   | Results and Discussion .....                                      | 98  |
| 5.3.1 | Bimetallic Ga Catalysts.....                                      | 98  |
| 5.3.2 | Microkinetic Modeling of DRM.....                                 | 100 |



|       |                                                                                                                                                           |     |
|-------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.3.3 | AIMD Simulations of Amorphous Ga.....                                                                                                                     | 102 |
| 5.4   | Conclusions.....                                                                                                                                          | 108 |
| 6     | Mechanistic Understanding of Support Effect on the Activity and Selectivity of Indium Oxide Catalysts for CO <sub>2</sub> Hydrogenation .....             | 110 |
| 6.1   | Introduction.....                                                                                                                                         | 110 |
| 6.2   | Methods Section.....                                                                                                                                      | 112 |
| 6.2.1 | Computational Methods.....                                                                                                                                | 112 |
| 6.2.2 | Catalyst Models .....                                                                                                                                     | 115 |
| 6.3   | Results and Discussion .....                                                                                                                              | 117 |
| 6.4   | Conclusions.....                                                                                                                                          | 126 |
| 7     | Conclusions and Outlook.....                                                                                                                              | 128 |
| 8     | References.....                                                                                                                                           | 132 |
|       | Appendix A - Molecular mechanism of methane dry reforming on Co <sub>3</sub> Mo <sub>3</sub> N catalyst with dual sites .....                             | 169 |
|       | Appendix B - Mitigating Coke Formations for Dry Reforming of Methane on Dual-Site Catalysts: A Microkinetic Modeling Study .....                          | 191 |
|       | Appendix C - Mechanistic Understanding of Support Effect on the Activity and Selectivity of Indium Oxide Catalysts for CO <sub>2</sub> Hydrogenation..... | 197 |
|       | Appendix D - Input Files for CatMAP .....                                                                                                                 | 199 |
|       | D.1. Input Energy File .....                                                                                                                              | 199 |
|       | D.2. Set Up Reaction Parameters.....                                                                                                                      | 219 |
|       | D.2.1. Single-site System.....                                                                                                                            | 219 |
|       | D.2.2. Dual-site System .....                                                                                                                             | 224 |

|                                       |     |
|---------------------------------------|-----|
| Appendix E - Reprint Permissions..... | 231 |
|---------------------------------------|-----|

## List of Figures

|                                                                                                                                                                                                                                                                                                                                                                                                                                            |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1.1. Possible chemical and fuel production catalytic routes based on CO <sub>2</sub> utilization. Major sources for Greenhouse gases (GHG) emissions in the United States are transportation (27%), power generation (25%), industrial activities (25%), residential consumption (13%), and agriculture (11%). The large portion of GHG emissions contribute to the CO <sub>2</sub> (79%), followed by CH <sub>4</sub> (11%). ..... | 2  |
| Figure 1.2. Possible synergistic effects in (a) a metal catalyst particle (pink) on the catalytic active substrate (blue), and (b) bifunctional alloy catalysts (represented in pink and blue). Comparison of dry reforming of methane on (c) Ni particle supported on inert SiO <sub>2</sub> and (d) Ni particle supported on Ce <sub>0.7</sub> Zr <sub>0.3</sub> O <sub>2</sub> , adapted from Ref. [39]. .....                          | 4  |
| Figure 1.3. The <i>volcano</i> plot for the rate (TOF, s <sup>-1</sup> ) of ammonia synthesis based on the binding energy of atomic N ( $E_N$ ). Adapted from Ref. [52]. .....                                                                                                                                                                                                                                                             | 7  |
| Figure 1.4. The cone diagram illustrating the structural evolution arranged diagonally. Adapted from Ref. [53]. .....                                                                                                                                                                                                                                                                                                                      | 8  |
| Figure 1.5. DRM reaction network including CH <sub>4</sub> decomposition (blue box), CO <sub>2</sub> activation (green box), CH <sub>x</sub> oxidation (red box), and coke formation (brown box).....                                                                                                                                                                                                                                      | 11 |
| Figure 1.6. CH <sub>3</sub> OH formation pathways via CO <sub>2</sub> hydrogenation.....                                                                                                                                                                                                                                                                                                                                                   | 13 |
| Figure 2.1. (a) Schematic illustration of the bonding and anti-bonding states on transition metal surfaces for a typical adsorption event, adapted from Ref. [152]. (b) Adsorption energy of O as a function of the transition metal <i>d</i> -band centers, adapted from Ref. [153]. .....                                                                                                                                                | 22 |
| Figure 2.2. (a) Binding energies of CH <sub>x</sub> intermediates, plotted against adsorption energies of C [160], (b) ammonia production rates as a function of N adsorption energy and N <sub>2</sub> transition                                                                                                                                                                                                                         |    |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| state energies (both in eV). Solid and dashed lines indicate the linear relationships between $E_{N-N}$ and $E_N$ on flat and stepped surfaces, respectively [28].                                                                                                                                                                                                                                                                                                                                              | 26 |
| Figure 2.3. (a) Ammonia synthesis rate as a function of nitrogen adsorption energy and $N_2$ dissociation barrier. $E_{N-N}$ is a linear function of $E_N$ [5], (b) calculated limiting potential for the $O_2$ reduction [169].                                                                                                                                                                                                                                                                                | 28 |
| Figure 2.4. (a) Three basic structures, triangle, square, and pentagon identified from the shortest-path rings (gray), bonds between ring particles are shown in white, spindle particles are shown in yellow (they build a pyramid shape structure), and the extra particle (red). This figure is adapted from Ref. [183]. (b) Motifs used in the TCC algorithms: to three-fold symmetric (5A), four-fold symmetric (6A and sp4b) local order, and five-fold symmetric (7A and sp5b). Adapted from Ref. [184]. | 33 |
| Figure 3.1. (a) Dissection of the molybdenum nitride ( $Mo_3N$ ) and cobalt in bulk ternary $Co_3Mo_3N$ single crystal. (b-d) Top views the cleavage close-packed (111) orientation of $Co_3Mo_3N$ , $Co(0001)$ , and (d) $Mo_2N(110)$ surfaces, respectively. Accessible adsorption sites are also labelled. The Co, Mo, and N atoms are depicted in dark blue, pink, and light blue, respectively. The supercell boundaries are depicted with solid lines.                                                    | 38 |
| Figure 3.2. Optimized structures of the DRM intermediates on $Co_3Mo_3N(111)$ . Atomic distances (in Å) are shown in dashed lines. The C, O, H, Co, Mo, and N atoms are depicted in brown, red, white, dark blue, pink, and light blue, respectively.                                                                                                                                                                                                                                                           | 43 |
| Figure 3.3. Optimized transition state structures (corresponding to the elementary steps in Table 3) on $Co_3Mo_3N(111)$ . Side views are shown as the inset figure. The C, O, H, Co, Mo, and N atoms are depicted in brown, red, white, dark blue, dark pink, and light blue, respectively. Atomic distances (in Å) are shown in dashed lines.                                                                                                                                                                 | 50 |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 3.4. Potential energy profiles for (a) direct (black) and O-assisted (red) C–H bond activation; (b) direct (black), H-assisted (blue), and C-assisted (red) CO <sub>2</sub> activation pathways on Co <sub>3</sub> Mo <sub>3</sub> N(111). The energy barriers are labeled in parentheses.....                                                                                                                                                                                                                                                                                                                                                                                                         | 51 |
| Figure 3.5. Coke formation pathway versus carbon removal pathways on Co <sub>3</sub> Mo <sub>3</sub> N(111).....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 55 |
| Figure 3.6. The free energy profiles depicting DRM on Co <sub>3</sub> Mo <sub>3</sub> N(111) - generated at 973.15 K and 1 bar. Gas phase CO <sub>2</sub> and CH <sub>4</sub> and clean surfaces are used as zero energy references. The main DRM routes are highlighted by thick lines including CO <sub>2</sub> (and subsequent OH formation) and CH <sub>4</sub> dissociation; C, CH oxidation via respective COH and CHO intermediates; and CO, H <sub>2</sub> formation that are illustrated in gold, purple, pink, blue, and black, respectively. The less competitive pathways (e.g., CHOH formation and subsequent C–H and O–H bond dissociation) are represented in thin dashed or dotted lines..... | 56 |
| Figure 3.7. Predicted Log <sub>10</sub> (TOF) (s <sup>-1</sup> ) for CH <sub>4</sub> activation according to Eqn. A34, as a function of <i>BEC</i> and <i>BEO</i> . The volcano heat map was generated using the linear correlations presented in Eqns. (A54-A58) as described in the Supporting Information. Reaction conditions used in the microkinetic model: T = 973.15 K, P = 1 bar, 55% CH <sub>4</sub> conversion, CH <sub>4</sub> /CO <sub>2</sub> ratio = 1:1 at a molar flow rate of 1 mol/s. The transition metals are represented by white squares, while nitrides and phosphide are represented by yellow circles. The data point for Ni <sub>2</sub> P was estimated based on Ref. [235].....  | 60 |
| Figure 3.8. Predicted surface coverage for (a) $\theta_C$ , (b) $\theta_O$ , (c) $\theta_*$ , (d) $\theta_{CH}$ , and (e) $\theta_H$ based on the same condition as in microkinetic modeling: T = 973.15 K, P = 1 bar, 55% CH <sub>4</sub> conversion, CH <sub>4</sub> /CO <sub>2</sub> ratio = 1:1 at a molar flow rate of 1 mol/s. The transition metals are represented by white squares, while nitrides and phosphide are represented by yellow circles.<br>.....                                                                                                                                                                                                                                         | 62 |

Figure 4.1. (a) Top and side views of  $\text{Co}_3\text{Mo}_3\text{N}$  (111); (b-c) terrace (111) and step (211) surfaces.

The Co, Mo, and N atoms in  $\text{Co}_3\text{Mo}_3\text{N}$  (111) are shown in blue, pink, and grey. The Co (site  $s_1$ ) and  $\text{Mo}_2\text{N}$  (site  $s_2$ ) domain boundaries are highlighted in blue and red dashed lines. High symmetry sites in (111) represent site  $s_1$ , while sites in (211) for site  $s_2$  in dual-site models. The dark grey color highlights the edge sites. .... 72

Figure 4.2. Top and side views of the optimized geometries of DRM intermediates on respective  $s_1$  (labeled with ‘\*’) and  $s_2$  (labeled with ‘■’) sites of  $\text{Co}_3\text{Mo}_3\text{N}$ (111). The C, O, H, Co, Mo, and N atoms are illustrated in brown, red, white, dark blue, pink, and light blue. .... 77

Figure 4.3. Potential energy profiles and the optimized TS structures at the interfacial sites (solid lines) versus at the Co domain (dashed lines) of  $\text{Co}_3\text{Mo}_3\text{N}$ (111). The C, O, H, Co, Mo, and N atoms are depicted in brown, red, white, dark blue, dark pink, and light blue. Atomic distances are shown in dashed arrows. .... 77

Figure 4.4. Linear scaling relationships for (a) OH adsorptions, (b) CHO adsorptions (blue: site  $s_1$  and orange:  $s_2$ ) based on binding energies of O and C on the  $s_1$  site. BEP relationships for (c) CH–O bond formation, and (d) O–H bond formation (blue: site  $s_1$  and orange: site  $s_2$ ). Data produced in this work are represented with solid symbols. Hollow symbols in (a, b, d) were reproduced using the data reported by Jalid and coworkers [250]. The BEP relationship in (c) on the  $s_2$  site was reproduced according to Ref. [261]. .... 80

Figure 4.5. Turnover frequencies ( $\text{Log}_{10}[\text{TOF}, \text{s}^{-1}]$ ) for (a)  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , (b) CO, and (c)  $\text{C}_6(\text{g})$  productions on dual-site models at 973 K and 1 bar. The active site ratio is set as  $s_1:s_2 = 7:3$ . The dashed line represents the boundaries between  $\text{H}_2$  and  $\text{H}_2\text{O}$  as the major reaction products. The labels are projected onto each heatmap based on the lower values of the

|                                                                                                                                                                                                                                                                                                                                                                                                                                |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| descriptors between the two sites. The error bars were generated from the Bayesian error estimation based on the BEEF-vdW functional.....                                                                                                                                                                                                                                                                                      | 84  |
| Figure 4.6. Performance gains ( $\text{Log}_{10}[r_{\text{dual}}/r_{\text{single}}]$ ,) for (a) $\text{H}_2$ , (b) $\text{CO}$ , and (c) $\text{C}_6$ productions achieved on dual-site models relative to the single-site models at 973 K and 1 bar. The dashed line in (c) indicates the sign change for the relative rates for $\text{C}_6$ production. The negative sign means $r_{\text{dual}} < r_{\text{single}}$ ..... | 86  |
| Figure 4.7. Surface coverage of (a) O, (b) C, (c) CH, (d) $\text{C}_2$ on site $s_1$ ; (e) O, (f) C on site $s_2$ ; and (g) H at 973 K and 1 bar. ....                                                                                                                                                                                                                                                                         | 88  |
| Figure 4.8. Comparisons of $\text{C}_6$ production rates by disabling (a) cross-site diffusion and (b) cross-site reaction steps in the dual-site mechanism at 973 K and 1 bar. The dashed lines indicate the sign change for the relative rates for $\text{C}_6$ production. The negative sign means $r_{\text{full}}$ decreases when compared to the rates from the modified mechanisms. ....                                | 90  |
| Figure 5.1. Top view of a Ru trimer embedded in Ga(100) surface. The Ga and Ru atoms are shown in green and pink. The Ru trimer (denoted as site $s_1$ ) is highlighted with blue dashed lines. The arrows indicate the top, bridge, and hcp sites associated with the Ru trimer. ....                                                                                                                                         | 96  |
| Figure 5.2. (a-c) Optimized structures of C on Ru trimer, dimer, and monomer; (d-f) optimized structures of O on Ru trimer, dimer, and monomer in RuGa. (g-h) Optimized structures of O and C on pure Ga(100) surfaces. The C, O, Ga, and Ru atoms are depicted in brown, red, green, and pink, respectively.....                                                                                                              | 99  |
| Figure 5.3. Turnover frequencies ( $\text{Log}_{10}[\text{TOF}, \text{s}^{-1}]$ ) for $\text{CO}$ , $\text{H}_2$ , and $\text{C}_6$ production at 973 K and 1 atm. The active site ratio used in the dual-site model is $s_1:s_2 = 1:9$ to represent Ga-rich systems. ....                                                                                                                                                     | 101 |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 5.4. The z-position of two (a) Pd and (b) Ni atoms in liquid PdGa and NiGa slab models as function of time, depicted in orange and blue lines. Inset figures show the liquid PdGa and NiGa surfaces with Numbered Pd and Ni atoms which are showing the final locations of chosen dopant atoms in this analysis. Ga, Pd, and Ni are shown in green, purple, and pink colors. Dash lines resemble the first maximum density of the Ga for the PdGa and NiGa surfaces. ....                                                                                                              | 104 |
| Figure 5.5. Radial distribution functions, $g(r)$ , for (a) Ga-Ga pair in pure Ga (blue), PdGa (orange), and NiGa (green); (b) Pd-Ga pair (orange) in PdGa system, and Ni-Ga pair (green) in NiGa; (c) Pd-Pd pair (green) in PdGa system, and Ni-Ni pair (red) in NiGa obtained from AIMD during the last 2 ps of AIMD simulations.....                                                                                                                                                                                                                                                       | 105 |
| Figure 5.6. Fractional populations for each cluster motif over the last 2 ps of AIMD simulations at 800 K. Orange: Ga; Blue: PdGa; and Grey NiGa. Inserted pictures of clusters are taken from Ref. [183]. ....                                                                                                                                                                                                                                                                                                                                                                               | 106 |
| Figure 5.7. Fractional populations for each cluster motif in PdGa during the last 2 ps of AIMD simulations at 303, 600, and 800 K.....                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 108 |
| Figure 6.1. Linear correlations between energy barrier ( $E_a$ ) and reaction energy ( $\Delta E$ ) for CO <sub>2</sub> hydrogenation (orange) and CH <sub>2</sub> O formation (blue). ....                                                                                                                                                                                                                                                                                                                                                                                                   | 114 |
| Figure 6.2. Optimized slab models: (a) In <sub>2</sub> O <sub>3</sub> (110), (b) Zr-In <sub>2</sub> O <sub>3</sub> (110), (c) Ce-In <sub>2</sub> O <sub>3</sub> (011), (d) Pr-In <sub>2</sub> O <sub>3</sub> (011), (e) ZrO <sub>2</sub> (011), (f) In-ZrO <sub>2</sub> (011), (g) CeO <sub>2</sub> (111), (h) In-CeO <sub>2</sub> (111), (e) PrO <sub>2</sub> (111), (f) In-PrO <sub>2</sub> (111), (g) Pr <sub>2</sub> O <sub>3</sub> (111), and (h) In-Pr <sub>2</sub> O <sub>3</sub> (111). The In, Zr, Ce, Pr, and O atoms are in pink, green, yellow, gold, and red, respectively. .... | 116 |
| Figure 6.3. (a) Optimized structures of CO <sub>2</sub> and its hydrogenation intermediates via the formate pathway on pristine and doped In <sub>2</sub> O <sub>3</sub> (1 1 0) surfaces with O <sub>v</sub> , and (b) the potential energy                                                                                                                                                                                                                                                                                                                                                  |     |



|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| profiles depicting methanol formation from CO <sub>2</sub> hydrogenation on pristine and doped In <sub>2</sub> O <sub>3</sub> .<br>.....                                                                                                                                                                                                                                                                                                                                                             | 119 |
| Figure 6.4. (a) Optimized structures of CO <sub>2</sub> and its hydrogenation intermediates via the formate<br>pathway on In-doped ZrO <sub>2</sub> (011) surface. (b) Potential energy profiles for CO <sub>2</sub> -to-CH <sub>3</sub> OH<br>conversion on Zr-doped In <sub>2</sub> O <sub>3</sub> (110) (denoted as Zr-In <sub>2</sub> O <sub>3</sub> (O <sub>v</sub> )) (red) versus In-doped ZrO <sub>2</sub><br>(011) (denoted as In-ZrO <sub>2</sub> (O <sub>v</sub> )) (blue) surfaces. .... | 120 |
| Figure 6.5. Indium-mass-normalized formation rates of (a) methanol, (b) CO and (c) methanol<br>selectivity of various supported In <sub>2</sub> O <sub>3</sub> catalysts as a function of reaction temperature.<br>Reaction conditions: 0.2 g catalyst, 1:3 CO <sub>2</sub> /H <sub>2</sub> , 20 ml/min, 0.1 MPa. ....                                                                                                                                                                               | 122 |
| Figure 6.6. Potential energy profiles for parallel CO and CH <sub>3</sub> OH formation pathways on In <sub>2</sub> O <sub>3</sub> and<br>doped In <sub>2</sub> O <sub>3</sub> surfaces with O <sub>v</sub> . ....                                                                                                                                                                                                                                                                                    | 124 |
| Figure 6.7. CO <sub>2</sub> adsorptions on various oxide surfaces. The In, Zr, Ce, Pr, C, and O atoms are in<br>pink, green, yellow, gold, brown, and red, respectively. ....                                                                                                                                                                                                                                                                                                                        | 125 |

## List of Tables

|                                                                                                                                                                                                                                                                                                                 |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 3.1. The calculated $d$ -band center (in eV) and Bader charge (in e) for Co(0001), Co <sub>3</sub> Mo <sub>3</sub> N(111), and Mo <sub>2</sub> N(110). Surface site notations are consistent with Figure 3.1d. ...                                                                                        | 39  |
| Table 3.2. Binding energies ( $BE$ in eV) and the preferred binding sites on Co <sub>3</sub> Mo <sub>3</sub> N(111), Co(0001), and Mo <sub>2</sub> N(110). ....                                                                                                                                                 | 43  |
| Table 3.3. Reaction energies ( $\Delta E$ in eV) and energy barriers ( $E_a$ in eV) on Co <sub>3</sub> Mo <sub>3</sub> N(111), Co(0001), and Mo <sub>2</sub> N(110). ....                                                                                                                                       | 47  |
| Table 4.1. Binding energies (eV) of reaction intermediates based on Eqn. (4.1) on the $s_1$ and $s_2$ sites of Co <sub>3</sub> Mo <sub>3</sub> N(111). The numbers in boldface highlight the site preference. ....                                                                                              | 76  |
| Table 4.2. Reaction energies ( $\Delta E$ ) and energy barrier energies for DRM reactions on $s_1$ (single-site catalysts), $s_2$ , and dual-site catalyst (most favorable binding site and the lowest barrier between the $s_1$ and $s_2$ sites were chosen) for Co <sub>3</sub> Mo <sub>3</sub> N (111). .... | 78  |
| Table 5.1. The $BEC$ and $BEO$ (in eV) on Pd(111), Ni(111), Ru(0001), Ga(100), and Pd-, Ni-, Ru-doped Ga(100) surfaces. ....                                                                                                                                                                                    | 100 |
| Table 5.2: the percentage of active sites appearing in each cluster associated in Figure 5.6. ....                                                                                                                                                                                                              | 107 |

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## **Dedication**

**“To My Dearests, Mohammadali and Sam.”**

**“To My Mother, in Loving Memory.”**

# 1 Introduction

Catalysts are vital to fuels and chemical production to meet societal needs [1-3]. Catalyst innovations focus on (i) maximizing the reactivities and targeted product selectivity; and (ii) minimizing the costs of catalyst manufacturing. However, the Sabatier principle often limits catalyst optimizations [4-7]. Recently, considerable emphasis has been placed on bifunctional catalysts, particularly systems with compatible functionalities [8-11]. This thesis employed state-of-the-art molecular modeling tools to understand the mechanisms relevant to the beneficial promotional effects of bifunctional catalysts for methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) conversions. In this chapter, I will focus on the working principles of bifunctional catalysts that demonstrate beneficial catalytic promotions. These fundamental chemical and physical insights serve as essential guidance for model construction and result interpretations.

## 1.1 Grand Challenge for Catalyst Design and the Sabatier Principle

Currently, atmospheric  $\text{CO}_2$  is a major source of concern about global climate change [12]. The rise of atmospheric  $\text{CO}_2$  level is a leading cause of global warming, ocean acidification [13], and more frequent destructive weather patterns [14]. UNEP (the United Nations Environment Programme) predicted that the global temperature will likely increase by more than  $3^\circ\text{C}$  by 2100 if current emission policies are maintained [15, 16]. To mitigate this issue, global greenhouse gas emissions must be cut by at least 50% of the 1990 level by 2050 [17]. Therefore, the utilization of  $\text{CO}_2$ , captured from emission sources or directly from the air [18, 19], for the production of value-added fuels or chemicals will play an essential role [20, 21] (Figure 1.1).

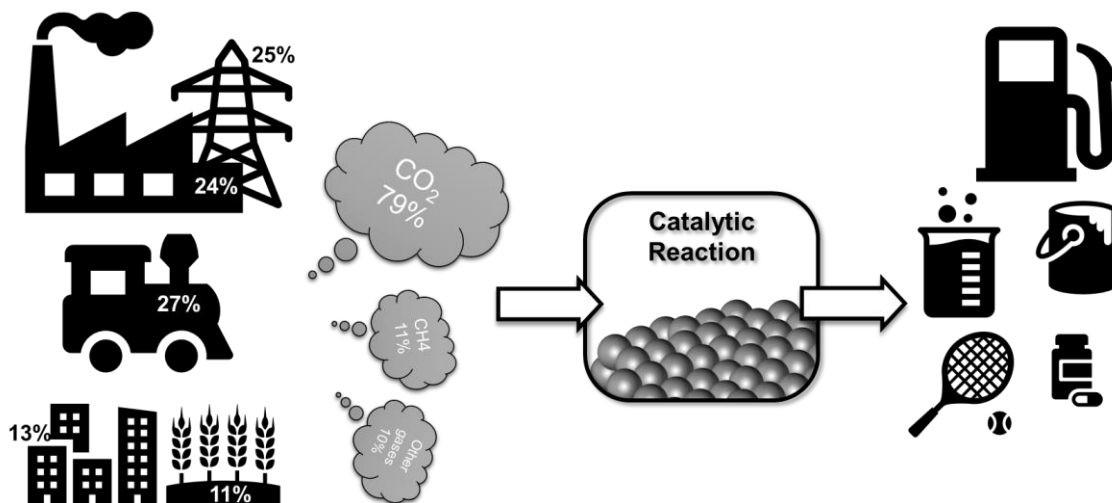


Figure 1.1. Possible chemical and fuel production catalytic routes based on CO<sub>2</sub> utilization. Major sources for Greenhouse gases (GHG) emissions in the United States are transportation (27%), power generation (25%), industrial activities (25%), residential consumption (13%), and agriculture (11%). The large portion of GHG emissions contribute to the CO<sub>2</sub> (79%), followed by CH<sub>4</sub> (11%).

CO<sub>2</sub> has long been considered a building-block chemical [22] and can be converted into carbonates [23], polymers [24], urea [25], methanol [26], and syngas [27]. However, the challenge for CO<sub>2</sub> utilization is that it is thermodynamically stable. The chemical stability results in low conversion efficiency, making relevant processes economically not profitable.

The central theme in technological innovation is to design and optimize catalysts suitable for industrial-scale applications. For rational catalyst design, the Sabatier principle states that optimal catalysts should bind reactants moderately. The criterion is that neither initial reactant activation nor final product formation should be hindered [4]. This tradeoff imposes a fundamental limitation on the reactivities that currently available catalysts can achieve. An intrinsic limitation

on the maximum reactivity exists for many important catalytic reaction such as ammonia synthesis [28], and oxygen reduction reaction (ORR) reactions [29].

Moreover, economic costs for manufacturing and applying catalysts at the industrial scale should also be another critical factor in catalyst design. For instance, the most effective electrocatalysts for hydrogen evolution reaction (HER) and oxygen reaction (OER) are the platinum group metals (PGM) [30]. The scarcity of these noble metals prohibits the wide use of Pt-based fuel cells or other energy conversion devices despite their promising potential.

A change in the catalyst design paradigm is needed to address the above issues. In recent years, well-tailored bifunctional catalysts have enabled breakthroughs for ammonia synthesis [8, 31, 32], CO oxidation [9], water-gas-shift reaction [10], and hydrogen production [11]. More importantly, earth-abundant materials have been incorporated into these novel catalyst systems, meaningfully lowering the capital cost.

## 1.2 Bifunctional Catalysts

Recently, several promising bifunctional catalysts with two different active sites that promote surface reactions *synergistically* have been reported [33-35]. Fundamentally, catalytic synergy among active sites enables charge transfer and modifies surface electronic and geometrical structures of the surface to facilitate species spillover and alter reaction pathways. In principle, a plethora of benefits, such as unprecedented conversions and drastically improving catalytic efficiency, can be achieved [36]. For example, Au nanoparticles on MgO support would eliminate the energy barrier of the rate-limiting step (i.e., COOH formation) completely when compared to individual Au ( $E_a = 2.13$  eV) and MgO ( $E_a = 1.59$  eV) catalysts [37].

Bifunctional catalysts are frequently encountered in supported metal catalysts and alloys. Figure 1.2a illustrates a typical catalyst particle (pink) supported on a catalytically active substrate (blue). These active substrates are usually acidic or basic materials and will also participate in the reactions. The metal particles and substrate both provide the active sites that target different reaction intermediates in the reaction network due to their distinct chemical nature. As chemical reactions proceed, cross-site reactions become permissible.

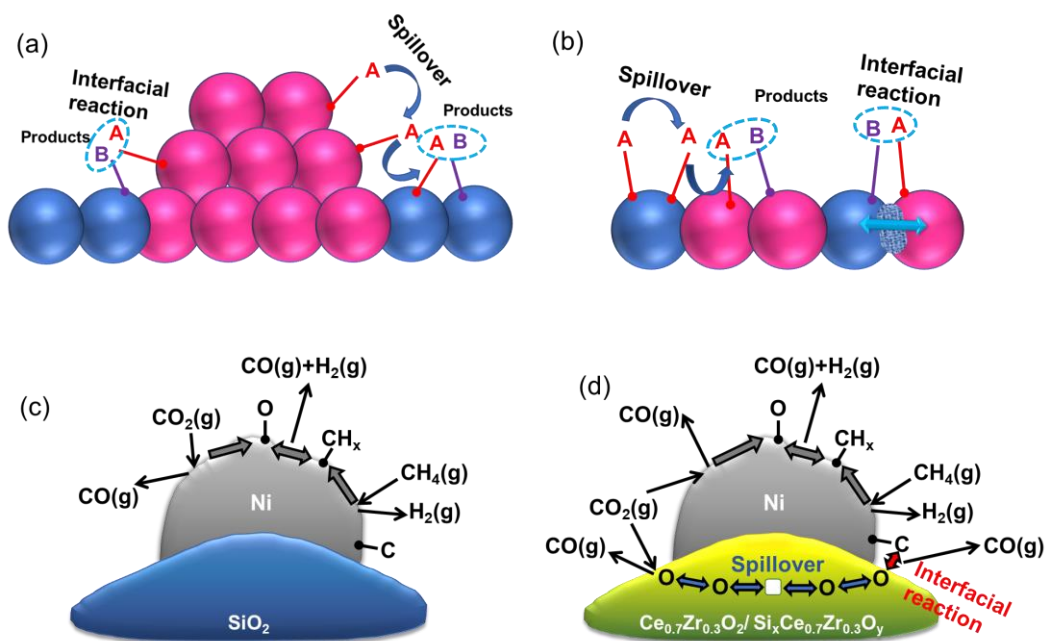


Figure 1.2. Possible synergistic effects in (a) a metal catalyst particle (pink) on the catalytic active substrate (blue), and (b) bifunctional alloy catalysts (represented in pink and blue). Comparison of dry reforming of methane on (c) Ni particle supported on inert  $\text{SiO}_2$  and (d) Ni particle supported on  $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ , adapted from Ref. [38].



Moreover, the migrations of reaction intermediates across the metal-support interface will also contribute to broadening the reaction network's capacity [39]. For instance, Lovell *et al.* [38] tested two Ni-supported catalysts for the dry reforming of methane (DRM), using SiO<sub>2</sub> as an inert substrate (Figure 1.2c) and Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> as the reducible support enabling oxygen spillover and interfacial reactions (Figure 1.2d). It has been shown that DRM on Ni/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> yields H<sub>2</sub>/CO at a stoichiometric ratio (i.e., ~1) and 42% less carbon formation, with a ~60% CH<sub>4</sub> conversion (after 24 hrs operation).

In general, alloy surfaces are subjected to three effects, i.e., ligand (electronic), ensemble (geometric), and strain effects [40]. The ensemble effect describes the changes in local chemisorption associated with the direct change in the neighboring atomic components at the adsorption site, leading to a change in adsorption configurations accordingly. The ligand effect describes tuning the surface electronic structure for the same surface ensemble but in a different atomic environment. The strain effect describes the changes in bond lengths of materials due to variations in lattice constants [40, 41]. DFT has proven as an effective technique for understanding these three alloying effects via surface-based descriptors, especially the d-band center [41, 42].

Tunable alloys with compatible elemental constituent or component and complementary configurations are vital to regulating lattice strain and ligand effect to achieve synergies. Furthermore, the ability to control catalyst synergy is especially advantageous for electrochemical reactions [43]. Synergy in bifunctional alloy catalysts includes two effects: species spillover and cross-site reactions, as depicted in Figure 1.2b. Xu and co-workers [44] found that biphasic Pd-Au nanoparticles are highly active for low-temperature CO oxidation. The authors found that the dissociative adsorption of O<sub>2</sub> and CO adsorption occur at the Pd-rich sites. In contrast, the Au-rich sites were active for CO oxidation. On Pd-Au, O\* (or CO\*) migrates from Pd to the neighboring

atoms or Au clusters through spillover and reacts with CO\* (or O\*) across both Au and Pd sites. Also, it has been found that high elemental dispersion increases the neighboring Pd–Au sites that promote the bifunctional mechanisms. Similar effects have been proposed by Neurock and Mei [45] for olefin hydrogenation, where Pd and Au sites are active for dissociative hydrogen adsorption and hydrogenation, respectively.

### 1.3 Rational Catalyst Design Using Molecular Mechanisms

Heterogeneous catalyst development originates from trial-and-error experiments, which is a tedious and very time-consuming method. Researchers often need to screen through millions of various potential material combinations before they find one that works. Experimental techniques such as temperature-programmed desorption (TPD) can be used to study the electronic structure of materials in some degree. Some advanced atomic-level imaging techniques (e.g., scanning tunneling microscope) can elucidate surface properties on single crystals in an ultrahigh vacuum. However, the required information needed to design a catalyst remains limited. The optimization of bifunctional catalysts is also challenged by the lack of *in situ* methods to identify active catalytic sites under reaction conditions, leading to uncertainties in mechanistic descriptions [40].

In the past twenty years, DFT and methods derived from DFT have significantly advanced our understanding of the intrinsic catalyst structure-property relationship for many systems [46]. The DFT-based catalyst screening procedure is established for almost any catalytic application. The binding energies and energy barriers from DFT calculation are essential design parameters [47]. Linear scaling relationships can be leveraged to accelerate the estimations of descriptor values for different surface species on different catalytic materials (metals, oxides, nitrides) [48]. Through microkinetic modeling, catalytic trends can be graphically described using the so-called

volcano plots for the interpretation of catalyst performance and predictions. As shown in Figure 1.3, too strong binding (i.e., Mo) or too weak binding (i.e., Co and Ni) will both slow down ammonia synthesis. On the other hand, the Co-Mo bimetallic alloy is predicted to boost the ammonia synthesis rate compared to its pure Co and Mo components. This prediction was subsequently confirmed experimentally [49-51].

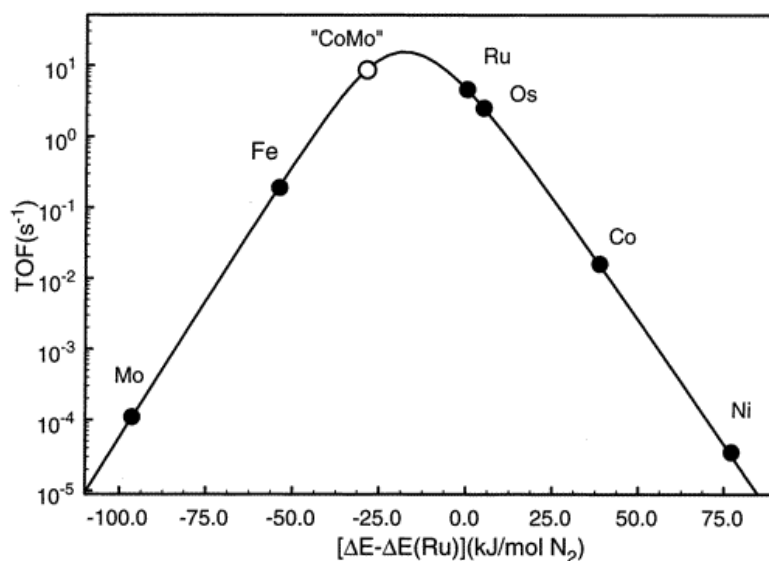


Figure 1.3. The *volcano* plot for the rate (TOF, s<sup>-1</sup>) of ammonia synthesis based on the binding energy of atomic N ( $E_N$ ). Adapted from Ref. [52].

The strong predictive power of these linear scaling relationships also severely binds the ultimate catalytic performance. Besides ammonia synthesis, many important catalytic reactions face a similar bottleneck, and the only solution is to design catalyst systems that *violate* the rules set by linear scaling relationships. Pérez-Ramírez and López [53] summarized the potential materials to accomplish this

goal. As illustrated in Figure 1.4, a range of materials with increasing complexity were proposed to *break* the linear scaling relationships.

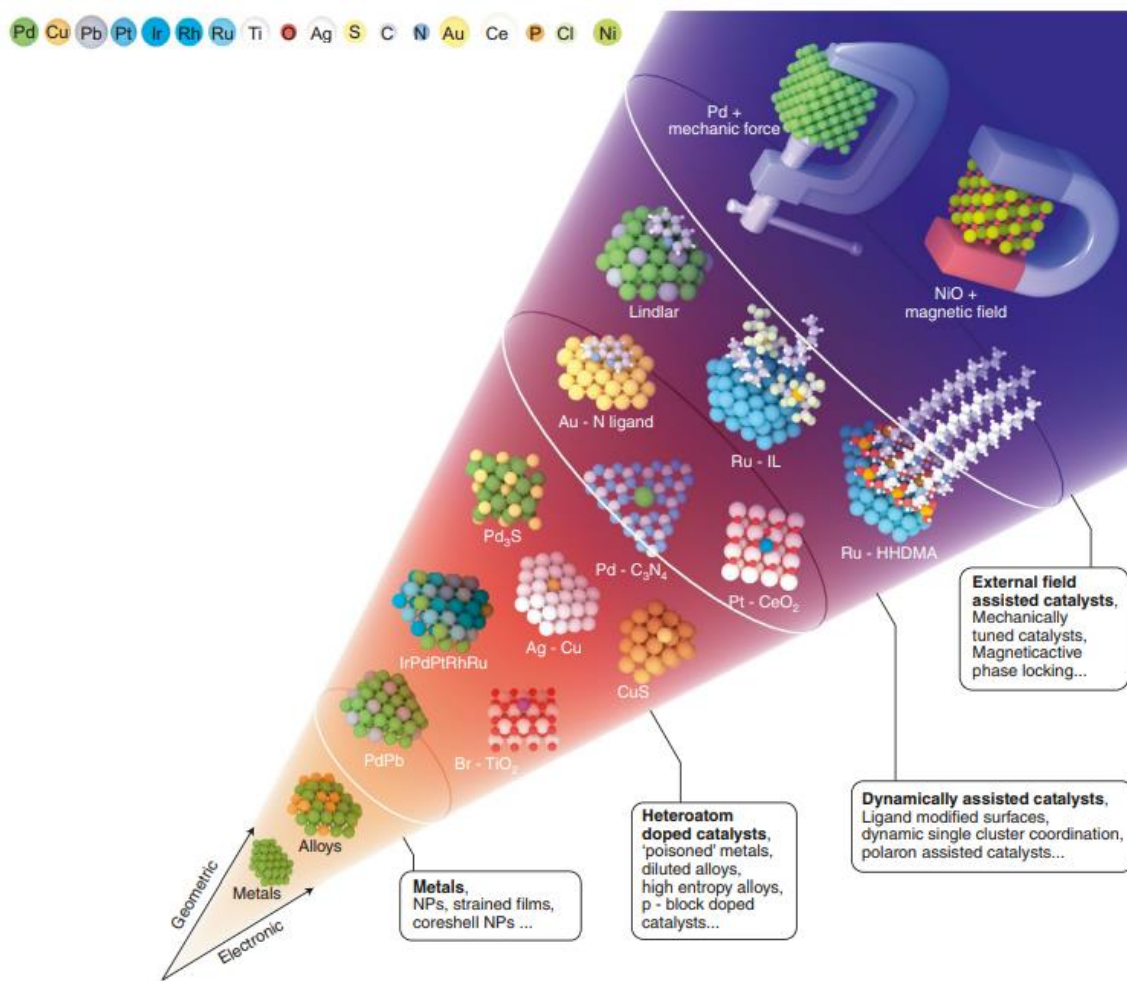


Figure 1.4. The cone diagram illustrating the structural evolution arranged diagonally. Adapted from Ref. [53].

Anderson and coworkers [54] demonstrated the full utility of the linear scaling relationships to help guide the search among a vast possibility of catalyst constructs. They found that not all bifunctional catalysts guarantee meaningful enhancement of performance. Instead, the reactant and product species must display different behaviors by breaking the linear correlations.

It is well known that the combination of the acidic and pH-neutral transition metal sites favors the conversion of furfural to cyclopentanone [55]. For ammonia synthesis, the addition of potassium promoter helps lower the activation energy for N<sub>2</sub> dissociation without significantly affecting the N adsorption energy [56]. In the latter case, experiments confirmed an order of magnitude increase of ammonia production rate [55].

The design of multicomponent synergistic catalytic systems can be challenging. But the reward is also highly rewarding. Multiple theoretical and experimental evidence pointed out that more work is necessary to gain further mechanistic understanding to continuously improve our ability to advance the bifunctional catalysis technology.

## **1.4 Case Studies**

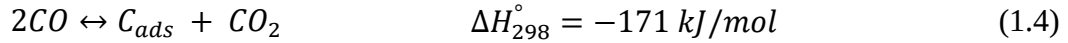
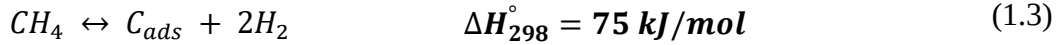
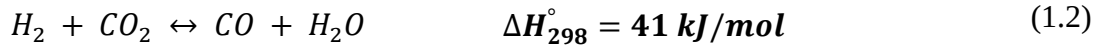
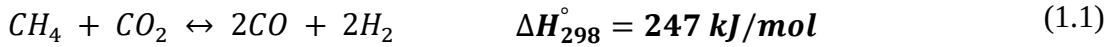
In this thesis, systematic studies on bifunctional catalysts also center on the chemistries of CO<sub>2</sub> conversions and utilization to produce useful, value-added chemical products. DFT calculations coupled with advanced modeling techniques such as molecular dynamics simulation, microkinetic modeling were employed as the primary research tool. The background and underlying chemistries of DRM and the CO<sub>2</sub>-to-methanol conversion will be reviewed in this section. Special attention will be given to recent advancement relevant to these reactions in relation to the beneficial effects by bifunctional catalysts.

### **1.4.1 Dry Reforming of Methane**

The US dry natural gas production, which is predominantly methane (CH<sub>4</sub>), has reached  $3.3 \times 10^6$  Mcf (million cubic feet) in June 2019 [57]. CH<sub>4</sub> is one of the most important energy carriers [58], but also a potent greenhouse gas. Dry reforming of methane (DRM) converts CH<sub>4</sub>

and CO<sub>2</sub> into syngas (gas mixture of CO and H<sub>2</sub>) [59-62], methanol, and sulfur-free diesel fuels [63, 64].

DRM is a highly endothermic reaction (Eqn. (1.1)), with the reverse water gas shift (RWGS) reaction as a side reaction. According to Eqn. (1.2), RWGS converts H<sub>2</sub> into H<sub>2</sub>O, and lowers the H<sub>2</sub>/CO ratio to less than 1. Both CH<sub>4</sub> and CO<sub>2</sub> are chemically stable. Thus, the activations of both chemical compounds are challenging. DRM are routinely conducted at high temperatures (800-1000°C) [65]. However, under such conditions, coke formation is favored [66, 67], mainly due to CH<sub>4</sub> cracking (Eqn. (1.3)) and the Boudouard reaction (Eqn. (1.4)). To alleviate coking, some partial oxidation [68], or steam reforming [69] is allowed during DRM.



A fundamental solution to suppress coking without sacrificing the reforming rate relies on innovative catalyst design [70]. The proposed DRM mechanism is illustrated in Figure 1.5 [59, 71, 72]. In this reaction network, the decomposition of CH<sub>4</sub> (blue box) via C–H bond cleavage releases H<sub>2</sub> and carbon residuals on the surface. The carbonaceous species (i.e., C, CH) are precursors inducing coking through the dimerization and polymerization reactions via C–C coupling (brown box). For DRM, the main mechanism responsible for suppressing the polymerization of carbon is the oxidations of C/CH by O/OH (red box), produced by CO<sub>2</sub> dissociation (green box) [73]. In

addition, the reverse Boudouard reaction (indicated by a purple dashed arrow) can convert surface carbons into CO at high temperatures.

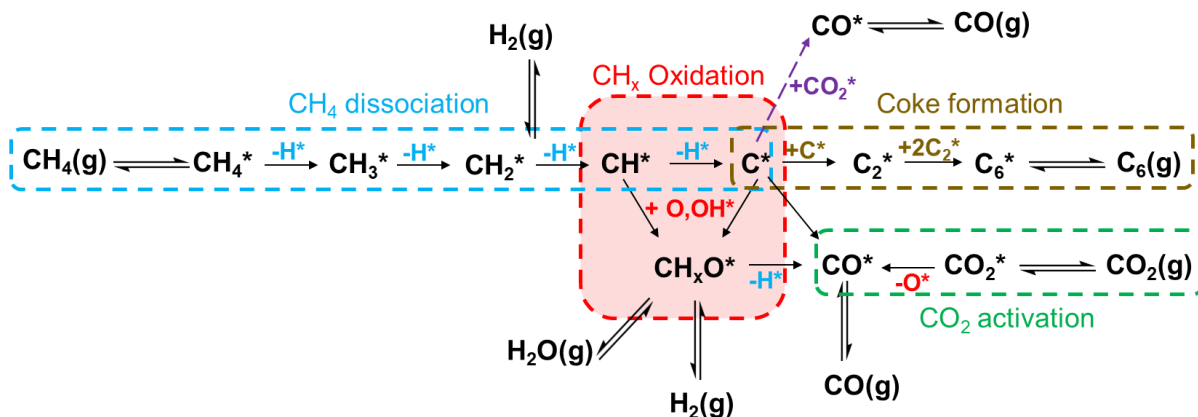


Figure 1.5. DRM reaction network including CH<sub>4</sub> decomposition (blue box), CO<sub>2</sub> activation (green box), CH<sub>x</sub> oxidation (red box), and coke formation (brown box).

Kinetically, the activation of the C–H bond in CH<sub>4</sub> is long recognized as the rate-determining step [74, 75]. However, there is much more debate on oxidation chemistry and their influence on coke formation. With DFT calculations, Zhu *et al.* [76] found the oxidation of CH via the formyl intermediate (i.e., CHO) is competitive. Moreover, the rate of CH oxidation also impacts the DRM rate.

For catalyst selection, the reactivity of CH<sub>4</sub> activation depends on the metal site (e.g., Ni, Pt, Co, Ru, Rh). Also, acidic (e.g., Al<sub>2</sub>O<sub>3</sub>) sites tend to induce coke formation; on the other hand, catalyst surfaces with abundant oxygen species are highly potent to boost the product selectivity and the removal of carbon deposits [77]. The synthesis of DRM catalysts already utilizes distinct functionalities of different catalytic materials, with some bifunctional capability to combat coking. For example, Pt supported on ZrO<sub>2</sub> shows significant improvement in catalyst stability [78].

The catalytic performance of transition metals on support is very sensitive to the amount of metal usage, particle dispersion, and preparation techniques. Variations in performance will be enhanced if the support is catalytically active. Recently, Fu and coworkers found that monolithic ternary nitrides such as  $\text{Co}_3\text{Mo}_3\text{N}$  are active and high durable during DRM [79]. Due to the strong metal *d*-orbitals hybridization with the nitrogen *2p* orbitals in the valance bands, the electronic structures of transition metal nitrides resemble closely to Group VIII metals (e.g., Pt) [80]. The procedure for the preparation of ternary nitrides is established.  $\text{Co}_3\text{Mo}_3\text{N}$  [81-83],  $\text{Fe}_3\text{Mo}_3\text{N}$  [81, 82], and  $\text{Ni}_3\text{Mo}_3\text{N}$  [82] have already been applied in numerous catalytic applications. Compared to  $\text{Mo}_2\text{N}$ ,  $\text{Co}_3\text{Mo}_3\text{N}$  exhibited significantly higher DRM reactivity, stability, and resistance to carbon deposition. Fu and coworkers attributed this enhanced catalytic performance of  $\text{Co}_3\text{Mo}_3\text{N}$  to the synergistic interactions of the Co- and Mo-containing components. However, the synergy among active sites remains poorly understood for ternary nitrides catalysts. A deep understanding of the origin of such synergistic effects in these materials is vital.

#### 1.4.2 Methanol Formation via $\text{CO}_2$ Hydrogenation

The production of methanol production is the second largest in terms of market volume (after urea) [84]. Products derived from methanol are commonly used in households, food, chemical industry, and fuels [85, 86]. As a liquid energy carrier, methanol production via  $\text{CO}_2$  hydrogenation can become a sustainable fuel production path [87].

The conversion of  $\text{CO}_2$  into methanol via hydrogenation is expressed by Eqn. (1.5), which can proceed through two main routes (Figure 1.6): (i) the formate ( $\text{HCOO}$ ) pathway and (ii) the carboxyl ( $\text{COOH}$ ) route followed by the reverse water-gas-shift (RWGS) and CO hydrogenation reactions [47]. CO and  $\text{H}_2\text{O}$  are the by-products during methanol production. Along the formate



route, the hydrogenation of HCOO and H<sub>2</sub>COO (dioxomethylene) are the rate-limiting steps [17,47,51]. In the carboxyl pathway, hydrogenation of CO forming formyl (HCO) is likely the rate-limiting step.

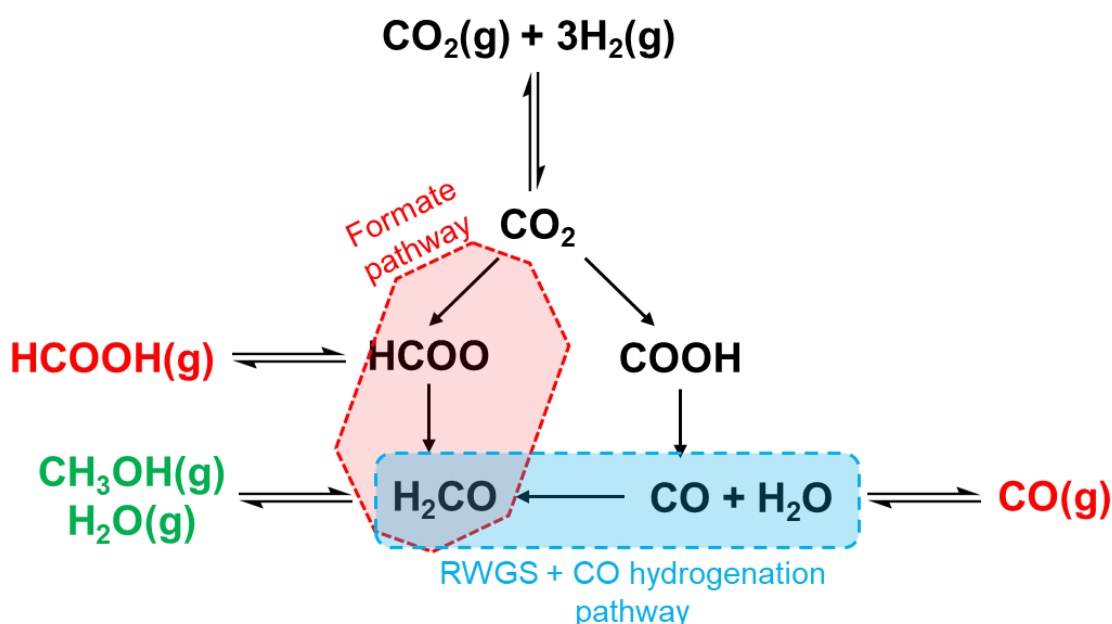


Figure 1.6. CH<sub>3</sub>OH formation pathways via CO<sub>2</sub> hydrogenation.

Indium oxide (In<sub>2</sub>O<sub>3</sub>) is a superior catalyst to carry out CO<sub>2</sub> hydrogenation to produce methanol at higher methanol yield and selectivity [88, 89], when compared to the industrial Cu [90-92] and Pd [93, 94] catalysts. Martin *et al.* [95] further showed that the RWGS side reaction can be suppressed completely on In<sub>2</sub>O<sub>3</sub> if hydrogenation occurs at 200–300°C, 50 bar, and a high space velocity (GHSV of 16000 h<sup>-1</sup>). The methanol selectivity becomes 100 %.

DFT studies revealed that the oxygen vacancies in  $\text{In}_2\text{O}_3$  play an important role in  $\text{CO}_2$  activation and subsequent hydrogenation steps [88, 96, 97]. The influence of oxygen vacancies becomes more pronounced for  $\text{In}_2\text{O}_3$  on reducible supports. For instance, the stable  $\text{In}_2\text{O}_3$  catalysts supported on  $\text{ZrO}_2$  show even higher methanol yield than pure  $\text{In}_2\text{O}_3$  catalysts at similar conditions [95, 98, 99]. Moreover, various methanol yields and selectivities were observed on  $\text{In}_2\text{O}_3$  supported on  $\text{ZrO}_2$  [95, 98-100],  $\text{CeO}_2$  [101], and  $\text{PrO}_x$  [102-104]. One possible explanation of such promotional effect is that the mixing of the metal ions from the support with  $\text{In}_2\text{O}_3$  alters the density and chemical nature of the oxygen vacancies [100]. Currently, the underlying mechanisms remain unclear.

## 1.5 Thesis Outline

This dissertation focuses on the computational studies of  $\text{CO}_2$ -to-chemical catalysis for reforming and hydrogenation applications. Chapter 1 (this chapter) presents an overview of my research scope and motivations. In Chapter 2, the theoretical background of DFT and the most essential computational techniques are introduced. Chapter 3 discusses the DFT modeling of DRM on  $\text{Co}_3\text{Mo}_3\text{N}$  and the reaction rates based on the steady-state analytical solutions. Chapter 4 revealed the trends of DRM reactivity and origin of the promotional effect on dual-site catalyst models. In Chapter 5, novel gallium-based liquid catalysts containing dispersed Ru, Ni and Pd species were investigated. Chapter 6 presents the an investigation of the reducible support effect on  $\text{In}_2\text{O}_3$  reactivity and product selectivity for  $\text{CO}_2$ -to-methanol conversions. The overall conclusions and research outlook are summarized in Chapter 7.

## 2 Computational Methods and Theory

Density Functional Theory (DFT) was used throughout this thesis. In this chapter, the fundamental elements in modern plane wave-based DFT framework will be discussed. In addition, the relevant computational methodologies derived from DFT will be introduced as well.

### 2.1 Density Functional Theory (DFT)

Over the past four decades, DFT has become deeply integrated into catalysis research and applications [46]. The theoretical framework of DFT was first introduced by Pierre Hohenberg and Walter Kohn in 1964 [105]. In the following year, based on Hohenberg and Kohn's work, Kohn and Sham established the Kohn–Sham (K-S) equations that became the foundation of the modern day DFT [106]. Nowadays, the Kohn–Sham formulation is being implemented in nearly all DFT packages such as Vienna ab initio Simulation Package (VASP) [107, 108], Quantum Espresso [109], CASTEP [110], and CP2K [111] so on.

#### 2.1.1 Kohn-Sham Formulation

According to the H-K theorem [105],

- **Theorem 1:** *The external potential  $V_{\text{ext}}(r)$  is a unique functional of the electron density  $\rho(r)$ .*
- **Theorem 2:** *The ground state energy is obtained variationally: the density that minimizes the total energy is the exact ground state density.*

Although the H-K theorems are theoretically exact, they do not offer a practical means to compute the ground-state density. The breakthrough was achieved by Kohn and Sham [106] by

solving the many-body problem using the  $i^{\text{th}}$  single-particle K-S equation expressed by Eqn. (2.1), Known as Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}[\rho(r)] \right] \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (2.1)$$

Where,  $\rho(r) = \sum_i |\varphi_i(r)|^2$ , and the  $-\frac{\hbar^2}{2m} \nabla^2$  and  $V(r)$  terms represent the electron kinetic energy and the external potential energies, respectively. The third term describes the electron-electron Coulomb repulsion. The  $V_{xc}(r) = \frac{\delta E_{xc}(\rho)}{\delta \rho(r)}$  is the ‘functional derivative’ of the exchange-correlation energy. In the K-S formulation, all exchange-correlation effects in the many-body systems are embedded into the  $V_{xc}(r)$  term.  $\varphi_i(r)$  is K-S orbital, and  $\varepsilon_i$  is the eigenvalue of the corresponding K-S orbital. The  $\varphi_i$  will be solved iteratively to achieve self-consistency.

### 2.1.2 Electron Exchange-Correlation Functional

The accuracy of DFT calculations depends on the approximation of  $V_{xc}(r)$ . Several empirical and semi-empirical functionals were developed over the past few decades to find more accurate approximation for this term. The exchange-correlation functional developed from various level of theoretical formulations form the so-called functional Jacob’s ladder [112, 113]. The three main types of exchange-correlation functionals are local density approximation (LDA) [114], generalized gradient approximation (GGA) [115-118], and hybrid functionals (e.g., BLYP [115, 119, 120]).

The LDA functional is one of the simplest approximations of  $E_{xc}(r)$ , which assumes a homogeneous electron gas. Although LDA predicts satisfactory molecular geometries and

vibrational frequencies, it is also known to severely underestimate the binding energies [121]. The GGA functionals include both the local electron density and the local gradient of electron density to approximate  $E_{xc}(r)$ . GGA functionals are generally more accurate than LDA for transition metals, interfaces, and some chemical systems [122]. The accuracies in binding energy calculations are improved broadly over LDA. Several variations, including Perdew-Burke-Ernzerhof (PBE) [123], Perdew-Wang (PW91) [124], and the revised PBE (RPBE) [125], are available for the implementation of DFT calculations yielding similar level of accuracy.

The GGA-PBE functional will be employed in this thesis unless specified otherwise due to the balanced accuracy versus computational cost for structure optimizations and total energy calculations [126].

Hybrid functionals are particularly useful for electronic structure calculations to obtain energy band gaps, which are often underestimated by GGA and LDA methods. However, the hybrid functionals are much more expensive. Also, the material band structures will not be a main research topic in this thesis.

### 2.1.3 Self-Interaction Errors (SIE)

The SIE can be encountered in DFT calculations involving d- and f- transition metal oxides (e.g.,  $\text{In}_2\text{O}_3$  [127, 128],  $\text{ZrO}_2$  [128, 129],  $\text{CeO}_2$  [129-131],  $\text{PrO}_2$  [130]). SIE in standard DFT calculations leads to erroneous lattice parameters, magnetic moments, band gaps, oxygen vacancy formation, and reaction energies. This error arises when the self-Coulomb term and exchange part failed to completely cancel each other exactly [132].

The Hubbard U method applied in LDA or GGA functionals (known as LDA+U or GGA+U) is effective in compensating the SIEs for *d* and *f* electron systems [133-135]. However,

it is widely acknowledged that there is not a universal  $U$  value for all material properties [136]. Hence, it is necessary to carry out benchmark testing to determine  $U$  empirically based on known material properties (e.g., lattice parameters, band gaps, formation energies). In this thesis, the Hubbard- $U$  method was applied to  $\text{In}_2\text{O}_3$  and related systems. The  $U$  values were acquired from my own testing or taken from literature.

#### 2.1.4 Plane Wave Basis Set and Pseudopotential

For solid-state systems, the wavefunction of an electron occupying a state of  $k$  in the first Brillouin zone of cell can be expanded using the Bloch's theorem [137]. A wavefunctions taking the form of the plane wave basis set is expressed in Eqn.(2.2):

$$\psi_i(\mathbf{r}) = \sum_j C_{i,j} \Phi_{i,j}(\vec{r}) = \sum_G C_{i,k+G} e^{i(k+G)r}, \quad (2.2)$$

where  $\vec{G}$  is the lattice vector in the reciprocal space,  $C_{i,k+G}$  is the Fourier coefficient and  $k$  is a wave vector limited to the first Brillouin zone in the reciprocal space. For very large kinetic energies  $|k+G|^2$ ,  $C_{i,k+G}$  is negligible. With a finite number of plane waves (up to the cutoff energy of  $E_{cut}$ ), the ground state energy and density converge quickly. Once the wavefunctions are converged at the end of the self-consistent loop, electron density  $\rho(\mathbf{r})$  will be calculated from  $\langle\psi|\psi\rangle$ .

The plane wave-based approach are implemented in many packages such as ABINIT [138], GAMESS [139], Quantum Espresso [109], and VASP [140].

All electron calculations with the full Coulombic potential can be very expensive because the wave function in the proximity to the nuclei oscillate rapidly. Moreover, only valence electrons

determine the material properties or participate in chemical bonding. In order to make DFT calculations computationally tractable, pseudopotentials (PPs) were introduced.

Generally, the wave functions for core electrons are approximated with a much smoother mathematical formulation for a given PP. The ultrasoft PP [141] and the projector augmented wave (PAW) method [142] are the most commonly used. The ultrasoft PP (USPP) is cost effective, requiring few planewaves. The PAW method constructs the PP to resemble the all-electron wavefunctions. Hence, the PAW pseudopotential is superior and tends to be more accurate than the USPP. In this thesis, the calculations were performed using a pseudopotential generated from the PAW method.

### **2.1.5 Bader Charge Analysis**

The electron charge density is a main product from DFT calculations. Charge density analyses yield valuable information to help understand charge transfer, charge delocalization, and chemical bonding [143, 144].

The original concept of the Bader charge analysis was proposed by Richard Bader [145], who offered an intuitive means to reveal charge distributions within the molecular system. In this thesis, charge transfers between active sites were used to understand the change in reactivity. In this method, individual atomic charge is determined through the partitioning of a molecular volume at the zero flux surfaces [146]. This algorithm is implemented in the Perl-based *vtstscripts* package provided by Henkelman *et al.* [146].

## 2.2 Reaction Thermodynamics

The total energies produced directly from DFT calculations represent the ground state energies. To account for the temperature effect, the Gibbs free energies should be used as expressed by Eqn. (2.3):

$$G = E_{DFT} + ZPE - TS \quad (2.3)$$

$$ZPE = \frac{1}{2} \sum_i h c v_i \quad (2.4)$$

where  $E_{DFT}$ ,  $ZPE$ , and  $TS$  represent the DFT total energy, the zero-point energy (Eqn.(2.4)), and the entropic term, respectively [46].  $h$  is the Planck's constant ( $6.63 \times 10^{-34}$  m<sup>2</sup> kg s<sup>-1</sup>),  $v_i$  is the  $i^{th}$  vibrational mode, and  $c$  is the speed of light ( $2.99 \times 10^{10}$  cm/s). The entropy energy for gaseous species can be calculated based on standard statistical mechanical formulations [147]. Once the molecular free energy is known, the reaction free energy can be calculated from Eqn. (2.5):

$$\Delta G = \sum G_{products} - G_{reactants} \quad (2.5)$$

## 2.3 Climbing Image-Nudged Elastic Band (CI-NEB)

To estimate the reaction rates, it is necessary to know the activation energy. For DFT calculations, the nudged elastic band (NEB) method is one of the most implemented approaches to determine the transition state structures and saddle point energies on the potential energy surface [148]. To carry out the NEB transition state search, a set of linearly interpolated images are generated using the DFT optimized initial and final configurations. Fictitious springs are imposed between adjacent images so that the images on the path can be continuously nudged toward the



true minimum energy path (MEP). Upon the completion of the search, the transition state is located, so is the energy barrier of the MEP via Eqn. (2.6).

$$E_a = E_{TS} - E_{IS} \quad (2.6)$$

where  $E_a$  is the barrier energy and  $E_{TS}$  and  $E_{IS}$  are the total energies of the transition state (TS), the initial state (IS), respectively.

The Climbing Image NEB (CI-NEB) [149] method helps mitigate the slipping of the image, especially near the saddle point. The slipoff may result in underestimation of the true energy barriers. In practice, CI-NEB moves the highest energy image towards the energy uphill by turning off the tangential forces to maximize its energy along the band.

## 2.4 Dimer Method

The dimer method [150] allows one to locate the transition state without the knowledge of the final state configuration. The dimer search for the saddle point is driven by the first derivatives of the potential energy [150, 151]. A pair of images (i.e., dimer), which are slightly displaced from each other along the axis, is used for each optimization stage. The search is complete when the dimer forces are minimized and meet the convergence criterion.

The dimer method is often applied along with the CI-NEB to accelerate the search of transition state. In practice, the initial structures for Dimer calculations are acquired from the prior CI-NEB step.

## 2.5 *d*-Band Theory

For a chemisorption event depicted in Figure 2.1a, the *p* orbitals of an adsorbate and the *d* orbitals of the transition metal substrate will couple forming bonding and anti-bonding states. In this case, the bond strength will depend on the filling of the antibonding state, which varies with the substrate elements [152, 153].

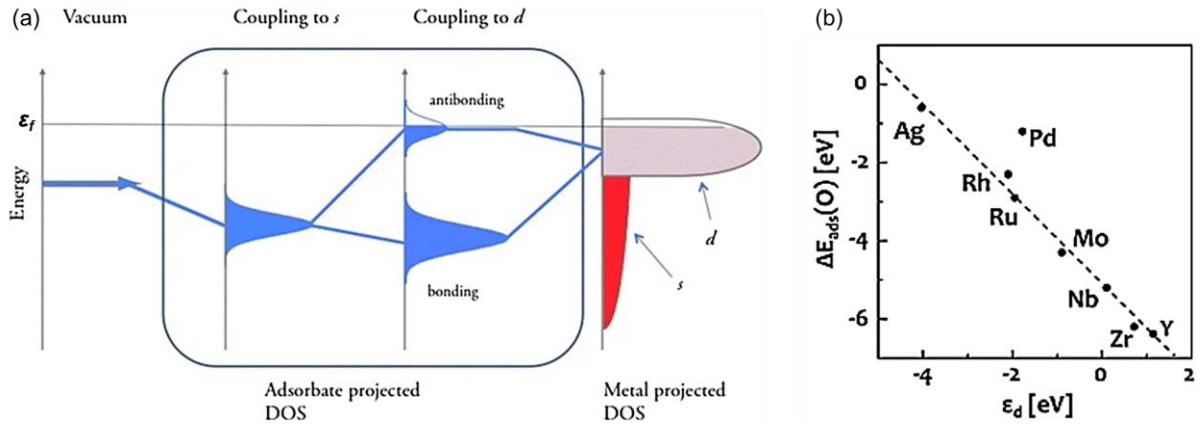


Figure 2.1. (a) Schematic illustration of the bonding and anti-bonding states on transition metal surfaces for a typical adsorption event, adapted from Ref. [154]. (b) Adsorption energy of O as a function of the transition metal *d*-band centers, adapted from Ref. [155].

Such behavior gives rise to the so-called *d*-band theory, in which a single state at energy  $\epsilon_d$ , known as the *d*-band center, bears the predictive power of the characteristic adsorbate-substrate interactions.  $\epsilon_d$  is calculated as the first moment of the projected *d*-band density of states (DOS) relative to the Fermi level ( $\epsilon_f$ ) according to Eqn. (2.7):

$$\epsilon_d = \frac{\int_{-\infty}^{\epsilon_f} \epsilon \times \rho_d(\epsilon) d\epsilon}{\int_{-\infty}^{\epsilon_f} \rho_d(\epsilon) d\epsilon}, \quad (2.7)$$

where  $\rho_d$  represents the projected density of state (PDOS). Hammer and Nørskov [122, 153, 156] declared that the bond strength of an adsorbate on different transition metals correlates linearly with the relative position of the metal  $d$ -band center (Figure 2.1b). The larger upward shift toward the Fermi level the stronger binding energy, due to larger possibility of the formation of a larger number of empty anti-bonding states [157].

The  $d$ -band center is the most relevant descriptor to predict the trend in activation energies on alloys [158]. When a metal is modified with a second metal with a larger lattice constant, the parent metal is under tensile strain and its  $d$ -orbital overlap decreases, which results in a narrower  $d$ -band and an up-shifted  $\epsilon_d$ . Conversely, if the second metal has a smaller lattice constant, the overlap of the  $d$ -orbital of first metal increases. As a result, the  $d$ -band becomes broader and the  $d$ -band center decreases. The subtle downshift of the  $d$ -band center can also be induced by the ligand effect. According to Nørskov's, the  $d$  electrons in less noble metals such as Ni, Co, Fe and Ag tend to transfer to Pt or Pd which consequently downshifts the  $d$ -band of the latter [42].

In practical applications, Ma *et al.* [43] studied the electrocatalytic reduction of CO<sub>2</sub> on Au-Pt bimetallic catalysts (with different compositions) and observed a correlation between the catalytic activity and the surface composition of bimetallic electrocatalysts. They found that the syngas ratio (CO:H<sub>2</sub>) on the Au-Pt films can be tuned by controlling the binary compositions. This tunable catalytic selectivity is attributed to the variation of binding strength of COOH and CO intermediates, influenced by the composition-dependent  $d$ -band centers.

### 2.5.1 Rate Theory for Elementary Steps

The rate constant of an elementary step can be represented according to the transition state theory (TST), as in Eqn. (2.8):

$$k = \frac{k_B T}{h} \exp\left(\frac{-E_a}{RT}\right), \quad (2.8)$$

where T is temperature (in K),  $E_a$  is the activation energy. For instance, the forward and reverse rate constants of CH<sub>4</sub> dissociative adsorption can be explicitly written as Eqns. (2.9) and (2.10):

$$k_f = \frac{k_B T}{h} \frac{q_{TS}}{q_{CH_4(g)}} \exp\left(-\frac{E_{af}}{RT}\right), \quad (2.9)$$

$$k_r = \frac{k_B T}{h} \frac{q_{TS}}{q_{CH_3^*} q_{H^*}} \exp\left(-\frac{E_{ar}}{RT}\right), \quad (2.10)$$

where  $q_{TS}$ ,  $q_{CH_4}$ ,  $q_{surf}$ ,  $q_{CH_3^*}$ , and  $q_{H^*}$  are the partition functions for the transition state (TS), the reactant, and product states with respect to their ground states, respectively. These partition functions were estimated based on the standard statistical mechanical approach [147]. For regular adsorption and desorption events, the rate constants for molecular adsorption and desorption can be expressed by Eqns. (2.11) and (2.12) [159]:

$$k_{adsorption} = \frac{1}{N_0 \sqrt{2\pi k_B T M_A}} \frac{q_{A^*}}{q_{rA(g)} q_{vA(g)}}. \quad (2.11)$$

$$k_{desorption} = e \frac{k_B T}{h} \exp\left(-\frac{\Delta E}{RT}\right) \quad (2.12)$$

where  $N_0$  is the number of surface sites of the exposed surface.  $M_A$  is the molecular mass of the adsorbate (A).  $q_{r_{A(g)}}$  and  $q_{v_{A(g)}}$  are the rotational and vibrational partition functions of the gas-phase adsorbate, respectively.  $E_{af}$  and  $E_{ar}$  correspond to the activation energies of the forward and reverse elementary step, respectively, while  $\Delta E$  is the reaction energy for any given reaction step. Activation and reaction energies can be obtained from DFT calculations or estimation based on linear relationships (see sections 2.5.2 and 2.5.3).

## 2.5.2 Linear Scaling Relationship

Driven by systematic DFT calculations on a vast number of adsorbates on various substrates, researchers realized that some chemical species follow species adsorption patterns. Their binding energies are also bounded by linear correlations, known as the linear scaling relationship in modern computational catalysis.

As shown in Figure 2.2a, the binding energies of the main group atomic species C are linearly correlated with the binding of CH<sub>3</sub>, CH<sub>2</sub>, and CH, all of which are bound to the substrate through their C atoms [52]. Abild-Pederson *et al.* [160] summarize the DFT calculations for several main group elements (i.e. C, O, N, S) and their hydrogenated counterparts AH<sub>x</sub> (A = C, N, O, S) with Eqn. (2.13).

$$E^{AH_x} = \gamma E^A + \xi \quad (2.13)$$

where  $E$ ,  $\gamma$ , and  $\xi$  are binding energy, slope, and intercept, respectively. Interestingly, the  $\gamma$  parameters can be interpreted with a simple geometric argument as in Eqn. (2.14):

$$\gamma = \frac{x_{max} - x}{x_{max}} \quad (2.14)$$

where  $x_{max}$  is the maximum number of bonds acceptable to the central atom A. For example, C  $x_{max} = 4$ , hence,  $\gamma$  of  $\text{CH}_3$  will be 0.25. The positive value of  $\xi$  indicates that the binding of  $\text{AH}_x$  intermediate will be weaker than the corresponding A species. Moreover, for large positive  $\xi$ , the conversion of A into  $\text{AH}_x$  is thermodynamically unfavorable, while a small positive  $\xi$  indicate that A and  $\text{AH}_x$  intermediates are energetically similar. On the other hand, the large negative  $\xi$  shows that the conversion of A into  $\text{AH}_x$  will be exothermic [161]. Thermodynamical linear scaling relationships have been proven to facilitate catalyst design and material discovery with minimal computational cost.

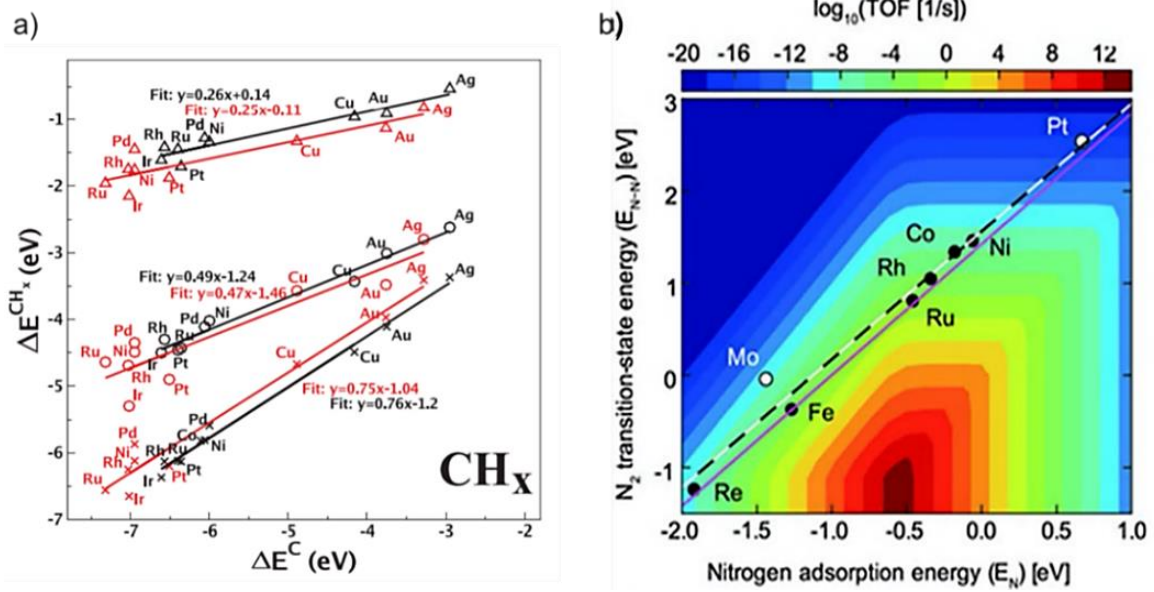


Figure 2.2. (a) Binding energies of  $\text{CH}_x$  intermediates, plotted against adsorption energies of C [160], (b) ammonia production rates as a function of N adsorption energy and  $\text{N}_2$  transition state

energies (both in eV). Solid and dashed lines indicate the linear relationships between  $E_{N-N}$  and  $E_N$  on flat and stepped surfaces, respectively [28].

### 2.5.3 Brønsted–Evans–Polanyi (BEP) Relationship

Besides the linear scaling relationships discussed above for surfaces adsorptions, Nørskov and coworkers also showed that linear relationships exist between reaction energies of gas phase reactants ( $\Delta E$ ) and activation energies ( $E_a$ ), as shown in Eqn. (2.15) [162-164]:

$$E_a = \alpha \cdot \Delta E + \beta \quad (2.15)$$

Both NEB and dimer calculations are much more computationally expensive than total energy calculations. In this regard, the advantage of the BEP is obvious. Both  $\alpha$  and  $\beta$  in Eqn. (2.15) depend on reaction types and catalytic materials. Physically,  $\alpha$  indicates the similarity between transition states and the reactant (early transition state reaction) or the product (late transition state reaction) state [165, 166]. A change in  $\alpha$  can be associated with the electronic effect ( $d$ -band center), while the surface geometrical effect is reflected in  $\beta$  [167]. Therefore, the BEP relationship can serve as a tool to evaluate the geometrical and electronic properties of catalysts, and to link these properties to their intrinsic activities [168].

At this point, the combination of linear scaling relationship and BEP enables researchers to rapidly screen for the desired catalysts using the energetic and kinetic descriptors, allowing significant advancement in catalyst discovery in the past 10-15 years. However, as discussed in Chapter 1, these linear scaling relationships also pose a stringent constraint for oxygen reduction reaction (ORR) and ammonia synthesis catalysts.

As shown in Figure 2.2b, it is evident that any catalyst located on the BEP relationships (solid or dashed line) is unable to achieve the optimal turnover frequency displayed in the heatmap. In theory, to inch closer toward the peak of the reactivity volcano, the  $N_2$  activation transition state should be much lower in energy without significantly strengthening the binding of atomic N. That is to say, the linear scaling relationships presented in Figure 2.2b must be *broken*.

Liu *et al.* [8] constructed a dual-site model of manganese nitride ( $Mn_4N$ )-supported  $Ni_3$  and  $Fe_3$  clusters for  $NH_3$  synthesis (Figure 2.3a). As shown in Figure 2.3b, both dual-site composite catalysts yield superior turnover frequency to  $Mn_4N$  and the Fe, Ni catalysts. DFT calculations showed that the  $N_v$  site activates  $N_2$  with a barrier of approximately 0.55 eV, while the Ni or Fe site is responsible for hydrogenation and  $NH_3$  formation.

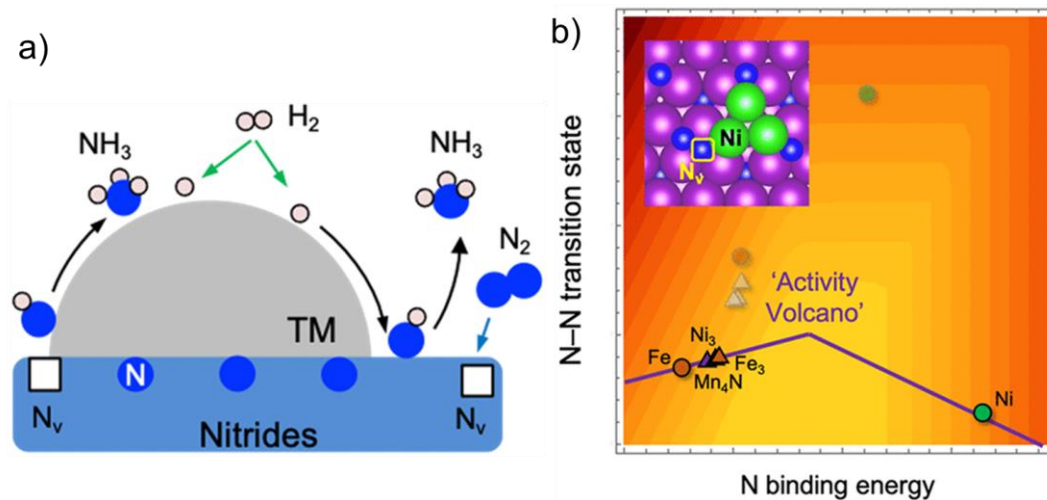


Figure 2.3. (a) Ammonia synthesis rate as a function of nitrogen adsorption energy and  $N_2$  dissociation barrier.  $E_{N-N}$  is a linear function of  $E_N$  [5], (b) calculated limiting potential for the  $O_2$  reduction [169].



## 2.6 Microkinetic Modeling

Microkinetic modeling was first introduced by Jim Dumesic [170], and is designed to solve for the rates of a reaction network composed of a series of elementary steps. Modern microkinetic modeling, based on catalytic descriptors, was pioneered by Nørskov *et al.* [171, 172], with strong emphasis on rational catalysts design. The microkinetic modeling reported in this thesis is based on the mean-field approximation that assumes homogeneous distributions of reaction species on the catalyst surface. A general first step to construct a microkinetic model is to identify all the elementary steps involved in the catalytic process [173]. The DFT-calculated binding energies will be used to obtain reaction free energies (see Eqns. (2.3-2.5)), and to estimate the activation energies (see Section 2.5.3). The energy barriers of each elementary step will be used to estimate the rate constants [47], followed by the estimations of equilibrium constants.

In the microkinetic model, the reaction rate of each elementary step ( $r_i$ ) is obtained by solving Eqn. (2.16), with a site conservation constraint (Eqn. (2.17)), under the assumptions of mean-field theory (Eqn. (2.18)) and pseudo-steady-state condition (Eqn. (2.19)), all rate equations can be solved simultaneously. All elementary step rates and species coverages ( $\theta_i$ ) will be obtained.

$$r_i = k_{i,f} \prod_j \theta_{ij} \prod_j p_{ij} - k_{i,r} \prod_l \theta_{il} \prod_l p_{il} \quad (2.16)$$

$$\sum_i \theta_i = \theta^{total} = 1 \quad (2.17)$$

$$\frac{\delta \theta_i}{\delta t} = \sum_j S_{ij} r_j \quad (2.18)$$

$$\frac{\delta\theta_i}{\delta t} = 0 \quad (2.19)$$

$k_{i,f}$  and  $k_{i,r}$  are the forward and reverse rate constants (see Section 2.5.1), respectively.  $p_{ij}$  and  $p_{il}$  are the unitless pressures of the gas phase species.  $S_{ij}$  are coefficients for the stoichiometry of species  $i$  in elementary step  $j$ .

Most microkinetic modeling reported in literature assume a single-type active site uniformly distributed on catalyst surfaces. The modeling of bifunctional catalysts is a research frontier. In this work, elementary steps are allowed to proceed on different active sites in parallel. Intermediate diffusion or spillover and interfacial reactions are carefully chosen using the inputs from DFT analyses. It has been shown that hydrogen spill-over from the metal particle to the support [174] and CO oxidation on Pt-Fe/M bimetallic [9] is vital to catalyst activity and selectivity.

As discussed in Chapters 3, a *Mathematica* script developed in-house, and the Catalysis Micro-kinetic Analysis Package (CatMAP) developed by Medford and coworkers [175] were used to carry out the microkinetic modeling tasks.

## 2.7 *Ab initio* Molecular Dynamics (AIMD)

Molecular dynamics (MD) is one of the most powerful tools in physical science and engineering. In particular, MD simulations are uniquely positioned to probe large scale molecular systems (up to millions of atoms) [176]. However, reliable MD simulations rely on accurate descriptions of the interatomic potentials, which can pose significant challenges to reactive systems.

AIMD simulations do not require empirical inter-atomic potentials; instead, the system Hamiltonians are evaluated on the fly. The forces on the nuclei at each MD step are calculated from electronic structure calculations. Then, the nuclei motions are numerically propagated in time. Two approaches are commonly implemented for AIMD: (1) the Born–Oppenheimer molecular dynamics (BOMD) [177], and (2) Car–Parrinello molecular dynamics (CPMD) [178]. AIMD can yield highly accurate descriptions of many-body forces, electronic polarization, and bond-breaking and formations [177]. Results produced from AIMD have been linked to experimental infrared [179], Raman spectra [180], and nuclear magnetic resonance (NMR) chemical shifts [181]. However, the self-consistent electronic calculations are far more expensive than classic MD simulations that use empirical potentials. The computational cost increases rapidly with the number of simulation atoms.

AIMD simulations reported in this thesis were carried out using VASP. For all simulations, the Nose-Hoover thermostat was chosen to control the simulations temperature in the canonical (NVT) ensemble. The simulation results were analyzed and visualized using the Ovito software [182].

## **2.8 Topological Cluster Classification (TCC)**

The topological cluster classification (TCC) algorithm was proposed by Malin and coworkers [183] to identify the local structure in the condensed matter systems. The TCC algorithm identifies a number of local structures and then compares these structures to a library of pre-defined elementary motifs (Figure 2.4a) [183]. In practice, the neighbors of each particle are identified first, followed by the search of 3-, 4-, and 5-membered rings within the neighbors’

network in the shapes of triangle, square, and pentagon shapes. Larger clusters can be constructed by combining these basic structure motifs that minimize the local potential energy Figure 2.4b.

In this thesis, TCC was used to directly link the interactions in the system with any cluster structural identified to for the liquid gallium (Ga) catalysts. Using the AIMD simulation trajectories, the Pd and Ni active sites in the Ga solution were investigated to collect information on the spatial locations of Ni or Pd, configurations (i.e., monomer, dimer), and the coordination with Ga solvent.

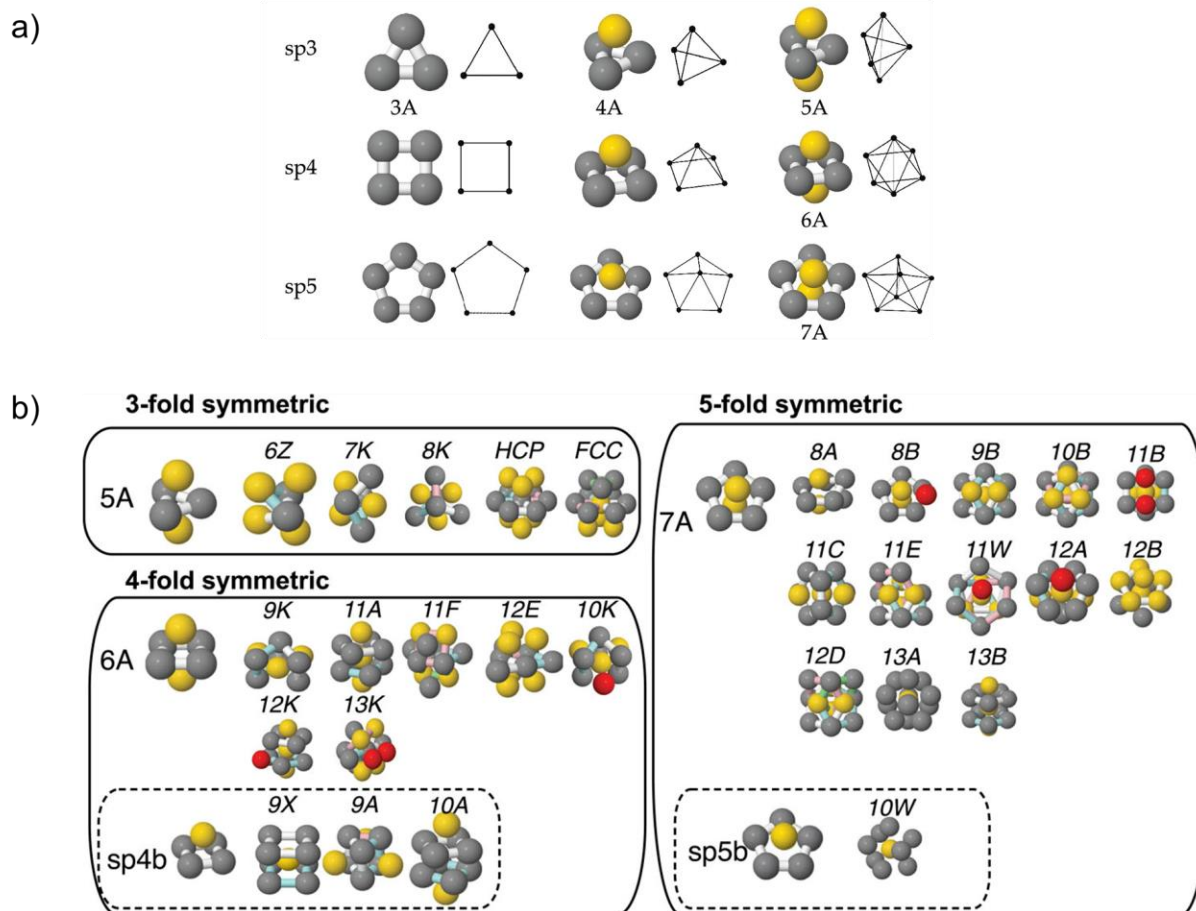


Figure 2.4. (a) Three basic structures, triangle, square, and pentagon identified from the shortest-path rings (gray), bonds between ring particles are shown in white, spindle particles are shown in yellow (they build a pyramid shape structure), and the extra particle (red). This figure is adapted from Ref. [183]. (b) Motifs used in the TCC algorithms: to three-fold symmetric (5A), four-fold symmetric (6A and sp4b) local order, and five-fold symmetric (7A and sp5b). Adapted from Ref. [184].

### 3 Molecular Mechanisms of Methane Dry Reforming on Dual-Site $\text{Co}_3\text{Mo}_3\text{N}$ Catalysts

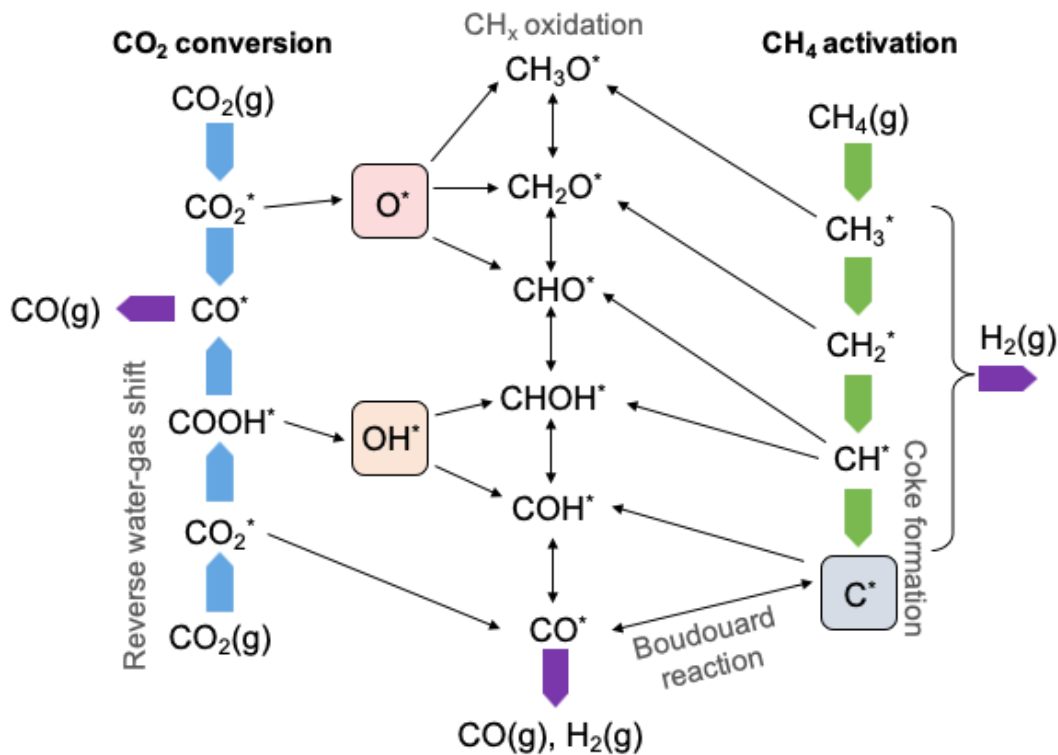
Chapter 3 is reproduced from Ref. [34] with permission from the Royal Society of Chemistry.

#### 3.1 Introduction

Dry reforming of methane (DRM), as described by Eqn. (3.1), converts methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) into a range of value-added chemicals including syngas, [59-62] methanol, [60] and sulfur-free diesel fuels; [63, 64] and thus engenders environmental and economic benefits. For DRM, however, carbon formation results in rapid catalyst deactivation, and remains a technological obstacle that hinders large-scale processes to realize its beneficial potentials. [66, 185, 186]

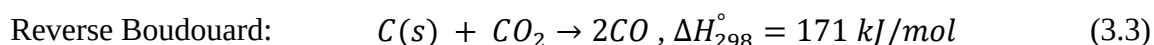
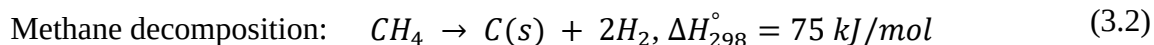


Scheme 3.1. Parallel  $\text{CH}_4$  and  $\text{CO}_2$  conversion pathways (indicated by respective green and blue arrows) in the DRM reaction network. Potentially relevant intermediate steps and species are also presented. The hydrogenation/dehydrogenation steps are not explicitly labeled. CO and  $\text{H}_2$  productions are also indicated by purple arrows.



The reaction network derived from transition metal DRM catalysts based on various reviews on this topic is summarized in Scheme 3.1. [59, 71, 72] Akin to most C1 chemistries related to  $\text{CH}_4$ , the initial C–H bond activation is a rate-limiting step (RLS), where the  $\text{CH}_4$  turnover frequency is often a reliable metric for the catalyst efficacy. [59] Specifically, Rostrup-Nielsen and Hansen [187] showed that the DRM rates on transition metals follow an order of:  $\text{Ru} > \text{Rh} > \text{Ir} > \text{Pt} > \text{Pd}$  in a low-to-medium temperature range (773–923 K) and at the ambient pressure. For earth abundant metal catalysts such as nickel (Ni) and cobalt (Co), Ferreira-Aparicio and coworkers [188] demonstrated that supported Ni catalysts may outperform noble-metal Rh and Ru catalysts. However, Ni-based catalysts are notoriously susceptible to coke-related deactivation, [187] doping atoms like Sn may slow down carbon deposition at 1000 K. [189] Chen *et al.* [190] showed that coking on Co(111) at high temperatures.

Methane decomposition yielding H<sub>2</sub> at the metallic sites, according to Eqn. (3.2), can be presented in a stepwise sequence (green arrows in Scheme 3.1). [187, 191] In parallel, CO<sub>2</sub> activation (indicated by blue arrows in Scheme 3.1), supplies O or OH to manage surface carbonaceous (C, CH<sub>x</sub>) intermediates.



The reverse Boudouard reaction is able to convert solid-state carbon into CO via Eqn. (3.3). As such, higher temperatures (above 1000 K) generally favor carbon removal. [186] In addition, reverse water-gas shift (RWGS) reaction plays a role in DRM to produce H<sub>2</sub>O as a side product. CO<sub>2</sub> chemisorption and dissociation are sensitive to surface structures, and can be enhanced by surface defects. [192, 193] To some extent, the C–O bond activation in CO<sub>2</sub> competes for the same active sites against CH<sub>4</sub> activation. Hence, there is a constraint on monofunctional transition metal catalysts to maintain a balance between C–H activation and C/CH conversion into CO.

There is plenty of evidence that DRM benefits from bifunctional catalysts. Commonly, CH<sub>4</sub> activation occurs at the metal sites, while CO<sub>2</sub> activation may take place on either acidic or basic oxide supports. [72] For instance, noble metal Pt catalysts supported on ZrO<sub>2</sub> promote CO<sub>2</sub> conversion during DRM while suppressing the carbon residue. [194, 195] The insights revealing what DRM mechanisms are enabled by specific metal-support functionalities can be leveraged to overcome the limiting DRM performance issues in future catalyst design endeavor. [71, 72]

Transition metal nitrides are metalloids with characteristic hybridization between the *d*- and 2*p*-orbitals of respective metal and N elements. These materials are less expensive and



intrinsically coke resistant, and thus, have long been employed as alternatives to transition metal catalysts in many applications. [196] Many ternary metal nitrides exist as stable multi-component monolithic materials, and add one more compositional parameter for fine-tuning of their catalytic properties. One notable example is  $\text{Co}_3\text{Mo}_3\text{N}$ , which has been long recognized as an outstanding material for ammonia synthesis. [50, 197] Recently, Fu *et al.* [79] demonstrated that  $\text{Co}_3\text{Mo}_3\text{N}$  exhibits promising reactivity toward DRM at temperatures below 873 K, and remains functional at up to 1073 K without significant catalyst deterioration. This appealing behavior has been attributed to the synergistic effects between Mo and Co components, high active site density, and the ability to balance  $\text{CH}_4$  and  $\text{CO}_2$  consumption rates.

Without a consensus on the DRM mechanism catalyzed by  $\text{Co}_3\text{Mo}_3\text{N}$ , in this work, periodic Density Functional Theory (DFT) was employed to reveal the origin of the DRM reactivity and coke resistance based on a close-packed  $\text{Co}_3\text{Mo}_3\text{N}$  facet that exposes coexisting Co and molybdenum nitride functional regimes, as geometric configurations among active sites could play significant roles in directing the occurrence of RLS to mitigate site crowding and competition. With DFT calculations, we were also able to draw contrast between the  $\text{Co}_3\text{Mo}_3\text{N}$  ternary nitride and individual single crystalline  $\text{Co}(0001)$  and  $\text{Mo}_2\text{N}(110)$  surfaces to show that the superior performance indeed results from the synergistic effects stemming from the dual-site configuration. Moreover, the DRM kinetics on  $\text{Co}_3\text{Mo}_3\text{N}$  is quantified using a newly developed microkinetic model that accommodates the dual-site functionalities.

## 3.2 Methods

### 3.2.1 Catalyst Models

The x-ray and neutron diffraction revealed that  $\text{Co}_3\text{Mo}_3\text{N}$  has a cubic  $Fd\bar{3}m$  lattice structure. [198] The bulk ternary  $\text{Co}_3\text{Mo}_3\text{N}$  nitride can be dissected into  $\text{Co}_8$  octameric clusters and a  $\text{Mo}_3\text{N}$  framework with bridging nitrogen species (Figure 3.1a).

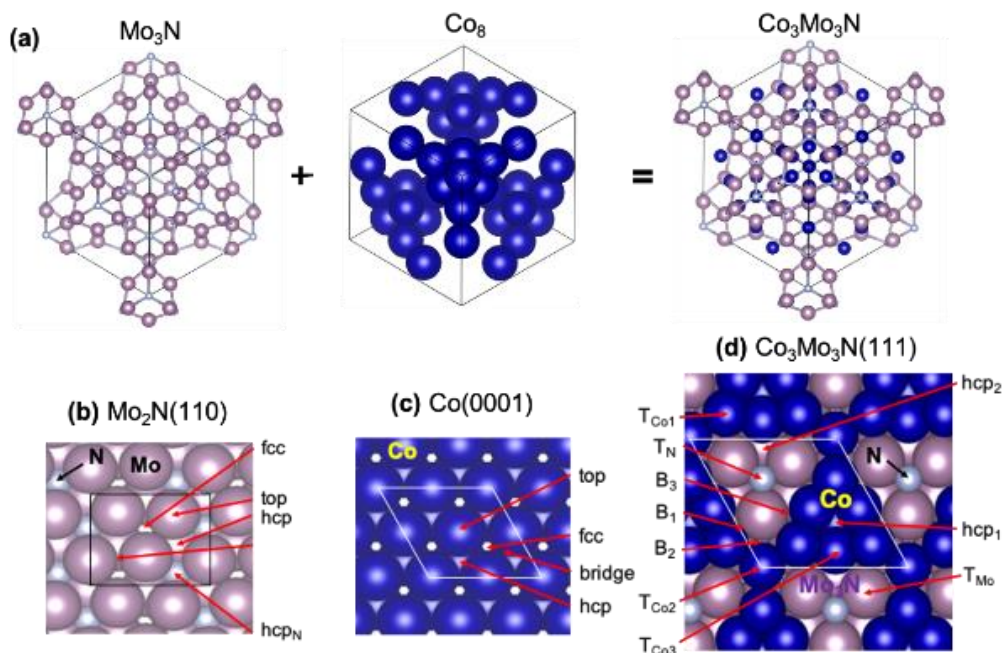


Figure 3.1. (a) Dissection of the molybdenum nitride ( $\text{Mo}_3\text{N}$ ) and cobalt in bulk ternary  $\text{Co}_3\text{Mo}_3\text{N}$  single crystal. (b-d) Top views the cleavage close-packed (111) orientation of  $\text{Co}_3\text{Mo}_3\text{N}$ ,  $\text{Co}(0001)$ , and (d)  $\text{Mo}_2\text{N}(110)$  surfaces, respectively. Accessible adsorption sites are also labelled. The Co, Mo, and N atoms are depicted in dark blue, pink, and light blue, respectively. The supercell boundaries are depicted with solid lines.

The  $\text{Co}_3\text{Mo}_3\text{N}(111)$  surface exhibits patterned Co and molybdenum nitride ( $\text{Mo}_x\text{N}$ ) domains (Figure 3.1d). The neighboring Co domains are connected via a single corner  $\text{Co}_2$  atom,

while the Mo domains are isolated and bounded by three Co domains. Such alternating patterns help break up continuous active site domains that would be susceptible to the establishment of large-area carbon structures. Indeed, Rostrup-Nielsen *et al.* [199-201] suggested that interruptions of continuous domains help suppress coking because the size of active-site ensemble for coke formation is typically larger than what is needed for reforming. Cleavage along the (111) orientation may yield a number of possible close-packed configurations. Here, the chosen facet represents the highest density of active sites; and was employed by Zeinalipour-Yazdi *et al.* [202] for the modeling of N<sub>2</sub> and H<sub>2</sub> adsorptions.

The Co domains in Figure 3.1d exhibit a 3-fold symmetry. The center of the 3-fold site is denoted as hcp<sub>1</sub>. Three distinct Co sites can be identified, denoted as **T<sub>Co1</sub>**, **T<sub>Co2</sub>**, and **T<sub>Co3</sub>**. In the top layer, the Co<sub>1</sub> atom is bonded to one Co<sub>2</sub>, two Co<sub>3</sub>, and two Mo atoms. The Co<sub>2</sub> species is bonded with three Co<sub>1</sub> atoms and three Mo atoms. The Co<sub>3</sub> species is bonded to two Co<sub>1</sub>, two Co<sub>3</sub>, and two Mo atoms. All three Co sites are located at the boundary with the Mo domain, and the Co<sub>1</sub> species are undercoordinated relative to the other two Co sites in Co<sub>3</sub>Mo<sub>3</sub>N(111). Due to the varying numbers of coordination and ligand, each Co site is considered electronically distinct, corroborated by the *d*-band centers listed in Table 3.1. The *d*-band centers for all Co sites shift toward the Fermi level relative to Co atoms in Co(0001) (Figure 3.1 c) following an order of Co<sub>3</sub> > Co<sub>2</sub> > Co<sub>1</sub>. Also, all Co sites are negatively charged (Table 3.1), indicating there is charge transfer from Mo to the nearest Co.

Table 3.1. The calculated *d*-band center (in eV) and Bader charge (in e) for Co(0001), Co<sub>3</sub>Mo<sub>3</sub>N(111), and Mo<sub>2</sub>N(110). Surface site notations are consistent with Figure 3.1d.

| Surface                                | Atomic site     | <i>d</i> -band center | Bader charge |
|----------------------------------------|-----------------|-----------------------|--------------|
| Co(0001)                               | Co              | -1.27                 | 0            |
| Co <sub>3</sub> Mo <sub>3</sub> N(111) | Co <sub>1</sub> | -1.14                 | -0.10        |
|                                        | Co <sub>2</sub> | -1.09                 | -0.37        |
|                                        | Co <sub>3</sub> | -0.92                 | -0.26        |
|                                        | N               | -                     | -1.17        |
|                                        | Mo              | 0.00                  | 0.88         |
| Mo <sub>2</sub> N(110)                 | N               | -                     | -1.44        |
|                                        | Mo              | -0.04*                | 0.32*        |

\* Such labeled values represent an average of the *d*-band center or Bader charge of different Mo atoms in the surface layer.

The Mo domains also exhibit 3-fold symmetry, consisting of three equivalent Mo atoms (labeled as T<sub>Mo</sub>) and one bridging N in the top layer. The boundary sites are denoted as B<sub>1</sub> (Mo-Co<sub>1</sub>), B<sub>2</sub> (Mo-Co<sub>2</sub>), and B<sub>3</sub> (Mo-Co<sub>3</sub>) for the Mo atoms bounded with different Co, respectively. The exposed bridging N, carrying a net charge of -1.17 e, is designated as T<sub>N</sub>.

We also included the close-packed facets of respective Mo<sub>2</sub>N (Figure 3.1 b) and Co (Figure 3.1 c) single crystals to represent the pure components of Co<sub>3</sub>Mo<sub>3</sub>N for later comparisons. The selection of Mo-terminated Mo<sub>2</sub>N(110) facet is because this surface exhibits a similar atomic arrangement to the Mo domain of Co<sub>3</sub>Mo<sub>3</sub>N(111).

### 3.2.2 Density Functional Theory

All periodic DFT calculations were performed using the *Vienna Ab initio* Simulation Package (VASP) [140]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof

functional (GGA-PBE) was used to account for the electron exchange and correlation. [123] The interactions between valence electrons and ion cores were described by the projector augmented wave (PAW) method [142], with a cutoff for the expanded plane wave basis set up to 400 eV. The Brillouin-zone was sampled using the Monkhorst-Pack  $k$ -point mesh [203]. The convergence criterion for self-consistent iterations is  $1.0 \times 10^{-6}$  eV, with a residual force smaller than 0.02 eV/Å for ionic relaxations.

The binding energies ( $BE$ ) reported in Table 3.2 are defined according to Eqn. (3.4):

$$BE = E_{total} - E_{adsorbate(g)} - E_{surface}, \quad (3.4)$$

where  $E_{total}$ ,  $E_{adsorbate(g)}$ , and  $E_{surface}$  represent the total energies of the adsorbed surface species, adsorbate in gas phase, and clean surface, respectively. Furthermore, the energy barriers ( $E_a$ ) and reaction energies ( $\Delta E$ ) for each elementary step reported in Table 3.3 were obtained according to Eqns. (3.5-3.6):

$$E_a = E_{TS} - E_{IS}, \quad (3.5)$$

$$\Delta E = \sum_i E_{product,i} - \sum_j E_{reactant,j}, \quad (3.6)$$

where  $E_{TS}$ ,  $E_{IS}$ ,  $\sum_i E_{product,i}$ , and  $\sum_j E_{reactant,j}$  are the total energies of the transition state (TS), the initial state (IS), and the summation of total energies for all product and reactant species, respectively. The total energies for the TS were obtained from the Climbing Image-Nudged Elastic Band (CI-NEB) and the dimer methods. [149, 150] All TS structures were confirmed with only one imaginary frequency.

All Gibbs free energies were estimated at 973.15 K and 1 bar by employing the standard statistical mechanical approach. [204] Under such conditions, the rate constants on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ ,  $\text{Co}(0001)$ ,  $\text{Mo}_2\text{N}(110)$ , and  $\text{Ni}(111)$  were evaluated based on the transition state theory (TST), see Table A.3 in ESI. Based on the order-of-magnitude analysis of the rate constants, a reduced DRM mechanism - consisting of 10 elementary steps, five gas phase species ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$ ), and eight surface intermediates (\*, C, CH,  $\text{CO}_2$ , CO, O, H, and OH) - was proposed to obtain the turnover frequencies (see Appendix A). The rate constants and equilibrium constants on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  and  $\text{Ni}(111)$  are summarized in Table A.4 in ESI.

The effective charges were obtained based on the Bader charge analyses [146]. The  $d$ -band centers ( $\epsilon_d$ ) were calculated as the first moment of the projected density of states (PDOS) relative to the Fermi level ( $\epsilon_f$ ) according to Eqn. (3.7): [122]

$$\epsilon_d = \frac{\int_{-\infty}^{\epsilon_f} \epsilon \rho_d(\epsilon) d\epsilon}{\int_{-\infty}^{\epsilon_f} \rho_d(\epsilon) d\epsilon}. \quad (3.7)$$

where  $\rho_d$  represents the PDOS.

### 3.3 Results and Discussion

#### 3.3.1 DRM Intermediates on $\text{Co}_3\text{Mo}_3\text{N}(111)$ and Site Preference

The optimized surface bound intermediates  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  at their preferred locations on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  are shown in Figure 3.2. The binding energies (**BE**) and their preferred binding sites are listed in Table 3.2, along with the **BE** values on  $\text{Co}(0001)$  and  $\text{Mo}_2\text{N}(110)$ . The optimized structures on  $\text{Co}(0001)$  and  $\text{Mo}_2\text{N}(110)$  are illustrated in Figure A.1-A.2 in ESI.

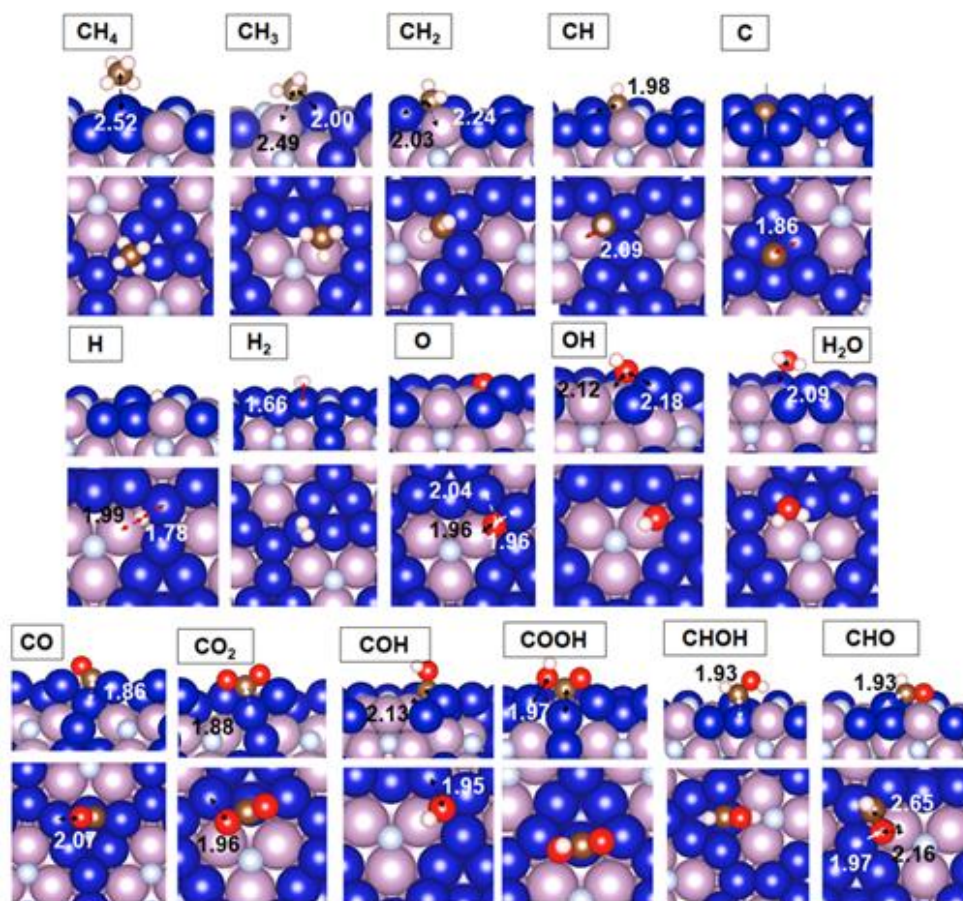


Figure 3.2. Optimized structures of the DRM intermediates on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . Atomic distances (in Å) are shown in dashed lines. The C, O, H, Co, Mo, and N atoms are depicted in brown, red, white, dark blue, pink, and light blue, respectively.

Table 3.2. Binding energies ( $BE$  in eV) and the preferred binding sites on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ ,  $\text{Co}(0001)$ , and  $\text{Mo}_2\text{N}(110)$ .

| Species       | <b><math>\text{Co}_3\text{Mo}_3\text{N}(111)</math></b> |       | <b><math>\text{Co}(0001)</math></b> |       | <b><math>\text{Mo}_2\text{N}(110)</math></b> |       |
|---------------|---------------------------------------------------------|-------|-------------------------------------|-------|----------------------------------------------|-------|
|               | Binding site                                            | $BE$  | Binding site                        | $BE$  | Binding site                                 | $BE$  |
| $\text{CH}_4$ | $\text{T}_{\text{Co}_1}$                                | -0.08 | NP                                  | -0.06 | NP                                           | -0.01 |

|                  |                             |       |        |       |        |       |
|------------------|-----------------------------|-------|--------|-------|--------|-------|
| CH <sub>3</sub>  | T <sub>Co<sub>1</sub></sub> | -1.93 | fcc    | -1.98 | fcc    | -3.01 |
| CH <sub>2</sub>  | B <sub>2</sub>              | -4.49 | hcp    | -4.04 | fcc    | -5.22 |
| CH               | B <sub>2</sub>              | -7.07 | hcp    | -6.39 | fcc    | -7.41 |
| C                | hcp <sub>1</sub>            | -7.97 | hcp    | -7.04 | hcp    | -8.33 |
| H <sub>2</sub>   | T <sub>Co<sub>1</sub></sub> | -0.39 | -      | -     | -      | -     |
| H                | B <sub>2</sub>              | -2.87 | fcc    | -2.82 | fcc    | -3.31 |
| O                | B <sub>2</sub>              | -6.22 | hcp    | -5.77 | fcc    | -7.71 |
| OH               | B <sub>1</sub>              | -3.80 | fcc    | -3.48 | fcc    | -4.78 |
| H <sub>2</sub> O | T <sub>Co<sub>1</sub></sub> | -0.67 | top    | -0.30 | top    | -0.77 |
| CO               | T <sub>Co<sub>3</sub></sub> | -1.99 | hcp    | -1.69 | hcp    | -2.54 |
| CO <sub>2</sub>  | T <sub>Co<sub>3</sub></sub> | -1.50 | hcp    | -0.05 | bridge | -0.82 |
| COH              | B <sub>2</sub>              | -4.70 | hcp    | -4.33 | fcc    | -5.13 |
| CHO              | B <sub>2</sub>              | -3.04 | bridge | -2.21 | hcp    | -3.17 |
| COOH             | T <sub>Co<sub>3</sub></sub> | -2.82 | bridge | -2.29 | hcp    | -3.47 |
| CHOH             | T <sub>Co<sub>3</sub></sub> | -4.27 | fcc    | -3.77 | hcp    | -4.52 |

---

Molecular CH<sub>4</sub> prefers the T<sub>Co<sub>1</sub></sub> site, with a binding energy of -0.08 eV. This value is on a similar order of magnitude to the adsorption of closed-shell, nonpolar species on metal or metalloid surfaces. Still, as shown in Table 3.2, CH<sub>4</sub> binds slightly stronger than on Co(0001) and Mo<sub>2</sub>N. Similar to CO<sub>2</sub>, CO also prefers the T<sub>Co<sub>3</sub></sub> site, with a binding energy of -1.99 eV. However, unlike CH<sub>4</sub> and CO<sub>2</sub>, both H and CO bind stronger than on Co(0001) but weaker than on Mo<sub>2</sub>N(110).



The carbonaceous  $\text{CH}_x$  intermediates (i.e.,  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ , and  $\text{C}$ ) prefer the  $\text{T}_{\text{Co}_1}$ ,  $\text{B}_2$ ,  $\text{B}_2$ , and  $\text{hcp}_1$  site, respectively. In fact for  $\text{CH}_x$ , a similar pattern has been observed elsewhere by Kua and Goddard on  $\text{Pt}(111)$ . [205] The geometric interpretation of such site preferences is that  $\text{CH}_x$  ( $x = 0 - 3$ ) favors the site that would satisfy the valence of the central C atom in  $\text{CH}_x$ . Similar to H and CO,  $\text{CH}_x$  (except for  $\text{CH}_3$ ) species continue a trend where the binding energies are weaker on  $\text{Co}(0001)$ , but stronger on  $\text{Mo}_2\text{N}(110)$ .

The O, OH, and  $\text{H}_2\text{O}$  species prefer the respective  $\text{B}_2$ ,  $\text{B}_1$ , and  $\text{T}_{\text{Co}_1}$  site. For the oxygenated carbon species, CHO prefers the  $\text{B}_2$  site, whereas the primary binding sites for COH, COOH, and CHOH are  $\text{B}_2$ ,  $\text{T}_{\text{Co}_3}$ , and  $\text{T}_{\text{Co}_3}$ , respectively. The binding energies of all above species also follow the order of  $\text{Mo}_2\text{N}(110) > \text{Co}_3\text{Mo}_3\text{N}(111) > \text{Co}(0001)$ .  $\text{N}(110)$ . At the  $\text{T}_{\text{Co}_1}$  site, the distance (2.52 Å) between  $\text{CH}_4$  and the surface (a surface Co site) is the shortest. Electronically, the stronger  $\text{CH}_4$  binding can be associated with the negatively charged, undercoordinated  $\text{Co}_1$  site that facilitates electron back donation to the  $\text{CH}_4$  anti-bonding orbitals.

$\text{CO}_2$  prefers the  $\text{T}_{\text{Co}_3}$  site and also binds stronger (-1.50 eV) than on both  $\text{Co}(0001)$  and  $\text{Mo}_2\text{N}(110)$ . The chemisorbed  $\text{CO}_2$  structure is bent; as illustrated in Figure 3.2, its C atom is located at the  $\text{T}_{\text{Co}_3}$  site, and the two O atoms bind at the two neighboring  $\text{T}_{\text{Co}_1}$  sites.

Molecular  $\text{H}_2$  prefers the  $\text{T}_{\text{Co}_1}$  site with a binding energy of -0.39 eV. The dissociation of  $\text{H}_2$  is facile, then the dissociated H atom migrates to the  $\text{B}_2$

Based on their site preferences (Figure 3.2), it is evident that DRM intermediates (except for C) predominantly occupy two types of active sites: (1) the negatively charged Co sites ( $\text{T}_{\text{Co}_1}$  or  $\text{T}_{\text{Co}_3}$ ) for  $\text{CH}_4$ ,  $\text{CH}_3$ ,  $\text{H}_2$ , CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , CHOH, and COOH; and (2) the boundary sites ( $\text{B}_1$  or  $\text{B}_2$ ) for H, O, OH, CH,  $\text{CH}_2$ , COH, and CHO. Interestingly, we observed that all the reactants and products prefer one of the two Co sites:  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$  on the  $\text{T}_{\text{Co}_1}$  site, while CO and  $\text{CO}_2$  on

the  $T_{Co_3}$  site. On the other hand, the reaction intermediates are more likely to occupy along the Co and Mo domain boundaries. Hence, the variety of  $Co_3Mo_3N(111)$  surface sites enables the fine differentiation of the site preference that potentially benefit DRM in terms of mitigating active site competition blockage.

The tuning of binding energies due to the electronic effects in alloys (including  $Co_3Mo_3N$ ) is well-known and also crucial in catalytic applications such as  $NH_3$  synthesis. [197] As reported in Table 3.2, we noted a familiar alloying effect for DRM catalysis as well, that is, a majority of DRM intermediates bind stronger on  $Mo_2N(110)$  but weaker on  $Co(0001)$  relative to  $Co_3Mo_3N(111)$ , except for  $CH_4$ ,  $CH_3$ ,  $CO_2$ . In this case, stronger adsorptions of  $CO_2$  ( $T_{Co_3}$ ) and  $CH_4$  ( $T_{Co_1}$ ), particularly the latter, will favor the conversions of both chemically inert molecules thermodynamically.

Last, the binding energies of reaction intermediates on  $Co_3Mo_3N(111)$  are also put to comparison with  $Ni(111)$ ,  $Ni(100)$ , and  $Ni(211)$  as the benchmark systems. [206] Again, the stronger adsorptions of  $CH_4$  and  $CO_2$  on  $Co_3Mo_3N(111)$  are considered as an enhancement favoring DRM. Among the reaction intermediates, only the atomic O binds notably stronger on  $Co_3Mo_3N(111)$  than on all three Ni facets. The remaining  $CH_xO$ ,  $CH_x$ , and OH bind similarly to the most active sites among all facets. Overall, we anticipate that the energetics the reaction routes will unlikely be very different from Ni. For the products, the bindings of  $H_2$  and CO are also comparable to those on Ni; [206] thus, CO poisoning will not be a serious concern. However,  $H_2O$ , a side product of DRM, does bind stronger on  $Co_3Mo_3N(111)$ .

### 3.3.2 Elementary DRM Steps on Co<sub>3</sub>Mo<sub>3</sub>N(111)

A total of 25 elementary steps can be adapted from Scheme 3.1 to characterize DRM. The associated reaction energies ( $\Delta E$ ) and energy barriers ( $E_a$ ) from DFT calculations are summarized in Table 3.3, with the TS structures depicted in Figure 3.3. In addition, TS structures on Co(0001) and Mo<sub>2</sub>N(110) are shown in Figures A.3 and A.4 in the accompanying ESI.

Table 3.3. Reaction energies ( $\Delta E$  in eV) and energy barriers ( $E_a$  in eV) on Co<sub>3</sub>Mo<sub>3</sub>N(111), Co(0001), and Mo<sub>2</sub>N(110).

| Elementary step |                                                                        | Co <sub>3</sub> Mo <sub>3</sub> N(111) |       | Co(0001)   |       | Mo <sub>2</sub> N(110) |       |
|-----------------|------------------------------------------------------------------------|----------------------------------------|-------|------------|-------|------------------------|-------|
|                 |                                                                        | $\Delta E$                             | $E_a$ | $\Delta E$ | $E_a$ | $\Delta E$             | $E_a$ |
| R1              | CH <sub>4</sub> (g) + 2* $\leftrightarrow$ CH <sub>3</sub> * + H*      | -0.08                                  | 0.65  | 0.01       | 1.02  | -1.60                  | 0.51  |
| R2              | CH <sub>4</sub> (g) + O* + * $\leftrightarrow$ CH <sub>3</sub> * + OH* | 0.60                                   | 0.97  | 0.36       | 1.60  | -0.08                  | 1.89  |
| R3              | CH <sub>3</sub> * + * $\leftrightarrow$ CH <sub>2</sub> * + H*         | -0.46                                  | 0.51  | 0.13       | 0.72  | -0.12                  | 0.85  |
| R4              | CH <sub>2</sub> * + * $\leftrightarrow$ CH* + H*                       | -0.63                                  | 0.16  | -0.33      | 0.22  | -0.66                  | 0.40  |
| R5              | CH* + * $\leftrightarrow$ C* + H*                                      | -0.02                                  | 0.96  | 0.40       | 1.13  | -0.14                  | 1.11  |
| R6              | CO <sub>2</sub> (g) + * $\leftrightarrow$ CO <sub>2</sub> *            | -1.52                                  | -     | -0.05      | -     | -0.82                  | -     |
| R7              | CO <sub>2</sub> * + * $\leftrightarrow$ CO* + O*                       | -0.50                                  | 0.69  | -1.03      | 0.46  | -3.13                  | 0.10  |
| R8              | C* + O* $\leftrightarrow$ CO* + *                                      | 0.72                                   | 2.11  | -0.57      | 1.84  | 1.14                   | 2.76  |
| R9              | H* + O* $\leftrightarrow$ OH* + *                                      | 0.67                                   | 1.38  | 0.35       | 1.27  | 1.51                   | 1.99  |
| R10             | C* + OH* $\leftrightarrow$ COH* + *                                    | 0.86                                   | 1.38  | -0.14      | 1.75  | 0.99                   | 2.26  |
| R11             | COH* + * $\leftrightarrow$ CO* + H*                                    | -0.81                                  | 0.71  | -0.79      | 0.99  | -1.36                  | 1.27  |
| R12             | CH* + O* $\leftrightarrow$ CHO* + *                                    | 1.34                                   | 1.65  | 0.90       | 1.59  | 1.95                   | 2.13  |
| R13             | CHO* + * $\leftrightarrow$ CO* + H*                                    | -0.64                                  | 0.40  | -1.08      | 0.14  | -0.96                  | 0.76  |
| R14             | CH* + OH* $\leftrightarrow$ CHOH* + *                                  | 1.57                                   | 1.95  | 0.93       | 1.51  | 2.17                   | 2.56  |

|     |                                                                          |       |      |       |      |       |      |
|-----|--------------------------------------------------------------------------|-------|------|-------|------|-------|------|
| R15 | $\text{CHOH}^* + * \leftrightarrow \text{CHO}^* + \text{H}^*$            | -0.91 | 0.54 | -     | -    | -1.73 | 0.41 |
| R16 | $\text{CHOH}^* + * \leftrightarrow \text{COH}^* + \text{H}^*$            | -0.73 | 0.23 | -     | -    | -1.32 | -    |
| R17 | $\text{CO}_2^* + \text{H}^* \leftrightarrow \text{COOH}^* + *$           | 1.28  | 1.43 | 0.23  | 1.38 | 0.37  | 0.93 |
| R18 | $\text{CO}_2^* + \text{OH}^* \leftrightarrow \text{COOH}^* + \text{O}^*$ | 0.61  | 0.98 | -0.12 | 1.06 | -     | -    |
| R19 | $\text{COOH}^* + * \leftrightarrow \text{CO}^* + \text{OH}^*$            | -1.11 | 0.44 | -0.98 | 0.24 | -1.99 | 0.28 |
| R20 | $\text{CO}_2^* + \text{C}^* \leftrightarrow 2\text{CO}^*$                | 0.21  | 1.80 | -1.68 | 1.78 | -1.99 | 1.42 |
| R21 | $\text{CO}^* \leftrightarrow \text{CO (g)} + *$                          | 1.99  | -    | 1.69  | -    | 2.54  | -    |
| R22 | $2\text{H}^* \leftrightarrow 2* + \text{H}_2 \text{ (g)}$                | 1.26  | -    | 1.09  | -    | 2.13  | -    |
| R23 | $\text{H}^* + \text{OH}^* \leftrightarrow \text{H}_2\text{O (g)} + 2*$   | 1.29  | -    | 0.85  | -    | 2.71  | -    |

### 3.3.2.1 CH<sub>4</sub> Activation

Both direct and O-assisted C–H bond activation of CH<sub>4</sub>, as the RLS for DRM, were considered for DFT calculations. Xing *et al.* [207] reported that CH<sub>4</sub> dissociation can be promoted on O-covered IB group metals (e.g., Cu, Ag, Au). Most recently, the C–H bond activation were extended over transition metal-based facets, clusters, complexes, and oxides by Latimer and coworkers, [208] who revealed a linear correlation between the C–H bond activation energies and the cohesive energies of respective materials.

**Direct CH<sub>4</sub> activation ( $\text{CH}_4 + 2* \rightarrow \text{CH}_3^* + \text{H}^*$ ):** In R1, CH<sub>4</sub> was treated as a loosely bound molecule, due to its weak binding (-0.08 eV), prior to activation. The  $\Delta E$  and  $E_a$  are -0.08 eV and 0.65 eV, respectively, producing CH<sub>3</sub> (T<sub>Co1</sub>) and H (B2). As illustrated in Figure 3.3 (TS1), the C–H bond activation occurs at the T<sub>Co1</sub> site, also preferred by the initial CH<sub>4</sub> adsorption. Also, in Figure 3.3 (TS1), the C–H bond length in the TS is stretched to 1.66 Å. This barrier is significantly higher than on Mo<sub>2</sub>N(110), but much lower than on Co(0001), as well as Pt (1.01 eV), [209] Ni(111) (0.91 eV), [206, 210] and Ni bimetallic alloys. [211]

**O-Assisted CH<sub>4</sub> activation ( $CH_4 + O^* \rightarrow CH_3^* + OH^*$ ):** The pre-adsorbed O species may participate in the abstraction of H from hydrocarbons to assist C–H bond activation (R2). As illustrated in Figure 3.3 (TS2), the participating O needs to move closer to the H by migrating from its preferred B<sub>2</sub> site to the B<sub>1</sub> site. The O–H distance decreases from 2.55 Å in the IS to 1.15 Å. DFT calculations showed that the O-assisted step is more endothermic (0.60 eV) than R1, with a barrier of 0.97 eV. A comparison between the direct and O-assisted C–H activation is also displayed in Figure 3.4 a. The higher C–H bond activation barrier can be attributed to the nonacidic nature of the C–H bond, and the energy compensation to displace O from its preferred site in the TS structure.

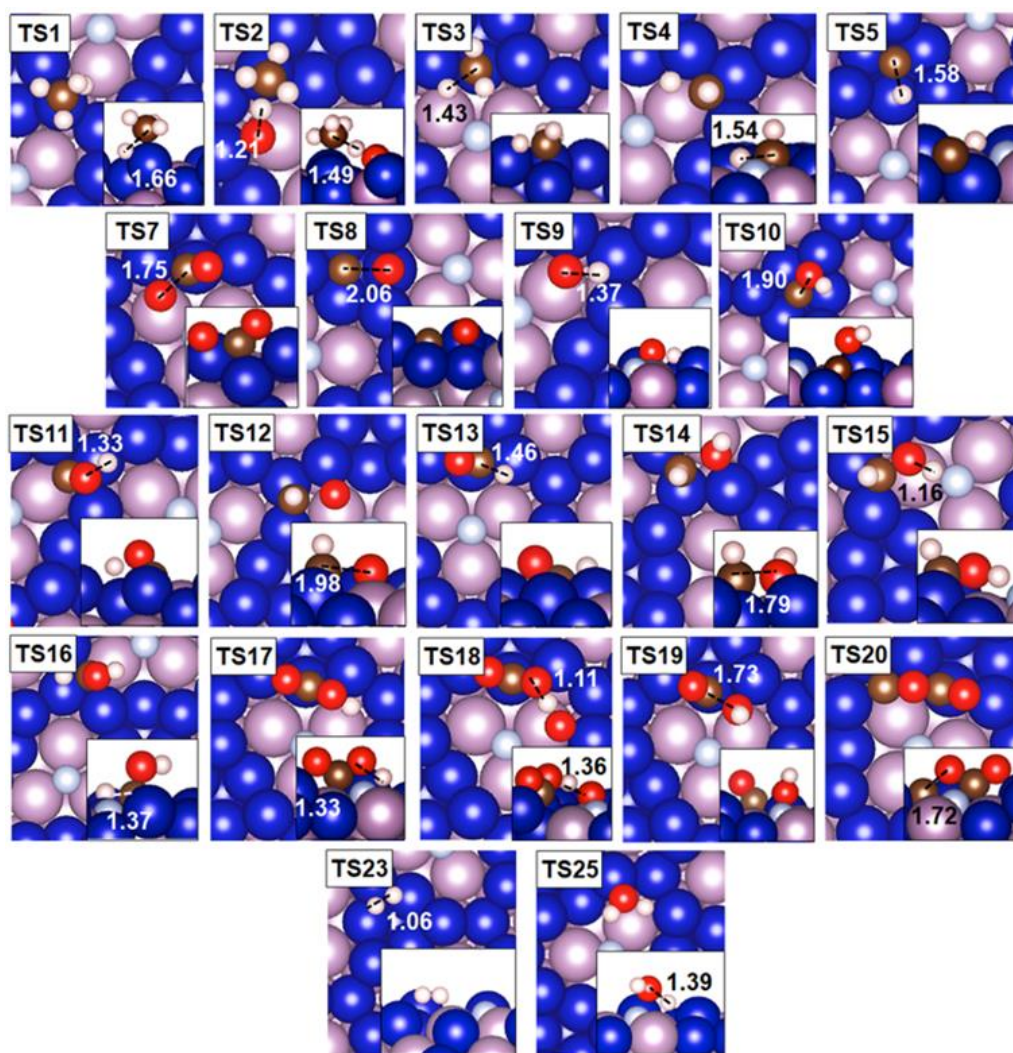


Figure 3.3. Optimized transition state structures (corresponding to the elementary steps in Table 3) on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . Side views are shown as the inset figure. The C, O, H, Co, Mo, and N atoms are depicted in brown, red, white, dark blue, dark pink, and light blue, respectively. Atomic distances (in Å) are shown in dashed lines.

**$\text{CH}_x$  decomposition ( $\text{CH}_x \rightarrow \text{CH}_{x-1}^* + \text{H}^*$ ):** The decompositions of  $\text{CH}_3$  and  $\text{CH}_2$  (R3 and R4) occur with quite modest energy barriers at 0.51 and 0.16 eV, respectively. Facile  $\text{CH}_3$  and  $\text{CH}_2$  dissociation following the initial  $\text{CH}_4$  activation is common, e.g., on Ni catalysts. [209-212] The energy barrier for CH decomposition (R5), however, increases substantially to 0.96 eV. Therefore,

we anticipate that the CH could be a relevant species to CO formation. From the above analysis, a lumped CH<sub>4</sub> activation step was used in lieu of an explicit CH<sub>4</sub> decomposition sequence, with the overall kinetics determined by the energy barrier for the first C–H bond dissociation (see Appendix A in ESI).

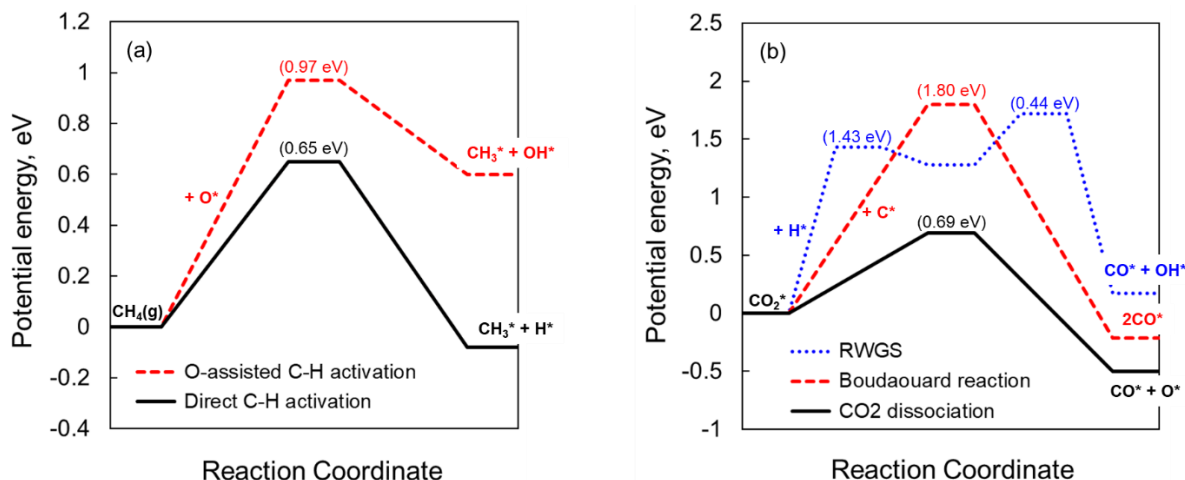


Figure 3.4. Potential energy profiles for (a) direct (black) and O-assisted (red) C–H bond activation; (b) direct (black), H-assisted (blue), and C-assisted (red) CO<sub>2</sub> activation pathways on Co<sub>3</sub>Mo<sub>3</sub>N(111). The energy barriers are labeled in parentheses.

### 3.3.2.2 CO<sub>2</sub> Activation

Three CO<sub>2</sub> activation pathways, the direct, H-assisted, and C-assisted, were considered.

**Direct CO<sub>2</sub> activation ( $\text{CO}_2^* + * \rightarrow \text{CO}^* + \text{O}^*$ ):** On Co<sub>3</sub>Mo<sub>3</sub>N(111), R7 is moderately exothermic (-0.50 eV) with an energy barrier of 0.69 eV, with the C–O bond elongated to 1.75 Å (TS7). This barrier (0.69 eV) is similar to that (0.67 eV) on Ni(111), [206, 210] but lower than on Pt(111) (1.81 eV [209, 213]) and on NiSn [214].

**H-Assisted CO<sub>2</sub> activation ( $\text{CO}_2^* + \text{H}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}^* + \text{OH}^*$ ):** The H-assisted CO<sub>2</sub> activation (R17) is a critical step in RWGS, [215-217] in which H species (originating from CH<sub>4</sub> decomposition) is utilized to convert CO<sub>2</sub> into a carboxyl (COOH). However, on Co<sub>3</sub>Mo<sub>3</sub>N(111), the R17 step is quite endothermic (1.28 eV in Table 3.3). In addition, an energy barrier of 1.43 eV is required to enable the O–H bond formation. This barrier is much higher than that on Ni(111) (1.13 eV [206, 210]) and on Pt(111) (0.75 eV [209]), respectively. Once COOH is formed, the C–O bond cleavage (R19) is rather exothermic (-1.11 eV) with a modest barrier of 0.44 eV.

**Reverse Boudouard reaction ( $\text{CO}_2^* + \text{C}^* \rightarrow 2\text{CO}^*$ ):** The reverse Boudouard process (R20) converts solid carbon into CO using CO<sub>2</sub> as the co-reactant. On Co<sub>3</sub>Mo<sub>3</sub>N(111), R20 is moderately endothermic (0.21 eV), versus Eqn. (3.3). Nevertheless, the energy barrier is prohibitively high at 1.80 eV when compared to Ni(111), i.e., 1.13 eV. [218]

The potential energy profiles depicting the three routes are summarized in Figure 3.4b. The direct reaction pathway is clearly is the most competitive route for C–O bond cleavage and will be adopted to represent for CO<sub>2</sub> activation in the microkinetic model.

**C and CH oxidation by O and OH.** The oxidation pathways of C and CH species are less straightforward than CH<sub>4</sub> and CO<sub>2</sub> dissociations. Here, four pathways converting C and CH into CO were considered.

**Direct C oxidation ( $\text{C}^* + \text{O}^* \rightarrow \text{CO}^*$ ):** CO formation via the combination of atomic C and O (R8) takes place at the T<sub>Co<sub>3</sub></sub> site and requires both atoms to migrate from their respective hcp<sub>1</sub> and B<sub>2</sub> sites to T<sub>Co<sub>3</sub></sub> for C–O bond formation. This process is quite endothermic (0.72 eV) with a high energy barrier of 2.11 eV.

**C oxidation via COH ( $\text{C}^* + \text{OH}^* \rightarrow \text{COH}^* + * \rightarrow \text{CO}^* + \text{H}^*$ ):** An alternative path is to enable the C–O bond formation via the COH intermediate (R10), which then decomposes into CO and H



(R11). The  $\Delta E$  and  $E_a$  are 0.86 eV and 1.38 eV, respectively. The O–H bond cleavage is exothermic (-0.81 eV) with an energy barrier of 0.71 eV. The only limitation to this oxidation route is the surface concentration of OH species, which is produced from R9, with  $\Delta E$  and  $E_a$  being 0.67 eV and 1.38 eV, respectively.

**CH oxidation via CHO** ( $CH^* + O^* \rightarrow CHO^* + * \rightarrow CO^* + H^*$ ): CH from incomplete  $CH_4$  decomposition can be oxidized by O via the formyl (CHO) intermediate as in R12. This step is quite endothermic (1.34 eV) and will need to overcome an energy barrier of 1.65 eV for C–O bond formation. Still, the energy barrier related to CHO formation is lower than R8. The dissociation of CHO into CO and H is an exothermic step (-0.64 eV), with an energy barrier of 0.40 eV.

**CH oxidation via CHOH** ( $CH^* + OH^* \rightarrow CH-OH^* + * \rightarrow CHO^*(COH^*) + H^* \rightarrow CO^* + 2H^*$ ): Like C, CH can also be oxidized by OH via R14. However, the formation of CHOH is highly endothermic (1.57 eV), with a prohibitive energy barrier of 1.95 eV. The subsequent CHOH decomposition forming CHO is exothermic (-0.91 eV) with a moderate energy barrier of 0.54 eV. Alternatively, CHOH can form COH and H via C–H bond scission (R16), which is exothermic (-0.73 eV) with a low energy barrier (0.23 eV).

Based on DFT calculations, the RLS for all oxidation elementary steps involve the C–O bond formation.

### 3.3.2.3 Coke Formation

The sources of coke formation are frequently attributed to  $CH_4$  cracking and Boudouard reaction. [219] According to Nikoo and Amin, [220]  $CH_4$  cracking is favored over the Boudouard reaction between 900 K and 1273 K. On  $Co_3Mo_3N(111)$ , the Boudouard reaction (reverse of R20 in Table 3.3) proceeds with a very high energy barrier 1.80 eV. Here, we focused on CH dissociation (R5) and CO decomposition (R8), both of which have lower energy barriers (0.96 eV

and 1.39 eV) than that in the Boudouard pathway. With the CO desorption energy of 0.13 eV on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ , the likelihood of CO decomposition (R8) is much diminished, as CO is more likely to desorb. Hence,  $\text{CH}_4$  decomposition will be considered as the main mechanism for coke formation on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ .

According to Bradford and Vannice, [59] carbon diffusion resulting in coke formation is sensitive to catalyst structures, especially the presence of large ensemble of metallic sites. Because the  $\text{Co}_3\text{Mo}_3\text{N}(111)$  facet is dominated by interspersed Co and  $\text{Mo}_3\text{N}$  domains, large and continuous metallic domains for coke formation are absent. The electronic structures modulated by the interactions between the Co and  $\text{Mo}_3\text{N}$  domains also suppress coke formation. On  $\text{Co}_3\text{Mo}_3\text{N}(111)$ , the most preferred binding site for C is hcp1 with a binding energy of -7.97 eV. A stronger carbon binding on  $\text{Mo}_2\text{N}(110)$  indicates that, on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ , C atom likely prefers the  $\text{Mo}_3\text{N}$  over the Co domain. However, the top layer N species at the Mo hcp site blocks the access of carbon, hence, C binds at a secondary binding site ( $\text{hcp}_1$ ). As a result, carbon binding is weakened on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . Figure 3.5 illustrates four possible carbon removal pathways on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  versus C–C bond formation producing the  $\text{C}_2$  aggregates. We observed that the oxidation of C by OH should be the most competitive against C–C bond formation with the lowest energy barrier (1.38 eV versus 1.90 eV).

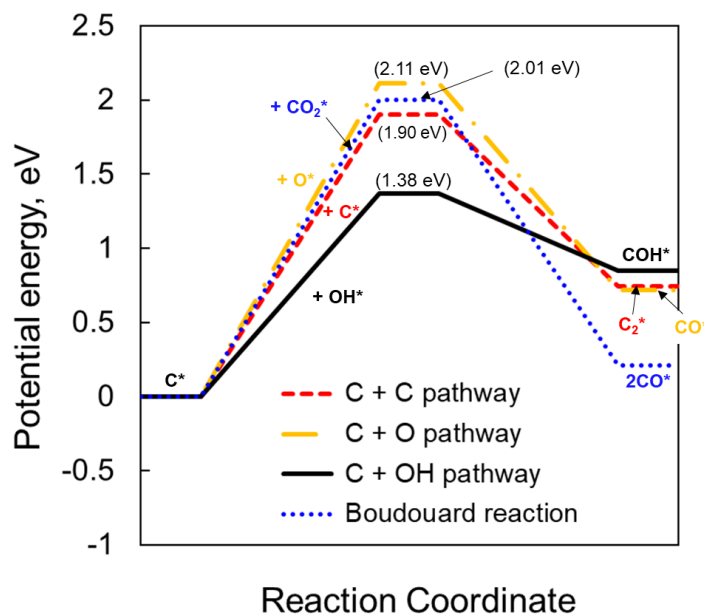


Figure 3.5. Coke formation pathway versus carbon removal pathways on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ .

### 3.3.2.4 DRM Pathways on $\text{Co}_3\text{Mo}_3\text{N}(111)$

Figure 3.6 graphically depicts the free energy profile (at 973.15 K and 1 bar) of the DRM processes on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  based on the above analysis of DFT calculations. By adopting Scheme 3.1, we emphasize the parallel  $\text{CH}_4$  and  $\text{CO}_2$  conversion pathways (distinguished by respective solid purple and dashed gold lines) at the initial stage. It is evident that the initial  $\text{CH}_4$  C–H bond activation is the RLS. In comparison, subsequent  $\text{CH}_x$  decompositions follow free energy downhill upon the initial activation, while the  $\text{CO}_2$  dissociation free energy profile is much lower. The release of CO and  $\text{H}_2$  as the gas phase products also follow steep free energy downhill due to significant entropy gains. The multiple CH or C oxidation pathways are also displayed. According to Figure 3.6, indeed, the  $\text{CH} \rightarrow \text{CHO} \rightarrow \text{CO}$  (blue) and  $\text{C} \rightarrow \text{COH} \rightarrow \text{CO}$  (pink) routes are more competitive than the direct C oxidation and CHOH pathways. In fact, the conversions of

C and CH, as the most abundant carbonaceous species, still resemble the oxidation pathways proposed on transition metal DRM catalysts. [59]

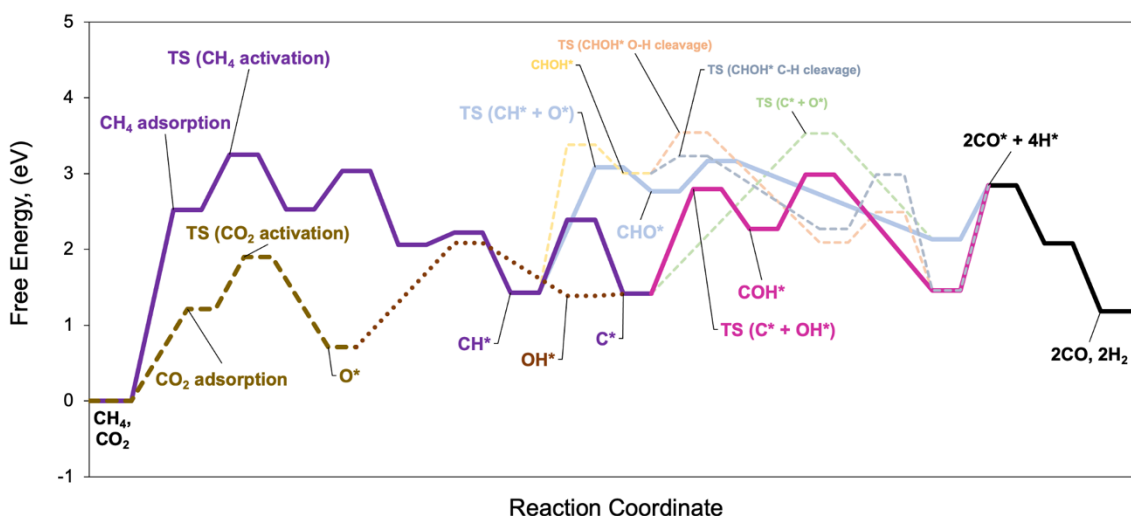


Figure 3.6. The free energy profiles depicting DRM on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  - generated at 973.15 K and 1 bar. Gas phase  $\text{CO}_2$  and  $\text{CH}_4$  and clean surfaces are used as zero energy references. The main DRM routes are highlighted by thick lines including  $\text{CO}_2$  (and subsequent OH formation) and  $\text{CH}_4$  dissociation; C, CH oxidation via respective COH and CHO intermediates; and CO,  $\text{H}_2$  formation that are illustrated in gold, purple, pink, blue, and black, respectively. The less competitive pathways (e.g., CHOH formation and subsequent C–H and O–H bond dissociation) are represented in thin dashed or dotted lines.

DFT calculations revealed that the sites in the  $\text{Co}_3\text{Mo}_3\text{N}$  Co domain can support parallel activations of  $\text{CH}_4$  and  $\text{CO}_2$  at two distinct sites; meanwhile, the bridge (Co–Mo) and hcp<sub>1</sub> sites permit C/CH oxidation to proceed without interference. Hence, the dual-site configuration in

Co<sub>3</sub>Mo<sub>3</sub>N(111) not only mitigates the site crowding and competition, but also allows both C–H activation and C–O bond formation to occur at their favoured sites.

The performance of DRM on Co(0001) and Mo<sub>2</sub>N(110) surfaces was also evaluated to better understand the synergy effect in Co<sub>3</sub>Mo<sub>3</sub>N(111). In Figure A.5, the DRM consisting of only CH<sub>4</sub> activation and the most competitive CH oxidation pathways were shown, with the activation of CO<sub>2</sub> shown in a separate inset figure. On Co(0001) and Mo<sub>2</sub>N(110), the C–H bond activation occurs at the T<sub>Mo</sub> and T<sub>Co</sub> sites, respectively. The C–H bond activation on Mo<sub>2</sub>N(110) is more exothermic (-1.60 eV), with a lower energy barrier (0.51 eV) than on Co<sub>3</sub>Mo<sub>3</sub>N(111). Still, the O-assisted C–H activations of CH<sub>4</sub> on Co(0001) and Mo<sub>2</sub>N(110) are not as competitive according to DFT calculations. This actually coincides with prior theoretical works, which already suggested that the C–H activation can sometimes be inhibited by the O and OH intermediates. [216, 221, 222]

The direct CO<sub>2</sub> dissociations on both Co(0001) and Mo<sub>2</sub>N(110) proceed with lower energy barriers. This process is particularly facile on Mo<sub>2</sub>N(110) with a barrier of only 0.10 eV. Morales-Salvador *et al.* [223] also suggested that Mo<sub>2</sub>N is highly reactive toward CO<sub>2</sub> activation. In contrast, Co(0001) is more inert with an energy barrier of 0.46 eV. The binding energy of CO<sub>2</sub> on Co obtained by Wang and co-workers is -0.04 eV, [224] in good agreement with this work (-0.05 eV in Table 3.3). Wang *et al.* [225] stated that the CO<sub>2</sub> binding strength correlates with the corresponding *d*-band center of on transition metal surfaces. By extrapolating this behavior to the T<sub>Co<sub>3</sub></sub> site in Co<sub>3</sub>Mo<sub>3</sub>N(111), the *d*-band of Co<sub>3</sub> atom on Co<sub>3</sub>Mo<sub>3</sub>N(111) is closer to the Fermi level. Also, Co<sub>3</sub> is more negatively charged than the Co atoms in Co(0001). Both factors result in more active Co sites in Co<sub>3</sub>Mo<sub>3</sub>N(111) than Co(0001) for CO<sub>2</sub> activation, and will ultimately favor DRM.

Facile CO<sub>2</sub> and CH<sub>4</sub> activations occur on Mo<sub>2</sub>N(110) based on DFT calculations. In principle, this surface may be susceptible to either coking related to strong C and CH binding, [79] or the hindrance of O passivation. The most probable oxidation pathway on Co(0001) proceeds via the CH oxidation by OH, with a relatively low energy barrier of 1.51 eV, while all oxidation pathways are hindered on Mo<sub>2</sub>N(110) due to the high reaction barriers ( $> 2$  eV). Conclusively, as illustrated in Figure A.5, Mo<sub>2</sub>N is predicted to lose its activity much more rapidly than Co and Co<sub>3</sub>Mo<sub>3</sub>N.

### 3.3.3 Microkinetic Modeling of DRM on Co<sub>3</sub>Mo<sub>3</sub>N

The microkinetic model consists of 10 chemical species (i.e., CH<sub>4</sub>, H<sub>2</sub>, C, O, H, CH, OH, CO, H<sub>2</sub>O, and CO<sub>2</sub>) in 10 elementary steps (see Appendix A in ESI). CH<sub>x</sub> (x = 2-3) dissociations following the initial CH<sub>4</sub> activation are quasi-equilibrated and were lumped into a single CH<sub>4</sub> decomposition step, producing CH, C, and H<sub>2</sub>; while CO<sub>2</sub> activation produces CO and O directly. The carbonaceous species (CH and C) are converted into CO coupled with O and OH, respectively. A Mathematica script was developed according to Appendix A to obtain the TOF for CH<sub>4</sub> activation and surface coverage values at 1 bar and 973.15 K. The initial feed consists of equimolar CH<sub>4</sub> and CO<sub>2</sub> (i.e.,  $p_{CH_4} = p_{CO_2} = 0.5$  bar) at a molar flow rate of 1 mol/s. The composition for the exiting gas stream consisting of CO, H<sub>2</sub>, and H<sub>2</sub>O, and the unreacted CH<sub>4</sub>, CO<sub>2</sub>, is determined by the equilibrium constant for Eqn. (3.1). The predicted TOFs were estimated based on a 55% CH<sub>4</sub> conversion as the function of  $BE_C$  and  $BE_O$ .

As shown in Figure A.7(a-d), a series of linear scaling relationships were established to estimate  $BE_H$ ,  $BE_{CH}$ ,  $BE_{CO}$ , and  $BE_{OH}$  for H, CH, CO, and OH, as the key intermediates of the developed DRM microkinetic model. The qualities of linear scaling relationships and BEP are

indicated by MAE, MAX values as discussed by Zaffran and coworkers. [226-228] The binding energies of H ( $BE_H$ ) exhibit a high degree of correlation simultaneously with  $BE_C$  and  $BE_O$  (Figure A.7a), with a standard error of 0.11 eV. The corresponding parameters associated with  $BE_C$  and  $BE_O$  are  $0.16 \pm 0.09$  and  $0.12 \pm 0.10$  (both are unitless), respectively. Conventional linear scaling forms were adopted based on respective  $BE_C$  and  $BE_O$  for CH and OH according to Ref. [64]. [229] Unlike other transition metal surfaces, the binding sites for C and O are uniquely distributed in different  $\text{Co}_3\text{Mo}_3\text{N}(111)$  regimes, i.e., the Co and the boundary sites. The acquired slopes of  $0.76 \pm 0.07$  (Figure A.7b) and  $0.63 \pm 0.09$  (Figure A.7d) for the 12 surfaces are in reasonable agreement to the values of 0.75 and 0.50, [229] and thus remain faithful to the empirical formulation  $(n_{max} - n)/n$ , where  $n_{max}$  and  $n$  represent the maximum H atoms bonded to C and O to fulfill their valency and the actual H atoms attached these central atoms. Because CO prefers to bind with its carbon end on transition metal and metalloid surfaces; [230] and thus, a correlation between  $BE_{CO}$  and  $BE_C$  was attempted. As shown in Figure A.7c, a linear scaling relationship does exist between  $BE_{CO}$  and  $BE_C$ , with a slope of  $0.52 \pm 0.11$  and a  $R^2$  value of 0.92. Thus far, all key DRM intermediates appearing in the microkinetic model can be related to  $BE_C$  and  $BE_O$ .

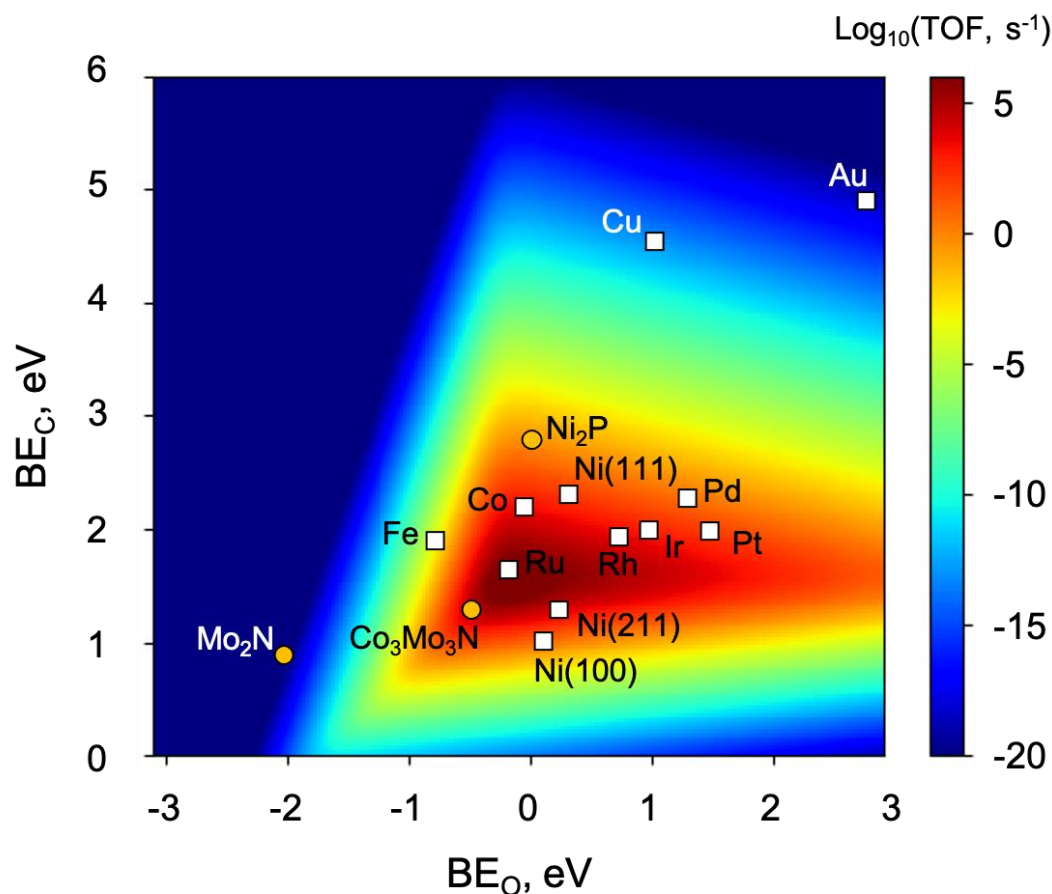


Figure 3.7. Predicted  $\text{Log}_{10}(\text{TOF})$  ( $\text{s}^{-1}$ ) for  $\text{CH}_4$  activation according to Eqn. A34, as a function of  $BE_C$  and  $BE_O$ . The volcano heat map was generated using the linear correlations presented in Eqns. (A54-A58) as described in the Supporting Information. Reaction conditions used in the microkinetic model:  $T = 973.15$  K,  $P = 1$  bar, 55%  $\text{CH}_4$  conversion,  $\text{CH}_4/\text{CO}_2$  ratio = 1:1 at a molar flow rate of 1 mol/s. The transition metals are represented by white squares, while nitrides and phosphide are represented by yellow circles. The data point for  $\text{Ni}_2\text{P}$  was estimated based on Ref. [231].

A descriptor-based microkinetic model based on  $BE_C$  and  $BE_O$  adopts both the linear scaling and Bronsted-Evans-Polanyi (BEP) relationships derived for the initial C–H bond



activation (see Figure A.8 in ESI). As indicated in Figure 3.7, a rather broad range of  $BE_O$  and  $BE_C$  values were covered with the chosen surfaces. Detailed reaction mechanism and the kinetic rate formulations are described in Appendix A.

The catalyst reactivities for both dual-site  $\text{Co}_3\text{Mo}_3\text{N}$  and single-site surfaces are characterized by the turnover frequencies (TOFs) of  $\text{CH}_4$  C–H bond activation. The trend describing the DRM rates is illustrated by the heatmap in Figure 3.7. The estimated  $\text{Log}_{10}(\text{TOF})$  values (in  $\text{s}^{-1}$ ) on 15 close-packed surfaces (including those of  $\text{Co}_3\text{Mo}_3\text{N}$ ,  $\text{Mo}_2\text{N}$ , and  $\text{Ni}_2\text{P}$ ) are explicitly identified on the heat map. The peak region encompasses Ru and  $\text{Co}_3\text{Mo}_3\text{N}$ . The majority of transition metals (e.g., Fe, Co, Ni, Rh, Ir, Pt, Pd) are dispersed in an area bounded by  $BE_C$  (1.0~2.8 eV) and  $BE_O$  (-0.9~1.5 eV). Au, Cu, and  $\text{Mo}_2\text{N}$  are located much further away corresponding to either much weaker or stronger  $BE_O$  and  $BE_C$  values. The microkinetic model predicts that Ru is among the most active single-site transition metals, followed by Co, Ni (both the 211 and 111 facets), and Rh; the next tier includes Ir, Pt, Pd, Ni(100), and Fe, with Cu and Au among the least active surfaces. This trend is reasonably consistent with the findings from Rostrup-Nielsen and Hansen, among other studies. [187, 232, 233]

The two metalloid catalysts,  $\text{Mo}_2\text{N}$  and  $\text{Ni}_2\text{P}$ , were also considered as single-site catalysts.  $\text{Mo}_2\text{N}$ , located in the lower left corner of Figure 3.7, is also significantly less active than most monofunctional transition metals, as well as  $\text{Co}_3\text{Mo}_3\text{N}$  according to Figure A.5.  $\text{Ni}_2\text{P}$ , reportedly an effective DRM catalyst resistant to carbon coking, [231] displays a competitive  $\text{Log}_{10}(\text{TOF})$ , similar to that of Pd or Pt thanks to moderate  $BE_C$  and  $BE_O$  on  $\text{Ni}_2\text{P}(0001)$ .

$\text{Co}_3\text{Mo}_3\text{N}(111)$  is adjacent to Ru on the heatmap in a close proximity to the activity peak of the volcano. The high  $\text{Log}_{10}(\text{TOF})$  exhibited on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  can be attributed to the unique dual-site configuration. From literature, conventional DRM catalysts often rely on functional metal

oxide supports (e.g., TiO<sub>2</sub>, [194, 195] ZrO<sub>2</sub>, [234] Ce/ZrO<sub>2</sub> [69]) to acquire the key functionality for CO<sub>2</sub> activation for carbon residual removal. [71] Relative to Ru on the heat map,  $BE_C$  and  $BE_O$  are both stronger on Co<sub>3</sub>Mo<sub>3</sub>N(111). On Co<sub>3</sub>Mo<sub>3</sub>N(111), the C and CH intermediates preferentially occupy the Co site, while the O and OH occupy the Co-MoN boundary site. Hence, CH<sub>4</sub> activation and carbon oxidation kinetics proceed at the respective Co and Mo<sub>3</sub>N domains simultaneously, which is an advantage for a catalyst consisting of a natural dual-site configuration.

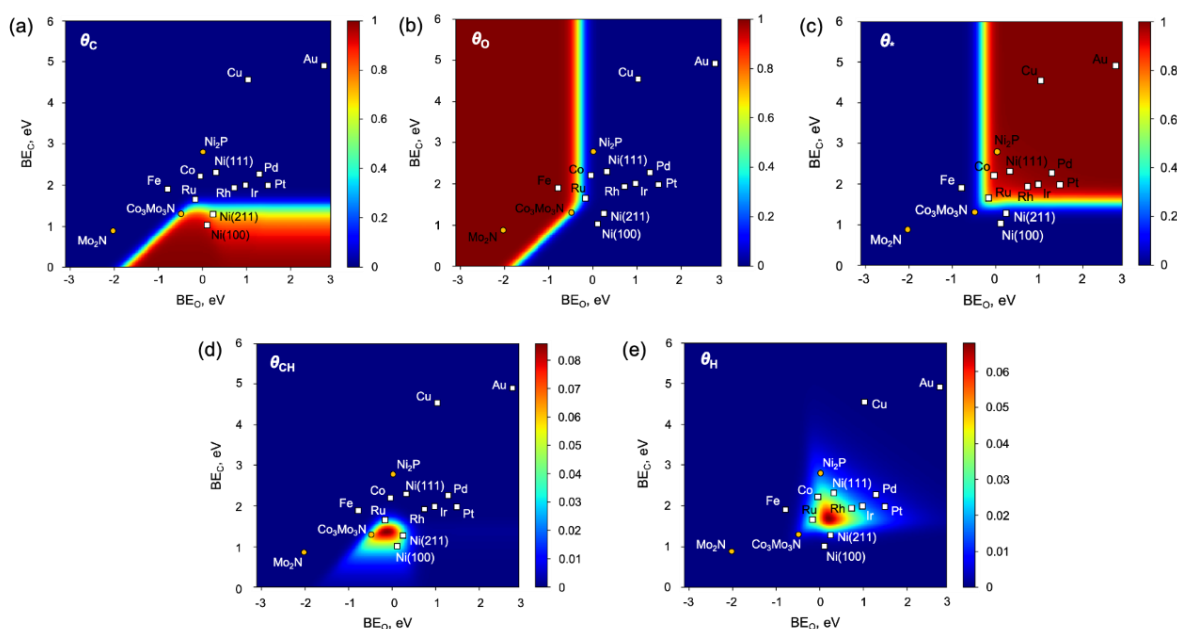


Figure 3.8. Predicted surface coverage for (a)  $\theta_C$ , (b)  $\theta_O$ , (c)  $\theta_*$ , (d)  $\theta_{CH}$ , and (e)  $\theta_H$  based on the same condition as in microkinetic modeling: T = 973.15 K, P = 1 bar, 55% CH<sub>4</sub> conversion, CH<sub>4</sub>/CO<sub>2</sub> ratio = 1:1 at a molar flow rate of 1 mol/s. The transition metals are represented by white squares, while nitrides and phosphide are represented by yellow circles.

The predicted coverages of key DRM intermediates (i.e., C, O, CH, H, and \*) from microkinetic modeling are summarized in Figure 3.8. Atomic C and O are shown to be the most

abundant surface intermediates (aka. MASIs). In Figure 3.8 a,  $\theta_C$  is relevant mainly in the bottom-right corner, i.e., the strong C binding regime ( $BE_C < 1.5$  eV). The absence of carbon coverage (in the lower left corner) suggests that strong O binding is able to counteract the dominance of C by occupying these active sites against C. This way, high  $\theta_O$  values are located on the left-hand side of the heatmap ( $BE_O < 0.2$  eV, see Figure 3.8b), a strong O binding region. Similarly, deep in the strong C binding region,  $\theta_O$  retreats and eventually yields to high  $\theta_C$  (Figure 3.8a) due to the competition from surface C species. The remaining area (Figure 3.8c) bounded at  $BE_C > 1.5$  eV and  $BE_O > 0.2$  eV corresponds to surfaces that are mostly adsorbate-free.

Based on  $BE_C$  and  $BE_O$ , the Sabatier principle dictating DRM suggests that too strong C or O binding may hinder the C–H bond activation due to active site blockage by C or O; while weak C or O binding results in intrinsically high activation barriers. For instance, when coupled with the predictions shown in Figure 3.7, the cause underlying low TOFs associated with Mo<sub>2</sub>N and Fe - due to the excessively high  $\theta_O$  (Figure 3.8a) - becomes evident. On clean Au(111) and Cu(111), the high C–H activation energy barriers reduce the TOF despite high open-site availability.

In fact, DRM rates on most close-packed surfaces shown in Figure 3.8a are not severely interfered by C species. Then, we focused on three Ni single crystal facets - (111), (100), and (211) - to validate the performance of the established DRM mechanism, as coking is a well-known issue specially on the low-coordinated Ni sites. [218] Using Figure 3.8a,  $\theta_C$  indeed follows a decreasing order of Ni(100) > Ni(211) > Ni(111), suggesting that, under current modeling conditions, coking only becomes a serious issue in the presence of low-coordination sites. We also noted that, as  $BE_C$  increases in the order of Ni(111) < Ni(211) < Ni(100), the TOFs of all three Ni facets can be projected onto the opposite sides of the volcano plot along the vertical direction (Figure 3.7).

Hence, despite similar magnitudes of TOF, low coordination Ni sites benefits from higher C—H activation rates while Ni(111) benefit from less hindrance of coke formation.

Due to stronger C binding on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  than on Ru, Co, Ni(111), as indicated in Figure 3.8a and Figure 3.8d, there are small fractions of C and CH on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  surface. Nevertheless,  $\text{Co}_3\text{Mo}_3\text{N}$  appears to tolerate such C presence. A plausible explanation is that: (i) C does not bind as strongly as on Ni(100); (ii) atomic O binds stronger than Ni, Ru, and Co. The left-shift of  $\text{Co}_3\text{Mo}_3\text{N}$  on the heatmap due to the latter is necessary to maintain sufficient active sites and sustain a high level of  $\text{CH}_4$  conversion.

Lastly, this work also suggests that a moderate  $\theta_{\text{C}}$  or  $\theta_{\text{O}}$  will not necessarily be detrimental to catalyst performance; and may even be beneficial to sustain the progression of DRM on the surface. However, the optimal surface conditions and the potential of co-catalyst related to reaction intermediates on catalyst surface should be more thoroughly and systematically explored.

### 3.4 Conclusions

DFT calculations were performed to elucidate the molecular mechanisms of DRM on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  so that the origins of its catalytic reactivity and coke resistance character can be understood. The proposed mechanism emphasizes initial parallel  $\text{CH}_4$  and  $\text{CO}_2$  activations, followed by oxidation and conversion of carbonaceous species into CO and  $\text{H}_2$ . The full mechanism revealed that  $\text{Co}_3\text{Mo}_3\text{N}(111)$  is capable of activating both inert molecules efficiently; and the dominant CO formation pathways proceed via the COH or CHO intermediates. DFT calculations revealed the varying site preferences for reaction intermediates at different catalytic regimes of  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . Generally,  $\text{CH}_4$  and  $\text{CO}_2$  activation favors the Co regime, while C oxidation and removal favor the boundary sites.

Trend analysis based on  $BE_C$  and  $BE_O$  (the catalytic descriptors) and linear scaling relationships confirmed that  $\text{Co}_3\text{Mo}_3\text{N}$  exhibits a superior DRM reactivity that is comparable to Ru. Also,  $\text{Co}_3\text{Mo}_3\text{N}$  performs significantly better than either of its single-site analogs (i.e.,  $\text{Mo}_2\text{N}$  and Co). Steady-state microkinetic modeling revealed that the electronic properties and a unique dual-site configuration collectively enable a high turnover rate for C–H bond activation on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  and higher tolerance for surface C species due to facile  $\text{CO}_2$  dissociation. It is also likely that the presence of moderate C and CH species help manage a moderate O coverage on the surface as well. The synergistic interactions between the Co- and Mo nitride regimes make  $\text{Co}_3\text{Mo}_3\text{N}$  a promising candidate for durable DRM.

#### **Author contributions**

Bin Liu conceptualized the project. Narges Manavi carried out the DFT calculations described in this paper and wrote the original draft. Bin Liu also participated in manuscript editing and revisions.

#### **Conflicts of interest**

There are no conflicts to declare.

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## **4 Mitigating Coke Formations for Dry Reforming of Methane on Dual-Site Catalysts: A Microkinetic Modeling Study**

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### **4.1 Introduction**

Innovative catalysis is vital to modern energy and chemical production to reduce energy consumption and prolong catalyst durability. Considerable attention has been given to bifunctional catalysts to acquire the necessary functionalities to carry out complex reactions [33, 235-238]. Tailored bifunctionalities enable synergistic cooperation that promotes charge transfer [31], facilitates species spillover [38], and lowers transition state energies [37].

Beneficial catalytic effects were observed in an array of carefully designed bifunctional systems. Bimetallic alloys were engineered to provide distinct geometric differences to enhance catalytic performance. For example, Wang *et al.* [239] demonstrated that CO and atomic O preferentially adsorb at the respective Au and the M sites in bimetallic Au-M (M = Cu, Ag, Co, and Ni) alloys during CO oxidation. The more electronegative Au atoms induce charge transfers away from the M sites that strengthen the binding of atomic O. Also, bifunctionality is observed on monometallic catalyst surfaces where steps and terraces act as distinct active sites. Tritsaris and Rossmeisl predicted that electrocatalytic methanol oxidation reaction (MOR) overpotentials on structured Pt

catalysts are lower than on either the step or the terrace sites [240]. Beyond alloys, Zhao *et al.* [37] argued that the activation energy of water dissociation during the water-gas shift reaction is reduced significantly to 0.1 eV at the interface of the Au/MgO dual-site model.

To reveal the underlying principle, Anderson *et al.* [54] showed that a meaningful boost to reactivity will most likely be achieved when reactant and product species display distinct behaviors between the two active site types in a bifunctional system. In computational catalysis, such behaviors can be intuitively described by Brønsted-Evans-Polanyi (BEP) [163, 241] and linear scaling relationships [229, 242, 243]. Generic models suggest that not only are different BEP parameters necessary to achieve bifunctionality, but the variations of these parameters at different active site types should also favor different reaction steps.

The best effect can be achieved for specific catalysts on composite systems composed of two different catalytic materials (e.g., metal catalyst particles and non-metallic supports). Using Ni<sub>3</sub> and Fe<sub>3</sub>-load Mn<sub>4</sub>N, N<sub>2</sub> activation and NH<sub>3</sub> formation occur at the interfacial nitrogen vacancy site (N<sub>v</sub>) and metallic sites. The coupled dual-site catalysts facilitate the migration of critical intermediates. The strong binding NH species can be transferred to the preferred N<sub>v</sub> onto the metallic site (Ni or Fe) to re-generate the N<sub>v</sub> sites. For this reason, ammonia turnover frequencies (TOF) from microkinetic analyses can be boosted by up to 7 orders of magnitude [8].

In this work, dry reforming methane (DRM) was chosen as a case study to demonstrate that bifunctional catalysts are particularly effective in coke mitigation. DRM yields value-added syngas from the CH<sub>4</sub> and CO<sub>2</sub> feedstocks. Nevertheless, there is a grand challenge for non-noble (i.e., Ni, Co) and noble metals (e.g., Rh [244], Pt [195], and Ir [245]) to sustain high reactivities without the hindrance of coking [65]. A common practice to suppress coking is to introduce a secondary active site that weakens C binding and increases the energy barriers of C–C coupling [246], as in Pt alloys



consisting of post-transition metals (i.e., PtM, M = Pb, Bi, and Tl) during ethane dehydrogenation [247]. Additionally, the diffusion of carbon species and coke (i.e., C<sub>2</sub> and C<sub>6</sub>) formation through the C-C coupling reaction depends on surface structures [248]. It has also been demonstrated that surface Sn in NiSn alloys lowers the rate of C-C bond formations versus C-O bond formations [249]. Moreover, transition metal particles supported on reducible oxide help prolong the catalyst durability [38, 194, 195, 250]. A comparative analysis performed by Lovell *et al.* [38] suggests that the SiO<sub>2</sub>/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> support plays a much more active role in oxygen spillover than silica, allowing the oxygen species to oxidize carbon residuals on Ni catalysts rapidly.

Recently, Fu *et al.* [79] reported a solid DRM performance displayed by a Co-Mo ternary nitride, Co<sub>3</sub>Mo<sub>3</sub>N, which is stable for over 50 hours at 800°C. They attributed the enhanced catalytic performance to the synergistic interactions between the Co and Mo<sub>2</sub>N phases. Previously, Co<sub>3</sub>Mo<sub>3</sub>N was investigated as a monolithic dual-site model system using Density Functional Theory (DFT) calculations [34]. The intrinsic reactivity of DRM on Co<sub>3</sub>Mo<sub>3</sub>N benefits from strong site preferences displayed by reaction intermediates. We observed that CH<sub>4</sub> decompositions favor the Co sites, while the CH<sub>x</sub> oxidations prefer the Co-Mo<sub>2</sub>N boundary sites. For DRM, these reaction steps dictate H<sub>2</sub> production and coke accumulation rates. The analytic CH<sub>4</sub> consumption rate indicates that Co<sub>3</sub>Mo<sub>3</sub>N should be competitive against some of the best transition metals (e.g., Ru, Ni) and metalloid catalysts (e.g., Ni<sub>2</sub>P) [34].

Here, Co<sub>3</sub>Mo<sub>3</sub>N was employed as an idealized model to understand how a dual-site system active toward both CH<sub>4</sub> activation and carbonaceous oxidation yield high reactivity yet durable performance during DRM. Also, a series of pure transition metals frequently appearing in DRM literature were included to obtain a general trend in H<sub>2</sub>, CO productions, and coking suppression. Using DFT-calculated binding energies of atomic C and O as descriptors, the catalytic

performance of the unique Co and Mo<sub>2</sub>N domains in Co<sub>3</sub>Mo<sub>3</sub>N is directly compared with functionalities derived from the step (211) and terrace (111) geometric features of pure transition metals. Aided by linear scaling relationships, the reaction intermediates and transition states of specific elementary steps that do not follow the same trend were identified. Mechanistically, the synergy in these dual-site systems was probed by examining the cross-site diffusion and cross-site reaction steps with mean-field microkinetic modeling. We showed that the site coupling will widely enhance the CO and H<sub>2</sub> production rates by facilitating species migration and lowering reaction barriers and is particularly effective in mitigating coke formations on surfaces that bind C and O strongly. The modeling results suggest that well-designed dual-site systems can achieve high reactivities without deactivations due to site blocking.

## 4.2 Methods

### 4.2.1 Catalyst Models

As described previously [34], the bulk of Co<sub>3</sub>Mo<sub>3</sub>N was cleaved along the (111) orientation. The resulting facet consists of patterned cobalt (Co) and molybdenum nitride (Mo<sub>2</sub>N) domains (Figure 4.1a). Here, the same surface was used to generate data to describe the dual-site system. We showed that three electronically distinct Co atoms exist in the cobalt domain (highlighted by the blue dashed triangle), donated as  $T_{Co1}$ ,  $T_{Co2}$ ,  $T_{Co3}$ , and hcp<sub>1</sub>. The geometry optimizations of each adsorbate were performed at different locations within the Co domain. The lowest binding energies (the preferred binding site) were used to represent the  $s_1$  site. The B<sub>1</sub>, B<sub>2</sub>, T<sub>Mo</sub>, and T<sub>N</sub> sites in the Mo<sub>2</sub>N domain (highlighted by the red triangle) were explored similarly to represent the  $s_2$  site.

As illustrated in Figure 4.1b and c, dual-site models based on pure transition metals (i.e., Ag, Au, Co, Cu, Ni, Pd, and Pt) comprise terrace and step sites. Surface geometries also influence fundamental catalytic behaviors and enable bifunctionality. By convention, the (111) and (211) facets were employed as the  $s_1$  and  $s_2$  sites, respectively. The (111) facet that dominates the terrace of transition metals shows the higher activity of  $\text{CH}_4$  and  $\text{CO}_2$  activations [248]. Coke formation via the C-C coupling reaction can also be enhanced on this facet for Ni, Rh, Pd [248], and Co [248, 251]. Atoms at the step sites in the (211) facet are highlighted in darker grey. Unlike the terrace, the step sites favor carbon oxidation (CO formation) [248, 251], OH formation [251, 252], and lower activity for C-C coupling reaction (reported on Co [248, 251]), resulting in lower coke forming rates.

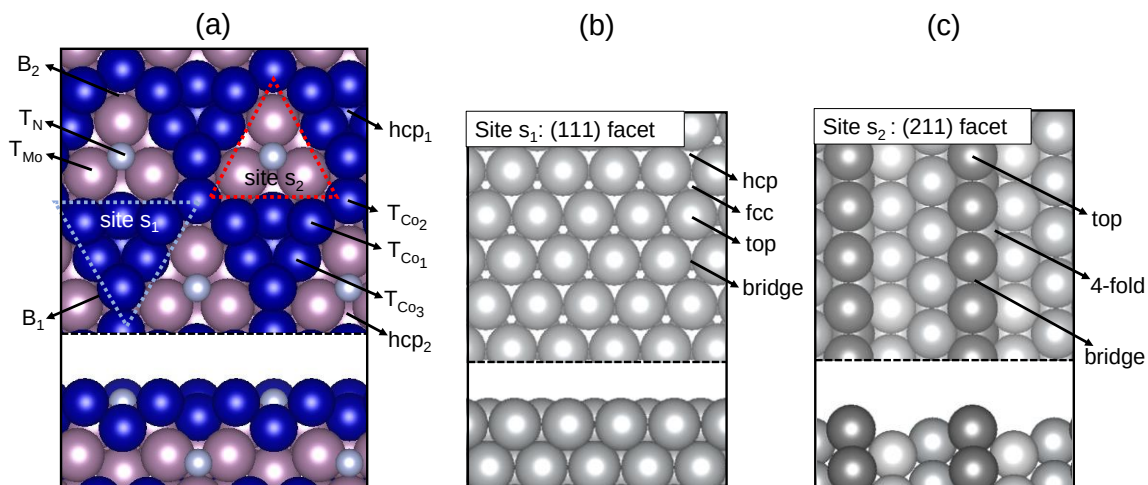


Figure 4.1. (a) Top and side views of Co<sub>3</sub>Mo<sub>3</sub>N (111); (b-c) terrace (111) and step (211) surfaces. The Co, Mo, and N atoms in Co<sub>3</sub>Mo<sub>3</sub>N (111) are shown in blue, pink, and grey. The Co (site  $s_1$ ) and Mo<sub>2</sub>N (site  $s_2$ ) domain boundaries are highlighted in blue and red dashed lines. High symmetry sites in (111) represent site  $s_1$ , while sites in (211) for site  $s_2$  in dual-site models. The dark grey color highlights the edge sites.

#### 4.2.2 Density Functional Theory

All spin-polarized, periodic DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [253, 254]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof functional (GGA-PBE) was used to account for the electron exchange and correlation [123]. The core electrons were described using the projector augmented wave (PAW) method [142], with a plane-wave basis set which was expanded up to a cutoff of energy of 400 eV. The reciprocal first Brillouin-zones of transition metal and Co<sub>3</sub>Mo<sub>3</sub>N surfaces were sampled using 4×4×1 and 2×2×1  $k$ -point meshes based on the Monkhorst-Pack scheme [203].

All reported binding energies ( $BE_{C_xH_yO_z^*}$ ) adopt the formulation expressed by Eqn. (4.1):

$$BE_{C_xH_yO_z^*} = E_{C_xH_yO_z^*} - xE_{CH_4} + \left(2x - \frac{1}{2}y + z\right)E_{H_2} - zE_{H_2O} - E_* \quad (4.1)$$

where  $E_{C_xH_yO_z^*}$ ,  $E_{CH_4}$ ,  $E_{H_2}$ ,  $E_{H_2O}$ , and  $E_*$  represent the total energies of the adsorbed surface species, gas-phase references (CH<sub>4</sub>, H<sub>2</sub>, and H<sub>2</sub>O), and clean surface, respectively. The Bayesian error estimation with van der Waals corrections was applied to quantify the uncertainties in  $BE_C$  and  $BE_O$  based on the BEEF-vdW functional [126].

The reaction energies ( $\Delta E$ ) and energy barriers ( $E_a$ ) were obtained from Eqns. (4.2) and (4.3):

$$\Delta E = \sum_i E_{product,i} - \sum_j E_{reactant,j}, \quad (4.2)$$

$$E_a = E_{TS} - E_{IS} \quad (4.3)$$

where  $\sum_i E_{product,i}$ ,  $\sum_j E_{reactant,j}$ ,  $E_{TS}$ , and  $E_{IS}$  represent summations of the total energies of all product and reactant species, the total energies of the transition state (TS), and the initial state (IS). The total energies of the TS were identified from the Climbing-Image Nudged Elastic Band (CI-NEB) followed by the dimer methods [149, 150] and then confirmed with a single imaginary frequency. The calculated  $\Delta E$  and  $E_a$  for dual-site systems in Table 2 are based on the preferred site preference and lowest TS energies.

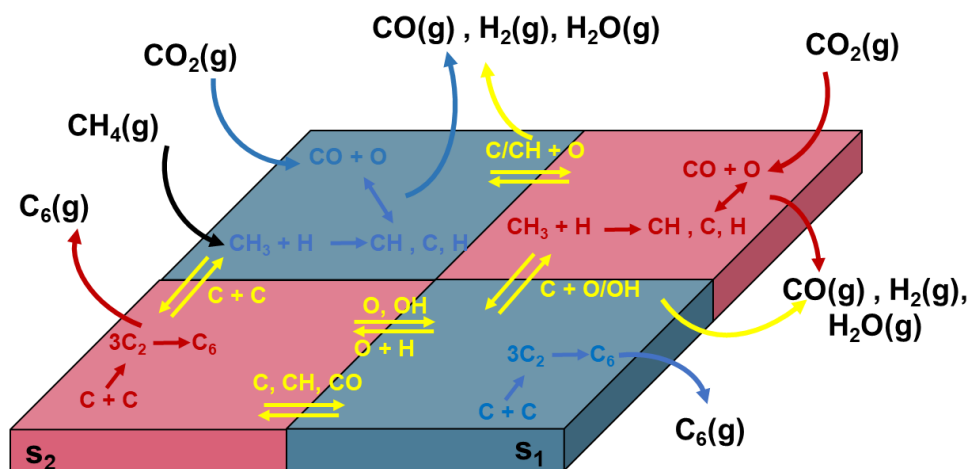
### 4.2.3 Linear Scaling Relationships

DRM reaction intermediates ( $C_xH_yO_z$ ,  $x = 1\sim 2$ ,  $y = 0\sim 3$ ,  $z = 0\sim 1$ ) bind with either their C or O end at the active site. For this reason, DFT-calculated binding energies of atomic C and O species (denoted as  $BE_C$  and  $BE_O$ ) are logical descriptor choices to discuss the trends of  $CH_4$  reforming [248, 255]. Through linear regressions,  $BE_{C_xH_yO_z^*}$  from Eqn. (4.1) were fitted to  $BE_C$  and  $BE_O$  to establish linear scaling relationships [160, 233, 243, 256], which, in turn, were used to interpolate reaction energies over the entire descriptor space. Similarly, the Bronsted-Evans-Polanyi (BEP) relationships were obtained through linear regressions using values (i.e.,  $\Delta E$  and  $E_a$ ) from Eqns. (4.2) and (4.3). Activation energies interpolated from BEP relationships are used to estimate the rate constants. We employ the combined linear scaling relationship and BEP

correlations to accelerate catalyst screening to reveal the dependence of DRM rates on an arbitrary catalyst surface [242, 243, 257]. Moreover, Andersen *et al.* [54, 258] demonstrated that the BEP relationship parameters were used to measure the extent of bifunctional promotion. Here, the linear scaling and BEP relationships were constructed specifically for the respective  $s_1$  and  $s_2$  sites.

#### 4.2.4 Microkinetic Modeling

Scheme 4.1. Schematic illustration of DRM on dual-site models. Different active site regimes are represented in blue and red, respectively. Blue and red arrows indicate reactions on  $s_1$  and  $s_2$  sites. Yellow arrows indicate cross-site reactions and diffusion steps.



The analytical results of DRM on single-site catalysts were derived under a quasi-steady-state approximation assuming the initial  $\text{CH}_4$  activation as the rate-limiting step [34]. In the full dual-site mechanism (Table B.1 in Supplementary Materials), these steps proceed in parallel on both  $s_1$  and  $s_2$  sites (see Scheme 4.1). Furthermore, the reaction network was expanded to incorporate coke formation steps. We adopted the coking process described by Jalid and coworkers

[248]. Specifically, dimerization and polymerization of C species via C–C coupling are used to represent C<sub>2</sub> and C<sub>6</sub> formations. The site couplings include five cross-site diffusion steps for C, CH, O, OH, and CO because these species will likely dominate on the surface. Seven cross-site reaction steps involving CH<sub>x</sub>-oxidation were included due to the site preferences of the participating reaction intermediates. The reactivities were represented by the turnover frequencies (TOF, s<sup>-1</sup>) of H<sub>2</sub> and CO productions. The extent of coking was measured in terms of the TOF of C<sub>6</sub> production. The reported numerical solutions were produced with a stoichiometry CH<sub>4</sub>:CO<sub>2</sub> ratio (= 1:1) at 973 K and 1 bar using the CatMAP package [175].

## 4.3 Results and Discussion

### 4.3.1 Binding Site Preference of DRM Intermediates

Table 4.1 compares the binding energies of DRM intermediates between the respective s<sub>1</sub> (Co) and s<sub>2</sub> (interfacial) sites. The carbonaceous species (i.e., CH<sub>3</sub>, C, C<sub>2</sub>, and C<sub>6</sub>) generally prefer the negatively charged s<sub>1</sub> sites of Co<sub>3</sub>Mo<sub>3</sub>N(111). Within the Co domain, CH<sub>3</sub> and CH predictably choose the sites that fulfill the tetrahedral valency of the central C atoms [34]. As illustrated in Figure 4.2, CH<sub>3</sub> prefers the T<sub>Co<sub>3</sub></sub> location of the s<sub>1</sub> site. The valence rule was initially discovered on transition metal facets and has been extended to the transition metal (Co) and nitride (Mo<sub>2</sub>N) domains in composite systems like Co<sub>3</sub>Mo<sub>3</sub>N. The valence rule is preserved for CH<sub>2</sub> and CH. However, CH<sub>2</sub> slightly prefers the B<sub>1</sub> location of the s<sub>2</sub> site instead, while CH exhibits negligible site preference. Although Mo chooses the more electronegative species, the negatively charged N (-1.17 e) at the center of the Mo<sub>2</sub>N domain (Figure 4.1a) forces O, H, OH, COH, and CHO toward the B<sub>1</sub> sites (Figure 4.2). The patterned Co<sub>3</sub>Mo<sub>3</sub>N Co and Mo<sub>2</sub>N domains highlighted that active site geometries and configurations influence the strength and locations of surface adsorptions, both

of which ultimately determine the performance of the dual-site system. The catalytic performance results will be discussed in the following sections.

Table 4.1. Binding energies (eV) of reaction intermediates based on Eqn. (4.1) on the  $s_1$  and  $s_2$  sites of  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . The numbers in boldface highlight the site preference.

| Site  | C           | O            | CH          | $\text{CH}_2$ | $\text{CH}_3$ | OH           | CHO         | COH         | H            | CO          | $\text{C}_2$ | $\text{C}_6$ |
|-------|-------------|--------------|-------------|---------------|---------------|--------------|-------------|-------------|--------------|-------------|--------------|--------------|
| $s_1$ | <b>1.27</b> | -0.37        | <b>0.67</b> | 0.76          | <b>0.54</b>   | -0.55        | 1.54        | 1.57        | -0.49        | <b>1.25</b> | <b>3.26</b>  | <b>10.26</b> |
| $s_2$ | 1.44        | <b>-0.73</b> | <b>0.67</b> | <b>0.69</b>   | 0.70          | <b>-0.67</b> | <b>1.27</b> | <b>1.45</b> | <b>-0.61</b> | 1.37        | 4.65         | 11.45        |

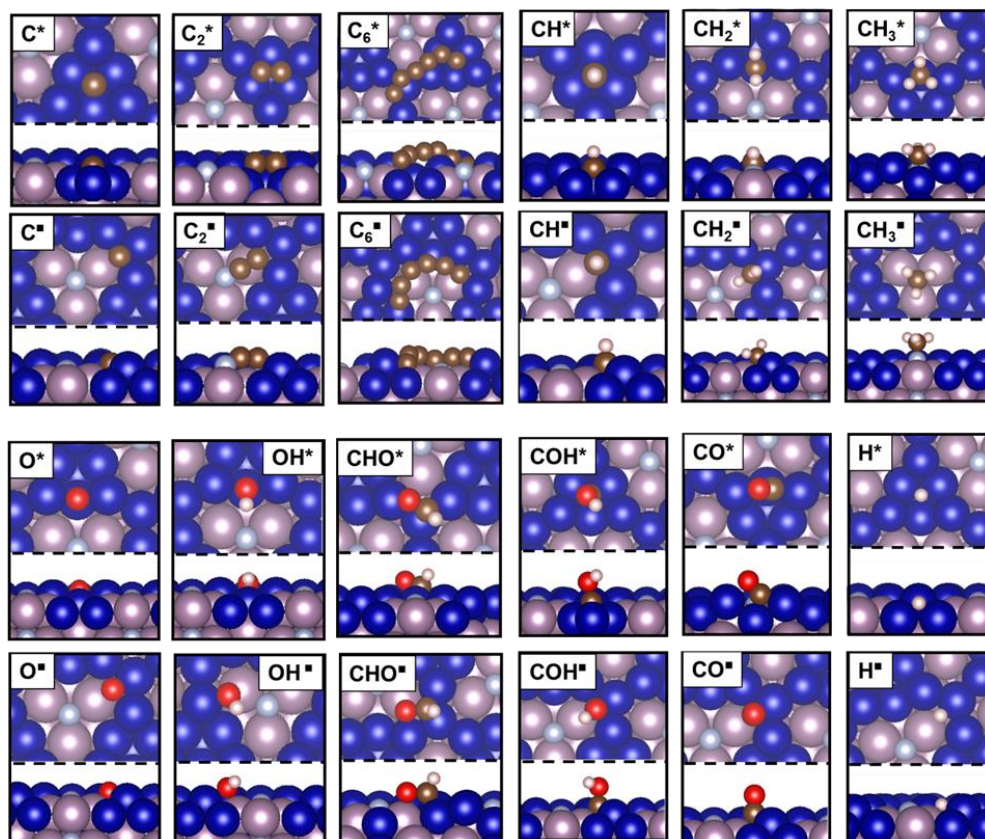




Figure 4.2. Top and side views of the optimized geometries of DRM intermediates on respective  $s_1$  (labeled with ‘\*’) and  $s_2$  (labeled with ‘■’) sites of  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . The C, O, H, Co, Mo, and N atoms are illustrated in brown, red, white, dark blue, pink, and light blue.

DRM at the terrace and steps sites of transition metal catalysts have been systematically investigated and discussed in the literature [248, 251, 259]. According to DFT calculations, DRM intermediates generally bind stronger on the low-coordinated edge site of the (211) facet (Figure 4.1c) than on the close-packed (111) facet (Figure 4.1b).

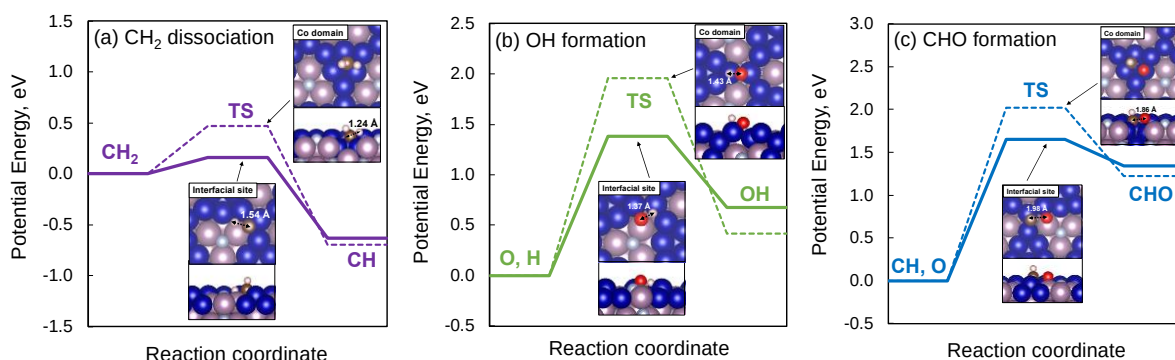


Figure 4.3. Potential energy profiles and the optimized TS structures at the interfacial sites (solid lines) versus at the Co domain (dashed lines) of  $\text{Co}_3\text{Mo}_3\text{N}(111)$ . The C, O, H, Co, Mo, and N atoms are depicted in brown, red, white, dark blue, dark pink, and light blue. Atomic distances are shown in dashed arrows.

We also identified the elementary steps displaying significant site dependence on  $\text{Co}_3\text{Mo}_3\text{N}(111)$ :  $\text{CH}_2$  dissociation (Figure 4.3a), OH (Figure 4.3b), and CHO (Figure 4.3c) formations. The TS structures obtained at the interfacial sites were compared with results based on the configurations in which reactants are confined within the Co domain. As shown in Figure

3, all cross-site reaction steps at the interfacial sites result in lower activation energies. For CH<sub>2</sub> dissociation,  $E_a$  is 0.4 eV lower than the reaction occurring at the Co domain (solid lines in Figure 4.3a). The  $E_a$  of OH formation is 0.58 eV lower even though  $\Delta E$  is more endothermic (Figure 4.3b), suggesting that  $\Delta E$  and  $E_a$  would not follow the same trend prescribed by the BEP relationship designed for pure Co. The C–O bond formation producing CHO is a critical step in CH<sub>x</sub>-oxidation. The corresponding  $E_a$  of the cross-site reaction between CH and O is 0.37 eV lower than on the Co domain (Figure 4.3c).

Table 4.2. Reaction energies ( $\Delta E$ ) and energy barrier energies for DRM reactions on s<sub>1</sub>(single-site catalysts), s<sub>2</sub>, and dual-site catalyst (most favorable binding site and the lowest barrier between the s<sub>1</sub> and s<sub>2</sub> sites were chosen) for Co<sub>3</sub>Mo<sub>3</sub>N (111).

| Elementary step |                                                                   | s <sub>1</sub> (Single-site) |       | s <sub>2</sub> |       | Dual-site  |       |
|-----------------|-------------------------------------------------------------------|------------------------------|-------|----------------|-------|------------|-------|
|                 |                                                                   | $\Delta E$                   | $E_a$ | $\Delta E$     | $E_a$ | $\Delta E$ | $E_a$ |
|                 |                                                                   | (eV)                         | (eV)  | (eV)           | (eV)  | (eV)       | (eV)  |
| R1              | CH <sub>4</sub> (g) + 2* $\leftrightarrow$ CH <sub>3</sub> * + H* | -0.08                        | 0.65  | 0.31           | NF    | -0.08      | 0.65  |
| R2              | CH <sub>3</sub> * + * $\leftrightarrow$ CH <sub>2</sub> * + H*    | -0.38                        | 0.51  | -0.62          | 0.42  | -0.46      | 0.51  |
| R3              | CH <sub>2</sub> * + * $\leftrightarrow$ CH* + H*                  | -0.70                        | 0.47  | -0.63          | 0.16  | -0.63      | 0.16  |
| R4              | CH* + * $\leftrightarrow$ C* + H*                                 | -0.03                        | 0.95  | 0.17           | 1.03  | -0.01      | 0.96  |
| R5              | CO <sub>2</sub> (g) + 2* $\leftrightarrow$ CO* + O*               | 1.07                         | 1.89  | 0.82           | 2.46  | 0.70       | 1.89  |
| R6              | C* + O* $\leftrightarrow$ CO* + *                                 | 0.34                         | 1.74  | 0.66           | 2.44  | 0.72       | 2.11  |
| R7              | H* + O* $\leftrightarrow$ OH* + *                                 | 0.42                         | 1.96  | 0.67           | 1.38  | 0.67       | 1.38  |
| R8              | C* + OH* $\leftrightarrow$ COH* + *                               | 0.86                         | 1.28  | 0.68           | 1.47  | 0.86       | 1.40  |
| R9              | COH* + * $\leftrightarrow$ CO* + H*                               | -0.93                        | 0.92  | -0.69          | 0.60  | -0.81      | 0.60  |

|     |                                                                                |       |      |       |      |       |      |
|-----|--------------------------------------------------------------------------------|-------|------|-------|------|-------|------|
| R10 | $\text{CH}^* + \text{O}^* \leftrightarrow \text{CHO}^* + *$                    | 1.22  | 2.02 | 1.34  | 1.65 | 1.34  | 1.65 |
| R11 | $\text{CHO}^* + * \leftrightarrow \text{CO}^* + \text{H}^*$                    | -0.90 | 0.96 | -0.52 | 0.78 | -0.64 | 0.78 |
| R12 | $\text{CO}^* \leftrightarrow \text{CO}(\text{g}) + *$                          | 1.99  | NA   | -0.49 | NA   | -0.37 | NA   |
| R13 | $\text{H}^* + \text{H}^* \leftrightarrow 2 * + \text{H}_2(\text{g})$           | 1.23  | NF   | 1.23  | NF   | 1.23  | NF   |
| R14 | $\text{H}^* + \text{OH}^* \leftrightarrow \text{H}_2\text{O}(\text{g}) + 2*$   | 1.17  | 1.20 | 1.29  | 1.29 | 1.29  | 1.29 |
| R15 | $\text{C}^* + \text{C}^* \leftrightarrow \text{C}_2^* + *$                     | 0.74  | 1.90 | 1.74  | 1.87 | 0.74  | 1.90 |
| R16 | $\text{C}_2^* + \text{C}_2^* + \text{C}_2^* \leftrightarrow \text{C}_6^* + 2*$ | 0.47  | NC   | -2.45 | NC   | 0.47  | NC   |
| R17 | $\text{C}_6^* \leftrightarrow \text{C}_6(\text{g}) + *$                        | -7.03 | NA   | -8.16 | NA   | -7.03 | NA   |

NF: Not Found, NC: Not Calculated, NA: Not Applicable.

The reaction energies ( $\Delta E$ ) and energy barriers ( $E_a$ ) of all elementary steps on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  are summarized in Table 4.2. The free energy diagram depicting DRM by incorporating the site preferences are presented in Figure B.1.

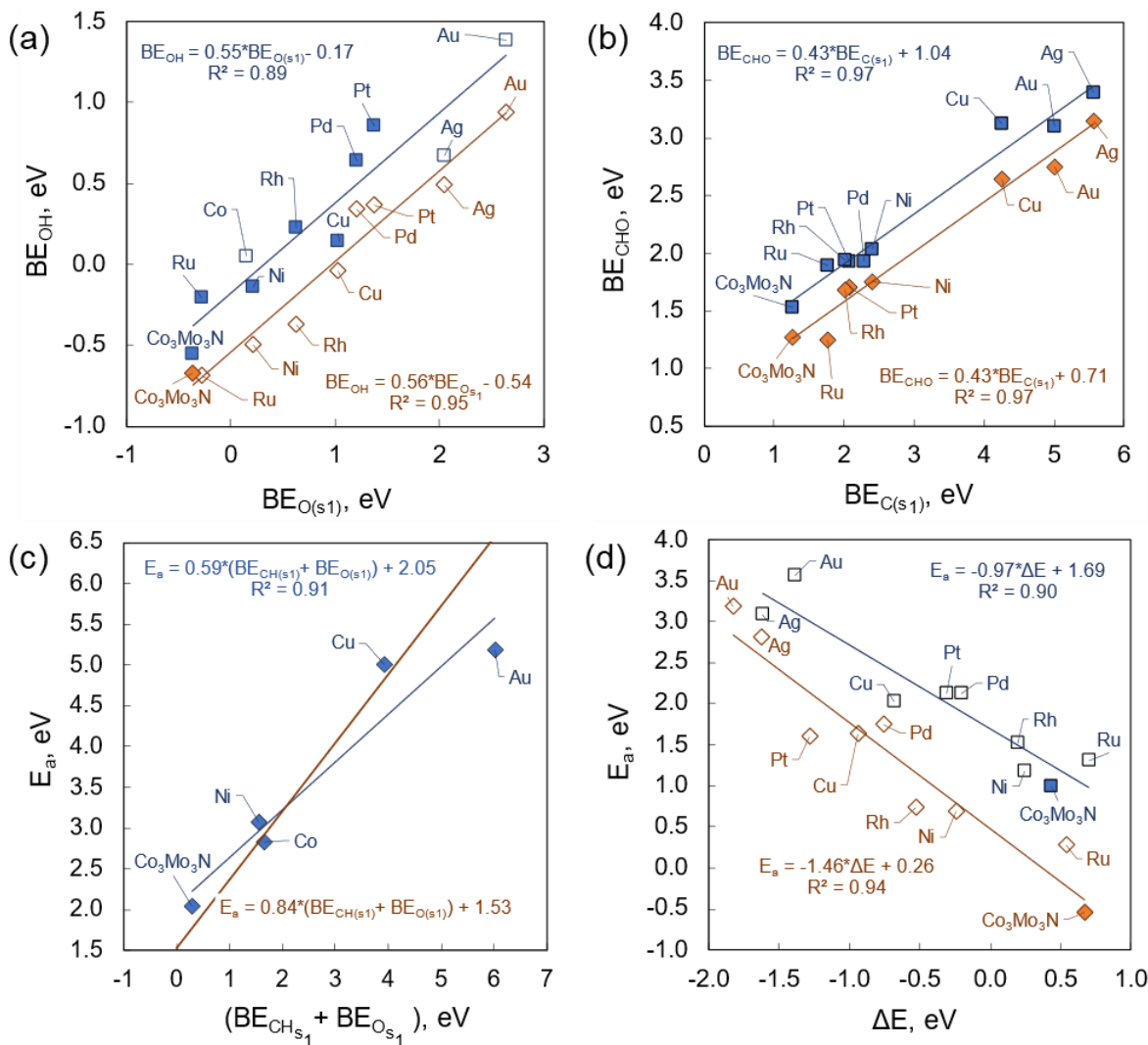


Figure 4.4. Linear scaling relationships for (a) OH adsorptions, (b) CHO adsorptions (blue: site  $s_1$  and orange:  $s_2$ ) based on binding energies of O and C on the  $s_1$  site. BEP relationships for (c) CH–O bond formation, and (d) O–H bond formation (blue: site  $s_1$  and orange: site  $s_2$ ). Data produced in this work are represented with solid symbols. Hollow symbols in (a, b, d) were reproduced using the data reported by Jalid and coworkers [248]. The BEP relationship in (c) on the  $s_2$  site was reproduced according to Ref. [259].

The calculated  $BE_{C_xH_yO_z^*}$  are also plotted against  $BE_{C(s_1)}$  or  $BE_{O(s_1)}$  at site  $s_1$ , as shown in Figure 4.4a-b and Figure B.2 (Supplementary Materials), to reveal the intrinsic trends. Based on the linear regression,  $CH_x$  ( $x = 1\sim3$ ) (Figures B.2a-c), CO (Figures B.2d), and COH (Figures B.2e) follow the trends that are indistinguishable between the  $s_1$  and  $s_2$  sites. The slopes and intercepts extracted from linear regression agree well with published literature values [255]. The identical parameters in these linear scaling relationships indicate that these species will be insensitive to the active site types.

The adsorptions of OH and CHO are the exceptions. As shown in Figure 4.4a, the slopes between the  $s_1$  and  $s_2$  sites are almost identical (i.e., 0.55 eV versus 0.56 eV), but the intercept of the  $s_2$  site is 0.37 eV lower. Similarly, the linear scaling relationship for CHO at the  $s_2$  site shifts downward from the  $s_1$  site while the slope remains the same (Figure 4.4b). The origins responsible for the observed trends in OH and CHO are similar. Although both  $BE_{OH}$  and  $BE_{CHO}$  strengthen with stronger O and C binding, given similar  $BE_O$  or  $BE_C$  values, the extra binding energy difference separates their site preferences between sites  $s_1$  and  $s_2$ . The relationship between O and OH can be understood straightforwardly. CHO often binds with both its C and O atoms. Hence, CHO acquires its additional binding strength at the  $s_2$  site owing to the contribution from its O site.

It has already been demonstrated that BEP parameters can be directly linked to the promotional effects of bifunctional catalysts [54]. We found that steps related to  $CO_2$  activation (Figure B.2f),  $CH_x$  ( $x = 1\sim3$ ) dissociations (Figures B.2g-i), and CO formation (Figure B.2j) do not display noticeable site preferences. Nevertheless, the slopes and intercepts in the BEP relationships for CHO (Figure 4.4c) and OH (Figure 4.4d) formations vary substantially. On the  $s_2$  site, the slope (0.84) is higher than that on the  $s_1$  site (0.59). On catalyst surfaces (e.g.,  $Co_3Mo_3N$ )

with strong CH and O bindings, we anticipate that the CHO formation - an essential step to remove carbonaceous surface species – becomes kinetically favorable due to the low  $E_a$  predicted by the BEP relationship. The activation energies of OH formations at the  $s_2$  sites are always lower than on the  $s_1$  site (Figure 4.4d). However, the negative slope indicates that OH formation activation energies vary inversely with the formation energies. The lowest activation energies occur on  $\text{Co}_3\text{Mo}_3\text{N}$  and Ru surfaces.

### 4.3.2 Coke Formation

In DRM, the rate of coke formation is influenced by the competition between the C-C coupling (e.g., R15, R16 in Table 4.2) and the rate of C or CH conversion into CO (e.g., R6, R8, R10 in Table 4.2). As discussed previously, a dual-site system that binds O or OH species strongly accelerates the conversion of C or CH to better compete against C–C coupling and thus suppress the coke formation pathways [246].

C and CH conversions (R8 and R10) with OH and O species are more kinetically favorable on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  than direct C oxidation (R6) due to a lower  $E_a$  [34]. Moreover,  $\text{Co}_3\text{Mo}_3\text{N}(111)$  facilitates step R7, which further favors C oxidation by providing sufficient OH species. As shown in Table 4.2, the reaction energy and energy barrier of C-C coupling on the  $s_2$  site are prohibitively high (1.87 eV). Also,  $\text{C}_2$  prefers the  $s_1$  site (Table 4.2) over the  $s_2$  site. Hence, the  $s_2$  site weakens the bindings of C,  $\text{C}_2$ , and  $\text{C}_6$  species, resulting in less coke forming on the surface.

### 4.3.3 Catalytic Trends in DRM Reactivity

The formation energies of 14 species and the energy barriers of 12 elementary steps (listed in Table 4.2) are compiled for microkinetic modeling. The rate expressions for the dual-site

mechanism are derived from Table B.1 in the Supplementary Material. The main DRM pathways are duplicated on  $s_1$  and  $s_2$  sites, using the respective energy set reported in Table 4.2. Cross-site reaction and diffusion steps account for processes related to  $\text{CH}_x$ -oxidation and coke formations. DFT calculations based on the  $s_1$  site were used to represent single-site systems. The energy dataset and the setup for the microkinetic modeling reported in this work were prepared in Appendices 1 and 2. The TOFs of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{C}_6$  production were obtained at 973 K and 1 bar with the active site ratio ( $s_1$ :  $s_2$ ) of 7:3 (by counting the Co and interfacial sites in the current  $\text{Co}_3\text{Mo}_3\text{N}$  model).

The catalytic reactivities ( $\text{Log}_{10}[\text{TOF}, \text{s}^{-1}]$ ) for  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{C}_6$  formations and their dependencies on  $BE_C$  and  $BE_O$  are presented in Figure 4.5. The rates of  $\text{H}_2$  and  $\text{H}_2\text{O}$  formations are shown in the same plot as their reactivities occupy different parts of the heatmap separated by the dashed lines (Figure 4.5a). The predicted  $\text{H}_2\text{O}$  TOFs indicate that the reactivities of RWGS peak at  $BE_C$  above 3 eV and  $BE_O$  close to 0 eV. Among the transition metals projected onto the heatmap, the Group IB metals (i.e., Cu, Ag, Au) appear near the reforming-RWGS boundary under the simulated conditions. Meaningful RWGS will likely occur on copper-based catalysts [260, 261].  $\text{H}_2$  is one of the main products in DRM. However, water is a side product of the reverse water-gas shift (RWGS) reaction. RWGS lowers  $\text{H}_2$  selectivity as H participates in R7 and R14 instead of the recombination reaction (R13). The  $\text{CO}$  production (Figure 4.5b), on the other hand, could be adversely impacted by coke formations.

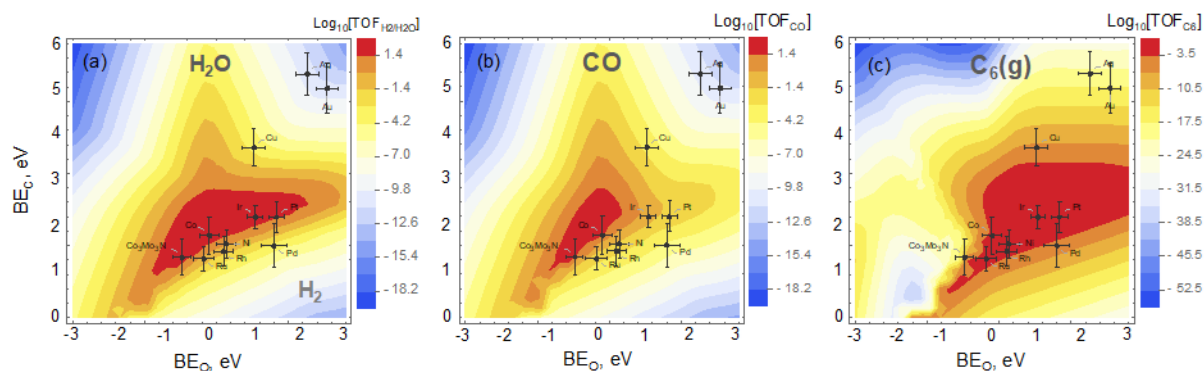


Figure 4.5. Turnover frequencies ( $\text{Log}_{10}[\text{TOF}, \text{s}^{-1}]$ ) for (a)  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , (b)  $\text{CO}$ , and (c)  $\text{C}_6(\text{g})$  productions on dual-site models at 973 K and 1 bar. The active site ratio is set as  $s_1:s_2 = 7:3$ . The dashed line represents the boundaries between  $\text{H}_2$  and  $\text{H}_2\text{O}$  as the major reaction products. The labels are projected onto each heatmap based on the lower values of the descriptors between the two sites. The error bars were generated from the Bayesian error estimation based on the BEEF-vdW functional.

$\text{H}_2$  and  $\text{CO}$  production rates represent the intrinsic DRM reactivities. As shown in Figure 4.5a-b, when  $BE_C$  is lower than 3 eV, the  $\text{H}_2$  production pathway will dominate RWGS. As  $BE_C$  continues to decrease, the  $\text{H}_2$  and  $\text{CO}$  production TOFs increase initially, then diminish before C binding becomes too strong. For a given  $BE_C$ , we observe a similar *volcano*-like dependence of the TOFs on  $BE_O$ . Overall, in the ranges of 1~2.5 eV and -1~2 eV for the respective  $BE_C$  and  $BE_O$ , resides the TOF maxima for both  $\text{H}_2$  and  $\text{CO}$ . We mapped a group of typical transition metal DRM catalysts on the reactivity heatmaps, using the descriptors based on the BEEF-vdW functional for van der Waals corrections and Bayesian error estimations [126]. As expected, Ru, Co, Ir, Ni, and Pt are among the best-performing catalysts for DRM [187, 262].

In the Supplementary Materials, the  $\text{H}_2$  and  $\text{CO}$  production TOFs on single-site models are also presented in Figures B.3a-b. Despite similar trends to the dual-site systems described above,



the high-performance area is now confined to a narrower range (i.e.,  $BE_C$ : 1.5~2.5 eV and  $BE_O$ : -1~1 eV). Beyond this range, the TOFs for H<sub>2</sub> and CO quickly drop due to the blockage by the strong C and O species. In comparison, the peaks of the reactivity plots (Figure 4.5a-b) broaden, and tilt along the off-diagonal direction, permitting catalysts like Co<sub>3</sub>Mo<sub>3</sub>N to sustain H<sub>2</sub> and CO production activities despite strong C and O binding.

Here, the rates of C<sub>6</sub> production as a gas-phase species were used as an indicator of how catalysts manage the accumulation of carbon residuals. As shown in Figure 4.5c, high C<sub>6</sub> production rates overlap partly with the H<sub>2</sub> production peak (e.g., Ir, Pt) on the heatmap because high CH<sub>4</sub> dissociation TOF tends to produce carbonaceous species at a higher rate as well. However, there is a notable shift toward the right, along the direction of weakening  $BE_O$ . This behavior emphasizes the roles of O and OH species in mitigating the accumulation of carbon residuals resulting from CH<sub>4</sub> decomposition.

Unlike H<sub>2</sub> and CO, a distinct C<sub>6</sub> production behavior can be observed in Figure 4.5c, i.e.,  $\text{Log}_{10}[\text{TOF}_{C_6}]$  decreases drastically for  $BE_O < -1$  eV. Unlike H<sub>2</sub> and CO, a distinct C<sub>6</sub> production behavior can be observed. On the other hand, strong C binding and high CH<sub>4</sub> dissociation TOF in single-site systems will produce rapid C<sub>6</sub> production and carbon accumulations that noticeably hinder H<sub>2</sub> and CO production (Figure B.3c).

When projected onto the heatmap (Figure 4.5c), the dual-site Co<sub>3</sub>Mo<sub>3</sub>N model appears superior to other transition metals. As discussed in the previous section, on Co<sub>3</sub>Mo<sub>3</sub>N (111), the O (s<sub>2</sub> site) converts the CH or C species (s<sub>1</sub> site) into CHO at a much lower energy barrier. Because CHO also favors the s<sub>2</sub> site, this step will boost CO production and free the s<sub>1</sub> sites from the occupation of C<sub>n</sub> (n = 1, 2, 6) for subsequent CH<sub>4</sub> activation and decomposition.

### 4.3.4 Bifunctionality and Coke Mitigation

We quantified the enhancement of  $H_2$ , CO productions, and coke suppression, using the relative performance gains, defined as  $\text{Log}_{10}[r_{\text{dual}}/r_{\text{single}}]$ , using the TOF results presented in Figure 4.5 (dual-site) and Figure B.3 (single-site). Although  $H_2$  production rates are promoted broadly (Figure 4.6a, below dashed lines), the performance gains are especially pronounced for catalysts with strong C binding, decreasing as O binding gradually becomes weaker. A similar trend can be observed for CO production (Figure 4.6b). It should be noted that  $H_2$  and CO productions benefit the most on  $\text{Co}_3\text{Mo}_3\text{N}$  and Ru surfaces, confirming the analyses conducted in the previous sections.

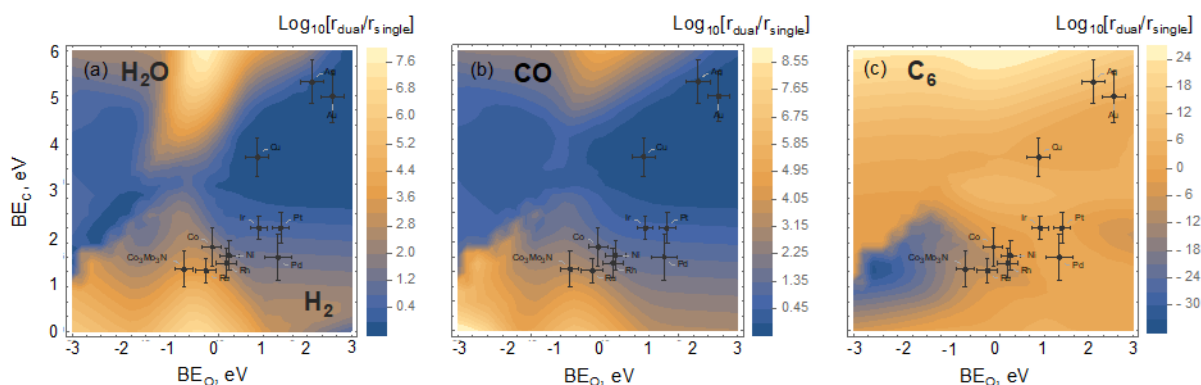


Figure 4.6. Performance gains ( $\text{Log}_{10}[r_{\text{dual}}/r_{\text{single}}]$ ) for (a)  $H_2$ , (b) CO, and (c)  $C_6$  productions achieved on dual-site models relative to the single-site models at 973 K and 1 bar. The dashed line in (c) indicates the sign change for the relative rates for  $C_6$  production. The negative sign means  $r_{\text{dual}} < r_{\text{single}}$ .

The suppression of coke formation was evaluated in Figure 4.6c. The rates of  $C_6$  production in the systems decrease when  $\text{BE}_\text{C} < 3$  eV and  $\text{BE}_\text{C} < 0$  eV, as indicated by the dashed boundary. We note the most significant suppression occurs when C and O bindings are strong (area

highlighted in blue). It can also be pointed out that the promotions of  $H_2$  and CO productions (Figure 4.6a-b) coincide substantially with the suppression of coke formation. We also noted that  $Co_3Mo_3N$  is one identified system capable of carrying out DRM at high intrinsic reactivity while mitigating coke formation simultaneously.

As shown in Figure 4.7, the most dominant surface intermediates on both  $s_1$  and  $s_2$  sites are C and O. The other traceable species include CH and  $C_2$  at the  $s_1$  site and H. We expect to see high C (Figure 4.7a and e) and O (Figure 4.7b and f) coverages concentrate in areas with low  $BE_C$  and  $BE_O$  values, respectively, regardless of the active site types. Coke formation precursors (i.e., C and CH) and carbon residuals ( $C_2$ ) can only be observed at the  $s_1$  site, as evidenced by their site preferences. The CH fragment is a product derived from incomplete  $CH_4$  decomposition. As shown in Figure 4.6c, catalysts with the most abundant CH species bind C moderately (with  $BE_C$  varying between 1~2 eV) but much weaker with O. At the  $s_1$  site, the  $C_2$  species is negligible and can only be observed along the boundary separating the C and O coverages. Even stronger O binding ( $BE_O < -2$  eV) will diminish coke accumulation and produce a catalyst surface covered by atomic O.

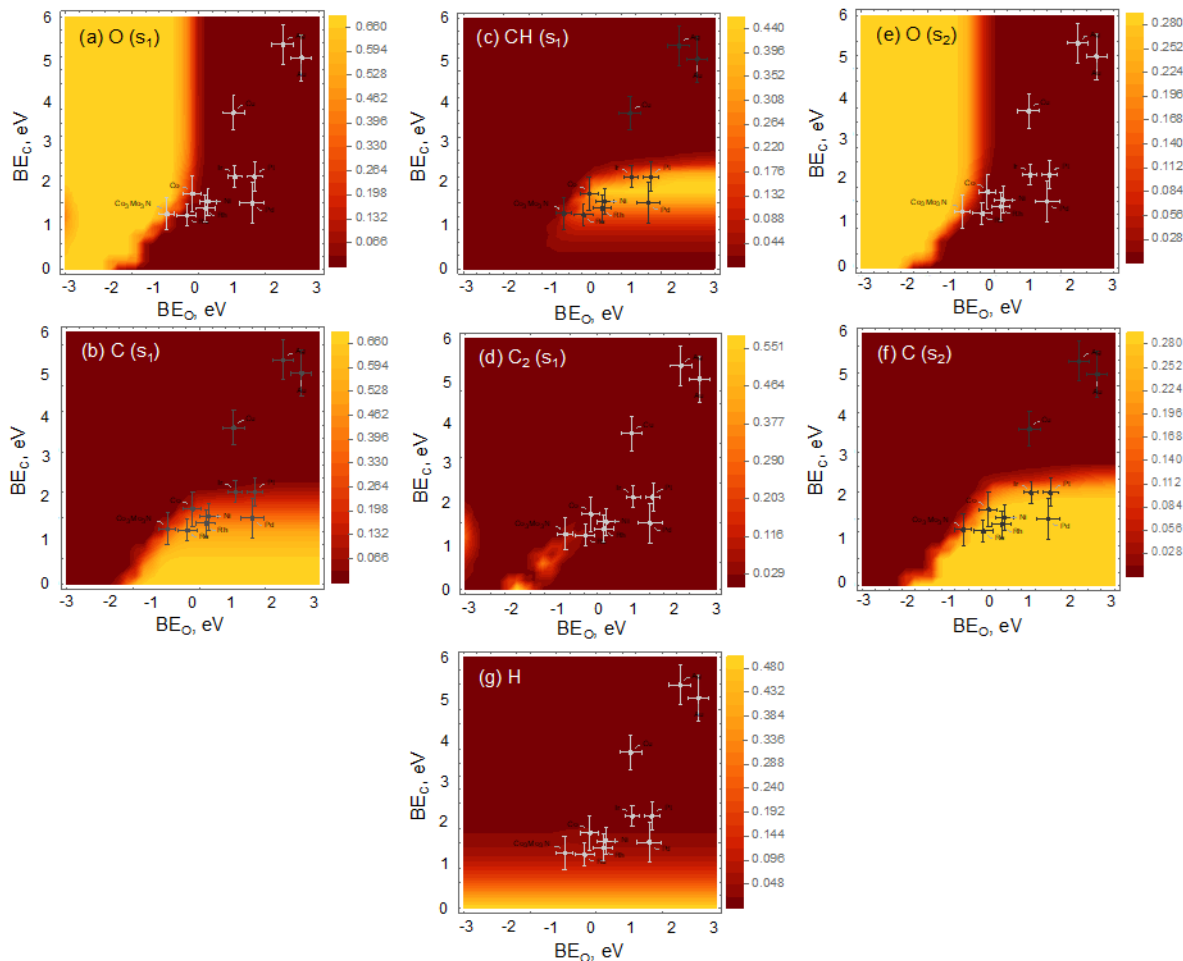


Figure 4.7. Surface coverage of (a) O, (b) C, (c) CH, (d) C<sub>2</sub> on site s<sub>1</sub>; (e) O, (f) C on site s<sub>2</sub>; and (g) H at 973 K and 1 bar.

### 4.3.5 Mechanisms Responsible for Coke Mitigation

To understand the origin of coke suppression due to site coupling, the cross-site diffusion or the cross-site reaction steps in the original dual-site model were artificially disabled. This time, the impacts on C<sub>6</sub> production rates were evaluated by comparing the TOFs between the full ( $r_{full}$ ) with the rates resulting from the respective modifications. As illustrated in Figure 4.8a, the rates of C<sub>6</sub> production increase in the absence of the cross-site diffusion steps (i.e.,  $r_{full} < r_{NoDiffusion}$ ).

The disabled steps prevent the migration of C, CH, O, and OH species between the two site types. Hence, we can conclude that upon the formations of C and CH (at their favored  $s_1$  site), the dimerization and polymerization of C species (i.e., R4, R15, and R16 in Table 4.2) will have to resume at the same site leading to  $C_6$ . Hence, the enhanced  $C_6$  production rates can be considered strong evidence regarding the roles of C, CH, O, and OH migrations in coke suppression. Such cross-site diffusion mechanisms would impact dual-site catalysts with strong C and O binding (highlighted in blue) because of the high  $CH_4$  decomposition TOFs and  $CH_x$ -oxidations, represented by systems such as  $Co_3Mo_3N$ .

When the cross-site reaction steps are removed from the original dual-site mechanism, the rates of  $C_6$  formation respond more complexly. Again, rates of  $C_6$  formation would increase (i.e., i.e.,  $r_{full} < r_{NoRxn}$ ) mainly on catalysts that bind C and O strongly (highlighted in shades of blue). Such a response suggests that interfacial reactions of C or CH at the  $s_1$  site with OH or O at the  $s_2$  site help mitigate carbon accumulation thanks to lower activation energies. However, for catalysts with moderate  $BE_C$  and  $BE_O$ , the rates of  $C_6$  formation will drop significantly (i.e.,  $r_{full} \gg r_{NoRxn}$ ) in the absence of cross-site reactions. This behavior is surprising and possibly due to the dominance of one species (e.g., C or O) for a given active site. Therefore, these catalysts will depend heavily on the cross-site reaction steps to carry out DRM.

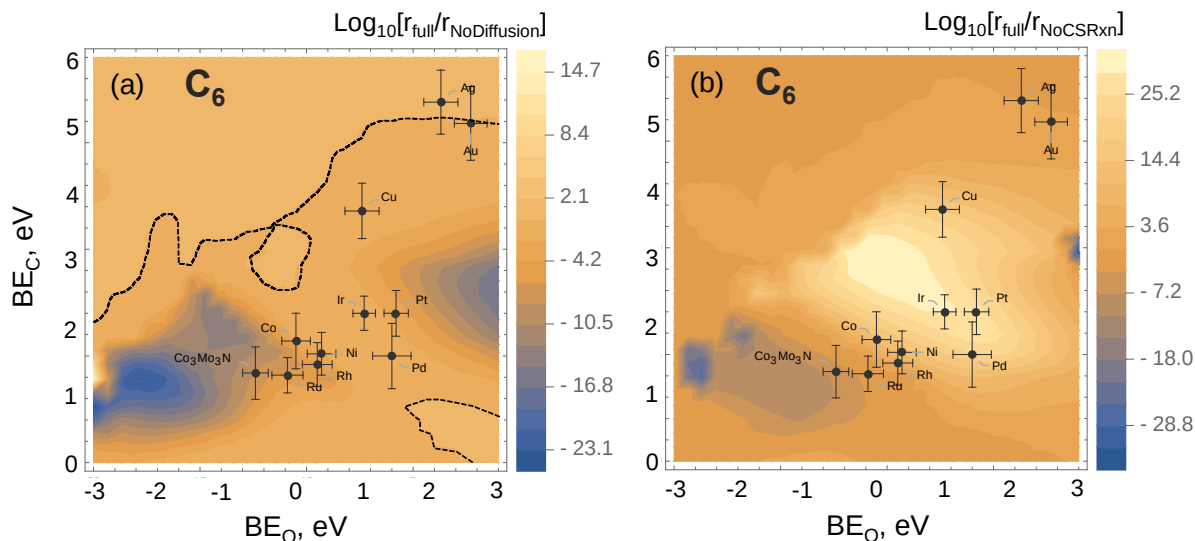


Figure 4.8. Comparisons of  $C_6$  production rates by disabling (a) cross-site diffusion and (b) cross-site reaction steps in the dual-site mechanism at 973 K and 1 bar. The dashed lines indicate the sign change for the relative rates for  $C_6$  production. The negative sign means  $r_{full}$  decreases when compared to the rates from the modified mechanisms.

#### 4.3.6 Rational Design of Bifunctional Catalysts for DRM

Finally, to guide future catalyst design, dual-site systems with other  $s_1:s_2$  site ratios (i.e., 1:1 and 3:7 versus 7:3) will be discussed. Both chosen ratios represent smaller fractions of the  $s_1$  sites. Such variations mean more abundant interfacial sites on  $Co_3Mo_3N$  to amplify their roles in  $CH_x$ -oxidation while limiting the supply of carbonaceous species from the Co sites. For transition metals, the concentrations of the step sites will rise.

The relative performance gains in  $H_2$ , CO, and  $C_6$  productions correspond to these site ratios (i.e.,  $\text{Log}_{10}[r_{1:1,dual}/r_{7:3,dual}]$  and  $\text{Log}_{10}[r_{3:7,dual}/r_{7:3,dual}]$ ) are presented in Figure B.4 in the Supplementary Materials. We found that modest gains can be obtained for  $H_2$  and CO productions for a composition of equimolar  $s_1$  and  $s_2$  sites (Figure B.4a). Transition metal catalysts

(e.g., Rh, Ni, Ir, Pd, Pt) with equimolar terrace and step sites ( $s_1:s_2 = 1:1$ ) acquire the most gains for ( $\sim 1$  order of magnitude). As the fraction of the  $s_1$  site decreases to 30% (i.e.,  $s_1:s_2 = 3:7$ ), the enhancement of the  $H_2$  production rate becomes uneven when compared to the original site composition. We observed pockets (enclosed by dashed lines) where the  $H_2$  production rates decreased slightly. The changes in  $H_2$  and CO production rates reflect a potential limit to boost syngas production by simply increasing the concentration of the oxyphilic  $s_2$  sites.

The impacts on  $C_6$  production by varying the  $s_1:s_2$  site ratio are reported in Figures B.4c and S4e. By lowering the fraction of the  $s_1$  site, the rates of  $C_6$  production decrease when  $BE_O < 0$  eV. This finding suggests that increasing the concentrations of the more oxyphilic site benefit coke suppression, thus confirming the catalytic role of such sites in prior discussion. On the other hand,  $C_6$  production may even increase if the second site binds too O weakly and will not play a role in coke mitigation.

## 4.4 Conclusions

In this work, DFT combined with microkinetic modeling was employed to investigate and understand how bifunctionality can be exploited to boost syngas production from DRM and mitigate the hindrance of rapid coking. The origin of enhanced catalytic performance resides in the site preferences displayed by DRM intermediates. Using DFT calculations, the site preference of each species was identified. More importantly, we showed that not all reaction intermediates (e.g., OH, CHO) follow the unified linear scaling relationships between two active site types. Specifically, the Co and Co-Mo<sub>2</sub>N interfacial sites in the Co-Mo ternary nitride (i.e., Co<sub>3</sub>Mo<sub>3</sub>N) show distinct reactivities toward CH<sub>4</sub> decomposition and CH<sub>x</sub>-oxidation respectively.

Furthermore, the impact on syngas production and coking was quantified using mean-field microkinetic modeling. The modeling results confirmed that  $\text{Co}_3\text{Mo}_3\text{N}$  is the most effective in mitigating coke formation by facilitating the oxidation and transportation of carbonaceous species (e.g., C, CH) from the initial active sites to sustain a high reactivity. In particular, cross-site diffusions of O, OH, C, and CH species effectively mitigate coke formation. Bifunctional catalysts also provide a valuable avenue for the consideration of earth-abundant catalytic materials with unconventional chemistries in the designs of novel systems.

## **Acknowledgments**

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## 5 Liquid Metal Gallium Catalysts for Dry Reforming of Methane

### 5.1 Introduction

Liquid metals have emerged as a new concept for catalytic reactions [263, 264] in the past ten years. They have displayed good selectivity and stable performance for hydrocarbon dehydrogenation reactions and graphitic carbon growth.

Gallium is a popular substrate for manufacturing liquid metal catalysts thanks to its low melting point (29.8 °C) and low toxicity. Moreover, alloys of Ga with Pd [265], Pt [266], and Rh [267] at low atomic percentages (1~10 at.%) may remain in the liquid state for targeted catalytic reactions. Taccardi and coworkers [268] reported that the dehydrogenation of *n*-butane catalyzed by liquid PdGa alloys yields butene with up to 85% selectivity. The catalyst remains stable over 20 hours of operation at 450 °C. The dissolved Pd atoms have a strong affinity to H atoms. Therefore, the Pd species at the gas-liquid enhance the activation and dehydrogenations of *n*-butane. The high butene selectivity can be attributed to the dissolved Pd widely dispersed in liquid Ga. The weakened alkene adsorptions facilitate product selectivity. Unlike conventional heterogeneous and homogeneous catalysts, liquid metal catalysts (e.g., Ga and Ga-based alloys) are highly dynamic. High active site mobility suppresses coke formation and accumulation [269].

Gallium-based liquid metal catalysts can catalyze CO<sub>2</sub> conversions as well. For example, bimetallic Pb-Ga [268, 270] and Ni-Ga [271] are applicable for CO<sub>2</sub> reduction to produce methanol (CH<sub>3</sub>OH). Gallium oxide (i.e., Ga<sub>2</sub>O<sub>3</sub>) is a suitable catalytic material for methanol steam reforming [272], photocatalytic water splitting [273], and CO<sub>2</sub> reductions [274].

Liquid bimetallic Ga systems have the potential to become cost-effective dry reforming of methane (DRM) catalysts [268, 275, 276]. Dispersed Ni, Pt, Pd atoms in Sn, Pb, Bi, In, and Ga

solutions can tolerate coking during CH<sub>4</sub> pyrolysis [269]. A robust coke-resistance character is a priority for DRM catalyst design. However, the primary challenge is the inadequate knowledge of the configurations and behaviors of catalytic active centers under realistic DRM conditions. Moreover, the characterization of liquid metal catalysts remains in its incubation stage. Grabau *et al.* [277] observed that Pd atoms are distributed non-homogeneously underneath the surface, covered mainly by Ga, and appear at the surface briefly. Liquid Ga systems have been subjected to *ab initio* molecular dynamics (AIMD), molecular dynamics (MD), and Density Functional Theory (DFT) investigations [265, 266, 278-282]. Liquid phase Ga and thermodynamic phase transitions were simulated by Niu *et al.* [278] using the potential derived from deep learning [283]. The phase diagram depicting the equilibrium among  $\alpha$ -Ga,  $\beta$ -Ga, Ga-II, and the liquid phase was generated. Liquid Ga under extreme pressures (to 33.4 GPa) and temperatures (up to 1000 K) were investigated by Drewitt *et al.* [284] using AIMD simulations and analyzed. The global and local liquid structures were analyzed using pair distribution functions (PDF) and topological cluster classification (TCC) analyses.

Molecular models representing pure and bimetallic Ga catalysts were constructed to elucidate the catalytic reactivity of Ga-based liquid catalysts for DRM. AIMD simulations were employed to generate configurations of Pd, Ni, and Ru species embedded in crystalline and amorphous Ga substrates. DFT calculations were performed to compute  $BE_C$  and  $BE_O$  as descriptors. In the first step, the performance of the solid-state catalyst was predicted using the dual-site model developed in Chapter 4. Microkinetic modeling revealed that the turnover frequency of H<sub>2</sub> production on RuGa increases by at least four orders of magnitude over pure Ga(100) due to strong carbon binding on Ru trimers. It is also found that the binding of C weakens on other Ru configurations such as dimer and monomer, suggesting that the clustering of Ru is the

key that guarantees sufficient reactivities. A similar trend can be applied to Ni and Pd. However, the binding of C is much weaker on Ni and Pd dimers and trimers when compared to Ru. The trajectories of Ni and Pd solutes in Ga solutions were generated using AIMD and then analyzed using the TCC algorithm to understand the clustering of transition metals in liquid Ga. As temperature decreases, the probability of observing transition metal species at the surface of liquid Ga becomes higher. Therefore, the active Ni and Pd configurations will more likely appear at the liquid-gas interface at low or moderate temperatures.

## 5.2 Computational Details

### 5.2.1 Solid-State Catalyst Models

The lattice of orthorhombic bulk crystal was used to construct solid-state Ga catalysts. Geometry optimizations of the bulk yield the lattice constants of pure Ga as  $a = 4.53 \text{ \AA}$ ,  $b = 4.59 \text{ \AA}$ , and  $c = 4.75 \text{ \AA}$ . X-ray analysis indicated lattice parameters at 297 K,  $a = 4.52 \text{ \AA}$ ,  $b = 4.49 \text{ \AA}$ ,  $c = 7.63 \text{ \AA}$  [285]. The core electrons were approximated using the PAW method [142], with the plane wave basis set expanded to 400 eV. The GGA-PBE functional was applied to account for the electron exchange-correlation effects [123]. The Brillouin zone was sampled using the Monkhorst-Pack  $k$ -point mesh [203]. All other computational details are the same as in Chapter 3.

A 4-layer Ga slab cleaved along the (100) facet was generated for surface reactions. The bottom two layers were fixed to the optimized bulk value. Monomers, dimers, and trimers of transition metals (i.e., Pd, Ni, and Ru) were embedded in Ga(100) surfaces for DFT calculations to obtain the baseline values for  $BE_C$  and  $BE_O$ . Figure 5.1 depicts the optimized Ru trimer (designated as the  $s_1$  site) embedded in Ga(100). The surface Ga atoms are labeled as  $s_2$ . Because

Ga itself is also known to be catalytically active, the functionalities of both the  $s_1$  and  $s_2$  sites will be investigated with DFT calculations.

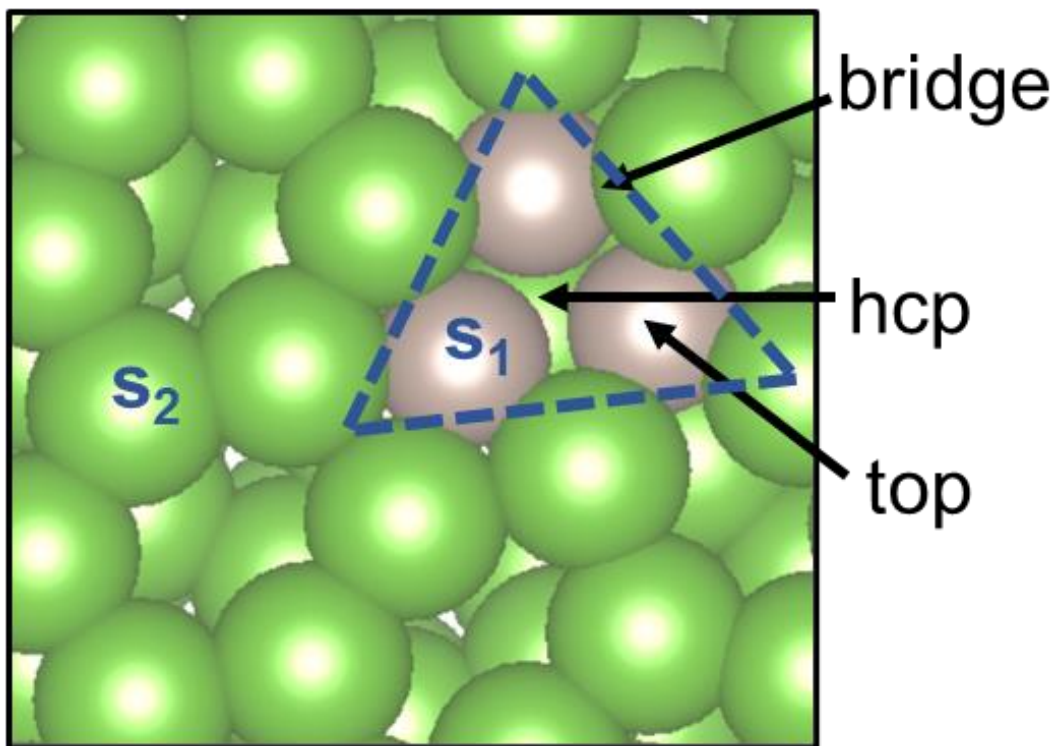


Figure 5.1. Top view of a Ru trimer embedded in Ga(100) surface. The Ga and Ru atoms are shown in green and pink. The Ru trimer (denoted as site  $s_1$ ) is highlighted with blue dashed lines. The arrows indicate the top, bridge, and hcp sites associated with the Ru trimer.

### 5.2.2 Liquid State Catalysts Models

AIMD simulations were performed in the canonical (NVT) ensemble with 96 Ga atoms in periodically bounded simulation cells. For bimetallic systems, the total number of atoms remains the same. Each bimetallic system consists of 9 Pd (Ni, Ru) atoms and 87 Ga atoms. System was heated to 1000 K for 2 ps to make sure that the original crystal lattice is eliminated. Then the system is cooled down to 303 (the melting point), 400, 500, 600, and 800 K for 4 ps, respectively.

The cell volume will be adjusted to match the liquid density corresponding to each temperature. The Nosé-Hoover thermostat was used to control the temperature. All systems were equilibrated for another 5 ps with a time step of 0.5 fs. For liquid systems, the Brillouin zone was sampled using the  $\Gamma$ -point.

Semi-periodic slab models were used to describe the molten catalyst surfaces. A vacuum of 20 Å was added to separate periodic images along the direction perpendicular to the open surfaces. The slabs were then equilibrated for 2 ps. The single  $\Gamma$  k-point was kept for the calculations.

The PDFs were generated from the trajectories of the last 2 ps of the simulations using the Ovito software [182]. The local structure of different liquid catalyst models was analyzed using the TCC algorithm. The basic principles of TCC were introduced in Section 2.13 of this thesis.

A total of 20 trajectories (each for an interval of 100 fs) were chosen from the last 2 ps of each simulation to examine if Pd or Ni species are present in the detected clusters by the TCC algorithm. In each frame, the numbers of Pd- or Ni-containing clusters were counted and then divided by the number of clusters that appeared in those 20 trajectories during the 2-ps time frame. The results are presented in Table 3 in terms of the percentages.

### 5.2.3 Microkinetic Modeling

The full dual-site DRM model (discussed in Chapter 4) was adopted for kinetic modeling and catalyst performance evaluations. That is, all the elementary steps in the reaction network are permitted on both sites. The catalyst reactivities will be assessed regarding the turnover frequencies of H<sub>2</sub> and CO productions. Similarly, coke formations were described by the elementary steps related to C<sub>2</sub> and C<sub>6</sub> formations [248]. To account for the active site synergies,

five equilibrated cross-site diffusion reactions (for C, O, OH, CH, and CO), seven cross-site reactions, and three coke formation steps are included to represent the synergistic interactions between different active site types. The descriptor-based kinetic modeling package CatMAP [175] was used to calculate steady-state turnover frequencies (TOFs) for H<sub>2</sub>, CO, and C<sub>6</sub> productions and the surface coverages at 973 K and 1 bar.

## 5.3 Results and Discussion

### 5.3.1 Bimetallic Ga Catalysts

The catalytic descriptors (i.e.,  $BE_C$  and  $BE_O$ ) were first calculated on crystalline Ga and Ga-derived systems. For instance, the optimized C and O atoms at their preferred locations on Ga(100) and Ga containing Ru monomer, dimer, and trimer are displayed in Figure 5.2. The  $BE_C$  and  $BE_O$  are listed in Table 5.1, along with the values on Pd(111), Ni(111), and Ru(0001). It is shown that adding transition metals to pure Ga alters the adsorption energies of C and O, that is, making C bind stronger at the  $s_1$  site and O binding weaker. For NiGa and RuGa, by increasing the number of dopant atoms from the monomer to the trimer, binding energy of C becomes even stronger while adding more Pd atoms further weakens the C binding at the  $s_1$  site. The O atom prefers the  $s_2$  sites. Also, its binding becomes stronger on monomers than on dimers and trimers.

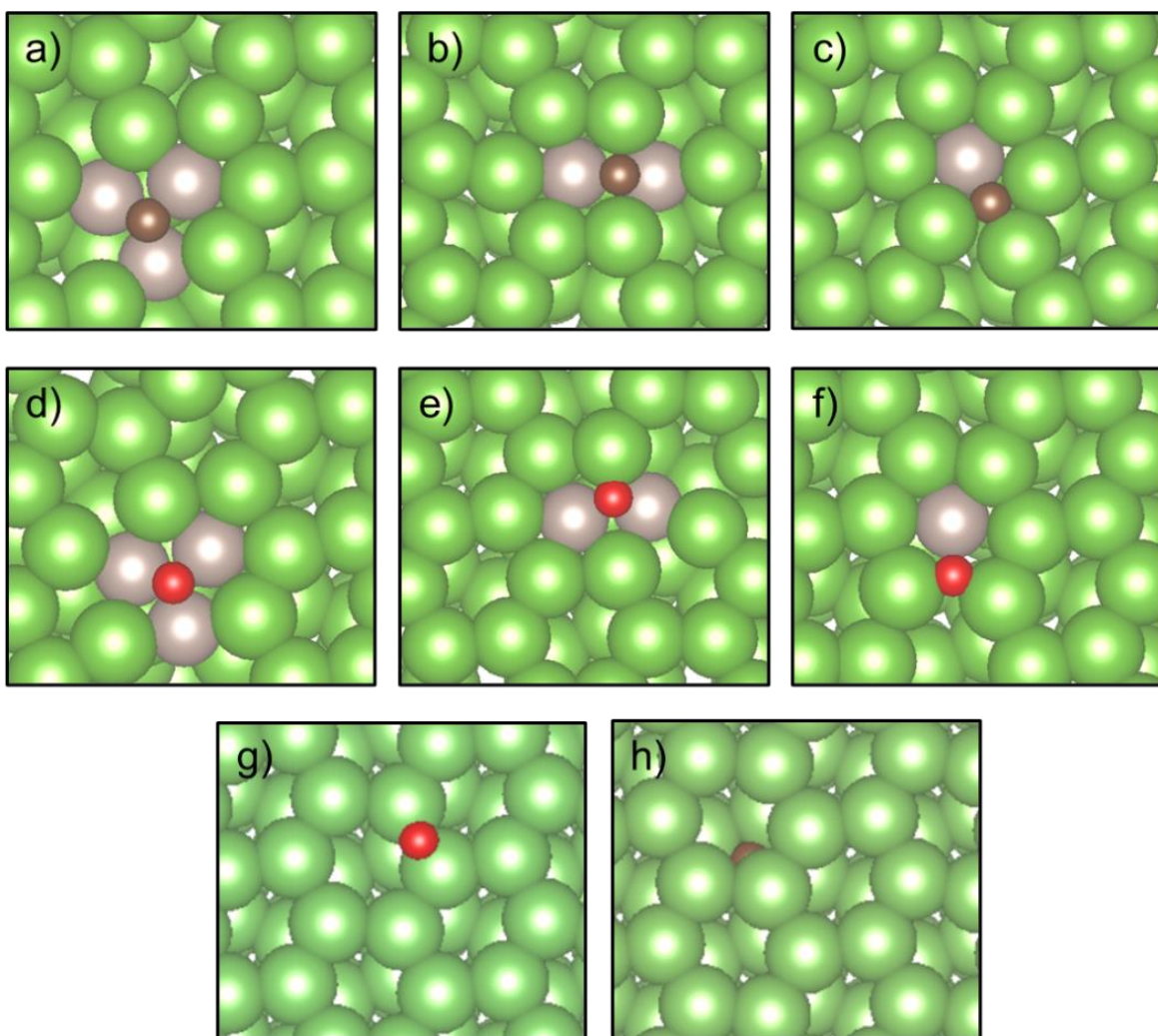


Figure 5.2. (a-c) Optimized structures of C on Ru trimer, dimer, and monomer; (d-f) optimized structures of O on Ru trimer, dimer, and monomer in RuGa. (g-h) Optimized structures of O and C on pure Ga(100) surfaces. The C, O, Ga, and Ru atoms are depicted in brown, red, green, and pink, respectively.

Table 5.1. The  $BE_C$  and  $BE_O$  (in eV) on Pd(111), Ni(111), Ru(0001), Ga(100), and Pd-, Ni-, Ru-doped Ga(100) surfaces.

| Surface   | C       |       |        | O       |       |        |
|-----------|---------|-------|--------|---------|-------|--------|
| Pd(111)   | 2.28    |       |        | 1.21    |       |        |
| Ni(111)   | 2.41    |       |        | 0.21    |       |        |
| Ru(0001)  | 1.76    |       |        | -0.27   |       |        |
| Ga(100)   | 3.97    |       |        | -0.08   |       |        |
|           | Monomer | Dimer | Trimer | Monomer | Dimer | Trimer |
| PdGa(100) | 3.62    | 4.32  | 4.00   | 0.33    | 1.20  | 1.43   |
| NiGa(100) | 3.50    | 3.21  | 2.96   | 0.21    | 0.47  | 0.54   |
| RuGa(100) | 3.26    | 3.35  | 2.35   | 0.21    | 1.09  | 0.47   |

### 5.3.2 Microkinetic Modeling of DRM

In this work, the alloyed Ga catalysts were described using two distinct active site types, denoted as  $s_1$  and  $s_2$ , where  $s_1$  represents the metallic site and  $s_2$  represents the Ga site.

The dual-site model for MKM was adapted from Chapter 4. The turnover frequencies (as  $\text{Log}_{10}[\text{TOF}]$ ) for  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , CO, and  $\text{C}_6$  productions were obtained at 973 K and 1 bar with an  $s_1:s_2$  ratio of 1:9.

The MKM results are summarized in Figure 5.3, in which the variations of  $\text{H}_2$  (or  $\text{H}_2\text{O}$ ), CO, and  $\text{C}_6$  productions with  $BE_O$  and  $BE_C$  are depicted. As shown in Figure 5.3a-b, the TOFs of  $\text{H}_2$  and CO production follow a decreasing order of  $\text{Co}_3\text{Mo}_3\text{N}(111) > \text{Ni}(111) \sim \text{RuGa}(100) > \text{Ru}(0001) > \text{Pd}(111) > \text{NiGa}(100) > \text{Pd}(111) > \text{Ga}(100) > \text{PdGa}(100)$ .



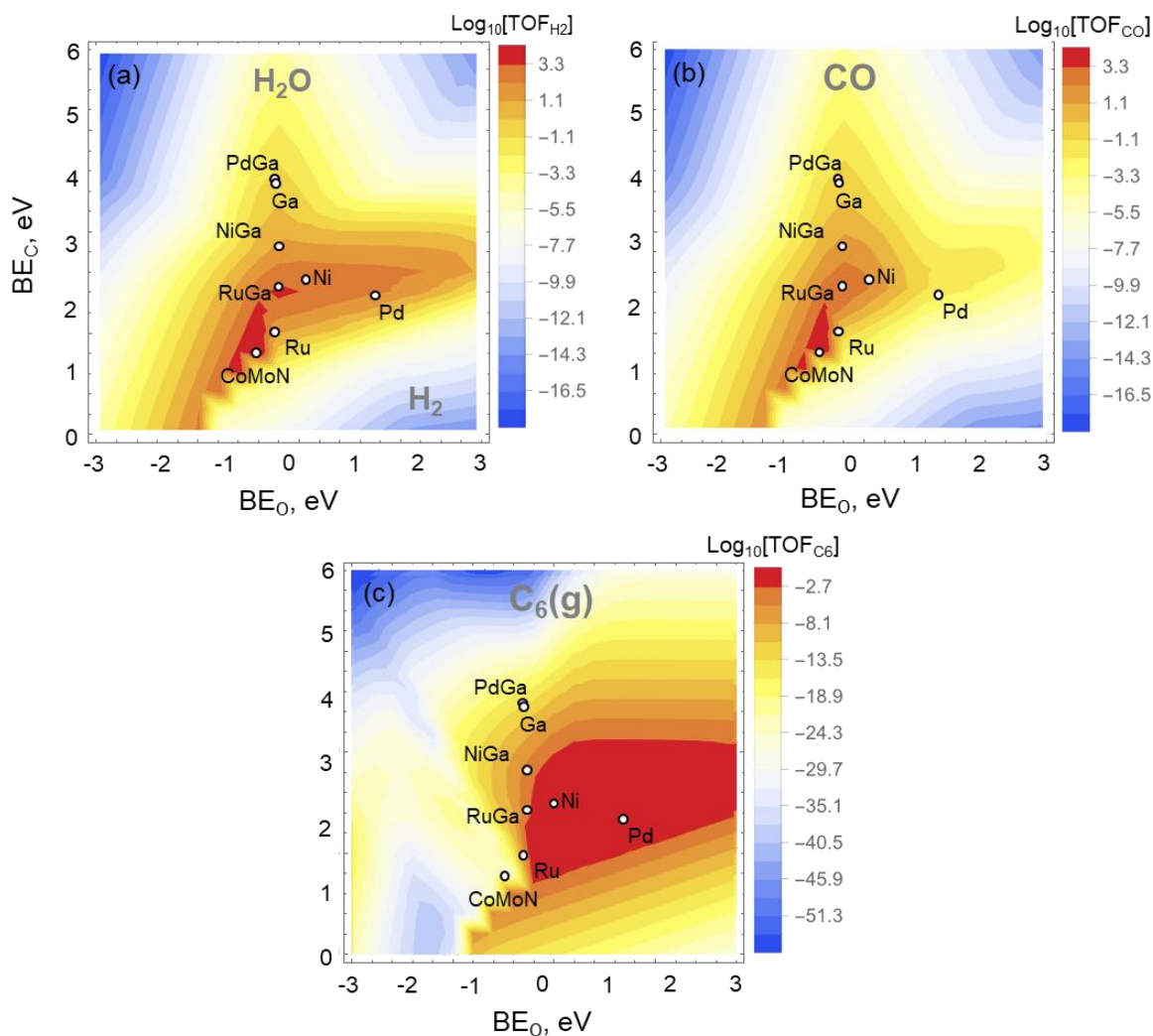


Figure 5.3. Turnover frequencies ( $\text{Log}_{10}[\text{TOF}, \text{s}^{-1}]$ ) for  $CO$ ,  $H_2$ , and  $C_6$  production at 973 K and 1 atm. The active site ratio used in the dual-site model is  $s_1:s_2 = 1:9$  to represent Ga-rich systems.

For alloyed Ga catalysts with diluted transition metal solutes, catalytic reactivity and product selectivity (e.g.,  $H_2$ ) will largely be determined by  $BE_C$ , as  $BE_O$  remains approximately constant. As shown in Figure 5.3a, the binding of C becomes stronger in the order of  $PdGa < Ga < NiGa < RuGa$ . When  $BE_C$  is above 3 eV, as on pure Ga or PdGa, RWGS will dominate,

producing H<sub>2</sub>O as the main product instead of H<sub>2</sub>. When  $BE_C$  is below 3 eV, H<sub>2</sub> becomes the main product. Overall, the H<sub>2</sub> and CO production rates peak when  $BE_C$  and  $BE_O$  are in the range of 1~2.5 eV, respectively. A more straightforward trend can be observed for CO production. The TOF frequency increase monotonously with increasing binding energies of C. Nevertheless, the TOF maxima still exist for all major products. This means that too strong C binding will eventually hinder H<sub>2</sub> and CO productions.

Guided by the heatmaps, it can be learned that the binding of C should be adequately strong to achieve DRM reactivities comparable to Ni or Ru. This is a potential challenge to alloyed Ga catalysts with low concentrations of Pd and Ni. DFT calculations showed that the formations of Ru or Ni trimers might be necessary to lower  $BE_C$  below 3 eV. This finding can be used as a guideline to optimize bimetallic liquid Ga catalysts for DRM.

Predictions of coke formations from DRM are shown in Figure 5.3c. Unlike H<sub>2</sub> and CO, C<sub>6</sub> formation drastically drops when  $BE_O$  is below -1 eV, suggesting that strong O binding is necessary to suppress coke formations. The rates of C<sub>6</sub> formation in Ga systems are lower than the transition metal catalysts. This promising result does indicate Ga alloys possess the potential to resist coking.

### 5.3.3 AIMD Simulations of Amorphous Ga

The liquid catalysts were modeled using the slabs taken from the last trajectory snapshot of the bulk simulation as the starting point. A vacuum of 30 Å along the dimension perpendicular to the surface was added. First, the changes of the z-position of Pd or Ni atoms (see the inset figures in Figure 5.4) in the slab are shown in Figure 5.5. It shows although both Ni atoms (Ni atoms number 2 and 5, see inset figure of Figure 5.4b) migrate away from the interface after 1.0 ps, and

prefer to stay in the sublayers. They re-emerge to the interface only occasionally afterwards. However, Pd atoms stay at the surface longer than Ni atoms. Pd and Ni surface atoms need to remain at the surface to be catalytically relevant. Next, the time evolution of Pd or Ni distance from the surface when CO is used as a probe molecule. Similar analysis for Ga-rich RhGa [267], PtGa [266] and PdGa [268] indicates that adsorbed CO can keep Pd and Ni atoms at the surface via adsorption.

The PDFs representing the Ga-Ga, Pd-Ga, Ni-Ga, Pd-Pd, and Ni-Ni pairs in liquid Ga, PdGa, and NiGa systems are shown in Figure 5.5. At short Ga-Ga distances ( $r < 2.5 \text{ \AA}$ ), the  $g(r)$  value is negligible, suggesting that liquid state does not contain the dimeric bond characteristic of the Ga-I structure. The first peak of Ga-Ga pair in  $g(r)$  is located at  $r = 2.75 \text{ \AA}$  which is in good agreement with the value ( $\sim 2.73 \text{ \AA}$ ) obtained by Xiong *et al.* [282] using *in-situ* high-temperature XRD method at 800 K. The location of the first peak remains unchanged for PdGa and NiGa (Figure 5.5a). This is because the PdGa and NiGa systems are quite diluted, and the Ga-Ga interactions are not notably affected by the presence of the Pd and Ni solutes. Figure 5.5b shows that the first peak of Pd-Ga and Ni-Ga pairs in  $g(r)$  are located at  $2.55 \text{ \AA}$  and  $2.45 \text{ \AA}$ , respectively, due to the smaller Ni-Ga bond length than the Pd-Ga bond. Figure 5.5c shows that at distances in the range of  $2.5 - 3.5 \text{ \AA}$ , Pd-Pd and Ni-Ni pairs can be detected. Since, these distance ranges perfectly describe the Pd-Pd and Ni-Ni bond distances, Figure 5.5c confirms the existence of at least Ni and Pd dimers in the liquid gallium.

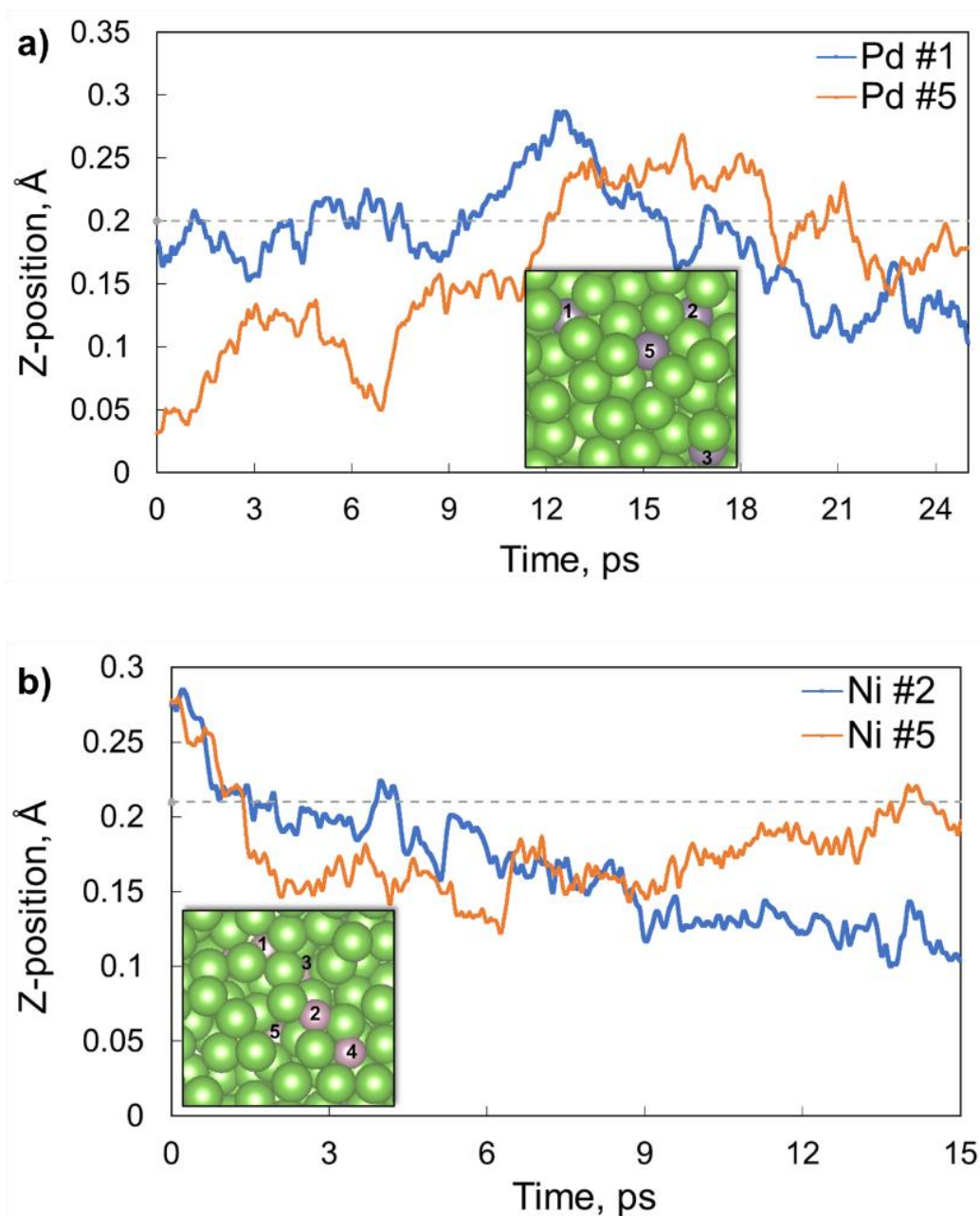


Figure 5.4. The z-position of two (a) Pd and (b) Ni atoms in liquid PdGa and NiGa slab models as function of time, depicted in orange and blue lines. Inset figures show the final locations of chosen dopant atoms in liquid PdGa and NiGa surfaces with numbered Pd and Ni atoms. Ga, Pd, and Ni are shown in green, purple, and pink colors. Dash lines resemble the first maximum density of the Ga for the PdGa and NiGa surfaces.

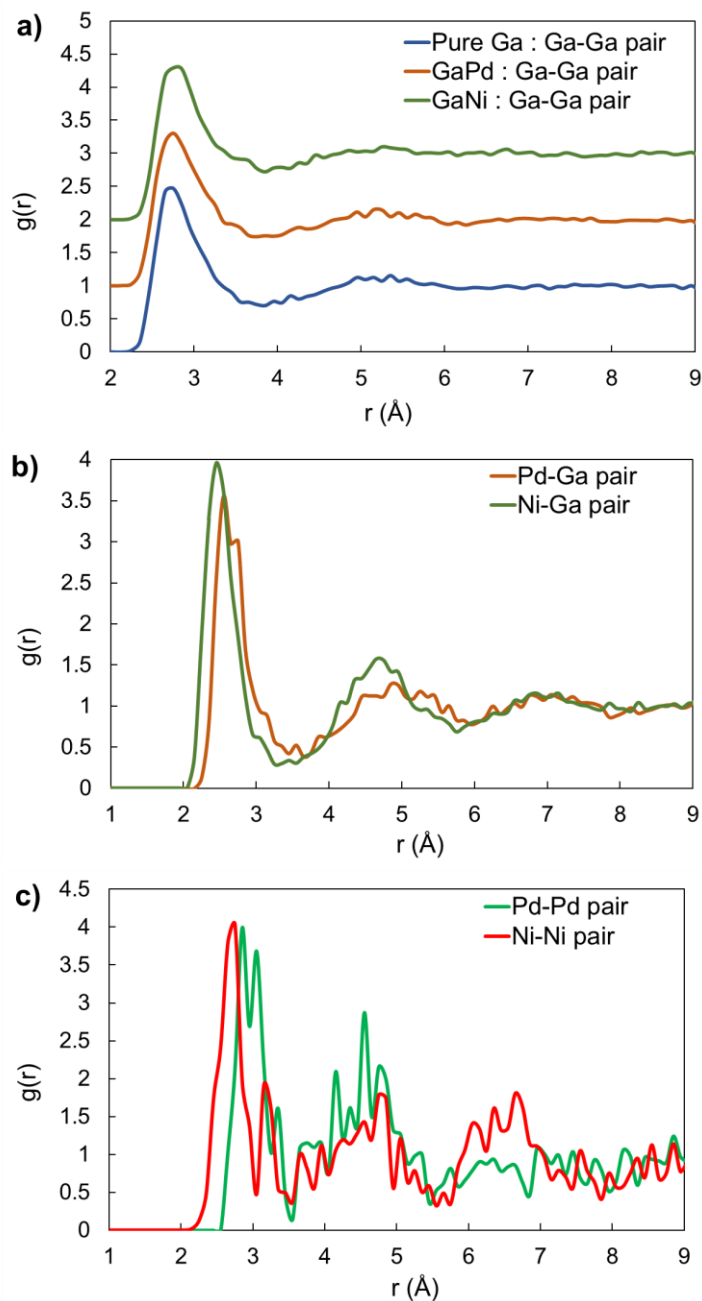


Figure 5.5. Radial distribution functions,  $g(r)$ , for (a) Ga-Ga pair in pure Ga (blue), PdGa (orange), and NiGa (green); (b) Pd-Ga pair (orange) in PdGa system, and Ni-Ga pair (green) in NiGa; (c) Pd-Pd pair (green) in PdGa system, and Ni-Ni pair (red) in NiGa obtained from AIMD during the last 2 ps of AIMD simulations.

To identify the bonds between neighboring atoms, the TCC method was applied with a maximum bond length cut-off of  $r_{Ga-Ga} = 3.70 \text{ \AA}$ ,  $r_{Pd-Ga} = 3.50 \text{ \AA}$ ,  $r_{Pd-Pd} = 3.31 \text{ \AA}$ ,  $r_{Ni-Ga} = 3.35 \text{ \AA}$ , and  $r_{Ni-Ni} = 3.01 \text{ \AA}$ . Also,  $f_c$  parameter is set to 0.82 to control the maximum degree of asymmetry of a fourfold ring of neighbors before it is detected, instead as two threefold rings of neighbors [183]. Figure 5.6 presents the results for fourteen specific motifs with different types of local environments: three-fold symmetry (6Z), motifs with four-fold symmetry (6A, 9A, 10A, 11F, 12E, BCC), and five-fold symmetric (7A, 8A, 8B, 9B, 10B, 11C, 11E, 12D). They were obtained by analyzing 20 frames from the last 2 ps of AIMD simulations of Ga, PdGa and NiGa systems. Results show that clusters larger than 8B will form for the bimetallic PdGa and NiGa systems.

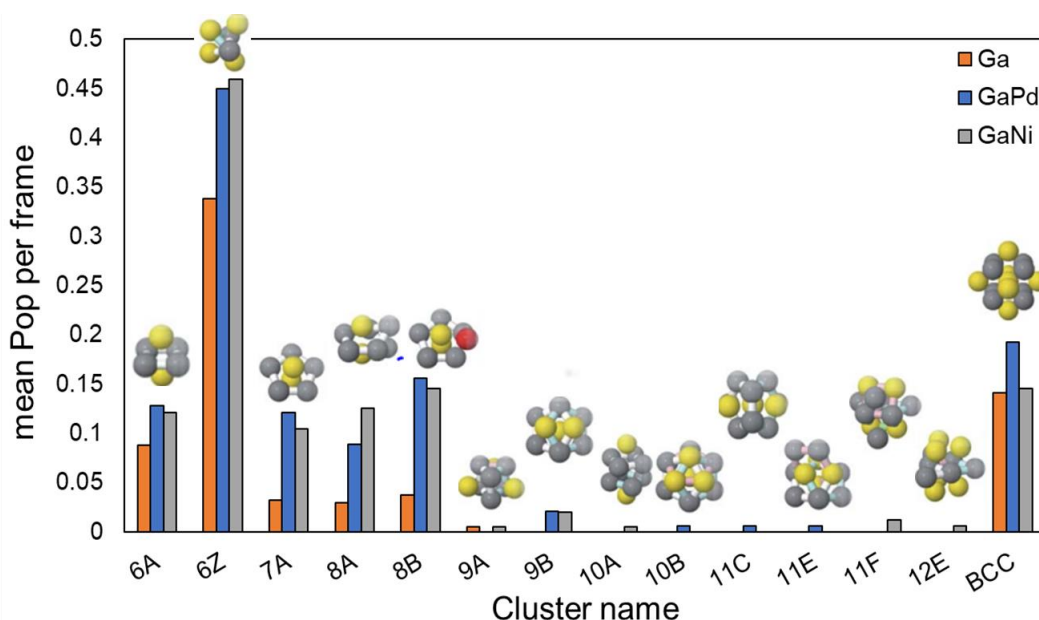


Figure 5.6. Fractional populations for each cluster motif over the last 2 ps of AIMD simulations at 800 K. Orange: Ga; Blue: PdGa; and Grey NiGa. Inserted pictures of clusters are taken from Ref. [183].

Table 5.2 lists the probabilities of finding Pd or Ni atoms in each cluster. For clusters smaller than 8B, there is no significant difference between the chance of finding Pd or Ni in the clusters (except for 6A). However, active sites are most likely to appear in the clusters larger than 8B. Therefore, the presence of active sites on the surface can be increased by controlling the cluster formation.

Table 5.2: the percentage of active sites appearing in each cluster associated in Figure 5.6.

| Cluster name | Active site appearance (%) |       |
|--------------|----------------------------|-------|
|              | PdGa                       | NiPd  |
| 6A           | 4.4                        | 16.7  |
| 6Z           | 32.2                       | 24.7  |
| 7A           | 34.2                       | 35.3  |
| 8A           | 16.0                       | 23.7  |
| 8B           | 40.3                       | 33.9  |
| 9A           | -                          | 100.0 |
| 9B           | 44.4                       | 60.0  |
| 10A          | -                          | 0.0   |
| 10B          | 50.0                       | -     |
| 11C          | 100.0                      | -     |
| 11E          | 0.0                        | -     |
| 11F          | -                          | 0.0   |
| 12E          | -                          | 0.0   |
| BCC          | 24.1                       | 16.7  |

Figure 5.7 shows the TCC analyses of the PdGa surfaces using 20 frames at last 2 ps of AIMD simulations at 303, 600, and 800 K. As temperature increases, the fraction of larger motifs (larger than 8B) decrease. Hence, at moderate or lower temperatures(303K-600K), clusters larger

than 8B are more likely to form. As discussed, the probability of the appearance of active sites in these clusters is higher (see Table 5.2). Therefore, at low and moderate temperatures, more active sites are expected to appear on the liquid Ga surface.

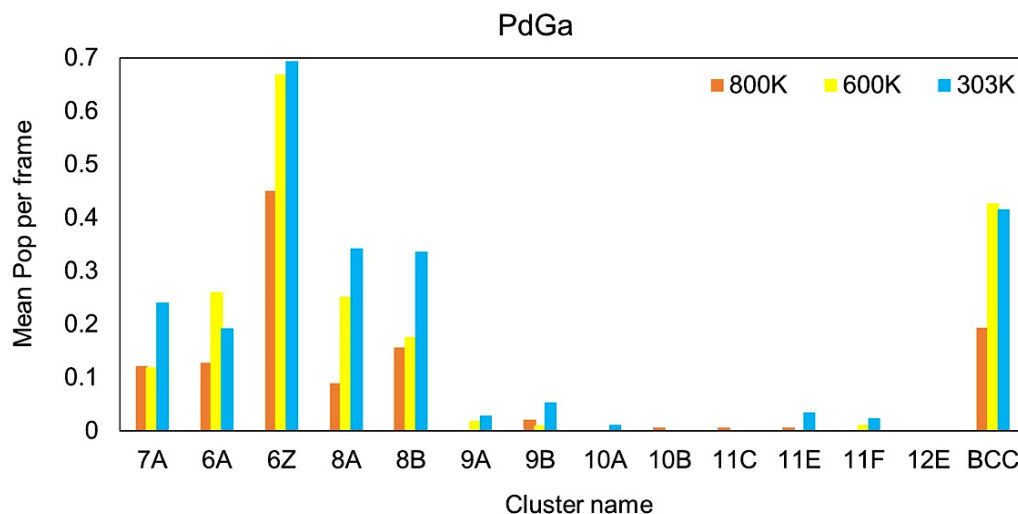


Figure 5.7. Fractional populations for each cluster motif in PdGa during the last 2 ps of AIMD simulations at 303, 600, and 800 K.

## 5.4 Conclusions

DFT calculations coupled with microkinetic modeling showed that the rate of hydrogenation production can be competitive against conventional transition metal catalysts when Ru trimers are formed in bimetallic Ga catalysts. Also, strong O binding is necessary to mitigate coke formation during DRM.

Although Ni and Pd have high tendency to diffuse into the Ga solution, we can anticipate that the transition metal active sites will be immediately available once adsorbents are introduced



to the system. The TCC analysis revealed that more transition metal species are likely to appear on the liquid Ga surface to participate catalytic reactions at low and moderate temperatures.

## 6 Mechanistic Understanding of Support Effect on the Activity and Selectivity of Indium Oxide Catalysts for CO<sub>2</sub> Hydrogenation

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C. Y. R. Vera, N. Manavi, Z. Zhou, L.-C. Wang, W. Diao, S. Karakalos, B. Liu, K.J. Stowers, M. Zhou, H. Luo, D. Ding, Mechanistic understanding of support effect on the activity and selectivity of indium oxide catalysts for CO<sub>2</sub> hydrogenation, *Chem. Eng. J.*, 426 (2021) 131767.

### 6.1 Introduction

Hydrogenation of CO<sub>2</sub> to methanol is a promising route to mitigate CO<sub>2</sub> emissions into the environment while producing an important constituent to the chemical industry [286-288]. Apart from efficient CO<sub>2</sub> capturing and hydrogen production from renewable sources, the successful deployment of this technology also relies on the development of highly active, selective, and stable catalyst for the CO<sub>2</sub> hydrogenation to methanol [287, 288]. Currently, the industrial production of methanol uses syngas (CO/CO<sub>2</sub>/H<sub>2</sub>) as the feedstock in a process that involves a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst [289-291]. In the absence of CO, Cu-based catalysts usually afford low methanol selectivity resulting from the competing side reaction of reverse water-gas shift (RWGS). In addition, Cu catalysts are susceptible to water-assisted sintering, which deteriorates its long-term stability [291].

Recently, indium oxide (In<sub>2</sub>O<sub>3</sub>) has been discovered as a highly selective and stable catalyst for methanol synthesis from CO<sub>2</sub>, even superior to Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> under the same conditions [89, 96, 97, 292-294]. Both experimental and theoretical studies suggested that the surface oxygen vacancies (O<sub>v</sub>) on In<sub>2</sub>O<sub>3</sub> play a key role in activating CO<sub>2</sub> and H<sub>2</sub> molecules during the reaction

[89, 96-98, 292-296]. The catalytic properties of bulk  $\text{In}_2\text{O}_3$  catalyst can be substantially affected by doping with a small amount of second metal or metal oxide, which provides an opportunity for tuning its activity and selectivity in  $\text{CO}_2$  conversion. For instance, the addition of Cu, [297] Co, [298] Ni, [299] or Pd [99, 300-302] has been shown to boost the activity of  $\text{In}_2\text{O}_3$  in methanol synthesis from  $\text{CO}_2$ , due to the promoted formation of surface  $\text{O}_\text{v}$  on  $\text{In}_2\text{O}_3$  as well as improved  $\text{H}_2$  dissociation. Similar promotional effect has also been reported for  $\text{In}_2\text{O}_3$  doped with rare earth metal oxides like Y or La, which was attributed to the enhanced reducibility [98]. From a practical point of view, however,  $\text{In}_2\text{O}_3$  catalyst should be dispersed on a support material to better utilize and stabilize the active indium species. Previous studies have shown that a remarkable support effect exists for  $\text{In}_2\text{O}_3$  catalysts in  $\text{CO}_2$  hydrogenation to methanol, with  $\text{ZrO}_2$  giving the best performance among various candidates [293, 296]. It has been suggested that the catalytic properties of supported  $\text{In}_2\text{O}_3$  should be determined by its electronic interactions with the support rather than by geometric effects [293]. The exceptional activity of  $\text{In}_2\text{O}_3$  supported on  $\text{ZrO}_2$ , especially in the monoclinic phase, has been correlated with the formation of abundant  $\text{O}_\text{v}$  resulting from tensile strain at the phase boundary due to a less favorable lattice matching [296]. Moreover, the synergy between indium oxide species and the zirconia substrate with variable interfacial structures has been proposed to have important consequences on the product selectivity of  $\text{CO}_2$  hydrogenation over In-Zr oxide catalyst [303]. Despite these efforts, the nature of the interfacial active sites as well as the role of surface  $\text{O}_\text{v}$  on both the active  $\text{In}_2\text{O}_3$  and the support in the performance of  $\text{In}_2\text{O}_3$ -based catalysts remains elusive.

The basicity and reducibility of oxide catalysts could have substantial impact on their ability in the adsorption and activation of  $\text{CO}_2$ , thus playing important roles in determining the catalytic properties for  $\text{CO}_2$  hydrogenation reactions [304, 305]. In this work, we have

systematically studied  $\text{In}_2\text{O}_3$  catalysts supported on three metal oxides (i.e.,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , and  $\text{PrO}_x$ ), with different reducibilities for  $\text{CO}_2$  hydrogenation under ambient pressure. Rare earth (lanthanide) metal oxides are known for their strong basic properties and reducible characteristics [306, 307].  $\text{CeO}_2$  is a well-known reducible oxide widely used in numerous catalytic reactions [307, 308]. For methanol production from  $\text{CO}_2$ ,  $\text{CeO}_2$  has been demonstrated to be an excellent support for Cu-based catalysts by generating a metal-oxide interface involving Cu and ceria nanoparticles [304, 305]. For In-based catalysts, a promoting effect of  $\text{CeO}_2$  as support was also observed in the  $\text{CO}_2$  conversion [101]. Due to their excellent oxygen ion mobility and variable stoichiometry, praseodymium oxides ( $\text{PrO}_x$ ) have found many applications as catalysts for different reactions, [102-104] as well as a promoter for the creation of oxygen vacancies on  $\text{CeO}_2$  and  $\text{ZrO}_2$  [309-311]. For  $\text{CO}_2$  hydrogenation reactions, it has been employed as a promoter of Pd/ $\text{SiO}_2$  catalyst with promising results, [104] but the use of  $\text{PrO}_x$  as a support for  $\text{In}_2\text{O}_3$  has not been reported. These catalysts were characterized by powder X-ray diffraction (XRD),  $\text{N}_2$  adsorption, transmission electron microscopy (TEM),  $\text{H}_2$ -temperature programmed reduction ( $\text{H}_2$ -TPR), temperature programmed desorption of  $\text{CO}_2$  ( $\text{CO}_2$ -TPD), *in situ* X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS). DFT modelling were also conducted to account for the support effect on the formation of oxygen vacancies and reaction mechanism in  $\text{CO}_2$  hydrogenation. The role of support in the activity and selectivity of  $\text{In}_2\text{O}_3$  catalysts has been discussed in light of the experimental and computational results.

## 6.2 Methods Section

### 6.2.1 Computational Methods

Periodic spin-polarized DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP) [253, 254]. The Perdew–Burke–Ernzerhof (PBE) functional

was used to account for electron exchange correlation effects [123], and the projector-augmented wave (PAW) method was used to approximate core electrons [142]. The plane-wave cutoff energy was set to be 520 eV for the optimization of bulk lattice. Integrations over the first Brillouin Zone were performed using the Monkhorst-Pack  $k$ -point sampling method with a  $4 \times 4 \times 4$  mesh [203]. For In, Zr, O, C, and H species, their respective (4d, 5s, 5p), (4s, 4p, 4d, 5s), (2s, 2p), (2s, 2p), and (1s) states are treated as valence electrons. The Hubbard U method is used to correct the self-interaction errors of In, Zr, Ce, and Pr oxides, [312] with respective  $U_{\text{eff}}$  values of 4.0 eV, 7.0 eV, 5.0 eV, [313] and 0.5 eV, [314] corresponding to each metal ion. These  $U_{\text{eff}}$  values were shown to produce reasonable geometric and electronic structures for the native metal oxides.

The adsorption energy ( $E_{\text{ads}}$ ) of adsorbate (A) is expressed by Eqn. (6.1):

$$E_{\text{ads}} = E_{A^*} - (E_{\text{surf}} + E_{A(g)}) \quad (6.1)$$

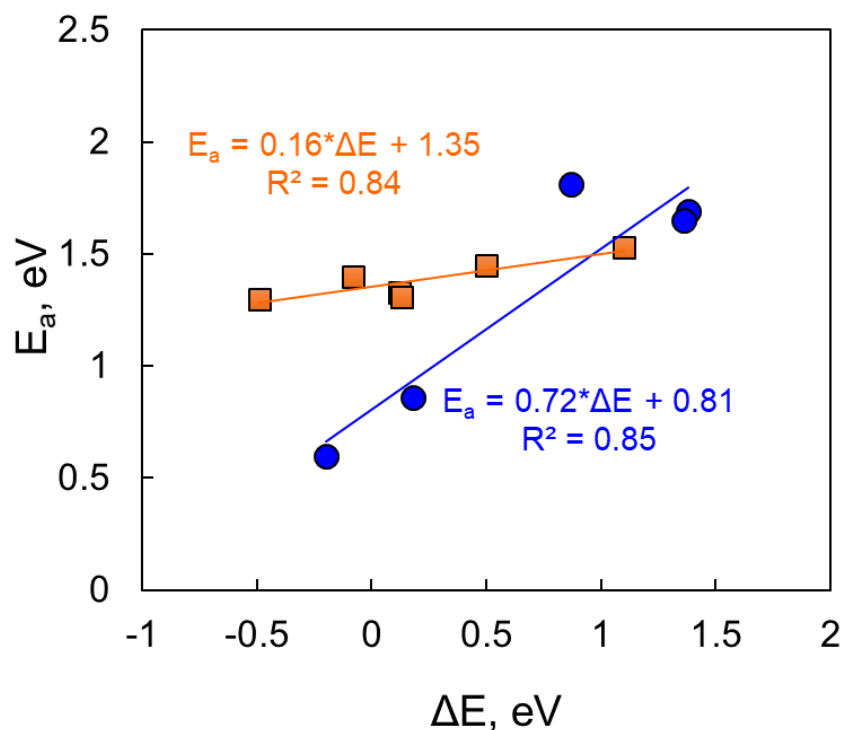
where  $E_{A^*}$ ,  $E_{\text{surf}}$ ,  $E_{A(g)}$  are total energies of the slab with adsorbate, clean surface, and the isolated adsorbate in the gas phase, respectively.

The reaction energy is expressed by Eqn. (6.2):

$$\Delta E_{\text{rxn}} = \sum E_{\text{Products}} - \sum E_{\text{Reactants}} \quad (6.2)$$

where  $\Delta E_{\text{rxn}}$ ,  $E_{\text{Products}}$ , and  $E_{\text{Reactants}}$  represent the reaction energy, the total energies of reactants and products, respectively.

The Nudged Elastic Band (NEB) method [149] was used to search transition states of CO<sub>2</sub> hydrogenation and C–O bond cleavage. All transition state structures were refined using the DIMER method [150].



**Figure 6.1.** Linear correlations between energy barrier ( $E_a$ ) and reaction energy ( $\Delta E$ ) for CO<sub>2</sub> hydrogenation (orange) and CH<sub>2</sub>O formation (blue).

As shown in Figure 6.1, DFT calculations revealed that the energy barriers ( $E_a$ ) and corresponding reaction energies ( $\Delta E$ ) for the elementary C–H bond formation (orange) and C–O bond scission (blue) steps on In<sub>2</sub>O<sub>3</sub> (110), In<sub>2</sub>O<sub>3</sub> (110) O<sub>v</sub>(O<sub>4</sub>), In<sub>2</sub>O<sub>3</sub> (110) O<sub>v</sub>(O<sub>1</sub>), Zr-In<sub>2</sub>O<sub>3</sub> (110) O<sub>v</sub>(O<sub>4</sub>), Ce-In<sub>2</sub>O<sub>3</sub> (110) O<sub>v</sub>(O<sub>4</sub>), and Pr-In<sub>2</sub>O<sub>3</sub> (110) O<sub>v</sub>(O<sub>4</sub>) follow linear relationships. Such relationships have been employed to estimate the energy barriers for the rate-determining steps related to initial CO<sub>2</sub> hydrogenation and CH<sub>2</sub>O formation during CO<sub>2</sub>-to-CH<sub>3</sub>OH conversion.

## 6.2.2 Catalyst Models

Semi-periodic slab models were employed to represent  $\text{In}_2\text{O}_3$  as active sites for  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversion. Slab models representing the most common facets of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , and  $\text{PrO}_x$  were also constructed. To account for the  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversion at the interfacial sites, mixed oxide models were used. Computationally, such models maintain well-defined active sites and allow probing the catalytic effect related to local mixing.

**$\text{In}_2\text{O}_3(110)$ :**  $\text{In}_2\text{O}_3$  has been frequently used as active component for  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversions. [96, 97] The (110) facet was adopted due to its low surface energy ( $0.969 \text{ J/m}^2$ ). [96] The (110) facet is cleaved from the pre-optimized  $\text{In}_2\text{O}_3$  bulk. A four-layer  $\text{In}_2\text{O}_3$  slab with lateral dimensions of  $10.30 \text{ \AA} \times 14.56 \text{ \AA}$  was built, with the bottom two layers fixed at the optimized bulk lattice values. A vacuum space of  $10 \text{ \AA}$  separates the periodic images of the slab along the perpendicular direction. A  $3 \times 3 \times 1$   $\Gamma$ -centered  $k$ -point mesh was employed, [315] with a plane-wave cutoff of  $400 \text{ eV}$ . The break condition for the ionic relaxation is  $0.05 \text{ eV/\AA}$ . Dipole corrections are included since only one side of the slab was used for adsorption.

As shown in Figure 6.2a, the top layer of  $\text{In}_2\text{O}_3(110)$  contains two types of O sites (denoted as  $\text{O}_1$  and  $\text{O}_4$ ); and three types of In sites (denoted as  $\text{In}_1$ ,  $\text{In}_2$ , and  $\text{In}_3$ ) differentiated by different coordination numbers with neighboring O atoms. In the mixed oxide models, only the most energetically stable substitutions for the support metal ions (i.e., Zr, Ce, and Pr) were considered. The Zr dopant favors the  $\text{In}_1$  site (Figure 6.2b), while Ce (Figure 6.2c) and Pr (Figure 6.2d) both prefer the  $\text{In}_2$  site. The oxygen vacancy ( $\text{O}_v$ ) was created at the  $\text{O}_1$ ,  $\text{O}_2$  and  $\text{O}_4$  sites.

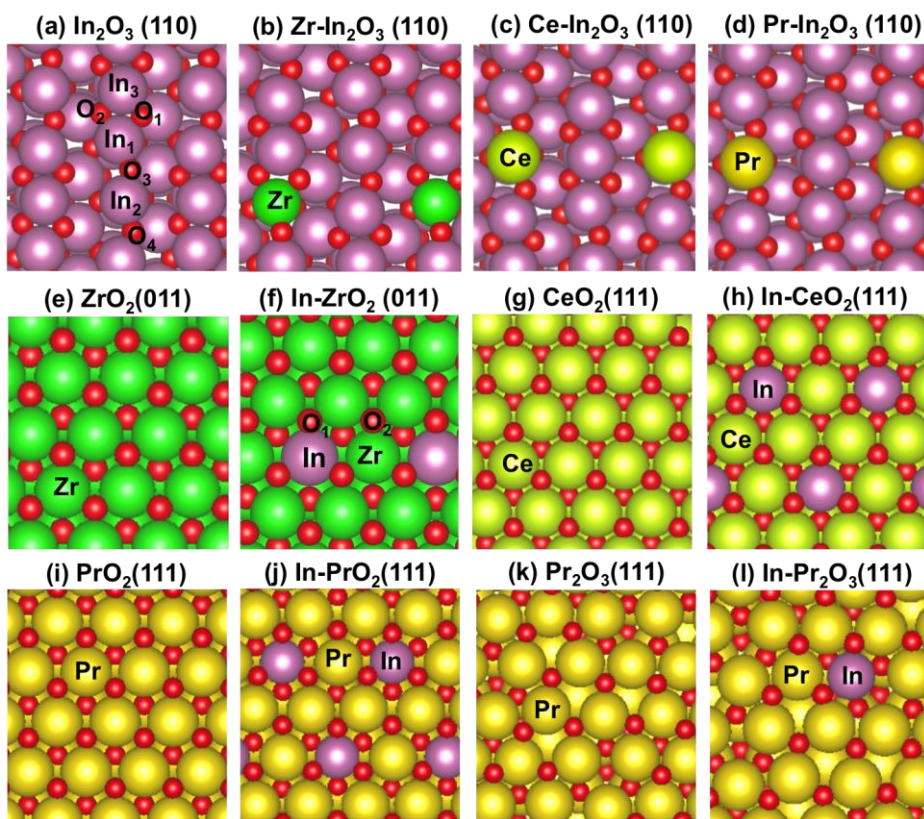


Figure 6.2. Optimized slab models: (a)  $\text{In}_2\text{O}_3$  (110), (b)  $\text{Zr-In}_2\text{O}_3$  (110), (c)  $\text{Ce-In}_2\text{O}_3$  (011), (d)  $\text{Pr-In}_2\text{O}_3$  (011), (e)  $\text{ZrO}_2$ (011), (f)  $\text{In-ZrO}_2$ (011), (g)  $\text{CeO}_2$ (111), (h)  $\text{In-CeO}_2$ (111), (i)  $\text{PrO}_2$ (111), (j)  $\text{In-PrO}_2$ (111), (k)  $\text{Pr}_2\text{O}_3$ (111), and (l)  $\text{In-Pr}_2\text{O}_3$ (111). The In, Zr, Ce, Pr, and O atoms are in pink, green, yellow, gold, and red, respectively.

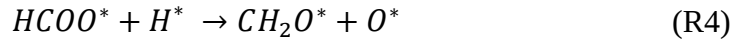
**Models for catalyst supports:** A three-layer  $\text{ZrO}_2$  (011) slab in a  $(3 \times 2)$  supercell based on the tetragonal  $\text{ZrO}_2$  lattice was chosen to represent the  $\text{ZrO}_2$  support (Figure 6.2e). Its bottom two layers were also fixed at the optimized bulk values. For  $\text{In-ZrO}_2$ (011), two types of O vacancies ( $\text{O}_1$  and  $\text{O}_2$ ) are produced as shown in Figure 6.2f. Similar approaches were applied to the cubic phase in a  $(1 \times 1)$  unit cell of  $\text{CeO}_2$  and  $\text{PrO}_x$ . The O-terminated close-packed (111) facets were chosen for both oxides and are illustrated in Figure 6.2g and Figure 6.2i, respectively. Similar mixed oxide support models containing In dopants are shown in Figure 6.2h and Figure 6.2j,



respectively. We identified that the cubic fluorite  $\text{PrO}_2$  is unstable and will likely transform into the more stable  $\text{Pr}_2\text{O}_3$  phase. [316] Experimental works showed that surface  $\text{PrO}_2$  can be reduced to  $\text{Pr}_2\text{O}_3$  at 830 K. Hence, the more stable  $\text{Pr}_2\text{O}_3$  phase, as shown in Figure 6.2k-l, was included the following analyses.

### 6.3 Results and Discussion

It has been shown that the  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversion pathway on  $\text{In}_2\text{O}_3$  proceeds according to R1-R7, , as indicated by the IR results and suggested by other researchers [96-98, 292, 297, 317] The  $\text{HCOO}$  (formate) and  $\text{CH}_2\text{O}$  are considered as key intermediates for  $\text{CH}_3\text{OH}$  formation.



The  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversion on  $\text{In}_2\text{O}_3(110)$  was studied as a benchmark system. As represented by the grey dashed line in Figure 6.3b, without any  $\text{O}_v$ , molecular  $\text{CO}_2$  binds at the O site moderately with a binding energy of -1.45 eV. The value obtained from this work agrees well with that reported by Ye and coworkers [97]. The formation of  $\text{HCOO}$  is endothermic on the

perfect  $\text{In}_2\text{O}_3$  surface. To enable the C–H bond formation, H needs to additional energy to migrate onto the In top site adjacent to the adsorbed  $\text{CO}_2$ , which also transforms into a metastable configuration (designated as  $[\text{H}_{\text{In}} + bi\text{-CO}_2]$  in Figure 6.3a). Once  $\text{HCOO}^*$  is formed, it is likely hydrogenated quickly and desorb as formic acid.

To understand the mechanism for the  $\text{O}_v$ -assisted  $\text{CO}_2$  conversion, the  $\text{O}_v(\text{O}_4)$  site in  $\text{In}_2\text{O}_3(110)$  (Figure 6.2a) was chosen. As shown by the purple dashed line in Figure 6.3b, the  $\text{CO}_2$  binding energy remains unchanged, but the dissociated H atom binds much stronger at the In site adjacent to  $\text{O}_v(\text{O}_4)$ . This favors  $\text{HCOO}$  formation and lowers the overall potential landscape, and the formed  $\text{HCOO}$  intermediate will be more stable at the  $\text{O}_v(\text{O}_4)$  site as well. The  $\text{HCOO}$ -to- $\text{CH}_2\text{O}$  conversion (R4) produces one  $\text{O}^*$  species that fills the  $\text{O}_v(\text{O}_4)$  site. Nevertheless, R5 ( $\text{CH}_3\text{O}$  formation) is endothermic with a substantial energy barrier ( $>1.18$  eV) and has become a potential rate-limiting step for  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversion.

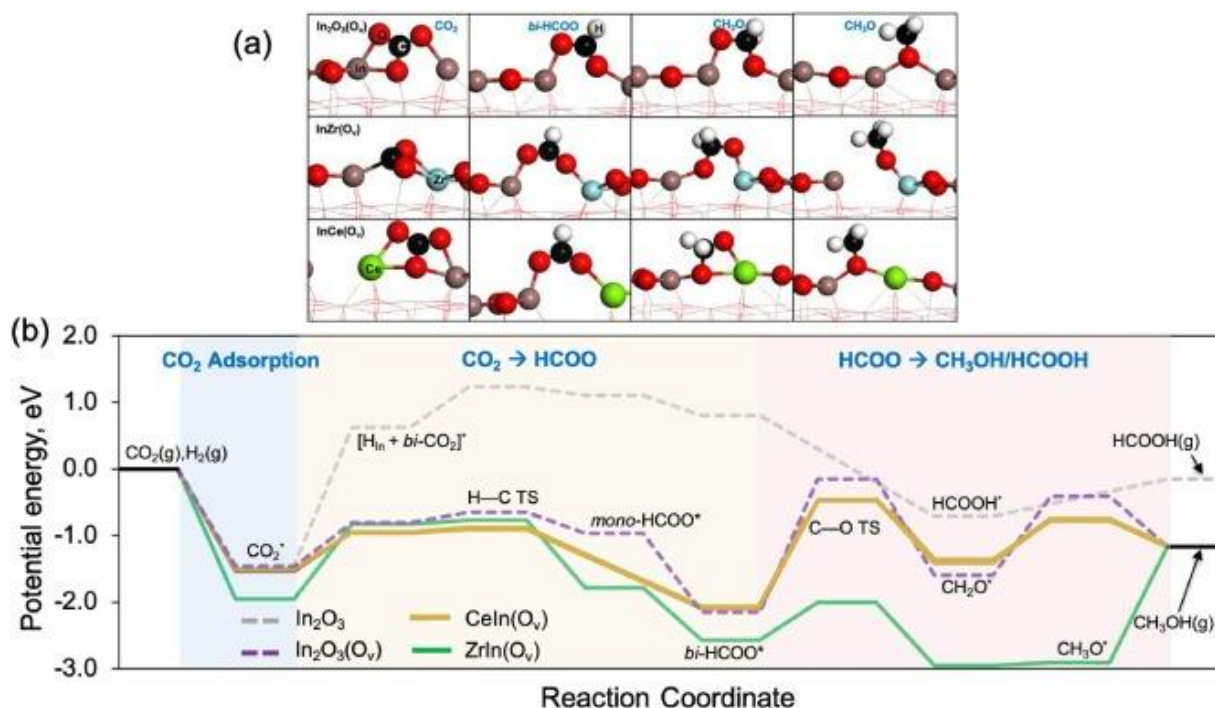


Figure 6.3. (a) Optimized structures of CO<sub>2</sub> and its hydrogenation intermediates via the formate pathway on pristine and doped In<sub>2</sub>O<sub>3</sub>(1 1 0) surfaces with O<sub>v</sub>, and (b) the potential energy profiles depicting methanol formation from CO<sub>2</sub> hydrogenation on pristine and doped In<sub>2</sub>O<sub>3</sub>.

As stated earlier, experimental evidence suggests that methanol formation from CO<sub>2</sub> hydrogenation occur via the formate pathway over In<sub>2</sub>O<sub>3</sub> catalysts regardless of the support materials, and the variations in catalyst activities are influenced by the mixing of support metal ions in In<sub>2</sub>O<sub>3</sub>. Mixed oxide models are adopted to mimic the intimate interactions between In<sub>2</sub>O<sub>3</sub> and its support at the interface that modified the structural properties (e.g., O<sub>v</sub> formation) of the catalyst. Firstly, two possible model surfaces, i.e., Zr-doped In<sub>2</sub>O<sub>3</sub> with O<sub>v</sub> (denoted as Zr-In<sub>2</sub>O<sub>3</sub>(O<sub>v</sub>)) and In-doped ZrO<sub>2</sub> with O<sub>v</sub> (denoted as In-ZrO<sub>2</sub>(O<sub>v</sub>)) are chosen to study the dominance of either In<sub>2</sub>O<sub>3</sub> or support materials in activity and selectivity of CH<sub>3</sub>OH production. As energy profile in Figure 6.4b shows, although the CO<sub>2</sub>-to-HCOO conversion on In-ZrO<sub>2</sub>(O<sub>v</sub>) (Figure 6.4a) is more exothermic, further conversion to form CH<sub>2</sub>O and CH<sub>3</sub>OH will be more challenging when compared with the conversion on Zr-In<sub>2</sub>O<sub>3</sub>(O<sub>v</sub>). Hence, the overall activity and CH<sub>3</sub>OH production rate are determined by the In<sub>2</sub>O<sub>3</sub> catalyst rather than the support. This result is consistent with the experimental results that In<sub>2</sub>O<sub>3</sub> phase is the major contributor to the activity of supported In catalysts.

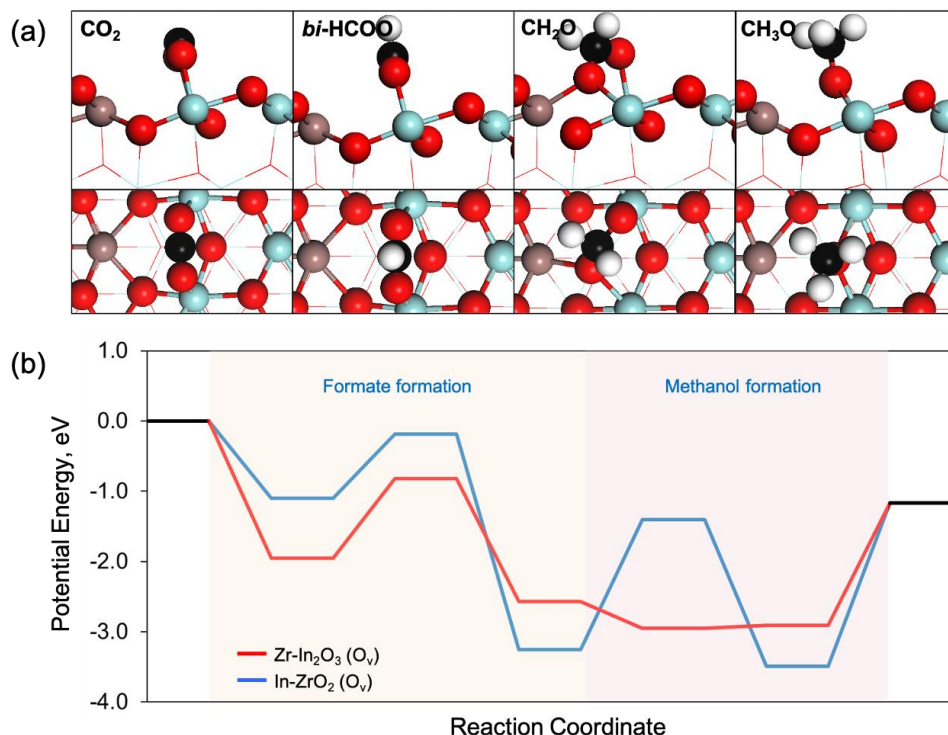


Figure 6.4. (a) Optimized structures of  $\text{CO}_2$  and its hydrogenation intermediates via the formate pathway on In-doped  $\text{ZrO}_2$  (011) surface. (b) Potential energy profiles for  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  conversion on Zr-doped  $\text{In}_2\text{O}_3$  (110) (denoted as  $\text{Zr-In}_2\text{O}_3(\text{O}_v)$ ) (red) versus In-doped  $\text{ZrO}_2$  (011) (denoted as  $\text{In-ZrO}_2(\text{O}_v)$ ) (blue) surfaces.

Next, the  $\text{M-In}_2\text{O}_3$  (110) models ( $\text{M}=\text{Zr}$ ,  $\text{Ce}$ , and  $\text{Pr}$ , see Figure 6.2b-d) were employed to understand the impact of different M ions on  $\text{In}_2\text{O}_3$  activity. In  $\text{Zr-In}_2\text{O}_3(\text{O}_v)$ ,  $\text{CO}_2$  binds at the  $\text{O}_v(\text{O}_4)$  site in a bent configuration, with both of its O atoms coordinated with the same Zr atom. A similar configuration has also been reported by Zhang *et al.* [100]. Also,  $\text{CO}_2$  binds even stronger on  $\text{Zr-In}_2\text{O}_3(\text{O}_v)$  than on  $\text{In}_2\text{O}_3(\text{O}_v)$  by ca. 0.5 eV (Table C.1), indicating additional promotional effect related to Zr doping. The potential energy profiles on  $\text{In}_2\text{O}_3$  doped with Ce (blue) and Pr (green) in the presence of  $\text{O}_v$  sites are also included in Figure 6.3 for comparison. Even in the presence of the energetically stable  $\text{O}_v$  sites, which are as the active sites for  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$

conversion, molecular CO<sub>2</sub> binds at the lattice O site in a *carbonate*-like configuration. The CO<sub>2</sub> binding energies both Ce-In<sub>2</sub>O<sub>3</sub> O<sub>v</sub>(O<sub>3</sub>) and Pr-In<sub>2</sub>O<sub>3</sub> O<sub>v</sub>(O<sub>3</sub>) are weaker than on Zr-In<sub>2</sub>O<sub>3</sub> O<sub>v</sub>(O<sub>4</sub>) (Table C.1), suggesting that the stronger CO<sub>2</sub> binding on Zr-In<sub>2</sub>O<sub>3</sub>(O<sub>v</sub>) is due to its unique configuration. The O<sub>v</sub> sites in the Ce- and Pr-doped In<sub>2</sub>O<sub>3</sub> surfaces are still capable of facilitating HCOO formation and stabilization, but the CH<sub>2</sub>O and CH<sub>3</sub>O formations are more endothermic than on Zr-doped In<sub>2</sub>O<sub>3</sub>(110). This comparison suggests that all doped surfaces are anticipated to promote CH<sub>3</sub>OH formation, while the Zr-doped In<sub>2</sub>O<sub>3</sub> shall exhibit the most promotional effect. This trend is consistent with the activity results in terms of methanol formation rate Figure 6.5a).

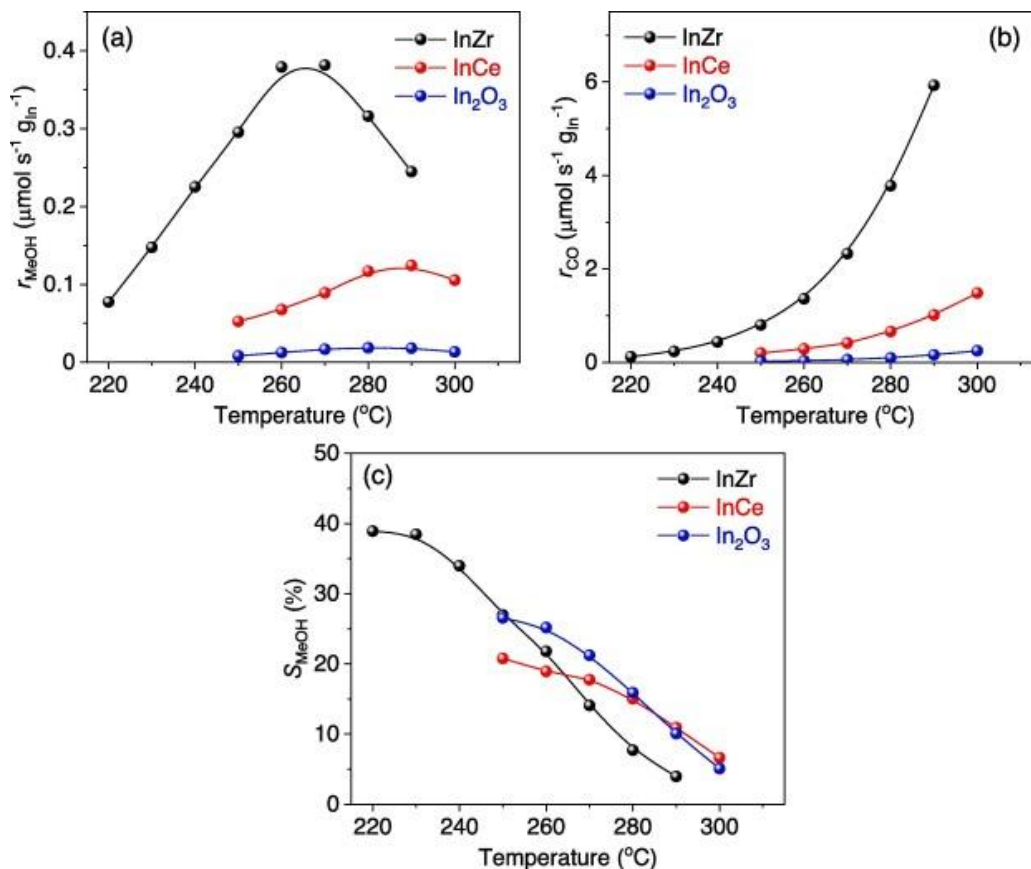


Figure 6.5. Indium-mass-normalized formation rates of (a) methanol, (b) CO and (c) methanol selectivity of various supported  $\text{In}_2\text{O}_3$  catalysts as a function of reaction temperature. Reaction conditions: 0.2 g catalyst, 1:3  $\text{CO}_2/\text{H}_2$ , 20 ml/min, 0.1 MPa.

To understand the support effect on the methanol selectivity, the CO formation pathways on Zr- and Ce-doped  $\text{In}_2\text{O}_3$  catalysts were investigated. It has been reported that CO formation through direct dissociation of adsorbed  $\text{CO}_2^*$  or carboxyl species ( $\text{OCOH}^*$ ) on  $\text{In}_2\text{O}_3(110)$  and Zr- $\text{In}_2\text{O}_3(110)$  is energetically unfavorable, even in the presence of  $\text{O}_v$  sites. [97, 100, 292] Our calculations also showed that  $\text{OCOH}^*$  is much less stable than  $\text{HCOO}^*$ , and will likely decompose into  $\text{CO}_2^*$  and  $\text{H}^*$ . We are also able to show that direct  $\text{CO}_2$  dissociation pathway is the least competitive on all surfaces, and thus, can be eliminated from the consideration. Ye *et al.* [96] and Zhang *et al.* [100] also separately reported that  $\text{CO}_2$  dissociation into CO on  $\text{In}_2\text{O}_3(110)$  and Zr- $\text{In}_2\text{O}_3(110)$  consisting of  $\text{O}_v$  are prohibited. Although the  $\text{HCOO}$  formation is challenging on the  $\text{O}_v$ -free  $\text{In}_2\text{O}_3(110)$ , continuing hydrogenation of  $\text{HCOO}$  will likely produce  $\text{COOH}$ , the precursor for CO formation (data is not shown). Here, in the context of support influence, we propose that CO formation would proceed via the much more stable  $\text{HCOO}^*$  intermediate, which undergoes C–O and C–H bonds cleavage and a simultaneous O–H bond formation producing CO and OH species. This is treated as a parallel pathway to  $\text{CH}_2\text{O}$  formation, resulting in  $\text{CH}_3\text{OH}$  eventually. The energy profiles (Figure 10) showed that the energy barriers for CO formation (blue dashed lines) are higher than that for  $\text{CH}_2\text{O}^*$  formation (red solid lines), in order to overcome C–O and C–H bond cleavage followed by the migration of H (in  $\text{HCOO}^*$ ) onto the oxide lattice O. This trend is corroborated by the higher  $E_a$  for CO formation from the kinetic measurements (Table C.2), suggesting CO formation could become more competitive at only higher temperatures (Figure 6.5).

Moreover, the potential energies corresponding to the doped  $\text{In}_2\text{O}_3$  surfaces are lower than on the pristine  $\text{In}_2\text{O}_3$ , indicating that CO production will also be promoted at the  $\text{In}_2\text{O}_3$ -support interface, again in agreement with the experimental results. The largest difference ( $\Delta E_a$ ) between the formation energy of  $\text{CO}(\text{g})$  and  $\text{CH}_2\text{O}^*$  was obtained on Zr-promoted  $\text{In}_2\text{O}_3$  surface (2.08 eV), followed by  $\text{In}_2\text{O}_3(\text{O}_v)$  and Ce- $\text{In}_2\text{O}_3(\text{O}_v)$  surfaces, which was 1.12 and 0.89 eV, respectively (Figure 6.6). This trend is qualitatively consistent with the kinetic results and may account for the superior selectivity of InZr (see Figure 6.5c) over InCe and  $\text{In}_2\text{O}_3$  especially at low temperatures (<250 °C).

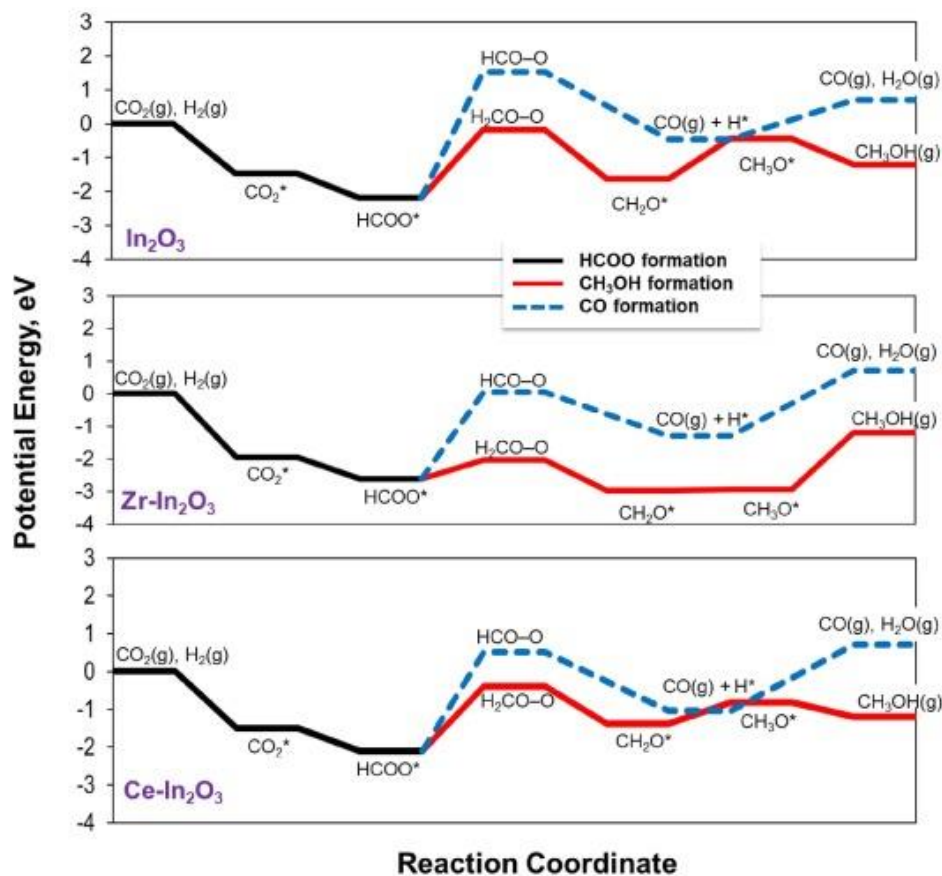


Figure 6.6. Potential energy profiles for parallel CO and CH<sub>3</sub>OH formation pathways on In<sub>2</sub>O<sub>3</sub> and doped In<sub>2</sub>O<sub>3</sub> surfaces with O<sub>v</sub>.

The XRD analyses showed that there is a large fraction of Pr<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> in the bulk phases of InPr, suggesting that the CO<sub>3</sub> fraction increases after reaction. In this section, the adsorbed CO<sub>2</sub> structures on surfaces with O<sub>v</sub> site were obtained (Figure 6.7), with their binding energies (BE<sub>CO<sub>2</sub></sub>) listed in Table C.1. Except on Zr-In<sub>2</sub>O<sub>3</sub> O<sub>v</sub>(O<sub>4</sub>) and ZrO<sub>2</sub>(011) O<sub>v</sub>, *carbonate*-like structures have been observed for CO<sub>2</sub> adsorption on both the In<sub>2</sub>O<sub>3</sub> catalyst and its support. It is also interesting to note that although CO<sub>2</sub> binds on support ZrO<sub>2</sub>(111)O<sub>v</sub> stronger than the Zr-doped In<sub>2</sub>O<sub>3</sub> (110) O<sub>v</sub> surface, carbonate is not formed. Therefore, the adsorbed CO<sub>2</sub> will be converted into HCOO instead.



Our calculations also indicate that CO<sub>2</sub> binds on PrO<sub>x</sub> and CeO<sub>2</sub> supports much stronger than on the In<sub>2</sub>O<sub>3</sub>-based surfaces. It has been observed that the presence of Pr in the catalyst's material (as support or dopant) facilitates carbonate species formation on the surface. The formation of Pr<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> has been clearly identified experimentally.

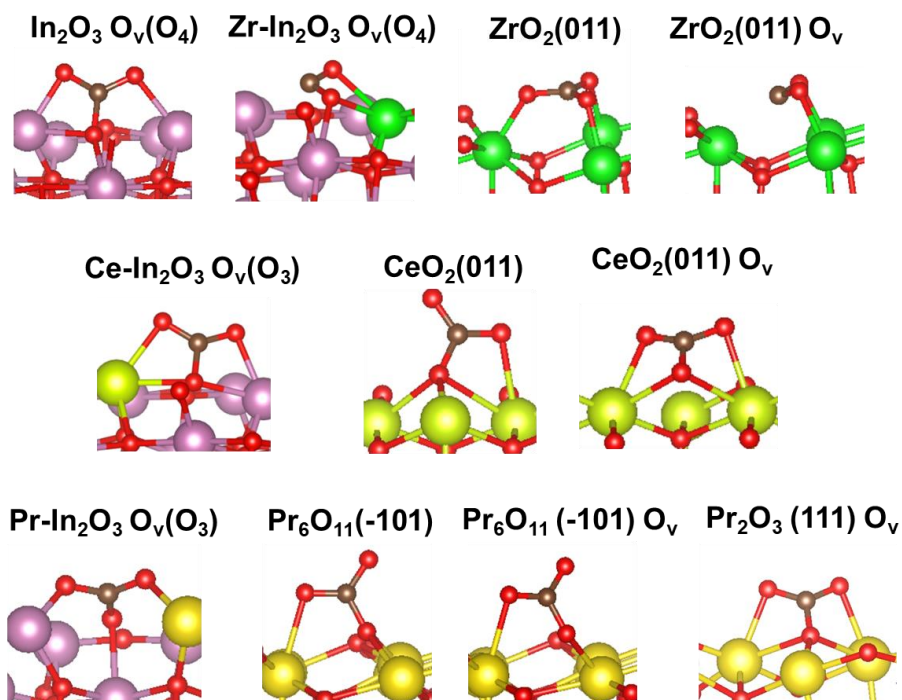


Figure 6.7. CO<sub>2</sub> adsorptions on various oxide surfaces. The In, Zr, Ce, Pr, C, and O atoms are in pink, green, yellow, gold, brown, and red, respectively.

Our DFT calculations suggested that at the In<sub>2</sub>O<sub>3</sub>-support interface the *surface active* O<sub>v</sub> should be located on the In<sub>2</sub>O<sub>3</sub> phase rather than the oxide support. In addition, the incorporation of metal dopants from the support oxide to In<sub>2</sub>O<sub>3</sub> results in higher O<sub>v</sub> formation energies as compared with that on undoped In<sub>2</sub>O<sub>3</sub> surface, being the highest on Zr-In<sub>2</sub>O<sub>3</sub> surface followed by Ce-In<sub>2</sub>O<sub>3</sub> surfaces (Table C.1). This trend is consistent with the calculation results reported in

previous theoretical work [100, 292]. Recently, it has been experimentally demonstrated that the catalytic activity of  $\text{In}_2\text{O}_3$  in  $\text{CO}_2$  hydrogenation is initiated by the formation of surface  $\text{O}_\text{v}$ , but the over-reduction of  $\text{In}_2\text{O}_3$  to  $\text{In}^0$  with time on stream could lead to catalyst deactivation [295]. Accordingly, our theoretical studies suggest that excessive formation of  $\text{O}_\text{v}$  or over-reduction on  $\text{In}_2\text{O}_3$  could be effectively suppressed by creating a mixed-metal-oxide interface between  $\text{In}_2\text{O}_3$  and a metal oxide support such as  $\text{ZrO}_2$ , thus benefiting the durability of the  $\text{In}_2\text{O}_3$  catalysts.

## 6.4 Conclusions

In this work, experimental measurements, presented in this thesis, were combined with DFT simulations to gain insights into the role of different oxide supports in tuning the activity and selectivity of supported  $\text{In}_2\text{O}_3$  catalysts for  $\text{CO}_2$  hydrogenation to methanol. In line with previous studies,  $\text{In}_2\text{O}_3$  supported on  $\text{ZrO}_2$  showed higher activity and selectivity than that on  $\text{CeO}_2$ . While the presence of surface  $\text{O}_\text{v}$  is important in activating the  $\text{In}_2\text{O}_3$  catalysts, the catalytic activity may not be directly correlated with either the  $\text{H}_2$ -reducibility or the abundance of heat-induced  $\text{O}_\text{v}$ , as suggested in prior work. DFT calculations indicated stronger binding of  $\text{CO}_2$  on the O-defective  $\text{InZr}$  surface with a unique bent configuration, in contrast to the carbonate structure on  $\text{InCe}$ . The latter resulted in a higher tendency in the formation of spectator (bi)carbonate species on reducible oxide supported  $\text{In}_2\text{O}_3$  catalysts as well as a lower reaction energy in the subsequent hydrogenation step. The superior activity of  $\text{InZr}$  in methanol formation may originate from the significantly lower energy barriers in the rate-limiting step, i.e., hydrogenation of formate ( $\text{HCOO}$ ) intermediates to  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{O}$ , in agreement with the kinetic results. The discrepancies in methanol selectivity may be accounted for by the energy barrier difference between the parallel competing reactions, i.e., hydrogenation vs. C-O bond cleavage of  $\text{HCOO}$ , which eventually lead

to the formation of methanol and CO products, respectively. The incorporation of metal oxide support to  $\text{In}_2\text{O}_3$  catalyst was also shown to be beneficial for the stable catalytic performance by creating a mixed metal oxide interface between  $\text{In}_2\text{O}_3$  and support, which can suppress the excessive formation of surface  $\text{O}_v$ .

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## 7 Conclusions and Outlook

This thesis focused on CO<sub>2</sub> utilization and the role of bifunctionality in boosting the chemical production from DRM and hydrogenation processes. DFT was used to construct dual-site model systems, identify reaction site preferences, establish catalytic trends, and evaluate catalyst performance. The main findings are summarized below:

- The ternary nitride Co<sub>3</sub>Mo<sub>3</sub>N, which has been shown to be durable for harsh DRM conditions, was studied as a model bifunctional catalyst.
- DFT calculations produced concrete evidence indicating notable site preference displayed by specific reaction intermediates and elementary steps. For instance, carbonaceous species prefer the Co site, while O and OH species favor the Co/Mo<sub>2</sub>N boundary site. Also, the activation of CH<sub>4</sub> favors the Co sites, while CH<sub>x</sub> (x = 0, 1) oxidations prefer the boundary sites.
- Furthermore, DFT calculations were utilized to confirm that dual-site systems permit reaction intermediates (i.e., OH and CHO) to break the bounds imposed by the linear scaling relationships.
- Mean-field, steady-state microkinetic modeling confirmed that the DRM turnover frequency on Co<sub>3</sub>Mo<sub>3</sub>N may exceed some of the best-known pure transition metal catalysts such as Ni, Pt, or even Ru.
- Most notably, the ability of Co<sub>3</sub>Mo<sub>3</sub>N to mitigate coke formation is far superior over transition metal catalysts by facilitating the oxidation and transportation of carbonaceous species (e.g., C, CH) thanks to the cross-site diffusions of O, C, OH, CO and CH species.
- The approach employed in this thesis to unravel the complex origin of catalytic performance will also impact on future discovery and design of bifunctional catalyst.

Ga-based alloys with Ni and Pd as active metals were set out to verify the reactivities of Ni, Pd, and Ru in liquid Ga solutions for DRM reaction as single atom alloy catalyst.

- DFT calculations coupled with microkinetic modeling on solid-state Ga systems showed that the trimer clustering of Ru in bimetallic Ga improves H<sub>2</sub> production rate.
- The TCC analysis on amorphous PdGa and NiGa revealed that more transition metal species are likely to appear on the liquid Ga surface to participate catalytic reactions at low and moderate temperatures.

For CO<sub>2</sub> hydrogenation, the support effects on the catalytic reactivity and product selectivity on In<sub>2</sub>O<sub>3</sub> catalysts were also investigated using DFT. The main findings are:

- Bicarbonates are the predominant species with little or no detectable formate (HCOO) or methoxy (CH<sub>3</sub>O) on the surface of the pure support oxides. Such experimental observations were confirmed with DFT calculations on CO<sub>2</sub> adsorptions. DFT further showed that the CO<sub>2</sub> adsorption at the oxygen vacancy (O<sub>v</sub>) is strengthened in Zr-In<sub>2</sub>O<sub>3</sub> in a unique bent binding configuration not observed on other surfaces.
- A stronger CO<sub>2</sub> binding facilitates subsequent formation and stabilization of the HCOO intermediate, which is a common intermediate for both methanol and CO formations. Carbonate-like structure is favored on CeO<sub>2</sub> supported or unsupported In<sub>2</sub>O<sub>3</sub> catalysts.
- DFT predicts that In<sub>2</sub>O<sub>3</sub> supported on ZrO<sub>2</sub> showed higher activity and selectivity toward CO<sub>2</sub> hydrogenation than on CeO<sub>2</sub>. This finding agrees well with the kinetic measurements. The hydrogenation of HCOO to CH<sub>2</sub>O is the rate-limiting step, which is thermodynamically favored on Zr-In<sub>2</sub>O<sub>3</sub>(O<sub>v</sub>) than on Ce-In<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>(O<sub>v</sub>) surfaces.

- The discrepancies in methanol selectivity can be explained based on the difference in the energy barriers between the hydrogenation and C–O bond cleavage pathways involving HCOO.
- The theoretical studies, consistent with experimental, indicated that the support of  $\text{In}_2\text{O}_3$  catalysts induce the formation of a mixed oxide phase at the interface to excessive formation of surface  $\text{O}_\text{v}$ .

In this thesis, DFT-based molecular modeling is demonstrated as a powerful tool to unequivocally clarify the catalytic functionality of well-defined active sites in model systems. I also demonstrated the potential of DFT in exploring sophisticated composite catalyst systems when coupled with AIMD and MKM techniques. Given the success of this work, there is a bright future for theoretical modeling in advancing the fundamental catalysis science and technology for  $\text{CO}_2$  utilization and other catalytic applications.

DFT calculations showed that  $\text{Co}_3\text{Mo}_3\text{N}$  is very active for DRM, however, additional studies are needed to explore other catalyst surface structures to obtain further insight into the catalytic activity of this catalytic material. One focal area is to understand if the other surface compositions of Co domain and  $\text{Mo}_3\text{N}$  domain can participate in the dual-site mechanisms. Although trends in DRM activity were predicted with MKM, several simplifications such as total neglect of lateral interactions between intermediates were made. In the future, such molecular interactions between adsorbates should be included. Besides  $\text{Co}_3\text{Mo}_3\text{N}$ , we shall be able to pursue other nitride alloys such as  $\text{Ni}_3\text{Mo}_3\text{N}$  or  $\text{Fe}_3\text{Mo}_3\text{N}$  to broaden the bifunctional catalytic material repertoire and boost the utilization of catalysts formed with earth-abundant metals.

In addition, we are still at the infant stage to study and understand the catalytic properties of liquid heterogenous catalysts. The performance of doped liquid Ga catalysts have not been fully

tested for DRM. For this reason, detailed fundamental investigations are needed to estimate the catalytic activity of this catalyst for DRM using different transition metals (Ni, Pd, or Ru) as an active site. For DRM active site engineering, dimer, trimer, or cluster transition metal configurations on liquid gallium will be explored to enhance catalyst reactivity. More systematic studies to suppress coke formation are desperately needed in order to apply these materials for meaningful DRM applications.

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# Appendix A - Molecular mechanism of methane dry reforming on

## Co<sub>3</sub>Mo<sub>3</sub>N catalyst with dual sites

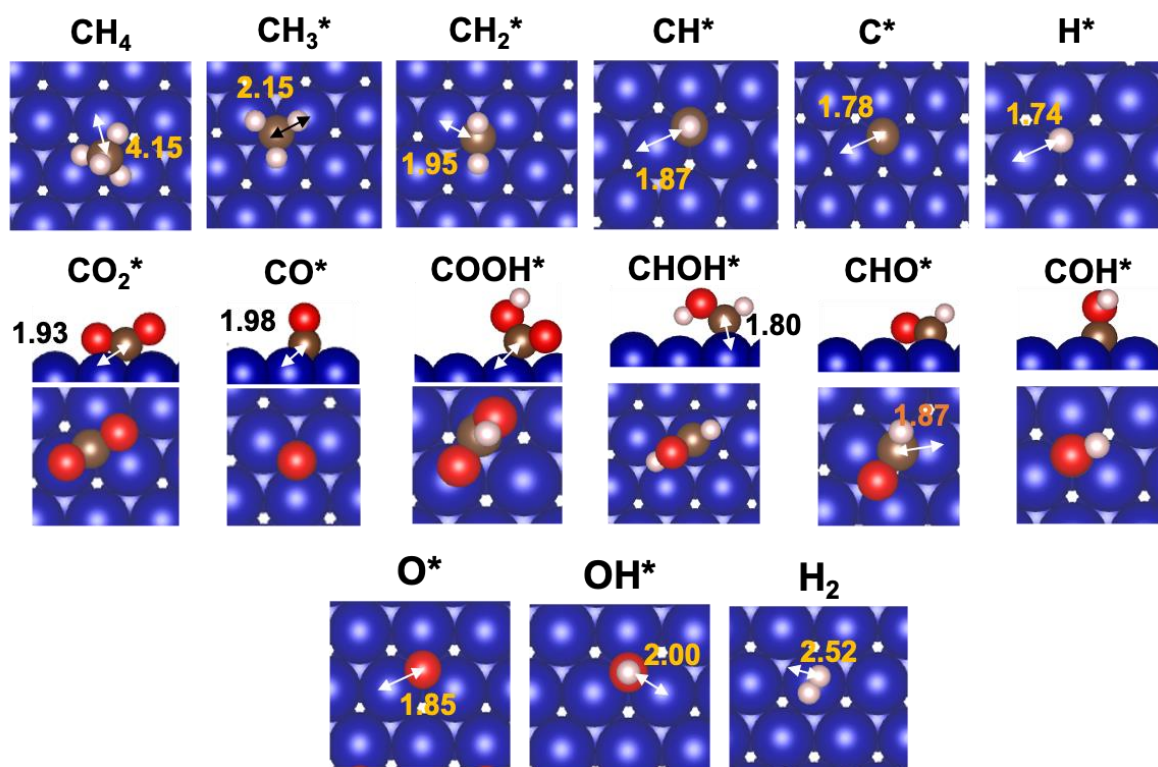


Figure A.1. Optimized structures of the intermediates listed in Table 3.2 on Co(0001). C, O, H, and Co are depicted in brown, red, light pink, and dark blue, respectively.

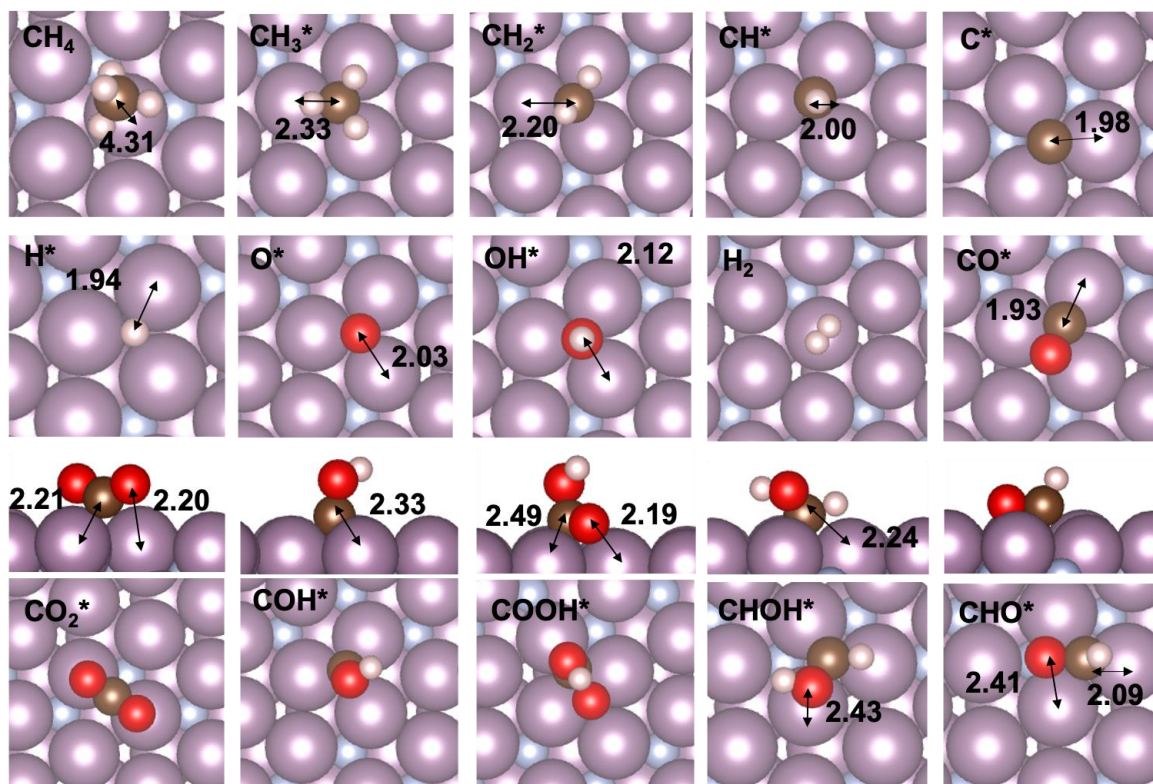


Figure A.2. Optimized structures of the intermediates listed in Table 3.2 on  $\text{Mo}_2\text{N}(110)$ . C, O, H, Mo, and N are depicted in brown, red, light pink, dark blue, and light blue, respectively.

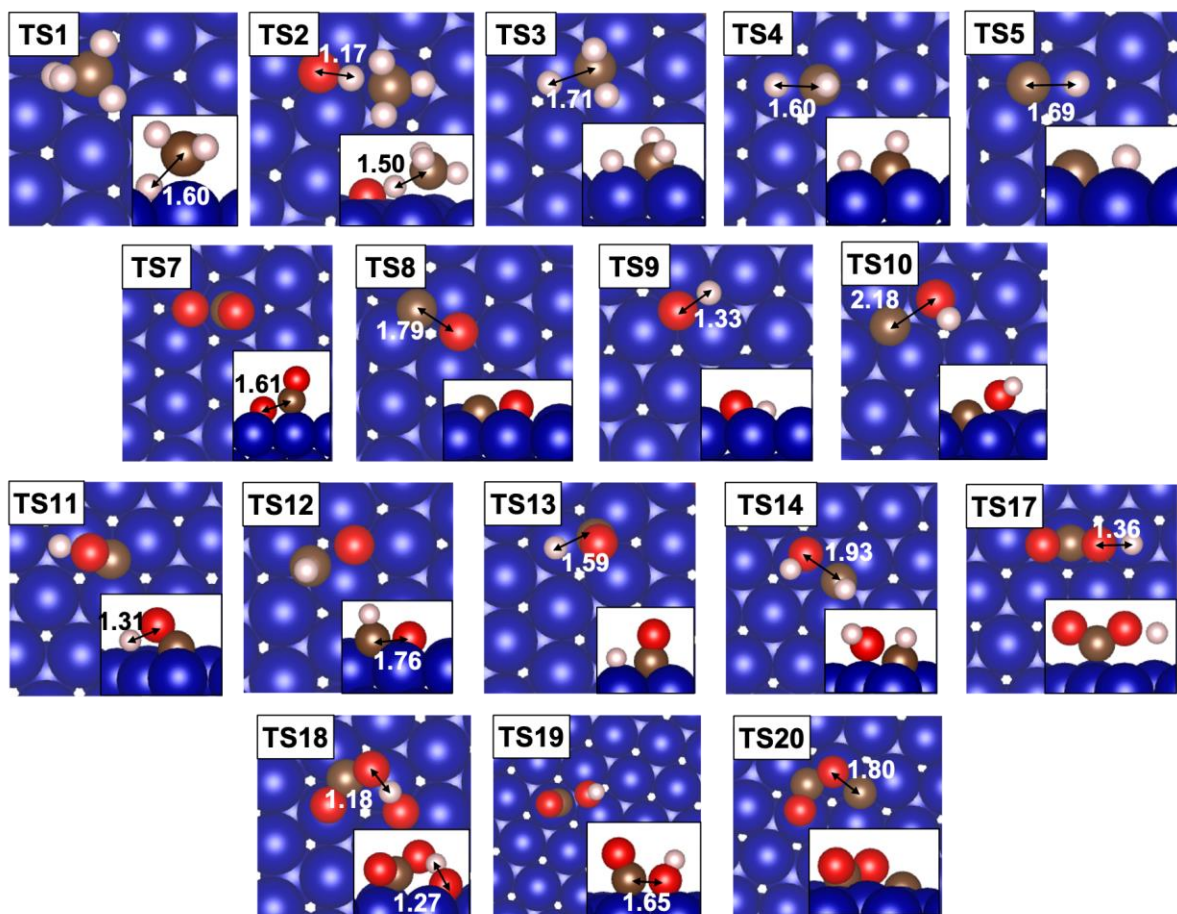


Figure A.3. Optimized transition state structures on Co(0001). Atomic distances (in Å) are labeled and indicated in dashed lines. C, O, H, and Co are depicted in brown, red, white, and dark blue, respectively.



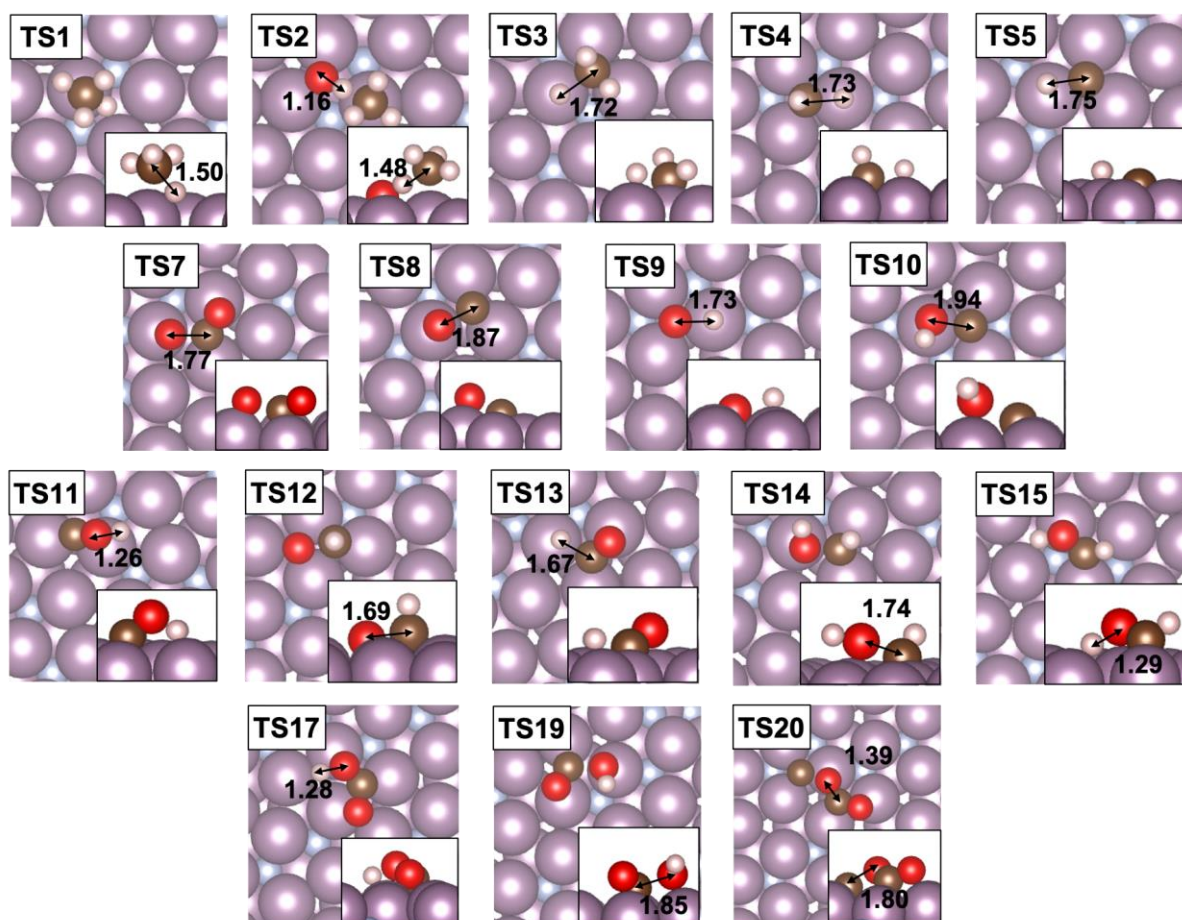


Figure A.4. Optimized transition state structures on Mo-terminated  $\text{Mo}_2\text{N}(110)$ . Atomic distances (in Å) are labeled and indicated in dashed lines. C, O, H, Mo, and N are depicted in brown, red, white, pink, and light blue, respectively.



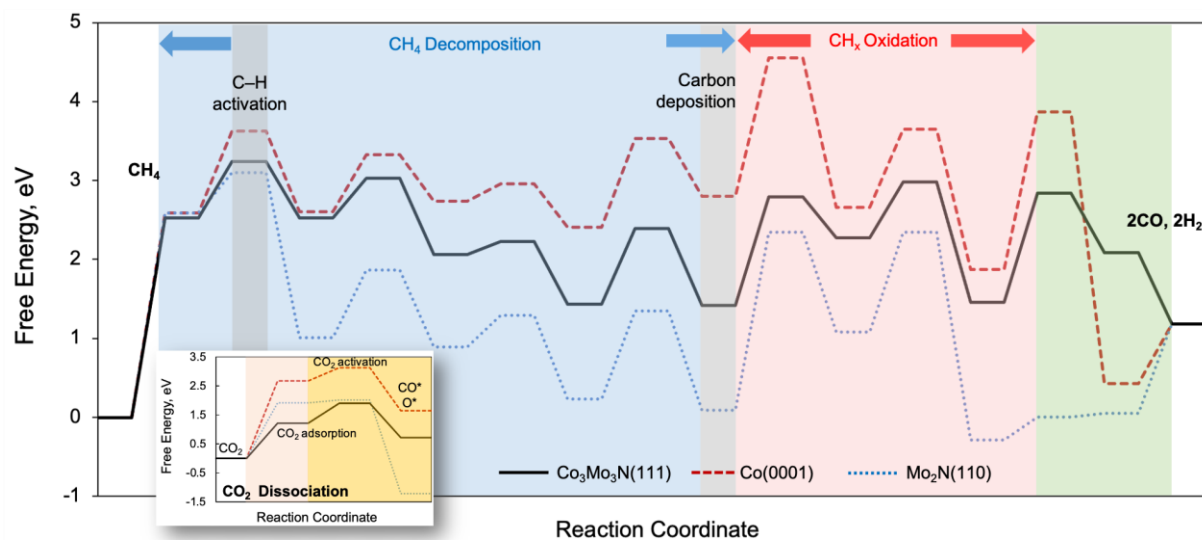


Figure A.5. Free energy profiles depicting on  $\text{Co}_3\text{Mo}_3\text{N}(111)$  (black),  $\text{Co}(0001)$  (red dashed), and  $\text{Mo}_2\text{N}(110)$  (blue dotted) emphasizing the  $\text{CH}_4$  activation and  $\text{COH}$  oxidation pathway at 1000 K and 1 bar. Gas phase  $\text{CO}_2$  and  $\text{CH}_4$  and corresponding clean surfaces were used as the zero energy references. Similarly, gas phase  $\text{CO}$  and  $\text{H}_2$ , following the reaction stoichiometry, are considered as the final products. The kinetically critical C–H activation step and carbon formation are highlighted with grey bars. The inset figure illustrates the accompanying  $\text{CO}_2$  dissociation on respective  $\text{Co}_3\text{Mo}_3\text{N}(111)$  (black),  $\text{Co}(0001)$  (red dashed), and  $\text{Mo}_2\text{N}(110)$  (blue dotted) surfaces under the same condition.

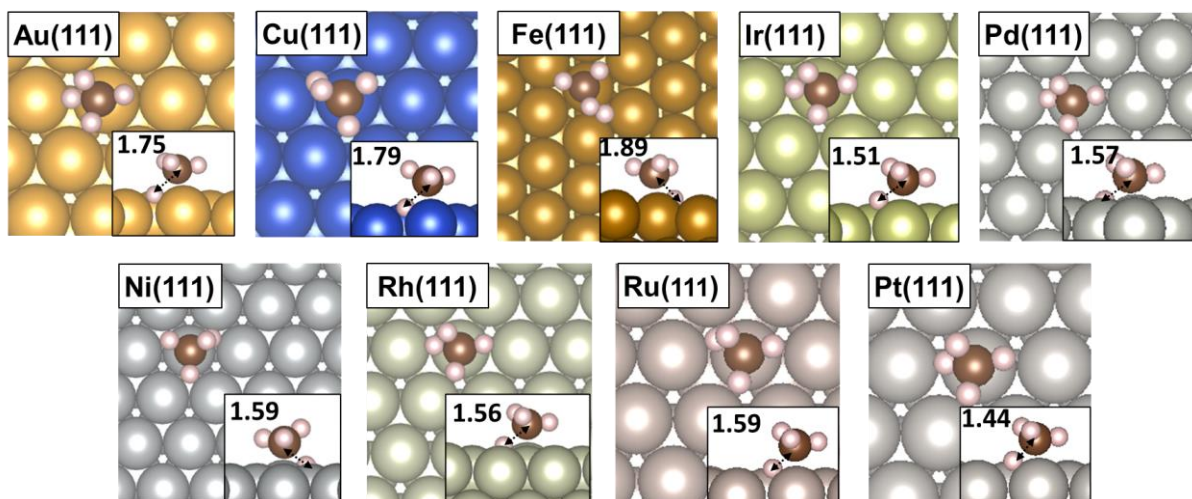


Figure A.6. Optimized transition states for CH<sub>4</sub> activation on transition metal surfaces. The distances (in Å) of the dissociating C–H bond are labeled and indicated in dashed lines.

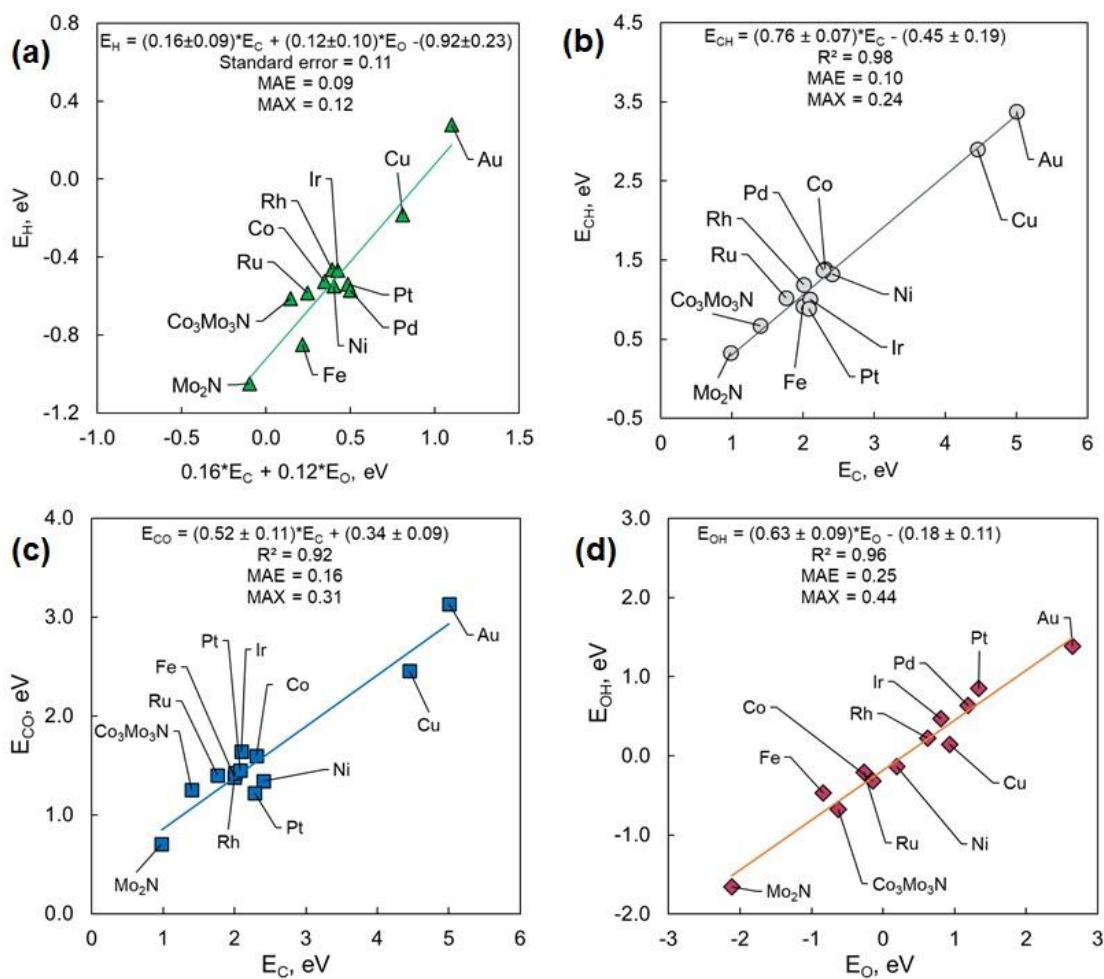


Figure A.7. Linear scaling relations of the binding energy corresponding to fragments bound in the most stable adsorption site for (a) H versus C/O, (b) CH versus C, (c) CO versus O, (d) OH versus O. The standard deviations, MAE, and MAX are also shown.

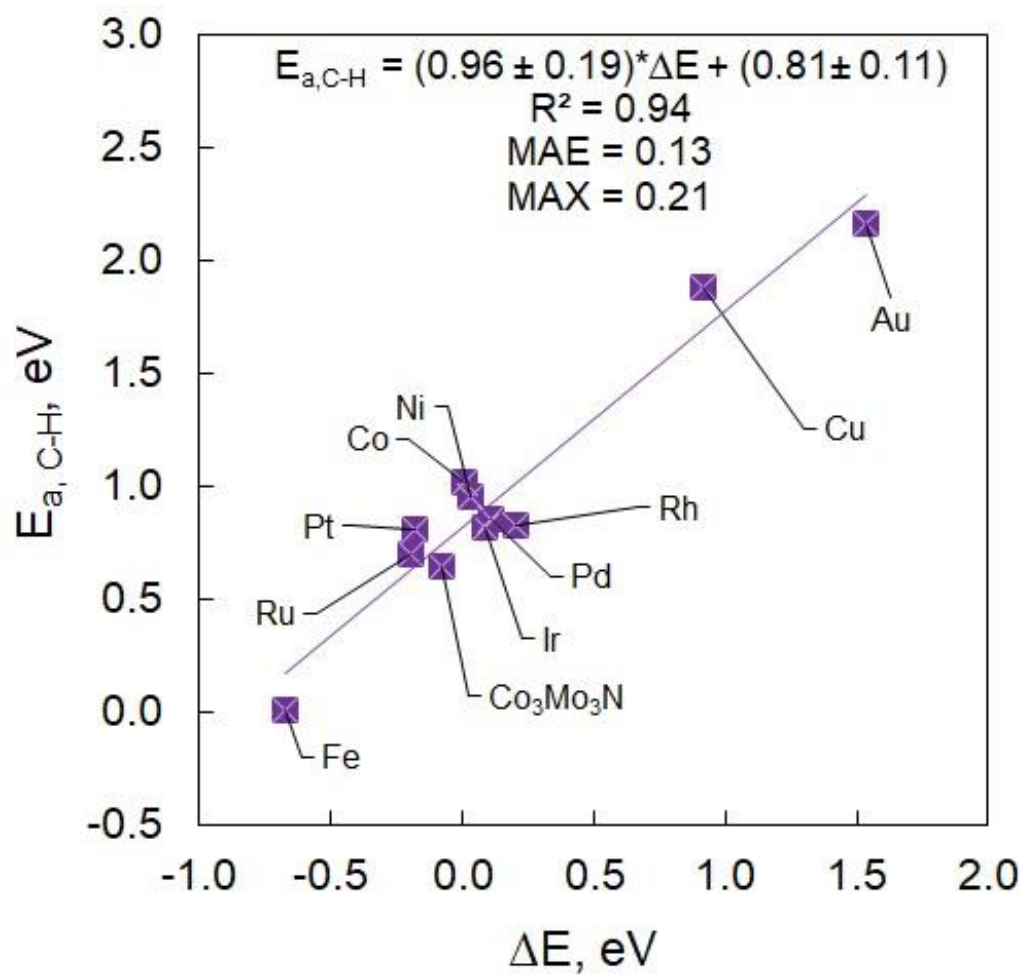


Figure A.8. BEP relationship for CH<sub>4</sub> C-H bond activation in terms of dissociation energies ( $\Delta E$ ) and energy barriers ( $E_a$ ). The standard deviations, MAE, and MAX are also shown.

Table A.1. Lattice parameters of surface models.

| Surface                                | Lattice<br>parameter (Å) | Experimental<br>lattice (Å) |
|----------------------------------------|--------------------------|-----------------------------|
| Co(0001)                               | 2.476                    | 2.501                       |
| Mo <sub>2</sub> N( <b>110</b> )        | 4.999                    | 5.044                       |
| Co <sub>3</sub> Mo <sub>3</sub> N(111) | 7.783                    | 7.813                       |
| Ni(111)                                | 2.491                    | 2.481                       |
| Pt(111)                                | 2.804                    | 2.812                       |
| Cu(111)                                | 2.580                    | 2.561                       |
| Au(111)                                | 2.949                    | 2.950                       |
| Ir(111)                                | 2.714                    | 2.741                       |
| Rh(111)                                | 2.705                    | 2.721                       |
| Fe(111)                                | 2.440                    | 2.578                       |
| Pd(111)                                | 2.751                    | 2.798                       |
| Ru(111)                                | 2.711                    | 2.705                       |

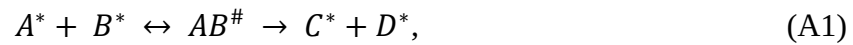
Table A.2. Binding energies (eV) of H and CH<sub>3</sub> and their preferred binding sites on close-packed transition metal surfaces; CH<sub>4</sub> dissociation energies ( $\Delta E$ ); and C–H bond activation energy barriers ( $E_a$ ). The literature values are shown in the parentheses.

| Surface        | H    |                                 | CH <sub>3</sub> |                                  | CH <sub>4</sub> dissociation               |                                                       |
|----------------|------|---------------------------------|-----------------|----------------------------------|--------------------------------------------|-------------------------------------------------------|
|                | Site | BE, eV<br>(BE <sub>lit.</sub> ) | Site            | BE (eV)<br>(BE <sub>lit.</sub> ) | $\Delta E$ , eV                            | $E_a$ , eV                                            |
| <b>Ir(111)</b> | top  | -2.72<br>(-2.73 [1])            | fcc             | -1.92<br>(-1.88 [1])             | 0.09<br>(0.06 [2])                         | 0.82<br>(0.95 [2])                                    |
| <b>Rh(111)</b> | fcc  | -2.72<br>(-2.86 [3])            | fcc             | -1.80<br>(-1.84 [4], -1.83 [5])  | 0.21<br>(0.12 [6], 0.09 [3], 0.05 [2])     | 0.83<br>(0.82 [6], 0.72 [3], 1.00 [2])                |
| <b>Ni(111)</b> | fcc  | -2.81<br>(-2.80 [7])            | top             | -1.89<br>(-1.91 [7])             | 0.03<br>(0.13 [8, 9], 0.01 [7], 0.15 [10]) | 0.95<br>(1.18 [8, 9], 1.17 [10], 0.90 [11], 0.88 [7]) |
| <b>Cu(111)</b> | fcc  | -2.44<br>(-2.51 [9])            | fcc             | -1.37<br>(-2.03 [12])            | 0.92<br>(1.07 [12], 1.25 [2])              | 1.88<br>(1.77 [12], 1.80 [2])                         |
| <b>Fe(111)</b> | hcp  | -2.98                           | fcc             | -2.29<br>(-2.81 [9])             | -0.67<br>(-0.63 <sup>14</sup> )            | 0.01                                                  |
| <b>Pt(111)</b> | top  | -2.79<br>(-2.74 [13])           | top             | -2.10<br>(-2.02 [13])            | -0.18<br>(-0.13 [14], 0.07 [15], 0.04 [2]) | 0.81<br>(0.84 [14], 0.77 [15], 1.10 [2])              |
| <b>Au(111)</b> | fcc  | -1.98                           | -               | -1.21                            | 1.53<br>(1.75 [2])                         | 2.16<br>(2.25 [2])                                    |
| <b>Pd(111)</b> | fcc  | -2.82<br>(-2.68)                | top             | -1.79<br>(-1.81 [16])            | 0.11<br>(0.26)                             | 0.85<br>(0.97)                                        |
| <b>Ru(111)</b> | fcc  | -2.84                           | fcc             | -2.08                            | -0.20<br>(-0.23)                           | 0.70<br>(0.80 [17])                                   |

Table A.3. Calculated rate constants for the elementary DRM steps on Co<sub>3</sub>Mo<sub>3</sub>N(111), Co(0001), Mo<sub>2</sub>N(110), and Ni(111). The elementary step indices correspond to the mechanism shown in Table 2 of the main text.

| Elementary<br>step | Co <sub>3</sub> Mo <sub>3</sub> N(111) |          | Co(0001) |          | Mo <sub>2</sub> N(110) |          | Ni(111)  |          |
|--------------------|----------------------------------------|----------|----------|----------|------------------------|----------|----------|----------|
|                    | $k_f$                                  | $k_r$    | $k_f$    | $k_r$    | $k_f$                  | $k_r$    | $k_f$    | $k_r$    |
| <b>R1</b>          | 1.85E-01                               | 1.60E+13 | 7.28E-02 | 7.44E+11 | 1.65E+00               | 6.69E+05 | 4.01E-02 | 9.08E+11 |
| <b>R2</b>          | 2.15E-02                               | 3.40E+13 | 1.52E-04 | 9.75E+08 | 5.44E-07               | 3.27E+06 | -        | -        |
| <b>R3</b>          | 6.62E+10                               | 1.92E+08 | 3.78E+09 | 1.78E+10 | 8.03E+08               | 1.92E+08 | 7.46E+09 | 1.11E+10 |
| <b>R4</b>          | 2.55E+10                               | 1.39E+07 | 1.47E+12 | 2.87E+10 | 1.72E+11               | 6.56E+07 | 2.87E+11 | 3.00E+09 |
| <b>R5</b>          | 2.44E+08                               | 3.93E+08 | 2.85E+07 | 3.36E+09 | 1.53E+11               | 2.87E+10 | 1.28E+06 | 7.13E+08 |
| <b>R6</b>          | 1.49E+01                               | 7.56E+05 | 2.65E+02 | 4.79E+13 | 2.78E+01               | 2.97E+09 | 4.01E+02 | 1.63E+13 |
| <b>R7</b>          | 5.41E+09                               | 1.39E+07 | 1.35E+11 | 3.89E+05 | 6.15E+11               | 3.79E+03 | 1.58E+10 | 1.69E+05 |
| <b>R8</b>          | 2.39E+02                               | 2.53E+07 | 5.99E+03 | 6.69E+00 | 1.03E-01               | 8.26E+04 | 1.05E+05 | 2.46E-02 |
| <b>R9</b>          | 3.33E+06                               | 9.83E+09 | 5.36E+06 | 3.49E+08 | 1.00E+03               | 6.62E+10 | 1.77E+07 | 1.70E+08 |
| <b>R10</b>         | 1.63E+06                               | 4.11E+10 | 1.75E+04 | 3.30E+03 | 4.00E+01               | 5.36E+06 | 2.33E+06 | 4.72E+03 |
| <b>R11</b>         | 4.26E+09                               | 2.72E+05 | 4.42E+08 | 3.59E+04 | 5.36E+06               | 4.85E-01 | 2.44E+08 | 2.60E+03 |
| <b>R12</b>         | 5.77E+04                               | 5.03E+11 | 1.18E+05 | 5.41E+09 | 1.89E+02               | 2.37E+12 | 2.14E+05 | 8.33E+07 |
| <b>R13</b>         | 1.72E+11                               | 8.33E+07 | 1.03E+12 | 2.62E+06 | 2.35E+09               | 2.51E+04 | 2.10E+12 | 7.07E+05 |
| <b>R14</b>         | 7.60E+03                               | 8.10E+11 | 3.07E+05 | 2.01E+10 | 1.12E+00               | 1.94E+11 | 6.27E+05 | 3.79E+09 |
| <b>R15</b>         | 3.24E+10                               | 6.27E+05 | -        | -        | 1.53E+11               | 1.67E+02 | 4.26E+09 | 2.53E+07 |
| <b>R16</b>         | 1.31E+12                               | 2.16E+08 | 1.03E+12 | 1.34E+08 | -                      | -        | 6.15E+12 | 1.02E+09 |
| <b>R17</b>         | 7.96E+05                               | 3.39E+12 | 8.97E+05 | 2.24E+07 | 3.09E+08               | 2.55E+10 | 7.96E+05 | 3.39E+12 |
| <b>R18</b>         | 1.70E+08                               | 2.46E+11 | 6.56E+07 | 1.57E+07 | -                      | -        | 1.70E+08 | 2.46E+11 |
| <b>R19</b>         | 1.07E+11                               | 1.90E+05 | 1.16E+12 | 9.74E+06 | 1.31E+12               | 6.45E+01 | 1.07E+11 | 1.90E+05 |
| <b>R20</b>         | 8.89E+02                               | 1.09E+04 | 7.60E+03 | 2.44E-05 | 8.97E+05               | 4.43E-05 | 8.89E+02 | 1.09E+04 |
| <b>R21</b>         | 2.72E+03                               | 1.07E-02 | 1.62E+05 | 2.82E-01 | 4.03E+00               | 2.40E-02 | 1.68E+04 | 1.29E-01 |
| <b>R22</b>         | 2.62E+07                               | 1.82E+01 | 2.07E+08 | 2.22E+01 | 8.15E+02               | 2.00E+01 | 1.26E+08 | 9.84E+00 |
| <b>R23</b>         | 1.22E+07                               | 1.60E+02 | 2.40E+09 | 6.42E+02 | 5.71E-01               | 1.93E+02 | 1.56E+10 | 3.38E+02 |

All elementary steps are generally described by Eqn. (A1),



where  $AB^\#$  represents the activated transition state. According to Eqn. (A2), the rate constants ( $k$ ) becomes:

$$k = \frac{k_B T}{h} \exp\left(\frac{-E_a}{RT}\right), \quad (\text{A2})$$

where  $k_B$  is the Boltzmann constant,  $h$  is the Planck's constant,  $R$  is the gas constant (i.e., 8.314 J/K mole), and  $T$  is temperature (in K). All  $E_a$  values were obtained from DFT CI-NEB and dimer calculations detailed in the main text.

Specifically, the forward and reverse rate constants for the rate-determining  $\text{CH}_4$  dissociative adsorption are expressed by Eqns. (A3-A4):

$$k_f = \frac{k_B T}{h} \frac{q^\#}{q_{\text{CH}_4(g)}} \exp\left(-\frac{E_{af}}{RT}\right), \quad (\text{A3})$$

$$k_r = \frac{k_B T}{h} \frac{q^\#}{q_{\text{CH}_3^*} q_{\text{H}^*}} \exp\left(-\frac{E_{ar}}{RT}\right), \quad (\text{A4})$$

where  $q_{\text{TS}}$ ,  $q_{\text{CH}_4}$ ,  $q_{\text{surf}}$ ,  $q_{\text{CH}_3^*}$ , and  $q_{\text{H}^*}$  are the partition functions for the transition state (TS), the reactant, and product states with respect to their ground states, respectively. These partition functions were estimated based on the standard statistical mechanical approach at 1 bar and 973.15 K.

$E_{af}$  and  $E_{ar}$ , with zero-point energy (ZPE) corrections included, correspond to the activation energies of the forward and reverse elementary step, respectively.

For molecular adsorption and desorption process (e.g.,  $\text{CO}_2$  adsorption), as expressed by Eqn. (A5),





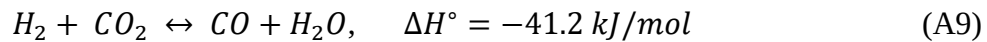
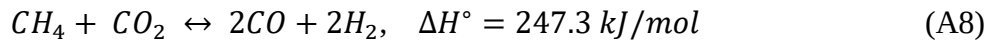
It can be shown that the rate constants for molecular adsorption and desorption can be expressed by Eqns. (A6) and (A7) [18]:

$$k_{adsorption} = \frac{1}{N_0 \sqrt{2\pi k_B T M_A}} \frac{q_{A^*}}{q_{rA(g)} q_{vA(g)}}. \quad (A6)$$

$$k_{desorption} = e \frac{k_B T}{h} \exp\left(-\frac{\Delta E}{RT}\right) \quad (A7)$$

where  $N_0$  is the number of surface sites of the exposed surface.  $M_A$  is the molecular mass of the adsorbate (A).  $q_{rA(g)}$  and  $q_{vA(g)}$  are the rotational and vibrational partition functions of the gas-phase adsorbate, respectively.  $\Delta E$  is approximated with the binding energy of the adsorbate.

A *Mathematica* script was developed to obtain the DRM turnover frequencies (TOFs) and surface coverage at  $P = 1$  bar and 973.15 K. The initial feed consists of equimolar  $CH_4$  and  $CO_2$  (i.e.,  $p_{CH_4} = p_{CO_2} = 0.5$  bar) at a molar flow rate of 1 mole/s. The composition for the exiting gas stream consisting of CO,  $H_2$  and  $H_2O$ , and the unreacted  $CH_4$ ,  $CO_2$ , was estimated based on the overall equilibrium constant. The relevant reactions consist of the DRM (A8) and the reverse water-gas shift reaction (A9):



The estimated equilibrium constants at 1 bar and 973.15 K are 5.92 and 0.594, respectively. Hence, thermodynamics will favor DRM strongly over the reverse water-gas shift reaction at high temperatures. The composition of the exiting gas stream were determined with Eqns. (A10) and (A11):

$$K_{DRM}(T) = \frac{\left(\frac{p_{H_2}}{P}\right)^2 \left(\frac{p_{CO}}{P}\right)^2}{\left(\frac{p_{CH_4}}{P}\right) \left(\frac{p_{CO_2}}{P}\right)}, \quad (A10)$$

$$K_{RWGS}(T) = \frac{p_{H_2} * p_{CO_2}}{p_{CO} * p_{H_2O}}, \quad (A11)$$

where the partial pressures are represented by Eqns. (A12-A16) in terms of CH<sub>4</sub> conversion ( $x_{CH_4}$ ) and the extent of reaction of RWGS ( $\xi$ ).

$$p_{CH_4} = \frac{1 - x_{CH_4}}{2 * (1 + x_{CH_4})} P \quad (A12)$$

$$p_{CO_2} = \frac{1 - x_{CH_4} * \xi}{2 * (1 + x_{CH_4})} P \quad (A13)$$

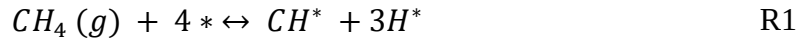
$$p_{CO} = \frac{2 * F_0 * x_{CH_4} + \xi}{2 * F_0 * (1 + x_{CH_4})} P \quad (A14)$$

$$p_{CO} = \frac{2 * F_0 * x_{CH_4} - \xi}{2 * F_0 * (1 + x_{CH_4})} P \quad (A15)$$

$$p_{H_2O} = \frac{\xi}{2 * F_0 * (1 + x_{CH_4})} P \quad (A16)$$

As mentioned in the main text, a reduced DRM mechanism was adopted to facilitate microkinetic modeling. The first activation of CH<sub>4</sub> was still treated as the rate-limiting step (RLS)

and will be used to determine the rate of DRM. In addition, the CH<sub>4</sub> decomposition sequence was represented as a *lumped* step (forming CH, see R), by neglecting the formation and oxidations of CH<sub>2</sub> and CH<sub>3</sub>. Because the formation of CHOH is significantly slower than its consumption (see Table A.3), the CHOH intermediate will be omitted. Instead, the oxidation of carbonaceous species (i.e., C and CH) is represented by R4 and R7, to form CO. The oxidants (i.e., O and OH) are generated via R3 and R6, respectively. Hence, there are 10 elementary steps, involving 5 gas phase species (CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>O) and 8 surface intermediates (\*, C, CH, CO<sub>2</sub>, CO, O, H, and OH) in the reduced DRM model.



The quasi-steady state assumption (QSSA) was applied to each surface species (excluding vacancies) in order to establish a set of differential equations describing each surface species, as in Eqns. (A17-A24):

$$r_1 = k_{1f}P_{CH_4}\theta_*^4 - k_{1r}\theta_{CH}\theta_H^3 \quad (A17)$$

$$\frac{d\theta_{CO_2}}{dt} = k_{2f}P_{CO_2}\theta_* - k_{2r}\theta_{CO_2} \quad (A18)$$

$$\frac{d\theta_O}{dt} = k_{3f}\theta_{CO_2}\theta_* - k_{3r}\theta_{CO}\theta_O \quad (A19)$$

$$\frac{d\theta_{CH}}{dt} = -k_{4f}\theta_{CH}\theta_O + k_{4r}\theta_{CO}\theta_H - k_{5f}\theta_{CH}\theta_* + k_{5r}\theta_C\theta_H \quad (A20)$$

$$\frac{d\theta_{OH}}{dt} = k_{6f}\theta_O\theta_H + k_{6r}\theta_{OH}\theta_* \quad (A21)$$

$$\frac{d\theta_C}{dt} = -k_{7f}\theta_C\theta_{OH} + k_{7r}\theta_{CO}\theta_H \quad (A22)$$

$$\frac{d\theta_{CO}}{dt} = -k_{8f}\theta_{CO} + k_{8r}P_{CO}\theta_* \quad (A23)$$

$$\frac{d\theta_H}{dt} = -k_{9f}\theta_{OH}\theta_H + k_{9r}P_{H_2O}\theta_*^2 - k_{10f}\theta_H^2 + k_{10r}P_{H_2}\theta_*^2 \quad (A24)$$

The rate constants corresponding to the above model are listed in Table A.4.

Table A.4. Rate constants and equilibrium constants on Co<sub>3</sub>Mo<sub>3</sub>N(111), Ni(111), Co(0001), and Mn<sub>2</sub>N(110) used in Eqns. (A3, A4, A6, A7).

| Elementary<br>step | Co <sub>3</sub> Mo <sub>3</sub> N(111) |          |          | Ni(111)  |          |          |
|--------------------|----------------------------------------|----------|----------|----------|----------|----------|
|                    | $k_{fi}$                               | $k_{ri}$ | $K_i$    | $k_{fi}$ | $k_{ri}$ | $K_i$    |
| <b>R1</b>          | 1.85E-01                               | 1.39E+07 | 1.33E-08 | 4.00E-02 | 3.00E+9  | 3.33E-11 |
| <b>R2</b>          | 1.48E+01                               | 7.57E+05 | 1.96E-05 | 4.01E+02 | 1.63E+13 | 2.46E-11 |
| <b>R3</b>          | 5.41E+09                               | 1.39E+07 | 3.89E+02 | 1.58E+10 | 1.69E+05 | 9.35E+04 |
| <b>R4</b>          | 5.77E+04                               | 8.33E+07 | 6.92E-04 | 2.14E+05 | 7.07E+05 | 3.03E-01 |
| <b>R5</b>          | 2.44E+08                               | 3.93E+08 | 6.21E-01 | 1.28E+06 | 7.13E+08 | 1.80E-03 |

|                    |                 |          |          |                             |          |          |
|--------------------|-----------------|----------|----------|-----------------------------|----------|----------|
| <b>R6</b>          | 3.33E+06        | 9.83E+09 | 3.39E-04 | 1.77E+07                    | 1.70E+08 | 1.04E-01 |
| <b>R7</b>          | 1.63E+06        | 2.72E+05 | 5.99E+00 | 2.33E+06                    | 2.60E+03 | 8.96E+02 |
| <b>R8</b>          | 2.72E+03        | 1.07E-02 | 2.54E+05 | 1.68E+04                    | 1.28E-01 | 1.31E+05 |
| <b>R9</b>          | 1.22E+07        | 1.60E+02 | 7.63E+04 | 1.56E+10                    | 3.38E+02 | 4.62E+07 |
| <b>R10</b>         | 2.62E+07        | 1.82E+01 | 1.44E+06 | 1.25E+08                    | 9.84E+00 | 1.27E+07 |
| Elementary<br>step | <b>Co(0001)</b> |          |          | <b>Mo<sub>2</sub>N(110)</b> |          |          |
|                    | $k_{fi}$        | $k_{ri}$ | $K_i$    | $k_{ri}$                    | $K_i$    |          |
| <b>R1</b>          | 7.28E-02        | 1.78E+09 | 4.09E-11 | 1.65E+00                    | 6.69E+05 | 2.46E-06 |
| <b>R2</b>          | 1.00E+00        | 4.79E+13 | 2.09E-12 | 2.78E+01                    | 2.97E+09 | 9.36E-09 |
| <b>R3</b>          | 1.35E+11        | 3.89E+05 | 3.47E+05 | 6.15E+12                    | 3.79E-04 | 1.62E+16 |
| <b>R4</b>          | 1.18E+05        | 2.62E+06 | 4.50E-02 | 1.89E+02                    | 2.51E+04 | 7.53E-03 |
| <b>R5</b>          | 2.85E+07        | 3.36E+09 | 8.48E-03 | 1.53E+11                    | 2.87E+10 | 5.33E+00 |
| <b>R6</b>          | 5.36E+06        | 3.49E+08 | 1.54E-02 | 1.00E+03                    | 6.62E+10 | 1.51E-08 |
| <b>R7</b>          | 1.75E+04        | 3.30E+02 | 5.30E+01 | 4.00E+01                    | 4.85E-01 | 8.25E+01 |
| <b>R8</b>          | 1.62E+05        | 2.82E-01 | 5.74E+06 | 4.03E+00                    | 2.40E-02 | 1.68E+02 |
| <b>R9</b>          | 2.40E+09        | 6.42E+02 | 3.74E+06 | 5.70E-01                    | 1.93E+02 | 2.95E-03 |
| <b>R10</b>         | 2.07E+08        | 2.22E+01 | 9.32E+06 | 8.15E+02                    | 2.00E+01 | 4.08E+01 |

According to QSSA, the surface coverage expressions are represented by Eqns. (A25-A32) for the *single-site* mechanism.

| Single-site mechanism |                                                                                                                                                                       | Dual-site mechanism |                                                                                                                                                                                        |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (A25)                 | $\theta_{CO_2} = K_2 p_{CO_2} \theta_*$                                                                                                                               | (A43)               | $\theta_{CO_2} = K_2 p_{CO_2} \theta_{1*}$                                                                                                                                             |
| (A26)                 | $\theta_O = \frac{K_3 \theta_{CO_2} \theta_*}{\theta_{CO}} = \frac{K_2 K_3 K_8 p_{CO_2}}{p_{CO}} \theta_*$                                                            | (A44)               | $\theta_O = \frac{K_3 \theta_{CO_2} \theta_{2*}}{\theta_{CO}} = \frac{K_2 K_3 K_8 p_{CO_2}}{p_{CO}} \theta_{2*}$                                                                       |
|                       | $\theta_{CH} = \frac{\frac{k_{4r} p_{CO}}{K_8} + \frac{k_{5r} p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}}}{\frac{k_{4f} K_2 K_3 K_8 p_{CO_2}}{p_{CO}} + k_{5f}} \times$ |                     | $\theta_{CH} = \frac{\frac{k_{4r} p_{CO}}{K_8} \theta_{2*} + \frac{k_{5r} p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}} \theta_{1*}}{\frac{k_{4f} K_2 K_3 K_8 p_{CO_2}}{p_{CO}} + k_{5f}}$ |
| (A27)                 | $\sqrt{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{\frac{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}}{p_{CO}} + k_{10f}}} \theta_*$                                                  | (A45)               | $\sqrt{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{\frac{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}}{p_{CO}} + k_{10f}}} \theta_{2*}$                                                                |
| (A28)                 | $\theta_{OH} = \frac{K_2 K_3 K_6 K_8 p_{CO_2}}{p_{CO}} \times$                                                                                                        | (A46)               | $\theta_{OH} = \frac{K_2 K_3 K_6 K_8 p_{CO_2}}{p_{CO}} \sqrt{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{\frac{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}}{p_{CO}} + k_{10f}}} \theta_{2*}$          |

|       |                                                                                                              |       |                                                                                                                 |
|-------|--------------------------------------------------------------------------------------------------------------|-------|-----------------------------------------------------------------------------------------------------------------|
|       | $\sqrt{\frac{k_{9r}p_{H_2O} + k_{10r}p_{H_2}}{K_2K_3K_6K_8k_{9f}p_{CO_2} + k_{10f}}}\theta_*$                |       |                                                                                                                 |
| (A29) | $\theta_C = \frac{\theta_{CO}\theta_H}{K_7\theta_{OH}} = \frac{p_{CO}^2}{K_2K_3K_6K_7K_8^2p_{CO_2}}\theta_*$ | (A47) | $\theta_C = \frac{\theta_{CO}\theta_H}{K_7\theta_{OH}} = \frac{p_{CO}^2}{K_2K_3K_6K_7K_8^2p_{CO_2}}\theta_{1*}$ |
| (A30) | $\theta_{CO} = \frac{p_{CO}}{K_8}\theta_*$                                                                   | (A48) | $\theta_{CO} = \frac{p_{CO}}{K_8}\theta_{1*}$                                                                   |
| (A31) | $\theta_H = \sqrt{\frac{k_{9r}p_{H_2O} + k_{10r}p_{H_2}}{K_2K_3K_6K_8k_{9f}p_{CO_2} + k_{10f}}}\theta_*$     | (A49) | $\theta_H = \sqrt{\frac{k_{9r}p_{H_2O} + k_{10r}p_{H_2}}{K_2K_3K_6K_8k_{9f}p_{CO_2} + k_{10f}}}\theta_{2*}$     |
| (A32) | $\theta_* + \theta_C + \theta_{CH} + \theta_{CO} + \theta_{CO_2} + \theta_O + \theta_{OH} + \theta_H = 1$    | (A50) | $\theta_{1*} + \theta_C + \theta_{CO} + \theta_{CO_2} = 0.7$                                                    |
|       |                                                                                                              | (A51) | $\theta_{2*} + \theta_O + \theta_{OH} + \theta_H + \theta_{CH} = 0.3$                                           |

The concentrations of all surface species are related to  $\theta_*$ . Then, the RLS ( $r_1$ ) can be expressed by Eqn. (A33).

$$r_1 = k_{1f}p_{CH_4} \left[ 1 - \frac{\frac{k_{4r}p_{CO}}{K_8} + \frac{k_{5r}p_{CO}^2}{K_2K_3K_6K_7K_8^2p_{CO_2}}}{K_1p_{CH_4} \left( \frac{k_{4f}K_2K_3K_8p_{CO_2}}{p_{CO}} + k_{5f} \right)} \left( \frac{k_{9r}p_{H_2O} + k_{10r}p_{H_2}}{K_2K_3K_6K_8k_{9f}p_{CO_2} + k_{10f}} \right)^2 \right] \theta_*^4 \quad (A33)$$

From a dimensional analysis, the RLS can be further simplified as Eqn. (A34):

$$r_1 = k_{1f}p_{CH_4}\theta_*^4 \left[ 1 - \frac{p_{CO}^2p_{H_2}^2}{K_1K_2K_3K_5K_6K_7K_8^2p_{CH_4}p_{CO_2}} \right] \quad (A34)$$

The *dual-site* mechanism accounts for DRM occurring on two distinct active sites, denoted as  $\theta_{1*}$  and  $\theta_{2*}$ , as established by Eqns. (A35-A42). We assumed that each species occupies their preferred binding sites and the diffusions between different active domains be neglected. The surface coverage for each intermediate are represented by Eqns. (A43-A51) listed in Table A.5.

$$r_1 = k_{1f}P_{CH_4}\theta_{1*}^4 - k_{1r}\theta_{CH}\theta_H^3 \quad (A35)$$

$$\frac{d\theta_{CO_2}}{dt} = k_{2f}P_{CO_2}\theta_{2*} - k_{2r}\theta_{CO_2} \quad (A36)$$

$$\frac{d\theta_O}{dt} = k_{3f}\theta_{CO_2}\theta_{1*} - k_{3r}\theta_{CO}\theta_O \quad (A37)$$

$$\frac{d\theta_{CH}}{dt} = -k_{4f}\theta_{CH}\theta_O + k_{4r}\theta_{CO}\theta_H - k_{5f}\theta_{CH}\theta_{1*} + k_{5r}\theta_C\theta_H \quad (A38)$$

$$\frac{d\theta_{OH}}{dt} = k_{6f}\theta_O\theta_H + k_{6r}\theta_{OH}\theta_{2*} \quad (A39)$$

$$\frac{d\theta_C}{dt} = -k_{7f}\theta_C\theta_{OH} + k_{7r}\theta_{CO}\theta_H \quad (A40)$$

$$\frac{d\theta_{CO}}{dt} = -k_{8f}\theta_{CO} + k_{8r}P_{CO}\theta_{1*} \quad (A41)$$

$$\frac{d\theta_H}{dt} = -k_{9f}\theta_{OH}\theta_H + k_{9r}P_{H_2O}\theta_{2*}^2 - k_{10f}\theta_H^2 + k_{10r}P_{H_2}\theta_{2*}^2 \quad (A42)$$

The heat map contour plot was generated using  $BE_C$  and  $BE_O$ , which are in general ( $C_xH_yO_z^*$ ) defined by Eqns. (A52-A53).

$$xCH_4 + (-2x + 1/2y - z)H_2 + zH_2O + * \rightarrow C_xH_yO_z^* \quad (A52)$$

$$E_{C_xH_yO_z^*} = E_{C_xH_yO_z^*}^{vasp} - xE_{CH_4}^{vasp} + (2x - 1/2y + z)E_{H_2}^{vasp} - zE_{H_2O}^{vasp} - E_*^{vasp} \quad (A53)$$

Then, the binding energies of H, CH, CO, and OH were estimated using Eqns. A54-A57. These linear scaling relationships were established and illustrated in Figure A7. Moreover, the C–H bond

activation energies were estimated using a BEP relationship based on Eqn. A58 (also see Figure A.8).

$$BE_H = 0.16BE_C + 0.12BE_O - 0.92 \quad (A54)$$

$$BE_{CH} = 0.76 BE_C - 0.45 \quad (A55)$$

$$BE_{CO} = 0.52 BE_C + 0.34 \quad (A56)$$

$$BE_{OH} = 0.63 BE_O - 0.18 \quad (A57)$$

$$E_{a,C-H} = 0.96 \Delta E + 0.81 = 0.96 (BE_{CH} + 3BE_H) + 0.81 \quad (A58)$$

## Notes and references

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# Appendix B - Mitigating Coke Formations for Dry Reforming of Methane on Dual-Site Catalysts: A Microkinetic Modeling Study

Formation energies of DRM intermediates on catalyst surfaces and transition state energies for dual-site microkinetic modeling. The formation energies at the step sites (denoted as “t”) were taken from Jalid and coworkers [1].

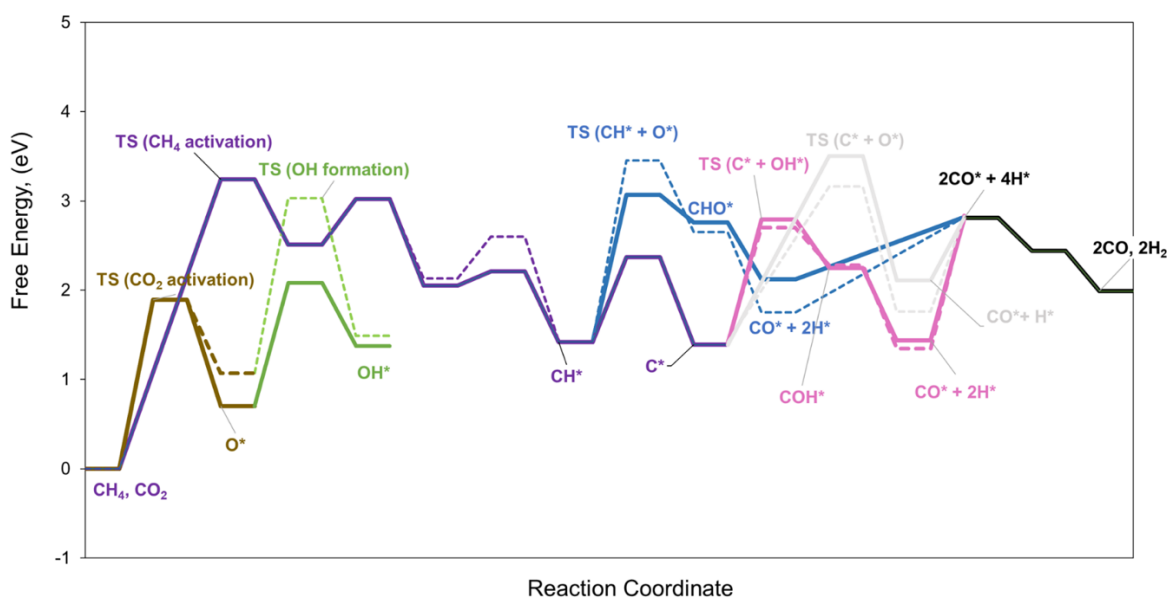


Figure B.1. DRM free energy profiles on the  $s_1$  and  $s_2$  sites of  $\text{Co}_3\text{Mo}_3\text{N}(111)$  at 973 K and 1 bar. Gas phase  $\text{CO}_2$  and  $\text{CH}_4$  and clean surfaces are used as zero energy references. DRM pathways representing the dual-site mechanism are shown with solid lines. The pathways representing single-site catalysts are shown with dash lines. Color scheme:  $\text{CO}_2$  dissociation (brown), OH formation (green),  $\text{CH}_4$  decompositions (purple), direct C oxidation (grey), COH formation (pink), CHO formation (blue),  $\text{H}_2$  and CO formations (black).

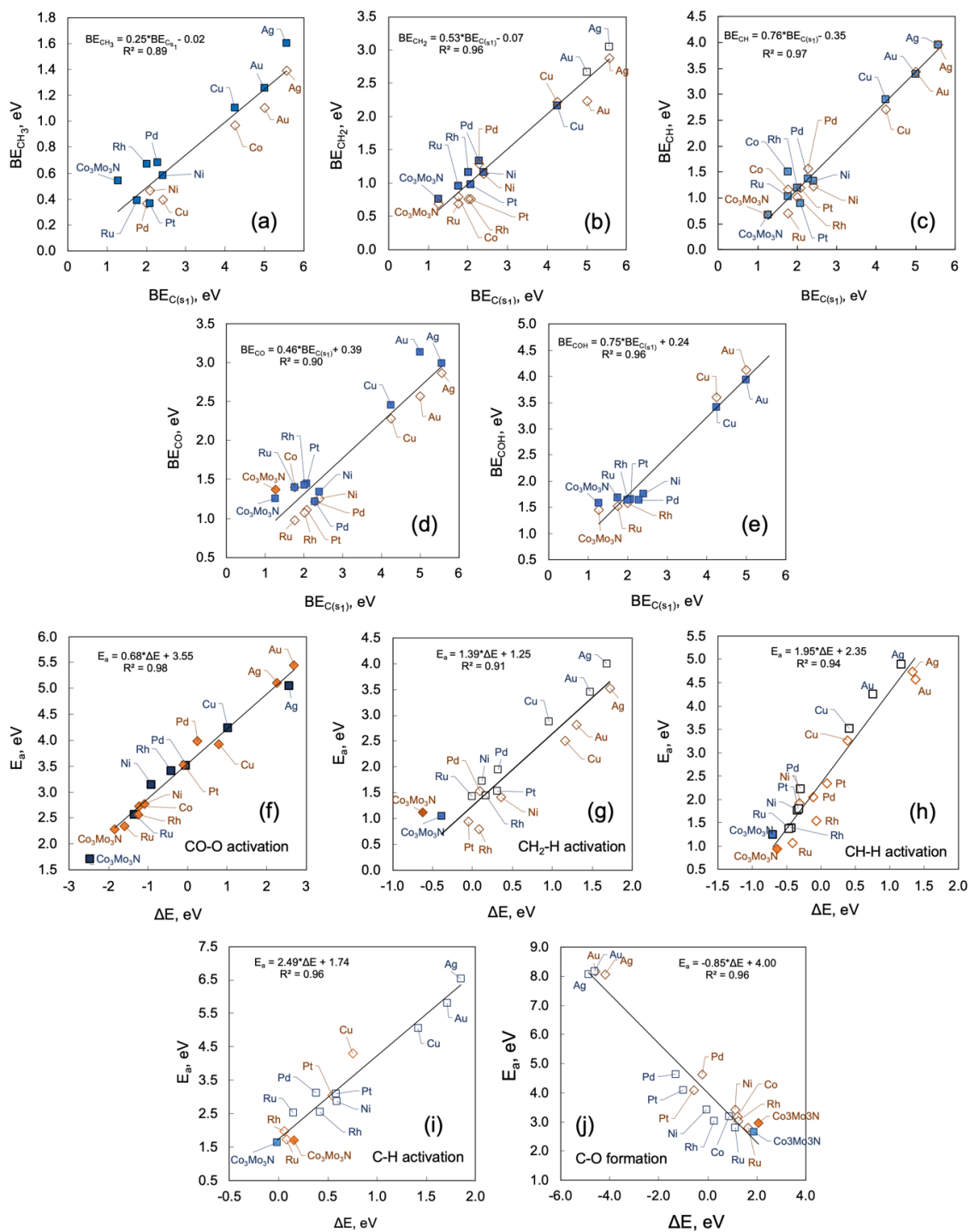


Figure B.2. (a-e) Linear scaling relationships for DRM intermediates; (f-j) Bronsted-Evans-Polanyi (BEP) relationships for DRM elementary steps.

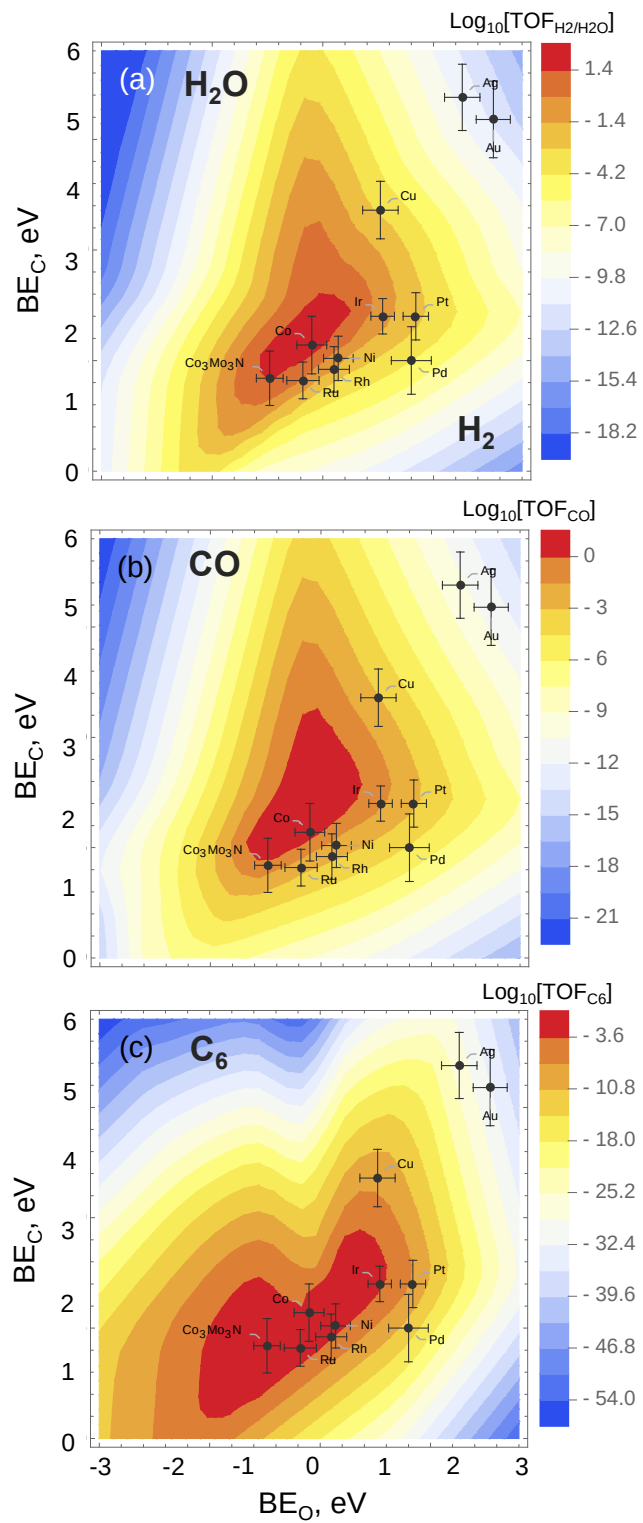


Figure B.3. Turnover frequencies on the single-site model for (a)  $H_2/H_2O$ , (b)  $CO$ , and (c)  $C_6$ .

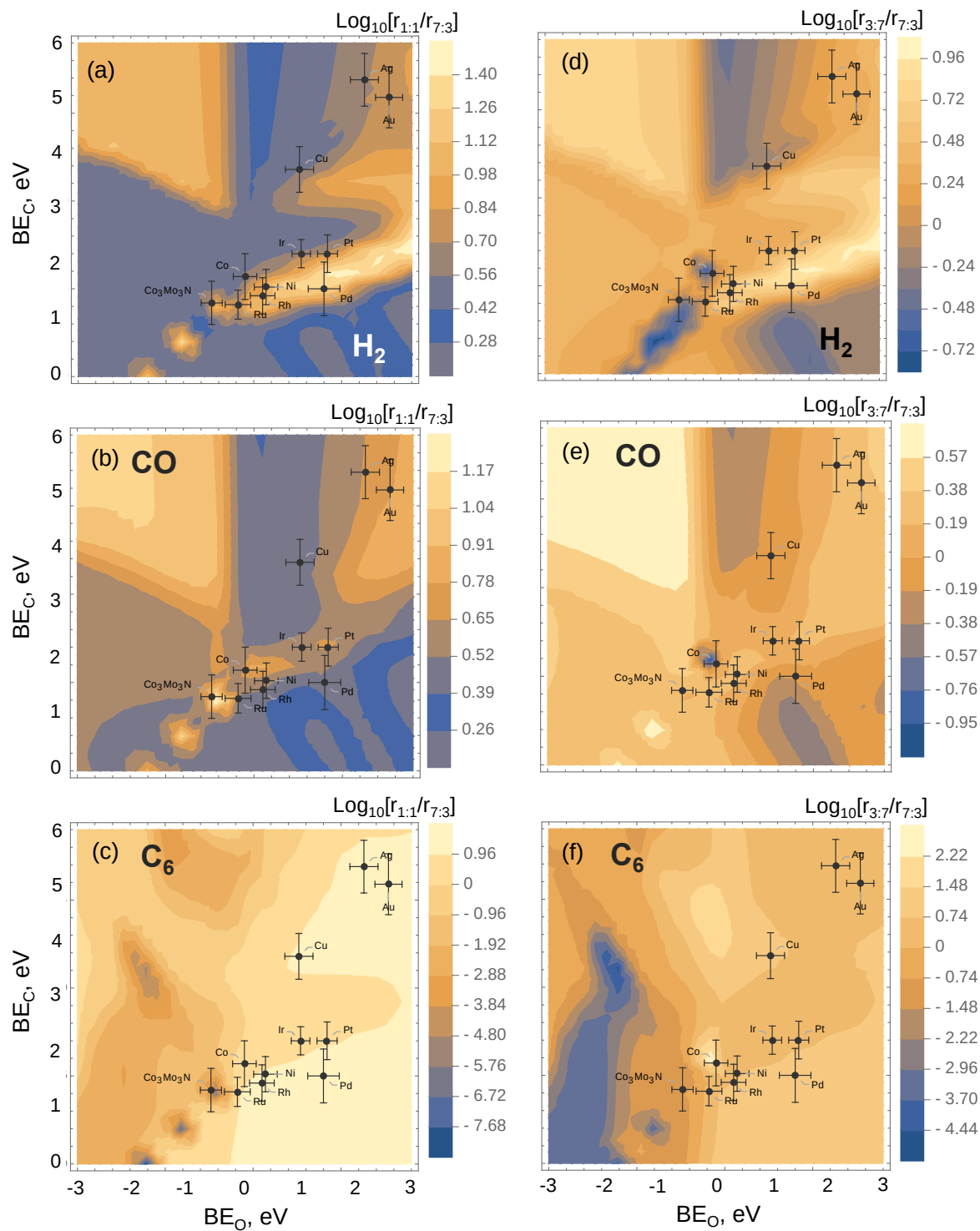


Figure B.4. Relative performance gains of  $H_2$ , CO, and  $C_6$  productions at  $s_1:s_2$  site ratios of 1:1 (a-c), and 3:7 (d-f) versus  $s_1:s_2 = 7:3$ .

Table B.1. Full dual-site model for DRM. “\*” and “■” are used to represent the active sites. The hydrogen reservoir site is represented by “Δ”.

| Elementary steps on site $s_1$ |                                                           | Elementary steps on site $s_2$ |                                                                                                            |
|--------------------------------|-----------------------------------------------------------|--------------------------------|------------------------------------------------------------------------------------------------------------|
| R1                             | $CH_4(g) + * + \Delta \leftrightarrow CH_3^* + H^\Delta$  | R15                            | $CH_4(g) + \blacksquare + \Delta \leftrightarrow CH_3^\blacksquare + H^\Delta$                             |
| R2                             | $CH_3^* + \Delta \leftrightarrow CH_2^* + H^\Delta$       | R16                            | $CH_3^\blacksquare + \Delta \leftrightarrow CH_2^\blacksquare + H^\Delta$                                  |
| R3                             | $CH_2^* + \Delta \leftrightarrow CH^* + H^\Delta$         | R17                            | $CH_2^\blacksquare + \Delta \leftrightarrow CH^\blacksquare + H^\Delta$                                    |
| R4                             | $CH^* + \Delta \leftrightarrow C^* + H^\Delta$            | R18                            | $CH^\blacksquare + \Delta \leftrightarrow C^\blacksquare + H^\Delta$                                       |
| R5                             | $CO_2(g) + 2 * \leftrightarrow CO^* + O^*$                | R19                            | $CO_2(g) + 2 \blacksquare \leftrightarrow CO^\blacksquare + O^\blacksquare$                                |
| R6                             | $C^* + O^* \leftrightarrow CO^* + *$                      | R20                            | $C^\blacksquare + O^\blacksquare \leftrightarrow CO^\blacksquare + \blacksquare$                           |
| R7                             | $H^\Delta + O^* \leftrightarrow OH^* + \Delta$            | R21                            | $H^\Delta + O^\blacksquare \leftrightarrow OH^\blacksquare + \Delta$                                       |
| R8                             | $C^* + OH^* \leftrightarrow COH^* + *$                    | R22                            | $C^\blacksquare + OH^\blacksquare \leftrightarrow COH^\blacksquare + \blacksquare$                         |
| R9                             | $COH^* + \Delta \leftrightarrow CO^* + H^\Delta$          | R23                            | $COH^\blacksquare + \Delta \leftrightarrow CO^\blacksquare + H^\Delta$                                     |
| R10                            | $CH^* + O^* \leftrightarrow CHO^* + *$                    | R24                            | $CH^\blacksquare + O^\blacksquare \leftrightarrow CHO^\blacksquare + \blacksquare$                         |
| R11                            | $CHO^* + \Delta \leftrightarrow CO^* + H^\Delta$          | R25                            | $CHO^\blacksquare + \Delta \leftrightarrow CO^\blacksquare + H^\Delta$                                     |
| R12                            | $CO^* \leftrightarrow CO(g) + *$                          | R26                            | $CO^\blacksquare \leftrightarrow CO(g) + \blacksquare$                                                     |
| R13                            | $H^\Delta + OH^* \leftrightarrow H_2O(g) + * + \Delta$    | R27                            | $H^\Delta + OH^\blacksquare \leftrightarrow H_2O(g) + \blacksquare + \Delta$                               |
| R14                            | $H^\Delta + H^\Delta \leftrightarrow H_2(g) + 2\Delta$    | R28                            | $H^\Delta + H^\Delta \leftrightarrow H_2(g) + 2\Delta$                                                     |
| Coke formations                |                                                           |                                |                                                                                                            |
| R29                            | $C^* + C^* \leftrightarrow C_2^* + *$                     | R32                            | $C^\blacksquare + C^\blacksquare \leftrightarrow C_2^\blacksquare + \blacksquare$                          |
| R30                            | $C_2^* + C_2^* + C_2^* \leftrightarrow C_6^* + 2 *$       | R33                            | $C_2^\blacksquare + C_2^\blacksquare + C_2^\blacksquare \leftrightarrow C_6^\blacksquare + 2 \blacksquare$ |
| R31                            | $C_6^* \leftrightarrow C_6(g) + *$                        | R34                            | $C_6^\blacksquare \leftrightarrow C_6(g) + \blacksquare$                                                   |
| Cross-site diffusions          |                                                           |                                |                                                                                                            |
| R35                            | $C^* + \blacksquare \leftrightarrow C^\blacksquare + *$   |                                |                                                                                                            |
| R36                            | $CH^* + \blacksquare \leftrightarrow CH^\blacksquare + *$ |                                |                                                                                                            |
| R37                            | $O^* + \blacksquare \leftrightarrow O^\blacksquare + *$   |                                |                                                                                                            |
| R38                            | $OH^* + \blacksquare \leftrightarrow OH^\blacksquare + *$ |                                |                                                                                                            |

|                      |                                                              |
|----------------------|--------------------------------------------------------------|
| R39                  | $CO^* + \blacksquare \leftrightarrow CO^\blacksquare + *$    |
| Cross-site reactions |                                                              |
| R40                  | $C^* + O^\blacksquare \leftrightarrow CO^* + \blacksquare$   |
| R41                  | $C^\blacksquare + O^* \leftrightarrow CO^\blacksquare + *$   |
| R42                  | $C^\blacksquare + C^* \leftrightarrow C_2^* + \blacksquare$  |
| R43                  | $CH^* + O^\blacksquare \leftrightarrow CHO^* + \blacksquare$ |
| R44                  | $CH^\blacksquare + O^* \leftrightarrow CHO^\blacksquare + *$ |
| R45                  | $C^* + OH^\blacksquare \leftrightarrow COH^* + \blacksquare$ |
| R46                  | $C^\blacksquare + OH^* \leftrightarrow COH^\blacksquare + *$ |

## References

[1] F. Jalid, M.A. Haider, M.I. Alam, T.S. Khan, Mechanistic Insights into the Dominant Reaction Route and Catalyst Deactivation in Biogas Reforming Using Ab Initio Microkinetic Modeling, Catalysis Science & Technology, 11 (2021) 2130-2143.



# Appendix C - Mechanistic Understanding of Support Effect on the Activity and Selectivity of Indium Oxide Catalysts for CO<sub>2</sub> Hydrogenation

Table C.1. Formation energy of oxygen vacancies (O<sub>v</sub>) and CO<sub>2</sub> binding energy ( $BE_{CO_2}$ ) on various surfaces.

| Surface                                                                  | O <sub>v</sub> formation energy (eV) | $BE_{CO_2}$ (eV)   |
|--------------------------------------------------------------------------|--------------------------------------|--------------------|
| In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>1</sub> )    | 2.17                                 | -0.78              |
| Zr-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>1</sub> ) | 2.80                                 | -1.42              |
| Pr-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>1</sub> ) | 2.57                                 |                    |
| Ce-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>1</sub> ) | 2.58                                 |                    |
| In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>3</sub> )    | 2.90                                 | -                  |
| Zr-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>3</sub> ) | 3.02                                 | -                  |
| Pr-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>3</sub> ) | 3.07                                 | -1.53 <sup>b</sup> |
| Ce-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>3</sub> ) | 3.05                                 | -1.51 <sup>b</sup> |
| In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>4</sub> )    | 2.47                                 | -1.47 <sup>b</sup> |
| Zr-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>4</sub> ) | 3.96                                 | -1.96 <sup>b</sup> |
| Pr-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>4</sub> ) | 3.25                                 | -                  |
| Ce-In <sub>2</sub> O <sub>3</sub> (110) O <sub>v</sub> (O <sub>4</sub> ) | 3.23                                 | -                  |
| CeO <sub>2</sub> (111) O <sub>v</sub>                                    | 2.58                                 | -2.12              |
| ZrO <sub>2</sub> (011) O <sub>v</sub>                                    | 6.05                                 | -3.31              |
| PrO <sub>2</sub> (111) O <sub>v</sub>                                    | -1.10 <sup>a</sup>                   | -                  |
| Pr <sub>2</sub> O <sub>3</sub> (111) O <sub>v</sub>                      | 5.74                                 | -2.75              |
| Pr <sub>6</sub> O <sub>11</sub> (-101) O <sub>v</sub>                    | -0.53 <sup>a</sup>                   | -1.97              |

|                                                        |                    |       |
|--------------------------------------------------------|--------------------|-------|
| In-CeO <sub>2</sub> (111) O <sub>v</sub>               | 0.01               | -0.87 |
| In-ZrO <sub>2</sub> (011) O <sub>v</sub>               | 2.23               | -0.78 |
| In-PrO <sub>2</sub> (111) O <sub>v</sub>               | -1.47 <sup>a</sup> | -     |
| In-Pr <sub>2</sub> O <sub>3</sub> (111) O <sub>v</sub> | 3.80               | -1.38 |

<sup>a</sup> Negative O<sub>v</sub> formation energies suggest that the PrO<sub>2</sub> and Pr<sub>6</sub>O<sub>11</sub> phases tend to decompose. <sup>b</sup> The  $BE_{CO_2}$  values in bold were used to construct the potential energy profiles.

Table C.2. Reaction rates, methanol selectivity, and apparent activation energies for CO<sub>2</sub> to methanol and reverse water gas shift (RWGS) reaction pathways. <sup>a</sup>

| Catalyst                       | Temperature | $r_{MeOH}$                                                   | $S_{MeOH}$ | $E_{a,MeOH}$ | $E_{a,RWGS}$ | $\Delta E_a^b$ |
|--------------------------------|-------------|--------------------------------------------------------------|------------|--------------|--------------|----------------|
|                                | (°C)        | ( $\mu\text{mol}\cdot\text{s}^{-1}\cdot\text{g}_{In}^{-1}$ ) | (%)        | (kJ/mol)     | (kJ/mol)     | (kJ/mol)       |
| InPr                           | 340         | 0.0855                                                       | 6.5        | 96 ± 9.5     | 169 ± 9.7    | 73             |
| InZr                           | 270         | 0.381                                                        | 14.1       | 69 ± 5.6     | 128 ± 1.3    | 59             |
| InCe                           | 290         | 0.124                                                        | 10.9       | 74 ± 4.6     | 101 ± 1.4    | 27             |
| In <sub>2</sub> O <sub>3</sub> | 280         | 0.0186                                                       | 10.1       | 92 ± 5.2     | 112 ± 1.7    | 20             |

<sup>a</sup> Reaction conditions: 0.2 g catalyst, 1:3 CO<sub>2</sub>/H<sub>2</sub>, 20 mL/min, 0.1MPa. <sup>b</sup> Difference between  $E_{a,MeOH}$  and  $E_{a,RWGS}$ .

## Appendix D - Input Files for CatMAP

### D.1. Input Energy File

| surface_<br>name | site_<br>name | species_<br>name | formation_<br>energy | frequencies                                            | reference                        |
|------------------|---------------|------------------|----------------------|--------------------------------------------------------|----------------------------------|
| None             | gas           | CH4              | 0                    | [3095, 3092, 3092, 2982, 1513, 1512, 1287, 1286, 1285] | Narges                           |
| None             | gas           | CO               | 2.77                 | [2125]                                                 | Narges                           |
| None             | gas           | CO2              | 2.47                 | [2365, 1319, 634, 633]                                 | Narges                           |
| None             | gas           | H2               | 0                    | [4381]                                                 | Narges                           |
| None             | gas           | H2O              | 0                    | [3824, 3710, 1582]                                     | Narges                           |
| None             | gas           | C6               | 4.66                 | [2119, 1965, 1668, 1178]                               | Jalid et al. Catal Sci Tech 2021 |
| Ga               | s             | C                | 3.73                 | []                                                     | Narges                           |
| Ga               | s             | C2               | 5.98                 | []                                                     | Narges                           |
| Ga               | s             | C6               | 14.68                | []                                                     | Narges                           |
| Ga               | s             | CH               | 2.62                 | []                                                     | Narges                           |
| Ga               | s             | CH3              | 0.83                 | []                                                     | Narges                           |
| Ga               | s             | CO               | 3.09                 | []                                                     | Narges                           |
| Ga               | s             | CO2              | 2.82                 | []                                                     | Narges                           |
| Ga               | s             | O                | 0.07                 | []                                                     | Narges                           |
| Ga               | h             | H                | 0.29                 | []                                                     | Narges                           |
| Ga               | s             | OH               | -0.23                | []                                                     | Narges                           |
| Ga               | s             | CHO              | 3.01                 | []                                                     | Narges                           |
| Ga               | s             | COH              | 3.83                 | []                                                     | Narges                           |
| Ga               | s             | CH3-H            | 2.4                  | []                                                     | Narges                           |
| Ga               | s             | CO-O             | 3.92                 | []                                                     | Narges                           |
| Ga               | s             | C-O              | 5.65                 | []                                                     | Narges                           |
| Ga               | s             | C+C              | 9.83                 | []                                                     | Narges                           |
| Ga               | t             | C                | 3.73                 | []                                                     | Narges                           |
| Ga               | t             | C2               | 5.98                 | []                                                     | Narges                           |
| Ga               | t             | C6               | 14.68                | []                                                     | Narges                           |
| Ga               | t             | CH               | 2.62                 | []                                                     | Narges                           |
| Ga               | t             | CH3              | 0.83                 | []                                                     | Narges                           |
| Ga               | t             | CO               | 3.09                 | []                                                     | Narges                           |
| Ga               | t             | CO2              | 2.82                 | []                                                     | Narges                           |
| Ga               | t             | O                | 0.07                 | []                                                     | Narges                           |
| Ga               | h             | H                | 0.29                 | []                                                     | Narges                           |
| Ga               | t             | OH               | -0.23                | []                                                     | Narges                           |
| Ga               | t             | CHO              | 3.01                 | []                                                     | Narges                           |
| Ga               | t             | COH              | 3.83                 | []                                                     | Narges                           |

|         |   |       |       |   |        |
|---------|---|-------|-------|---|--------|
| Ga      | t | CH3-H | 2.4   | □ | Narges |
| Ga      | t | CO-O  | 3.92  | □ | Narges |
| Ga      | t | C-O   | 5.65  | □ | Narges |
| Ga      | t | C+C   | 9.83  | □ | Narges |
| Ga(100) | s | C     | 3.97  | □ | Narges |
| Ga(100) | s | O     | -0.08 | □ | Narges |
| Ga(100) | t | C     | 3.97  | □ | Narges |
| Ga(100) | t | O     | -0.08 | □ | Narges |
| Pd3Ga   | s | C     | 4     | □ | Narges |
| Pd3Ga   | s | O     | 1.43  | □ | Narges |
| Pd3Ga   | t | C     | 3.97  | □ | Narges |
| Pd3Ga   | t | O     | -0.08 | □ | Narges |
| Ni3Ga   | s | C     | 2.95  | □ | Narges |
| Ni3Ga   | s | O     | 0.54  | □ | Narges |
| Ni3Ga   | t | C     | 3.97  | □ | Narges |
| Ni3Ga   | t | O     | -0.08 | □ | Narges |
| Ru3Ga   | s | C     | 2.34  | □ | Narges |
| Ru3Ga   | s | O     | 0.47  | □ | Narges |
| Ru3Ga   | t | C     | 3.97  | □ | Narges |
| Ru3Ga   | t | O     | -0.08 | □ | Narges |
| GaPd    | s | C     | 4.27  | □ | Narges |
| GaPd    | s | C2    | 6.74  | □ | Narges |
| GaPd    | s | C6    | 16.07 | □ | Narges |
| GaPd    | s | CH    | 3.33  | □ | Narges |
| GaPd    | s | CO    | 3.08  | □ | Narges |
| GaPd    | s | O     | 0.85  | □ | Narges |
| GaPd    | h | H     | 0.21  | □ | Narges |
| GaPd    | s | OH    | -0.04 | □ | Narges |
| GaPd    | s | CHO   | 3.15  | □ | Narges |
| GaPd    | s | COH   | 4.31  | □ | Narges |
| GaPd    | s | CH3-H | 2.05  | □ | Narges |
| GaPd    | s | CO-O  | 3.96  | □ | Narges |
| GaPd    | s | C-O   | 5.76  | □ | Narges |
| GaPd    | t | C     | 3.73  | □ | Narges |
| GaPd    | t | C2    | 5.98  | □ | Narges |

|      |   |       |       |   |        |
|------|---|-------|-------|---|--------|
| GaPd | t | C6    | 14.68 | □ | Narges |
| GaPd | t | CH    | 2.62  | □ | Narges |
| GaPd | t | CH3   | 0.83  | □ | Narges |
| GaPd | t | CO    | 3.09  | □ | Narges |
| GaPd | t | CO2   | 2.82  | □ | Narges |
| GaPd | t | O     | 0.07  | □ | Narges |
| GaPd | h | H     | 0.29  | □ | Narges |
| GaPd | t | OH    | -0.23 | □ | Narges |
| GaPd | t | CHO   | 3.01  | □ | Narges |
| GaPd | t | COH   | 3.83  | □ | Narges |
| GaPd | t | CH3-H | 2.4   | □ | Narges |
| GaPd | t | CO-O  | 3.92  | □ | Narges |
| GaPd | t | C-O   | 5.65  | □ | Narges |
| GaPd | t | C+C   | 9.83  | □ | Narges |
|      |   |       |       |   |        |
| GaNi | t | C     | 3.73  | □ | Narges |
| GaNi | t | C2    | 5.98  | □ | Narges |
| GaNi | t | C6    | 14.68 | □ | Narges |
| GaNi | t | CH    | 2.62  | □ | Narges |
| GaNi | t | CH3   | 0.83  | □ | Narges |
| GaNi | t | CO    | 3.09  | □ | Narges |
| GaNi | t | CO2   | 2.82  | □ | Narges |
| GaNi | t | O     | 0.07  | □ | Narges |
| GaNi | h | H     | 0.29  | □ | Narges |
| GaNi | t | OH    | -0.23 | □ | Narges |
| GaNi | t | CHO   | 3.01  | □ | Narges |
| GaNi | t | COH   | 3.83  | □ | Narges |
| GaNi | t | CH3-H | 2.4   | □ | Narges |
| GaNi | t | CO-O  | 3.92  | □ | Narges |
| GaNi | t | C-O   | 5.65  | □ | Narges |
| GaNi | t | C+C   | 9.83  | □ | Narges |
|      |   |       |       |   |        |
| GaNi | s | C     | 3.94  | □ | Narges |
| GaNi | s | C2    | 5.29  | □ | Narges |
| GaNi | s | C6    | 14.64 | □ | Narges |
| GaNi | s | CH    | 2.87  | □ | Narges |
| GaNi | s | CH3   | 0.7   | □ | Narges |
| GaNi | s | CO    | 1.66  | □ | Narges |
| GaNi | s | CO2   | 2.44  | □ | Narges |
| GaNi | s | O     | 0.4   | □ | Narges |
| GaNi | h | H     | -0.21 | □ | Narges |
| GaNi | s | OH    | -0.16 | □ | Narges |
| GaNi | s | CHO   | 2.18  | □ | Narges |
| GaNi | s | COH   | 2.3   | □ | Narges |
| GaNi | s | CH3-H | 1.71  | □ | Narges |

|        |   |      |       |   |                                   |
|--------|---|------|-------|---|-----------------------------------|
| GaNi   | s | CO-O | 3.57  | □ | Narges                            |
| GaNi   | s | C-O  | 5.7   | □ | Narges                            |
| Ag     | s | C    | 5.57  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | C    | 4.77  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | C    | 1.76  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | C-C  | 10.97 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | C-C  | 9.69  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | C-C  | 9.03  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | C-C  | 5.99  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | C-C  | 6.09  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | C-C  | 5.51  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | C-C  | 5.18  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | C-H  | 6.53  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | C-H  | 5.81  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | C-H  | 2.81  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | C-H  | 5.06  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | C-H  | 3.12  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | C-H  | 3.1   | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | C-H  | 2.56  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru     | s | C-H  | 2.53  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | C-O  | 8.15  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | C-O  | 7.96  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | C-O  | 6.4   | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | C-O  | 4.3   | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | C-O  | 5.31  | □ | Jalid et al. Catal Sci Tech 2021. |

|        |   |     |       |   |                                   |
|--------|---|-----|-------|---|-----------------------------------|
| Pt     | s | C-O | 5.08  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | C-O | 4.05  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | C2  | 6.71  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | C2  | 5.72  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | C2  | 4.55  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | C2  | 5.28  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | C2  | 5.55  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | C2  | 4.45  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru     | s | C2  | 3.95  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | C6  | 16.84 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | C6  | 15.18 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | C6  | 15.51 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | C6  | 16.16 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | C6  | 15.96 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru     | s | C6  | 14.74 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CH  | 3.96  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CH  | 3.23  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | CH  | 1.51  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CH2 | 3.04  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CH2 | 2.65  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | CH2 | 1.45  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CH3 | 1.6   | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CH3 | 1.35  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | CH3 | 0.89  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CO  | 2.99  | □ | Jalid et al. Catal Sci Tech 2021. |

|        |   |       |      |   |                                   |
|--------|---|-------|------|---|-----------------------------------|
| Au     | s | CO    | 3.04 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CO-OH | 4.98 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CO-OH | 5.59 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | CO-OH | 4.36 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | CO-OH | 3.51 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | CO-OH | 4.04 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | CO-OH | 4.18 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | CO-OH | 3.47 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru     | s | CO-OH | 3.24 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | COO-H | 3.79 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | COO-H | 2.92 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | COO-H | 3.05 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | COO-H | 3.14 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | COOH  | 3.13 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | COOH  | 3.01 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu     | s | COOH  | 2.82 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | COOH  | 2.25 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | COOH  | 2.39 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | COOH  | 1.41 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | COOH  | 1.23 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | h | H     | 0.24 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | h | H     | 0.17 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CH-H  | 4.9  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CH-H  | 4.26 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | CH-H  | 1.73 | □ | Jalid et al. Catal Sci Tech 2021. |



|                   |   |                    |      |   |                                   |
|-------------------|---|--------------------|------|---|-----------------------------------|
| Cu                | s | CH-H               | 3.52 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd                | s | CH-H               | 2.24 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt                | s | CH-H               | 1.8  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh                | s | CH-H               | 1.4  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru                | s | CH-H               | 1.39 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag                | s | CH <sub>2</sub> -H | 3.99 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au                | s | CH <sub>2</sub> -H | 3.45 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co <sub>111</sub> | s | CH <sub>2</sub> -H | 1.65 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd                | s | CH <sub>2</sub> -H | 1.95 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt                | s | CH <sub>2</sub> -H | 1.53 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh                | s | CH <sub>2</sub> -H | 1.44 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru                | s | CH <sub>2</sub> -H | 1.43 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag                | s | CH <sub>3</sub> -H | 2.49 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au                | s | CH <sub>3</sub> -H | 2.23 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co <sub>111</sub> | s | CH <sub>3</sub> -H | 1.43 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au                | h | H-H                | 1.15 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu                | h | H-H                | 0.78 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd                | h | H-H                | 0.12 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt                | h | H-H                | 0.19 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag                | s | OH-H               | 1.78 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au                | s | OH-H               | 2    | □ | Jalid et al. Catal Sci Tech 2021. |
| Co <sub>111</sub> | s | OH-H               | 1.03 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd                | s | OH-H               | 1.18 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt                | s | OH-H               | 0.85 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh                | s | OH-H               | 0.85 | □ | Jalid et al. Catal Sci Tech 2021. |

|        |   |      |       |   |                                   |
|--------|---|------|-------|---|-----------------------------------|
| Ru     | s | OH-H | 0.74  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | H2O  | -0.04 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | H2O  | -0.03 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | H2O  | -0.05 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni     | s | H2O  | -0.05 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | H2O  | -0.08 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | H2O  | -0.05 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru     | s | H2O  | -0.21 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | O    | 2.05  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | O    | 2.61  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | O    | 0.15  | □ | Jalid et al. Catal Sci Tech 2021. |
| #Cu    | s | O    | 1.07  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | CO-O | 5.05  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CO-O | 5.74  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | O-H  | 3.09  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | O-H  | 3.56  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | O-H  | 1.02  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd     | s | O-H  | 2.12  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt     | s | O-H  | 2.12  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh     | s | O-H  | 1.52  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru     | s | O-H  | 1.31  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag     | s | OH   | 0.67  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | OH   | 1.39  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co_111 | s | OH   | 0.05  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au     | s | CHO  | 3.1   | □ | Narges                            |
| Cu     | s | CHO  | 3.13  | □ | Narges                            |

|         |   |       |        |   |                     |
|---------|---|-------|--------|---|---------------------|
| Ni      | s | CHO   | 2.04   | □ | Narges              |
| Pd      | s | CHO   | 1.93   | □ | Narges              |
| Pt      | s | CHO   | 1.93   | □ | Narges              |
| Rh      | s | CHO   | 1.93   | □ | Narges              |
| Ru      | s | CHO   | 1.89   | □ | Narges              |
| Au      | s | CH-O  | 5.8    | □ | Narges              |
| Cu      | s | CH-O  | 5.21   | □ | Narges              |
| Ni      | s | CH-O  | 3.08   | □ | Narges              |
| Au      | s | COH   | 3.93   | □ | Narges              |
| Cu      | s | COH   | 3.4    | □ | Narges              |
| Ni      | s | COH   | 1.75   | □ | Narges              |
| Pd      | s | COH   | 1.64   | □ | Narges              |
| Pt      | s | COH   | 1.65   | □ | Narges              |
| Rh      | s | COH   | 1.64   | □ | Narges              |
| Ru      | s | COH   | 1.68   | □ | Narges              |
| Ni      | s | C-OH  | 3.61   | □ | Narges              |
|         |   |       |        |   |                     |
| Co3Mo3N | s | C     | 1.27   | □ | Cobalt site, Narges |
| Co3Mo3N | s | C2    | 3.26   | □ | Cobalt site, Narges |
| Co3Mo3N | s | C6    | 10.26  | □ | Cobalt site, Narges |
| Co3Mo3N | s | CH    | 0.67   | □ | Narges              |
| Co3Mo3N | s | C-H   | 1.629  | □ | Narges              |
| Co3Mo3N | s | C-C   | 4.44   | □ | Narges              |
| Co3Mo3N | s | CH2   | 0.76   | □ | Narges              |
| Co3Mo3N | s | CH-H  | 1.25   | □ | Narges              |
| Co3Mo3N | s | CH3   | 0.537  | □ | Narges              |
| Co3Mo3N | s | CH2-H | 1.045  | □ | Narges              |
| Co3Mo3N | s | CH3-H | 0.646  | □ | Narges              |
| Co3Mo3N | s | CO    | 1.251  | □ | Narges              |
| Co3Mo3N | s | C-O   | 2.65   | □ | Narges              |
| Co3Mo3N | s | CH-O  | 2.045  | □ | Narges              |
| Co3Mo3N | s | COH   | 1.57   | □ | Narges              |
| Co3Mo3N | s | CHO   | 1.537  | □ | Narges              |
| Co3Mo3N | s | C-OH  | 1.996  | □ | Narges              |
| Co3Mo3N | s | CO-H  | 2.495  | □ | Narges              |
| Co3Mo3N | s | CO2   | 1.02   | □ | Marges              |
| Co3Mo3N | h | H     | -0.613 | □ | Narges              |
| Co3Mo3N | s | H2O   | -0.665 | □ | Narges              |
| Co3Mo3N | s | O     | -0.368 | □ | Narges              |
| Co3Mo3N | s | OH    | -0.553 | □ | Narges              |
| Co3Mo3N | s | O-H   | 0.99   | □ | Narges              |
| Co3Mo3N | s | H-H   | -0.28  | □ | Narges              |
| Co3Mo3N | s | CO-O  | 1.709  | □ | Narges              |
|         |   |       |        |   |                     |
| Co3Mo3N | t | C     | 1.44   | □ | Narges              |

|         |   |       |        |   |                                      |
|---------|---|-------|--------|---|--------------------------------------|
| Co3Mo3N | t | C2    | 4.63   | □ | Narges                               |
| Co3Mo3N | t | C6    | 11.39  | □ | Narges                               |
| Co3Mo3N | t | C-C   | 4.7    | □ | Narges                               |
| Co3Mo3N | t | CH    | 0.67   | □ | Narges                               |
| Co3Mo3N | t | C-H   | 1.7    | □ | Narges                               |
| Co3Mo3N | t | CH-H  | 1.25   | □ | Narges                               |
| Co3Mo3N | t | CH2   | 0.69   | □ | Narges                               |
| Co3Mo3N | t | CH3   | 0.7    | □ | Narges                               |
| Co3Mo3N | t | CH2-H | 1.12   | □ | Narges                               |
| Co3Mo3N | t | O     | -0.733 | □ | Bounardy site,<br>Narges             |
| Co3Mo3N | t | CO    | 1.372  | □ | Narges                               |
| Co3Mo3N | t | H     | -0.613 | □ | Narges                               |
| Co3Mo3N | t | OH    | -0.673 | □ | Narges                               |
| Co3Mo3N | t | COH   | 1.452  | □ | Narges                               |
| Co3Mo3N | t | CHO   | 1.27   | □ | Narges                               |
| Co3Mo3N | t | C-O   | 2.97   | □ | Narges                               |
| Co3Mo3N | t | H2O   | 0.03   | □ | Narges                               |
| Co3Mo3N | t | CH-O  | 1.59   | □ | Narges                               |
| Co3Mo3N | t | C-OH  | 3.17   | □ | Narges                               |
| Co3Mo3N | t | O-H   | -0.539 | □ | Narges                               |
| Co3Mo3N | t | CO-O  | 2.285  | □ | Narges                               |
|         |   |       |        |   |                                      |
| Ni2Mo3N | s | C     | 4.33   | □ | Narges                               |
| Ni2Mo3N | s | O     | 1.7    | □ | Narges                               |
| Ni2Mo3N | t | C     | 1.35   | □ | Narges                               |
| Ni2Mo3N | t | O     | -1.72  | □ | Narges                               |
|         |   |       |        |   |                                      |
| Ni3Mo3N | s | C     | 1.74   | □ | Narges                               |
| Ni3Mo3N | s | O     | 0.66   | □ | Narges                               |
| Ni3Mo3N | t | C     | 1.69   | □ | Narges                               |
| Ni3Mo3N | t | O     | -0.61  | □ | Narges                               |
|         |   |       |        |   |                                      |
| Ag      | t | C     | 5.07   | □ | Jalid et al. Catal Sci<br>Tech 2021. |
| Au      | t | C     | 4.77   | □ | Jalid et al. Catal Sci<br>Tech 2021. |
| Co      | t | C     | 1.7    | □ | Jalid et al. Catal Sci<br>Tech 2021. |
| Cu      | t | C     | 3.54   | □ | Jalid et al. Catal Sci<br>Tech 2021. |
| Ni      | t | C     | 1.52   | □ | Jalid et al. Catal Sci<br>Tech 2021. |
| Pd      | t | C     | 1.51   | □ | Jalid et al. Catal Sci<br>Tech 2021. |

|    |   |     |       |   |                                   |
|----|---|-----|-------|---|-----------------------------------|
| Pt | t | C   | 2.1   | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | C   | 1.38  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | C   | 1.23  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | C-C | 11.02 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | C-C | 10.36 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | C-C | 5.07  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | C-C | 8.22  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | C-C | 6.03  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | C-C | 4.51  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | C-C | 4.37  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | C-H | 4.31  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | C-H | 2.25  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | C-H | 3.06  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | C-H | 1.97  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | C-H | 1.74  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | C-O | 8.07  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | C-O | 8.18  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | C-O | 3.19  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | C-O | 3.43  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | C-O | 4.63  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | C-O | 4.11  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | C-O | 3.03  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | C-O | 2.8   | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | C2  | 5.8   | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | C2  | 4.44  | □ | Jalid et al. Catal Sci Tech 2021. |

|    |   |     |       |   |                                   |
|----|---|-----|-------|---|-----------------------------------|
| Ni | t | C2  | 3.57  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | C2  | 4.03  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | C6  | 16.63 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | C6  | 15.28 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | C6  | 14.13 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | C6  | 13.44 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | C6  | 14.28 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | C6  | 12.22 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CH  | 3.96  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CH  | 3.43  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CH  | 1.16  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CH  | 2.7   | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CH  | 1.22  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CH  | 1.57  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CH  | 1.19  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CH  | 1.01  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CH  | 0.71  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CH2 | 2.87  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CH2 | 2.23  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CH2 | 0.79  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CH2 | 2.22  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CH2 | 1.14  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CH2 | 1.28  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CH2 | 0.76  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CH2 | 0.76  | □ | Jalid et al. Catal Sci Tech 2021. |

|    |   |                 |      |   |                                   |
|----|---|-----------------|------|---|-----------------------------------|
| Ru | t | CH <sub>2</sub> | 0.69 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CH <sub>3</sub> | 1.39 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CH <sub>3</sub> | 1.1  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CH <sub>3</sub> | 0.04 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CH <sub>3</sub> | 0.97 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CH <sub>3</sub> | 0.39 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CH <sub>3</sub> | 0.79 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CH <sub>3</sub> | 0.46 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CH <sub>3</sub> | 0.36 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CH <sub>3</sub> | 0.06 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CO              | 2.87 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CO              | 2.57 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CO              | 1.4  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CO              | 2.28 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CO              | 1.25 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CO              | 1.22 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CO              | 1.11 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CO              | 1.07 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CO              | 0.98 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CO-OH           | 3.75 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CO-OH           | 4.14 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CO-OH           | 2.97 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CO-OH           | 3.1  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CO-OH           | 2.8  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CO-OH           | 2.4  | □ | Jalid et al. Catal Sci Tech 2021. |

|    |   |       |       |   |                                   |
|----|---|-------|-------|---|-----------------------------------|
| Ru | t | CO-OH | 2.27  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | COO-H | 4.36  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | COO-H | 3.88  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | COO-H | 2.85  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | COO-H | 2.62  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | COO-H | 2.6   | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | COOH  | 3.05  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | COOH  | 2.7   | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | COOH  | 2.17  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | COOH  | 1.94  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | COOH  | 1.59  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | H     | 0.24  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | H     | 0.17  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | H     | -0.09 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | H     | -0.39 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | H     | -0.4  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | H     | -0.35 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | H     | -0.32 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | H     | -0.44 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CH-H  | 4.74  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CH-H  | 4.58  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CH-H  | 1.78  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CH-H  | 3.27  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CH-H  | 1.93  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CH-H  | 2.05  | □ | Jalid et al. Catal Sci Tech 2021. |



|    |   |                    |      |   |                                   |
|----|---|--------------------|------|---|-----------------------------------|
| Pt | t | CH-H               | 2.35 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CH-H               | 1.54 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CH-H               | 1.07 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CH <sub>2</sub> -H | 3.52 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CH <sub>2</sub> -H | 2.81 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CH <sub>2</sub> -H | 0.99 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CH <sub>2</sub> -H | 2.5  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CH <sub>2</sub> -H | 1.41 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CH <sub>2</sub> -H | 1.53 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CH <sub>2</sub> -H | 0.94 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CH <sub>2</sub> -H | 0.79 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CH <sub>2</sub> -H | 0.68 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CH <sub>3</sub> -H | 2.23 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | CH <sub>3</sub> -H | 1.83 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CH <sub>3</sub> -H | 0.86 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CH <sub>3</sub> -H | 1.7  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CH <sub>3</sub> -H | 1.13 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CH <sub>3</sub> -H | 0.83 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CH <sub>3</sub> -H | 0.73 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CH <sub>3</sub> -H | 0.66 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CH <sub>3</sub> -H | 0.52 | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | H-H                | 1.15 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | H-H                | 0.78 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | H-H                | 0.12 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | H-H                | 0.19 | □ | Jalid et al. Catal Sci Tech 2021. |

|    |   |                  |       |   |                                   |
|----|---|------------------|-------|---|-----------------------------------|
| Au | t | OH-H             | 1.82  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | OH-H             | 0.8   | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | OH-H             | 0.35  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | OH-H             | 0.82  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | OH-H             | 0.72  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | OH-H             | 0.49  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | OH-H             | -0.01 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | H <sub>2</sub> O | -0.12 | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | H <sub>2</sub> O | -0.37 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | H <sub>2</sub> O | -0.18 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | H <sub>2</sub> O | -0.32 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | H <sub>2</sub> O | -0.18 | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | H <sub>2</sub> O | -0.14 | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | H <sub>2</sub> O | -0.29 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | H <sub>2</sub> O | -0.57 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | O                | 1.88  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | O                | 2.32  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | O                | -0.15 | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | O                | 0.78  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | O                | 0.34  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | O                | 1.5   | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | O                | 1.26  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | O                | 0.16  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | O                | -0.1  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CO-O             | 5.1   | □ | Jalid et al. Catal Sci Tech 2021. |

|    |   |      |       |   |                                   |
|----|---|------|-------|---|-----------------------------------|
| Au | t | CO-O | 5.45  | □ | Jalid et al. Catal Sci Tech 2021. |
| Co | t | CO-O | 2.73  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | CO-O | 3.92  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | CO-O | 2.77  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | CO-O | 3.99  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | CO-O | 3.53  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | CO-O | 2.56  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | CO-O | 2.35  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | O-H  | 2.8   | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | O-H  | 3.18  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | O-H  | 1.63  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | O-H  | 0.68  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | O-H  | 1.75  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | O-H  | 1.6   | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | O-H  | 0.73  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | O-H  | 0.27  | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | OH   | 0.49  | □ | Jalid et al. Catal Sci Tech 2021. |
| Au | t | OH   | 0.94  | □ | Jalid et al. Catal Sci Tech 2021. |
| Cu | t | OH   | -0.04 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ni | t | OH   | -0.5  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pd | t | OH   | 0.34  | □ | Jalid et al. Catal Sci Tech 2021. |
| Pt | t | OH   | 0.36  | □ | Jalid et al. Catal Sci Tech 2021. |
| Rh | t | OH   | -0.37 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ru | t | OH   | -0.69 | □ | Jalid et al. Catal Sci Tech 2021. |
| Ag | t | CHO  | 3.15  | □ | narges                            |
| Au | t | CHO  | 2.75  | □ | narges                            |

|    |   |       |        |   |        |
|----|---|-------|--------|---|--------|
| Cu | t | CHO   | 2.65   | □ | narges |
| Ni | t | CHO   | 1.76   | □ | narges |
| Pt | t | CHO   | 1.71   | □ | narges |
| Rh | t | CHO   | 1.69   | □ | narges |
| Ru | t | CHO   | 1.25   | □ | narges |
|    |   |       |        |   |        |
| Ni | s | C     | 2.407  | □ | Narges |
| Ni | s | C-H   | 2.719  | □ | Narges |
| Ni | s | C-OH  | 3.613  | □ | Narges |
| Ni | s | CH    | 1.327  | □ | Narges |
| Ni | s | CH2   | 1.16   | □ | Narges |
| Ni | s | CH-H  | 1.52   | □ | Narges |
| Ni | s | CH-O  | 3.079  | □ | Narges |
| Ni | s | CH2-H | 1.24   | □ | Narges |
| Ni | s | CH3   | 0.581  | □ | Narges |
| Ni | s | CH3-H | 0.849  | □ | Narges |
| Ni | s | CHO   | 2.043  | □ | Narges |
| Ni | s | CHO-H | 2.64   | □ | Narges |
| Ni | s | CO    | 1.34   | □ | Narges |
| Ni | s | CO-H  | 2.7    | □ | Narges |
| Ni | s | CO2   | 2.518  | □ | Narges |
| Ni | s | COH   | 1.75   | □ | Narges |
| Ni | s | COO-H | 3.083  | □ | Narges |
| Ni | s | COOH  | 2.158  | □ | Narges |
| Ni | h | H     | -0.548 | □ | Narges |
| Ni | s | CO-H  | 2.234  | □ | Narges |
| Ni | s | H-COH | 2.029  | □ | Narges |
| Ni | s | OH-H  | 0.588  | □ | Narges |
| Ni | s | HCOH  | 1.928  | □ | Narges |
| Ni | s | O     | 0.212  | □ | Narges |
| Ni | s | CO-O  | 3.115  | □ | Narges |
| Ni | s | O-H   | 0.837  | □ | Narges |
| Ni | s | OH    | -0.138 | □ | Narges |
| Ni | s | CH-O  | 3.08   | □ | Narges |
|    |   |       |        |   |        |
| Cu | s | C     | 4.45   | □ | Narges |
| Cu | s | CH    | 2.898  | □ | Narges |
| Cu | s | CH-O  | 5.209  | □ | Narges |
| Cu | s | CH2   | 2.164  | □ | Narges |
| Cu | s | CH3   | 1.101  | □ | Narges |
| Cu | s | CH3-H | 1.882  | □ | Narges |
| Cu | s | CHO   | 3.131  | □ | Narges |
| Cu | s | CO    | 2.46   | □ | Narges |
| Cu | s | CO2   | 2.84   | □ | Narges |
| Cu | s | CO-OH | 3.92   | □ | Narges |

|    |   |       |        |   |        |
|----|---|-------|--------|---|--------|
| Cu | s | COH   | 3.401  | □ | Narges |
| Cu | h | H     | -0.184 | □ | Narges |
| Cu | s | CO-H  | 3.365  | □ | Narges |
| Cu | s | OH-H  | 1.216  | □ | Narges |
| Cu | s | H2O   | -0.157 | □ | Narges |
| Cu | s | O     | 1.027  | □ | Narges |
| Cu | s | CO-O  | 4.254  | □ | Narges |
| Cu | s | O-H   | 1.688  | □ | Narges |
| Cu | s | OH    | 0.141  | □ | Narges |
|    |   |       |        |   |        |
| Pd | s | C     | 2.28   | □ | Narges |
| Pd | s | CH    | 1.37   | □ | Narges |
| Pd | s | CH2   | 1.33   | □ | Narges |
| Pd | s | CH3   | 0.68   | □ | Narges |
| Pd | s | CH3-H | 0.85   | □ | Narges |
| Pd | s | CO    | 1.22   | □ | Narges |
| Pd | s | CO-O  | 3.52   | □ | Narges |
| Pd | h | H     | -0.57  | □ | Narges |
| Pd | s | O     | 1.21   | □ | Narges |
| Pd | s | OH    | 0.64   | □ | Narges |
| Pd | s | CO2   | 2.72   | □ | Narges |
| Pd | s | CHO   | 1.93   | □ | Narges |
|    |   |       |        |   |        |
| Ir | s | CH    | 1.01   | □ | Narges |
| Ir | s | C     | 2.1    | □ | Narges |
| Ir | s | CH2   | 0.6    | □ | Narges |
| Ir | s | CH3   | 0.551  | □ | Narges |
| Ir | s | CO    | 1.64   | □ | Narges |
| Ir | s | CO-O  | 3.613  | □ | Narges |
| Ir | h | H     | -0.466 | □ | Narges |
| Ir | s | OH    | 0.46   | □ | Narges |
| Ir | s | O     | 0.806  | □ | Narges |
| Ir | s | CH3-H | 0.796  | □ | Narges |
| Ir | s | CO2   | 2.7    | □ | Narges |
| Ir | s | CH    | 1.01   | □ | Narges |
|    |   |       |        |   |        |
| Rh | s | C     | 2.01   | □ | Narges |
| Rh | s | CH    | 1.188  | □ | Narges |
| Rh | s | CH2   | 1.15   | □ | Narges |
| Rh | s | CH3   | 0.669  | □ | Narges |
| Rh | s | CH3-H | 0.831  | □ | Narges |
| Rh | s | CO    | 1.424  | □ | Narges |
| Rh | s | CO-O  | 3.424  | □ | Narges |
| Rh | s | CO2   | 2.633  | □ | Narges |
| Rh | h | H     | -0.465 | □ | Narges |

|         |   |            |        |   |        |
|---------|---|------------|--------|---|--------|
| Rh      | s | O          | 0.627  | □ | Narges |
| Rh      | s | OH         | 0.22   | □ | Narges |
| Rh      | s | H2O        | -0.34  | □ | Narges |
|         |   |            |        |   |        |
| Ru      | s | C          | 1.76   | □ | Narges |
| Ru      | s | CH         | 1.02   | □ | Narges |
| Ru      | s | CH2        | 0.95   | □ | Narges |
| Ru      | s | CH3        | 0.39   | □ | Narges |
| Ru      | s | CH3-H      | 0.7    | □ | Narges |
| Ru      | s | CO         | 1.4    | □ | Narges |
| Ru      | s | CO-O       | 2.57   | □ | Narges |
| Ru      | h | H          | -0.59  | □ | Narges |
| Ru      | s | O          | -0.27  | □ | Narges |
| Ru      | s | OH         | -0.21  | □ | Narges |
| Ru      | s | CHO        | 1.89   | □ | Narges |
|         |   |            |        |   |        |
| Pt      | s | C          | 2.08   | □ | Narges |
| Pt      | s | CH         | 0.891  | □ | Narges |
| Pt      | s | CH2        | 0.98   | □ | Narges |
| Pt      | s | CH3        | 0.587  | □ | Narges |
| Pt      | s | CH3-H      | 0.81   | □ | Narges |
| Pt      | s | CO         | 1.45   | □ | Narges |
| Pt      | s | CO-O       | 4.266  | □ | Narges |
| Pt      | s | CO2        | 2.46   | □ | Narges |
| Pt      | h | H          | -0.537 | □ | Narges |
| Pt      | s | O          | 1.376  | □ | Narges |
| Pt      | s | OH         | 0.85   | □ | Narges |
|         |   |            |        |   |        |
| Co_0001 | s | C          | 2.311  | □ | Narges |
| Co_0001 | s | C2         | 4.2    | □ | Narges |
| Co_0001 | s | C-H        | 2.516  | □ | Narges |
| Co_0001 | s | C-C        | 5.85   | □ | Narges |
| Co_0001 | s | C-OH       | 3.742  | □ | Narges |
| Co_0001 | s | C-O        | 4.005  | □ | Narges |
| Co_0001 | s | CH         | 1.388  | □ | Narges |
| Co_0001 | s | CH-O       | 2.83   | □ | Narges |
| Co_0001 | s | CH-H       | 1.412  | □ | Narges |
| Co_0001 | s | CH2        | 1.187  | □ | Narges |
| Co_0001 | s | CH2-H      | 1.25   | □ | Narges |
| Co_0001 | s | CH3        | 0.531  | □ | Narges |
| Co_0001 | s | CH3-H      | 0.991  | □ | Narges |
| Co_0001 | s | CH3-<br>OH | 1.455  | □ | Narges |
| Co_0001 | s | CHO        | 2.146  | □ | Narges |
| Co_0001 | s | CHOH       | 2.347  | □ | Narges |

|         |   |      |        |    |        |
|---------|---|------|--------|----|--------|
| Co_0001 | s | CO   | 1.594  | [] | Narges |
| Co_0001 | s | CO-H | 2.831  | [] | Narges |
| Co_0001 | s | CO-O | 2.944  | [] | Narges |
| Co_0001 | s | CO2  | 2.728  | [] | Narges |
| Co_0001 | s | COH  | 1.855  | [] | Narges |
| Co_0001 | s | COOH | 2.26   | [] | Narges |
| Co_0001 | h | H    | -0.526 | [] | Narges |
| Co_0001 | s | H2   | -0.029 | [] | Narges |
| Co_0001 | s | HCO2 | 1.756  | [] | Narges |
| Co_0001 | s | O    | -0.143 | [] | Narges |
| Co_0001 | s | O-H  | 0.6    | [] | Narges |
| Co_0001 | s | OH-H | 0.59   | [] | Narges |
| Co_0001 | s | OH   | -0.316 | [] | Narges |

## D.2. Set Up Reaction Parameters

### D.2.1. Single-site System

#Microkinetic model parameters

rxn\_expressions = [

# "s": 111 facet

'CH4\_g + \*\_s + \*\_h <-> CH3-H\_s + \*\_h -> CH3\_s + H\_h',

'CH3\_s + \*\_h <-> CH2-H\_s + \*\_h -> CH2\_s + H\_h',

'CH2\_s + \*\_h <-> CH-H\_s + \*\_h -> CH\_s + H\_h',

'CH\_s + \*\_h <-> C-H\_s + \*\_h -> C\_s + H\_h',

'CH\_s + O\_s <-> CH-O\_s + \*\_s -> CHO\_s + \*\_s',

'CHO\_s + \*\_h <-> CO\_s + H\_h',

'H\_h + H\_h <-> H-H\_h + \*\_h -> H2\_g + 2\*\_h',

```

'O_s + H_h <-> O-H_s + *_h -> OH_s + *_h',
'OH_s + H_h <-> OH-H_s + *_h -> H2O_g + *_h + *_s',

'C_s + OH_s <-> C-OH_s + *_s -> COH_s + *_s',
'COH_s + *_h <-> CO_s + H_h',

'C_s + O_s <-> C-O_s + *_s -> CO_s + *_s',
'CO_s <-> CO_g + *_s',
'CO2_g + 2*_s <-> CO-O_s + *_s -> CO_s + O_s',

'C_s + C_s <-> C-C_s + *_s -> C2_s + *_s',
'C2_s + C2_s + C2_s <-> C6_s + 2*_s',
'C6_s <-> C6_g + *_s',
]

```

```

surface_names =

['Ag','Au','Cu','Ni','Pd','Pt','Rh','Ru','Co_111','Co3Mo3N','Ga(100)','Pd3Ga','Ni3Ga','Ru3Ga']

descriptor_names= ['O_s','C_s'] #descriptor names

descriptor_ranges = [[-3.0,3.0],[0.0,6.0]]

resolution = 20

temperature = 973 #Temperature of the reaction

species_definitions = {}

```



```

species_definitions['CO_g'] = {'pressure':0.005} #define the gas pressures
species_definitions['H2_g'] = {'pressure':0.005}
species_definitions['H2O_g'] = {'pressure':0.1}
species_definitions['CO2_g'] = {'pressure':0.4445}
species_definitions['CH4_g'] = {'pressure':0.4445} #define the gas pressures
species_definitions['C6_g'] = {'pressure':0.001}

species_definitions['s'] = {'site_names': ['s'], 'total':1.0}
species_definitions['h'] = {'site_names': ['h'], 'total':1.0}

data_file = 'DRM.pkl'

#

#Parser parameters

#

input_file = 'energies_Jalid_Narges2.txt' #input data

#

#Scaler parameters

#

gas_thermo_mode = "fixed_entropy_gas"
adsorbate_thermo_mode = "frozen_adsorbate"

#input the interaction paramters

scaling_constraint_dict = {'O_s':[1,0,0],
                           'C_s':[0,1,0],

```

'O\_t':[1.05,0,-0.23], #Jalid  
 'C\_t':[0,0.95,-0.28],#Narges  
 'H\_h':[0.0,0.18,-0.75],  
 'CH3\_s': [0.0,0.25,-0.02],  
 'CH2\_s': [0.0,0.53,0.40],  
 'CH\_s': [0.0,0.76,-0.35],  
 'CH3\_t': [0.0,0.25,-0.02],  
 'CH2\_t': [0.0,0.70,-0.07],  
 'CH\_t': [0.0,0.76,-0.35],  
 'CO\_s':[0,0.46,0.39],  
 'CO\_t':[0,0.46,0.39], #Narges  
 'CHO\_s':[0,0.43,1.04], #Narges  
 'CHO\_t':[0,0.43,0.71], #Narges  
 'COH\_s':[0,0.75,0.24], #Narges  
 'COH\_t':[0,0.75,0.24], #Narges  
 'OH\_s':[0.55,0,-0.17], #Narges  
 'OH\_t':[0.56,0,-0.54], #Narges  
 'CH3-H\_s': 'BEP[0.89,0.80]',  
 'CH2-H\_s': 'BEP[1.39,1.25]',  
 'CH-H\_s': 'BEP[1.95,2.35]',  
 'C-H\_s': 'BEP[2.49,1.74]',  
 'CH3-H\_t': 'BEP[0.89,0.80]',  
 'CH2-H\_t': 'BEP[1.39,1.25]',

```

        'CH-H_t': 'BEP[1.95,2.35]',
        'C-H_t': 'BEP[2.49,1.74]',
        'CO-O_s': 'BEP[0.68,3.35]',
        'CO-O_t': 'BEP[0.68,3.35]',
        'C-O_s': 'BEP[-0.85,4.00]', #Narges
        'C-O_t': 'BEP[-0.85,4.00]', #Jalid
        'O-H_s': 'BEP[-0.97,1.69]',
        'O-H_t': 'BEP[-1.46,0.26]', #Jalid ,
        'CH-O_s': 'initial_state[0.59,2.05]', #Narges
        'CH-O_t': 'initial_state[0.84,1.53]', #Yu
        'C-OH_t': 'final_state[1.18,1.13]', #Yu
        'C-C_s': 'BEP[-1.22,5.51]', #Narges
        'H-H_h': 'BEP[-0.93,0.87]'
    }

#

#Solver parameters

#

decimal_precision = 100 #precision of numbers involved

tolerance = 1e-50 #all d_theta/d_t's must be less than this at the solution

max_rootfinding_iterations = 100

max_bisections = 10

```

### D.2.2. Dual-site System

#Microkinetic model parameters

rxn\_expressions = [

# "s": 111 facet

'CH4\_g + \*\_s + \*\_h <-> CH3-H\_s + \*\_h -> CH3\_s + H\_h',

'CH3\_s + \*\_h <-> CH2-H\_s + \*\_h -> CH2\_s + H\_h',

'CH2\_s + \*\_h <-> CH-H\_s + \*\_h -> CH\_s + H\_h',

'CH\_s + \*\_h <-> C-H\_s + \*\_h -> C\_s + H\_h',

'CH\_s + O\_s <-> CH-O\_s + \*\_s -> CHO\_s + \*\_s',

'CHO\_s + \*\_h <-> CO\_s + H\_h',

'H\_h + H\_h <-> H-H\_h + \*\_h -> H2\_g + 2\*\_h',

'O\_s + H\_h <-> O-H\_s + \*\_h -> OH\_s + \*\_h',

'OH\_s + H\_h <-> OH-H\_s + \*\_h -> H2O\_g + \*\_h + \*\_s',

'C\_s + OH\_s <-> C-OH\_s + \*\_s -> COH\_s + \*\_s',

'COH\_s + \*\_h <-> CO\_s + H\_h',

'C\_s + O\_s <-> C-O\_s + \*\_s -> CO\_s + \*\_s',

'CO\_s <-> CO\_g + \*\_s',

'CO2\_g + 2\*\_s <-> CO-O\_s + \*\_s -> CO\_s + O\_s',

'C\_s + C\_s <-> C-C\_s + \*\_s -> C2\_s + \*\_s',

'C2\_s + C2\_s + C2\_s <-> C6\_s + 2\*\_s',

'C6\_s <-> C6\_g + \*\_s',

# "t": 211 facet

'CH4\_g + \*\_t + \*\_h <-> CH3-H\_t + \*\_h -> CH3\_t + H\_h',

'CH3\_t + \*\_h <-> CH2-H\_t + \*\_h -> CH2\_t + H\_h',

'CH2\_t + \*\_h <-> CH-H\_t + \*\_h -> CH\_t + H\_h',

'CH\_t + \*\_h <-> C-H\_t + \*\_h -> C\_t + H\_h',

'CH\_t + O\_t <-> CH-O\_t + \*\_t -> CHO\_t + \*\_t',

'CHO\_t + \*\_h <-> CO\_t + H\_h',

'O\_t + H\_h <-> O-H\_t + \*\_h -> OH\_t + \*\_h',

'OH\_t + H\_h <-> OH-H\_t + \*\_h -> H2O\_g + \*\_h + \*\_t',

'C\_t + OH\_t <-> C-OH\_t + \*\_t -> COH\_t + \*\_t',

'COH\_t + \*\_h <-> CO\_t + H\_h',

'C\_t + O\_t <-> C-O\_t + \*\_t -> CO\_t + \*\_t',

'CO\_t <-> CO\_g + \*\_t',

'CO2\_g + 2\*\_t <-> CO-O\_t + \*\_t -> CO\_t + O\_t',

'C\_t + C\_t <-> C-C\_t + \*\_t -> C2\_t + \*\_t',

'C2\_t + C2\_t + C2\_t <-> C6\_t + 2\*\_t',

'C6\_t <-> C6\_g + \*\_t',

# dual-site mechanism

'CH\_s + \*\_t <-> CH\_t + \*\_s',

'OH\_s + \*\_t <-> OH\_t + \*\_s',

'C\_s + \*\_t <-> C\_t + \*\_s',

'O\_s + \*\_t <-> O\_t + \*\_s',

'CO\_s + \*\_t <-> CO\_t + \*\_s',

'C\_s + O\_t <-> C-O\_s + \*\_t -> CO\_s + \*\_t',

'C\_t + O\_s <-> C-O\_t + \*\_s -> CO\_t + \*\_s',

'C\_t + C\_s <-> C-C\_s + \*\_t -> C2\_s + \*\_t',

'CH\_s + O\_t <-> CH-O\_s + \*\_t -> CHO\_s + \*\_t',

'CH\_t + O\_s <-> CH-O\_t + \*\_s -> CHO\_t + \*\_s',

'C\_s + OH\_t <-> C-OH\_s + \*\_t -> COH\_s + \*\_t',

'C\_t + OH\_s <-> C-OH\_t + \*\_s -> COH\_t + \*\_s',

]

surface\_names =

['Ag','Au','Co\_111','Cu','Ni','Pd','Pt','Rh','Ru','Co3Mo3N','Ga(100)','Pd3Ga','Ni3Ga','Ru3Ga']

descriptor\_names= ['O\_s','C\_s'] #descriptor names

descriptor\_ranges = [[-3.0,3.0],[0.0,6.0]]

resolution = 20

temperature = 973 #Temperature of the reaction

species\_definitions = {}

species\_definitions['CO\_g'] = {'pressure':0.005} #define the gas pressures

species\_definitions['H2\_g'] = {'pressure':0.005}

species\_definitions['H2O\_g'] = {'pressure':0.1}

species\_definitions['CO2\_g'] = {'pressure':0.4445}

species\_definitions['CH4\_g'] = {'pressure':0.4445} #define the gas pressures

species\_definitions['C6\_g'] = {'pressure':0.001}

species\_definitions['s'] = {'site\_names': ['s'], 'total':0.1}

species\_definitions['t'] = {'site\_names': ['t'], 'total':0.9}

species\_definitions['h'] = {'site\_names': ['h'], 'total':1.0}

```

data_file = 'DRM.pkl'

#

#Parser parameters

#

input_file = 'energies_Jalid_Narges2.txt' #input data

#

#Scaler parameters

#

gas_thermo_mode = "fixed_entropy_gas"

adsorbate_thermo_mode = "frozen_adsorbate"

{'cutoff':0.25,'smoothing':0.01}

scaling_constraint_dict = {'O_s':[1,0,0],
                           'C_s':[0,1,0],
                           'O_t':[0.83,0,0.12], #Narges
                           'C_t':[0,0.95,-0.28],#Narges
                           'H_h':[0.0,0.18,-0.75],
                           'CH3_s': [0.0,0.25,-0.02],
                           'CH2_s': [0.0,0.53,0.40],
                           'CH_s': [0.0,0.76,-0.35],
                           'CH3_t': [0.0,0.25,-0.02],
                           'CH2_t': [0.0,0.70,-0.07],
                           'CH_t': [0.0,0.76,-0.35],

```



'CO\_s':[0,0.46,0.39],  
 'CO\_t':[0,0.46,0.39], #Narges  
 'CHO\_s':[0,0.43,1.04], #Narges  
 'CHO\_t':[0,0.43,0.71], #Narges  
 'COH\_s':[0,0.75,0.24], #Narges  
 'COH\_t':[0,0.75,0.24], #Narges  
 'OH\_s':[0.55,0,-0.17], #Narges  
 'OH\_t':[0.56,0,-0.54], #Narges  
 'CH3-H\_s': 'BEP[0.89,0.80]',  
 'CH2-H\_s': 'BEP[1.39,1.25]',  
 'CH-H\_s': 'BEP[1.95,2.35]',  
 'C-H\_s': 'BEP[2.49,1.74]',  
 'CH3-H\_t': 'BEP[0.89,0.80]',  
 'CH2-H\_t': 'BEP[1.39,1.25]',  
 'CH-H\_t': 'BEP[1.95,2.35]',  
 'C-H\_t': 'BEP[2.49,1.74]',  
 'CO-O\_s': 'BEP[0.68,3.35]',  
 'CO-O\_t': 'BEP[0.68,3.35]',  
 'C-O\_s': 'BEP[-0.85,4.00]', #Narges  
 'C-O\_t': 'BEP[-0.85,4.00]', #Jalid  
 'O-H\_s': 'BEP[-0.97,1.69]',  
 'O-H\_t': 'BEP[-1.46,0.26]', #Jalid ,  
 'CH-O\_s': 'initial\_state[0.59,2.05]', #Narges

```

'CH-O_t': 'initial_state[0.84,1.53]', #Yu
'C-OH_t': 'final_state[1.18,1.13]', #Yu
'C-C_s': 'BEP[-1.06,6.06]', #Jalid
'C-C_t': 'BEP[-1.06,6.06]', #Narges
'H-H_h': 'BEP[-0.93,0.87]'
}

#
#Solver parameters
#
decimal_precision = 100 #precision of numbers involved
tolerance = 1e-50 #all d_theta/d_t's must be less than this at the solution
max_rootfinding_iterations = 100
max_bisections = 10

```

## Appendix E - Reprint Permissions



### Mechanistic understanding of support effect on the activity and selectivity of indium oxide catalysts for CO<sub>2</sub> hydrogenation

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