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DOCTORAL DISSERTATION

**The Multi-scale Simulations
of the Non-equilibrium States
of Cu Surfaces**

銅表面における非平衡状態の
マルチスケールシミュレーション

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Abstract

The Multi-scale Simulations of the Non-equilibrium States of Cu surfaces

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Understanding the nature of heterogenous catalysis is a non-trivial task especially when the catalyst is sensitively affected by the operating conditions. The challenge lies in the complex non-equilibrium states that are intractable in experiments as they occur in atomic size and timescale. A notable problem is the struggle in the identification of the active sites of Cu-based catalyst for methanol synthesis. By applying multi-scale simulations, this study aims to elucidate the non-equilibrium states of the Cu surface that are relevant to the development of catalyst for methanol synthesis. These include: (i) the step edge fluctuations, (ii) the surface alloying with Zn, and (iii) the surface transformation induced by CO molecules. The overview of these three works is provided as follows.

Graph Theoretical Kinetic Monte Carlo (GTKMC) simulation has been conducted to investigate the microscopic mechanism of surface diffusions of Cu with defects such as steps and kinks. Various diffusion events during the step fluctuations are discussed in detail. The diffusion along the step edge was found to be the dominant mass transport mechanism, indicated by the lowest energy barrier. The time correlation functions at 300 K, 400 K, and 500 K have been calculated and compared with experiments and theoretical studies.

The multi-scale simulation in the form of Machine Learning Molecular Dynamics (MLMD) has been conducted to investigate the structure and the formation process of Cu-Zn surface alloy on Cu(997). The simulation reveals atomistic details of the alloying process, i.e., the incorporation of deposited Zn adatoms to the Cu substrate. The surface alloying is found to start at upper and lower terraces near the step edge, which emphasize the role of steps and kinks in the alloying. The incorporation of Zn at the middle terrace was found at the later stage. The rationalization of alloying behavior and the connection to the STM experiment were performed based on statistics and barriers of various elementary events observed during simulation.

By applying the similar framework, the influence of CO adsorption upon the formation of Cu clusters on the Cu(111) has been elucidated. The simulations at 450 K to 550 K show Cu clusters are formed within a hundred of ns when the Cu surface is exposed with CO. On the other hand, no cluster is formed on the clean Cu surface even at 550 K. The clusters can be formed directly through instantaneous detachment of a group of step-atoms or indirectly by aggregation of wandering Cu-CO monomers and smaller CO-decorated clusters on the surface terrace. The preference to the indirect mechanism is indicated by the higher frequency of its occurrence. The DFT calculations also confirmed the promotion of CO adsorptions to the detachment of Cu step-atoms by lowering their detachment barriers.

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*This dissertation is dedicated to my loving parents
who have been my endless source of encouragement
and perseverance*

Chapter 1

Introduction

1.1 Overview

Heterogenous catalysts play indispensable roles in our sustainable civilization by facilitating the synthesis of various essential compounds [1]. Despite the massive needs, the development of heterogenous catalysts is challenged by the complex non-equilibrium states that are intractable in experiments as they occur in atomic size and timescale [2, 3]. These states hold critical knowledge about the mechanistic aspects of the catalysis, namely, the interaction between chemicals, kinetics and dynamics of reactions, the reaction pathway, and the structure of active sites where the catalysis actually takes place. Unfortunately, even in the raise of computing power, the conventional computational simulation has not been successful to reveal non-equilibrium states of heterogenous catalysis at operating condition due to severe trade-off between accuracy and computing cost.

For instance, Density Functional Theory (DFT) can accurately calculate the properties of the catalytic system, but simplified and nearly static model must be employed to compensate the demanding computing cost. The use of such model in the simulation should be handled with a great care to avoid a misleading interpretation of experimental results. Alternatively, the molecular simulation such as Kinetic Monte Carlo (KMC) and Molecular Dynamics (MD) can simulate catalysis at operating condition, but they rely on the inter-atomic potential that is very system-specific and often not reliable for chemical reactions. This trade-off inhibits the direct connection of the simulations to experiments which is ubiquitous in the rational design of the catalysts.

A notable evidence of the issue caused by the elusive non-equilibrium states is the difficulty in developing catalyst for methanol synthesis [4]. The industrial production of methanol has been well-established for decades by using

Cu/ZnO/Al₂O₃ (CZA) as the standard catalyst [5], but the exact nature of the active sites (i.e., promoting factor) of CZA, which are the key descriptors to design new catalyst, are still under controversy [6, 7]. This issue is particularly more pressing in the middle of global warming mitigation through CO₂ conversion to methanol and the invention of DMFC (Direct Methanol Fuel Cell) as renewable energy resource.

There have been various DFT-based studies to resolve such controversy, but unfortunately the results are not consistent with each other [8, 9]. The contradiction originates from different assumptions of the mechanistic aspects of the catalysis that must be employed in the model. These assumptions (e.g., rigid surface, non-interacting adsorbates, fixed reaction pathway) were used to simplify the model since the realistic system requires infeasible computing power and, more importantly, has not been fully elucidated. Meanwhile, the molecular simulation on methanol synthesis could be promising but only if a reliable interatomic potential is available. However, the crafting of the accurate inter-atomic potential suitable for chemical interactions is non-trivial due to the interactions of multiple species (e.g., Cu, Zn, C, H, O) during the catalytic reactions, the nature of which should depend on the electronic structure.

To break the trade-off between speed and accuracy of the computational approach, the integration of the frameworks with different scale is a promising alternative. This leads to a novel computational technique called multi-scale simulation which couple the atomic-scale framework (e.g., DFT) with the molecular-scale frameworks such as KMC and MD. Since the multiscale-simulation is highly accurate, capable to handle realistic model, and generally applicable for reactions in heterogeneous catalysis, this technique enables access to direct observation of catalysis under operating condition similar to experiments, which is the important link in the synergy between experiments and simulation.

By applying multi-scale simulations, namely, first-principles KMC and the machine-learning molecular dynamics (MLMD), I aim to contribute in resolving the long-standing puzzles of heterogeneous catalysis (e.g., methanol synthesis) by elucidating the relevant non-equilibrium states. As a starting point, I focus to elucidate the dynamics of the Cu catalyst in relation to its non-equilibrium properties, namely, step edge fluctuations, the surface alloying, and the change of surface morphology due to the adsorbates. These

works have relevance not only in the methanol synthesis, but also in various catalysis that utilizes Cu-based catalyst. The outcomes of this study can be used to provide information of realistic non-equilibrium states which are the ‘missing link’ between experimental and computational studies. A better link will close the gap between the two approaches, leading to more clear and confident understanding. In this way, the heterogenous catalysis in controversy can be resolved and better design can be realized.

1.2 Cu surface in Heterogenous Catalysis

The Cu surface, which becomes the focus of this study, holds primary importance in catalytic reactions especially in the water gas shift reaction (i.e. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) [10–12] and reverse water gas shift reaction (i.e. $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) [13–15]. Both of these reactions are attractive in the context of green energy, as the former reaction produces the H_2 and the latter utilizes the green-house gas CO_2 . The Cu surface also involves in the methanol synthesis in the form of CZA, which is the standard catalyst used in the industry [5]. Despite the well-establishment of methanol synthesis in industry, the active sites of CZA is still under controversy. There have been two proposals on the active site sites: the Cu-Zn bimetallic [6] vs the synergistic Cu-ZnO [7]. Though both of them involve the Cu surface, this current study mainly relates to the first proposal and can be considered as prerequisite in the active site elucidation of Cu/ZnO/ Al_2O_3 for methanol synthesis.

The origin of the first proposal comes from the experiment which have shown that deposition of Zn on Cu(111) promotes the activity of methanol production by an order of magnitude at Zn coverage of 0.197 [16]. In addition, the Cu-Zn alloy has been reported as a good model of CZA by sharing the similarity in the energy barrier [6, 17]. Thus, this alloy has been extensively involved in the investigation of the true active site of CZA which remains under controversy [6–9, 17–20]. Various studies have also shown that steps and kinks on Cu surfaces have non-negligible effect to the catalyst activity. For instances, Behrens et al. have shown experimentally that the intrinsic activity of Cu for methanol synthesis is proportional to the probability of stacking faults (including steps and kinks) [6]. Theoretical studies also showed that the steps and kinks on Cu surfaces can alter the thermodynamic and kinetic of intermediates during methanol synthesis from CO_2 , resulting in different adsorption state, reaction pathway and the product yield [21, 22].

The investigation of the effect of Cu surface defects to the overall catalyst activity in more realistic way must involve the dynamic of surface defects and general description of all structures that possibly formed during practical condition. For instance, it is well known that the Cu step-adatom migrates intensively along the step edge, resulting in step fluctuation even at room temperature [23, 24]. Moreover, the alloying or oxidation of the Cu surface (e.g., Cu-Zn alloy) and the interactions with the adsorbates might alter the morphology of the surface (thereby the active sites) which further raise the complexity of the realistic catalytic system. An evidence was provided by the high-pressure scanning tunneling microscopy (HPSTM) and ambient pressure x-ray photo-electron spectroscopy (APXPS) have shown that the Cu(111) surface is decomposed into small nanoclusters when exposed to CO molecules [25]. The CO-induced surface transformation on other Cu facets have also been reported [26–28]. This situation strongly emphasizes that the multi-scale simulation is required to include such dynamical change of the Cu surface that cannot be elucidated solely by the conventional DFT and molecular simulation.

1.3 General Idea of Multi-scale Simulation

The multi-scale simulation is defined as the integrated single-scale simulations which are connected by 'bridge' in a given architecture. Here, scale is referred to the spatial and temporal scale of the model. The low-scale model typically can be simulated accurately but cannot well represent the macroscopic scale observed in experiment, whereas the higher-scale links well to the experiment but cannot be reliably computed due to the demanding computing cost and the lost of accuracy upon assumptions and approximations. The overview on conventional single-scale simulations with the corresponding spatial and temporal scales is shown in Figure 1.1. At the bottom of the scale (i.e., the atomic and electronic level), the ab-initio simulation in the form of DFT can be applied without any empirical parameters to accurately elucidate the electronic structure or atomic arrangements of few to hundreds of atoms within a very short physical time. Model with more than hundreds of atoms can be handled with MD which can provide trajectory of the atoms in a molecular system based on the atomic interactions described by the inter-atomic potential. Much higher-scale model can be handled by MC or KMC that is based on the selection and execution of pre-defined events, of which

the probability of the selection is based on the kinetic constant of the particular event. Lastly, the finite element method can be used to simulate the behaviour of model with macroscopic scale by discretizing the model into meshes and solving a set of differential equations.

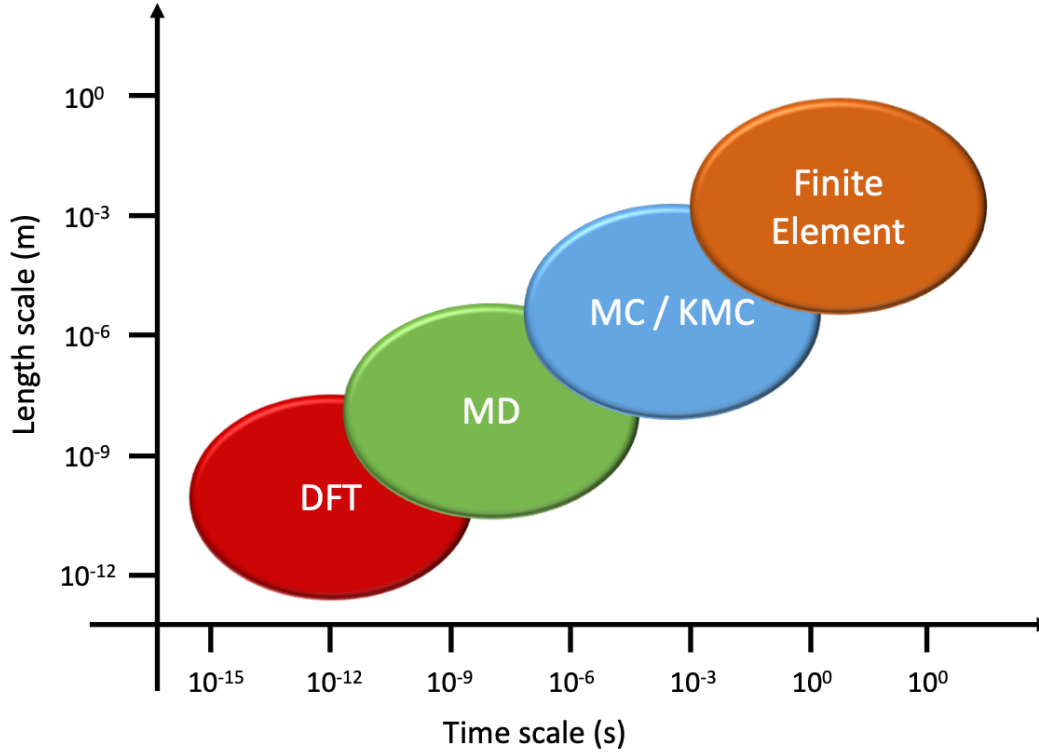


Figure 1.1: The conventional material simulations with the corresponding length and time scales.

Since more assumptions and approximations are typically introduced along the scale, the stand-alone simulation at high-scale typically loses accuracy and requires many empirical parameters that are not always available. The idea of multi-scale simulation is then introduced to overcome this issue. In this framework, the bridge is used to let the information propagates from the lower-scale to the higher-scale and thereby the simulation can retain the accuracy of the formerly accurate simulation such as DFT, and also eliminating the necessity of the empirical parameters. The propagation of the information from the lower-scale to upper-scale are handled by the additional framework called 'bridge'.

Two kinds of multi-scale simulation were implemented in this study, namely: the first-principles Graph Theoretical KMC (i.e., GTKMC) and the Machine Learning Molecular Dynamics (MLMD). In the former kind, the Cluster Expansion (CE) is used to bridge the DFT and KMC. The CE can provide the

ground state energy of the arbitrary structures based on the energy contribution of smaller building blocks (e.g., clusters) that can be easily computed with DFT. This energy then can subsequently be used to obtain the kinetic constants of the pre-defined events through the calculation of the energy barriers and the application of Arrhenius equation. On the other hand, MLMD utilizes the force-field that is built by applying a machine-learning algorithm to perform the interpolations and extrapolations of a DFT database. The forces given by this force-field then are in comparable with the results of DFT calculations and thereby allowing the dynamical simulation with DFT accuracy. More details on these methods are provided in Chapter 2. The first-principles KMC was applied to investigate the step edge fluctuation of the Cu surface (Chapter 3) and the MLMD was applied to elucidate the surface alloying (Chapter 4) and the CO decomposition of Cu surface to nanoclusters (Chapter 5).

1.4 Outline of Dissertation

The outline of the dissertation is straight-forward as follows. Chapter 1 provides the overview and the outline of the study. Chapter 2 presents the theoretical background on the methods applied in this study: first principles calculation, first principles KMC, and MLMD. Chapter 3 presents the investigation on the atomic scale mechanisms of step fluctuation on Cu(111) surface. Chapter 4 presents the elucidation of Cu-Zn surface alloying on the Cu(997) surface. Chapter 5 presents the investigation of CO-driven surface transformation on Cu(111) surface. Chapter 6 is the last chapter that summarizes the dissertation.

Chapter 2

Methods

2.1 First Principles Calculation

Progress in material research is a non-trivial task considering complex relations among the properties of materials, chemical reactivity, and practical operating conditions. Conventional approach involves trial-and-error experiments which are costly, time-consuming, and doesn't guarantee success. In order to establish more efficient approach, a paradigm called *rational catalyst design* emerges and steadily developing. The idea is to apply the theoretical understanding of material interest in the form of computational simulation. Such simulation is used to screen the promising materials and predict their corresponding properties before the actual synthesis. A well-developed method to perform this task is first principle calculation known as Density Functional Theory (DFT) that can calculate the thermodynamics properties of material at the atomic scale without any empirical parameters. The result then can be used to reveal many equilibrium properties of materials, such as elastic properties, thermal properties, enthalpy formation, and phase diagrams [29] [30]. This chapter is intended to briefly present the fundamental of DFT, which is born from the concept of quantum mechanics.

2.1.1 Many-body Schrödinger Equation

In quantum mechanics, any properties of materials can be calculated once the fundamental equation, Schrödinger equation, is solved. In the case of system with many electrons and nuclei, one then need to solve so called *many body Schrödinger equation* with wave-function Ψ , that depends on the position of each electron ($\mathbf{r}$) and each nucleus ($\mathbf{R}$) of the system [31]:

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) \quad (2.1)$$

Physically, $|\Psi|^2$ represents the probability of simultaneously finding electron number 1 at point $\mathbf{r}_1$, electron number 2 at point $\mathbf{r}_2$, and so forth. Based on this definition, the total electronic charge density $n(\mathbf{r})$, defined as the probability of finding any electron at position $\mathbf{r}$ can be obtained as follows.

$$P(\mathbf{r}_1 = \mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{R}_1 \dots d\mathbf{R}_M \quad (2.2)$$

Then the probability of finding any electron at position $\mathbf{r}$ is

$$n(\mathbf{r}) = P(\mathbf{r}_1 = \mathbf{r}) + P(\mathbf{r}_2 = \mathbf{r}) + \dots + P(\mathbf{r}_N = \mathbf{r}) \quad (2.3)$$

Since the electrons are *indistinguishable particles* all the terms in equation (2.3) are identical, which results in

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{R}_1 \dots d\mathbf{R}_M \quad (2.4)$$

The normalized wave function will satisfy the following property:

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{R}_1 \dots d\mathbf{R}_M = 1 \quad (2.5)$$

then the electronic charge density will be normalized to the total number of particles within the material, denoted as N .

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad (2.6)$$

The many-body wave function is used as eigenfunction in Schrödinger equation in such way that,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (2.7)$$

The eigenvalue E in equation (2.7) represents the total energy of the system. The lowest energy of which is called the *groundstate* of the system. Meanwhile, the $\hat{H}$ operator represents the Hamiltonian of the system which consists of kinetic and potential energies of the electrons and nuclei. Mathematically written as

$$\hat{H} = T_e + V_{ee} + V_{en} + T_n + V_{nn} \quad (2.8)$$

All the energy operators that are used are formulated (in Hartree atomic units) as follows. T_e represents the operator of electrons's kinetic energy:

$$T_e = - \sum_{i=1}^N \frac{\nabla_i^2}{2} \quad (2.9)$$

2.1. First Principles Calculation

T_n represents the operator of nuclei's kinetic energy:

$$T_n = - \sum_{I=1}^M \frac{\nabla_I^2}{2M_I} \quad (2.10)$$

V_{ee} represents the operator of internal potential or potential energy between electron and electron:

$$V_{ee} = \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.11)$$

V_{en} represents the operator of potential energy between electrons and nuclei:

$$V_{en} = - \sum_{iI} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (2.12)$$

V_{nn} represents the operator of potential energy between nuclei and nuclei:

$$V_{nn} = \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.13)$$

Finally by applying this operator to many-body wave function, we obtain the many-body Schrödinger equation in Hartree unit:

$$\hat{H} = - \sum_{i=1}^N \frac{\nabla_i^2}{2} - \sum_{I=1}^M \frac{\nabla_I^2}{2M_I} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.14)$$

In practice, solving many-body Schrödinger equation is extremely difficult since it is basically a 3N-dimension equation, where N equals to the total number of particles within the system.

2.1.2 Born-Oppenheimer Approximation

Since the mass of nuclei are much heavier than the mass of electrons (e.g. the mass of a proton is approximately 1800 times heavier than electron), the movement of nuclei are much slower relative to electrons to the point that they can be approximated to be clamped in known positions. This approximation, called as *Born-Oppenheimer approximation*, allows the kinetic energy of the nuclei to be neglected and the coulomb repulsion between nuclei to be treated as parameter[32]. Then the many-body wave function can be separated in such a way that:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \psi_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \psi_n(\{\mathbf{R}_I\}) \quad (2.15)$$

where ψ_e and ψ_n denote the electronic wave function and nuclei wave function, respectively.

Then by applying this wave function into many-body Schrödinger equation,

$$\begin{aligned}
 \hat{H}\Psi &= E\Psi \\
 \hat{H}\psi_e\psi_n &= E\psi_e\psi_n \\
 (\hat{H}_e + T_n + V_{nn})\psi_e\psi_n &= E\psi_e\psi_n \\
 (\hat{H}_e\psi_e)\psi_n + (T_n + V_{nn})\psi_e\psi_n &= E\psi_e\psi_n \\
 E_e\cancel{\psi_e}\psi_n + (T_n + V_{nn})\cancel{\psi_e}\psi_n &= E\cancel{\psi_e}\psi_n \\
 E_e\psi_n + T_n\psi_n + V_{nn}\psi_n &= E\psi_n \\
 (E_e + T_n + V_{nn})\psi_n &= E\psi_n
 \end{aligned} \tag{2.16}$$

it is found that indeed the electronic energy of the system E_e can be calculated separately from

$$\hat{H}_e\psi_e = E_e\psi_e \tag{2.17}$$

$\hat{H}_e$ is the Hamiltonian of many-electrons system which is expressed as:

$$\hat{H}_e = T_e + V_{ee} + V_{en} \tag{2.18}$$

We can approximate the complicated $3N$ -dimensional many-body Schrödinger equation ($4N$ if the spin variables are taken into account) into a set of single-particle Schrödinger equations by introducing independent electron approximation. The idea is to treat the electrons as ‘non-interacting particles’ which allow us to express the many-body wave function as a product of single-particle wave functions. Since electrons are fermion, Pauli’s exclusion principle states that the wave function Ψ must change sign if the variables of any two electrons are exchanged. To take this principle into account, the Hartree-Fock approximation was proposed in which the many-body wave function is written in terms of Slater determinant[33] :

$$\Psi_{HF} \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \phi_1(\mathbf{r}_2, \sigma_2) & \cdots & \phi_1(\mathbf{r}_N, \sigma_N) \\ \phi_2(\mathbf{r}_1, \sigma_1) & \phi_2(\mathbf{r}_2, \sigma_2) & \cdots & \phi_2(\mathbf{r}_N, \sigma_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1, \sigma_1) & \phi_N(\mathbf{r}_2, \sigma_2) & \cdots & \phi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix} \tag{2.19}$$

where N denotes the number of electrons in the system. The $\phi_i(\mathbf{r}, \sigma_j)$ are single particle *spin orbital* which can be decomposed into a product of spatial

2.1. First Principles Calculation

function $\psi_i^\sigma(\mathbf{r}_j)$ and spin function $\alpha_i(\sigma_j)$. If the hamiltonian is independent of spin, the expectation value of electronic Hamiltonian in Hartree atomic units is given by:

$$\begin{aligned} \langle \Psi_{HF} | H_e | \Psi_{HF} \rangle = & \sum_{i,\sigma} \int d\mathbf{r} \psi_i^{\sigma*}(\mathbf{r}) \left[T_e + V_{ext} \right] \psi_i^\sigma(\mathbf{r}) \\ & + \frac{1}{2} \sum_{i,j,\sigma_i,\sigma_j} \int d\mathbf{r} d\mathbf{r}' \psi_i^{\sigma_i*}(\mathbf{r}) \psi_j^{\sigma_j*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i^{\sigma_i}(\mathbf{r}) \psi_j^{\sigma_j}(\mathbf{r}') \\ & - \frac{1}{2} \sum_{i,j,\sigma} \int d\mathbf{r} d\mathbf{r}' \psi_i^{\sigma*}(\mathbf{r}) \psi_j^{\sigma*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^\sigma(\mathbf{r}) \psi_i^\sigma(\mathbf{r}') \quad (2.20) \end{aligned}$$

The first term consists of the kinetic energy of single electron and the *external potential*, namely the potential caused by the interaction between electron and nuclei. The second and third terms in the equation above represent the direct and exchange interaction between electrons, respectively. Note that the self interactions of $i = j$ are cancel out in the sum of direct and exchange terms. The exchange term only has value for parallel spin since the opposite one are orthogonal, resulting in zero value.

By taking the expectation value of many-electrons Hamiltonian as in equation 2.18 with respect to Ψ_{HF} and minimizing the expectation value with respect to N wave functions, the Hartree-Fock equation can be derived.

$$\begin{aligned} \left[T_e + V_{ext}(\mathbf{r}) + \sum_{j,\sigma_j} \int d\mathbf{r}' \psi_j^{\sigma_j*}(\mathbf{r}') \psi_j^{\sigma_j}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i^\sigma(\mathbf{r}) \\ - \sum_j \int d\mathbf{r}' \psi_j^{\sigma*}(\mathbf{r}') \psi_i^\sigma(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^\sigma(\mathbf{r}) = \epsilon_i^\sigma \psi_i^\sigma(\mathbf{r}) \quad (2.21) \end{aligned}$$

where the summation in the exchange term is run over all orbitals of the same spin including the self interaction $i = j$ which later cancels out with the one in the direct term.

2.1.3 Density Functional Theory

Even though the Hartree-Fock formalism has implemented the single particle approximation to obtain the ground state energy of the material, such formalism is still far from accurate since the correlation energy is neglected. In order to take into account the exchange and correlation energy while retaining the independent-electron treatment, new framework called Density Functional Theory was established.

Hohenberg-Kohn Theorem

The core concept of Density Functional is based on two theorems proposed by Hohenberg and Kohn [34] :

- Theorem I

For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, except for a constant, by ground state particle density $n_0(\mathbf{r})$.

- Theorem II

A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

Kohn-Sham Equation

The Hohenberg-Kohn theorems which proved that the ground state energy is a functional of electron density are very powerful, but they do not say anything about how to construct such functional. This problem was then later devised by Kohn and Sham by introducing Kohn-Sham equation[35]. In the absence of applied magnetic field, the Hamiltonian does not depend on the spin variables and thus the spin function $\alpha(\sigma)$ can be neglected. Considering only the spatial function of the single particle $\psi_i(\mathbf{r})$, the Kohn-Sham equation can be written as follow.

$$E = F[n] = \int d(\mathbf{r})n(\mathbf{r})V_n(\mathbf{r}) - \sum_i \int d\mathbf{r}\psi_i^*(\mathbf{r})\frac{\nabla^2}{2}\psi_i(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \quad (2.22)$$

In the independent electrons approximation, the electron density $n(\mathbf{r})$ is expressed as

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \quad (2.23)$$

The first, second, and third terms on the right hand side of the Kohn-Sham

equation are external potential, kinetic energy, and Hartree energy, respectively, obtained from the independent electrons approximation. The last term is called exchange correlation energy which contains everything that is left out. Now the remaining task is to determine the electron density $n(\mathbf{r})$. The Hohenberg-Kohn variational principle states that the ground-state density, $n_0(\mathbf{r})$, is precisely the function that minimizes the total energy, $E = F[n]$, mathematically expressed as:

$$\left. \frac{\delta F[n]}{\delta n} \right|_{n_0} = 0 \quad (2.24)$$

Stating that a functional derivative must be zero leads to an equation for the wave functions, $\psi_i(\mathbf{r})$, which can be used to construct the density. In fact, if we require these wave functions to be orthonormal then the Hohenberg-Kohn variational principle leads to:

$$\left[-\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.25)$$

The extra term, V_{xc} is called exchange and correlation potential.

$$V_{xc}(\mathbf{r}) = \left. \frac{\delta F[n]}{\delta n} \right|_{n(\mathbf{r})} \quad (2.26)$$

2.1.4 Self Consistent Algorithm

To computationally solve the Kohn-Sham equation, one can employ the so-called *self consistent algorithm* as shown schematically in Figure 2.1. The goal of this algorithm is to obtain the ground state electron density $n(\mathbf{r})$ which later can be used to calculate the ground state energy through equation 2.22.

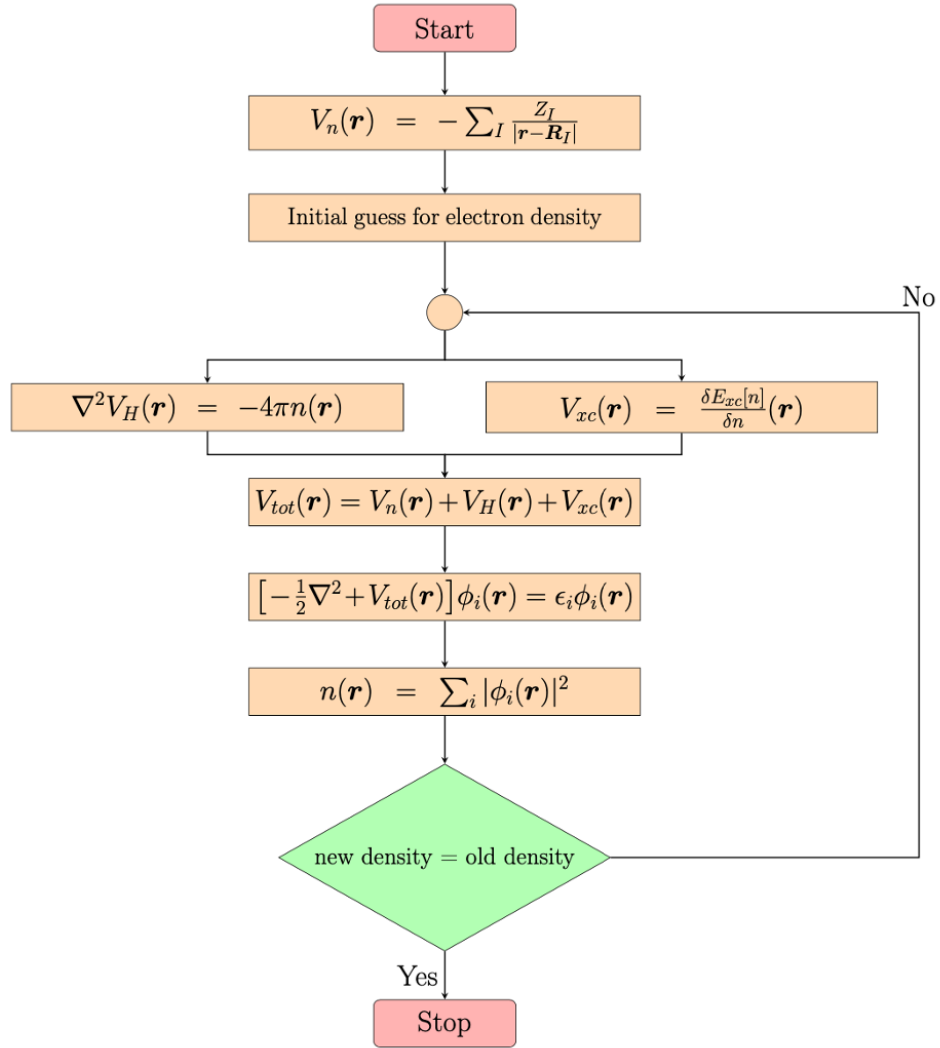


Figure 2.1: The flowchart of DFT algorithm.

2.2 First Principles Kinetic Monte Carlo

In the theoretical development of heterogeneous catalysts, kinetic modeling has become an indispensable tool to describe the dynamic phenomena of catalytic process. The advancement in the science of molecular simulation has given rise to several sophisticated methods to perform such task, one of which is kinetic Monte Carlo (KMC). Essentially, KMC is based on stochastic process or random walk on a discrete state space that occurs in continuous time[36]. By focusing on the propensity of transition (i.e. the probability of occurrence per unit time) instead of explicit transitions states, this method

enables the efficient kinetic simulation at temporal and spatial scale close to real experiment. KMC has been proved by numerous studies to successfully elucidate various enigmatic catalytic process involving complex catalyst's structure with ongoing complicated reaction networks[37]. The basic formalism and the computational implementation of this particular method is provided in this subchapter.

2.2.1 Master Equation and Detailed Balance

In KMC simulation, the dynamic of the catalytic process is described as the changes in the numbers and positions of molecules adsorbed on the catalyst. Such changes are caused by various *elementary events* (e.g. adsorption, diffusion, reaction, and desorption) which happen on the discrete lattice sites that are used to model the catalyst. Every changes will generate a *state*, defined as a specific adsorbates configuration with corresponding numbers of gas phase molecules.

Let w and w' denote two different states on the lattices with probability to occur equals to $P(w, t)$ and $P(w', t)$ respectively. These two states can change into each other with the rates specified by transition probabilities per unit time or *transition rates*, denoted as $k_{w \rightarrow w'}$ (transition from w to w') and $k_{w' \rightarrow w}$ (transition from w' to w). Then the stochastic equation that describes the dynamic of the system can be written as follows [38]:

$$\frac{dP(w, t)}{dt} = \sum_{w' \neq w} [k_{w' \rightarrow w} P(w', t) - k_{w \rightarrow w'} P(w, t)] \quad (2.27)$$

This equation is known as *master equation*, serves as the governing equation from which the KMC algorithm is derived. The first term in the right hand side stands for increases in $P(w, t)$ because of processes that change other configurations into w , whereas the second term stands for decreases because of processes in state w . In this respect, a KMC simulation is then a random walk governed by master equation that simulates elementary events with rate constants $k_{w \rightarrow w'}$ that allow for transitions from state w to w' . In addition, such random walk must satisfy the *Markov property*, which means that given the current state of the system, any future state is entirely independent from other states visited prior to the current state.

In order for any kinetic simulation to be able to reach the correct thermodynamic limits, first it must be ensured that detailed balance between any pair

of connected states w and w' is obeyed [39] [40]. Consider a system in which the equilibrium condition is reached i.e. the probability of each state is constant. According to the master equation, the total probability flux leaving a state must be balanced by the total probability flux towards that state. Such condition is mathematically written as follows.

$$\frac{dP^{eq}(w, t)}{dt} = 0 \quad (2.28)$$

$$\sum_{w' \neq w} [k_{w' \rightarrow w} P^{eq}(w', t) - k_{w \rightarrow w'} P^{eq}(w, t)] = 0 \quad (2.29)$$

$$\sum_{w' \neq w} k_{w' \rightarrow w} P^{eq}(w') = \sum_{w \neq w'} k_{w \rightarrow w'} P^{eq}(w, t) \quad (2.30)$$

$$k_{w' \rightarrow w} P^{eq}(w', t) = k_{w \rightarrow w'} P^{eq}(w, t) \quad (2.31)$$

From the above equations, it is shown that two constraints emerges: (i) for every elementary process w to w' , there is a reverse process w' to w , in other words each microscopic has a corresponding reverse process; and (ii) the average individual rates of the two processes must balance at thermodynamic equilibrium. The detailed balance principle is satisfied if equation (3.5) is satisfied, and must also hold true even if the system is still far from equilibrium. Hence, these fundamental constraints has to be applied to the definition of the rate constants, otherwise the evolution of the system may violate thermodynamics.

To apply this constraint, first the microscopic energy of the system with respect to configuration $\mathcal{E}(w)$ is introduced. Such energy has various free energy contributions: electronic ($E(w)$) and vibrational ($E_{vib}(w)$) free energies from the lattice species, as well as electronic ($E^{gas}(w)$), translational ($E_{transl}^{gas}(w)$), rotational ($E_{rot}^{gas}(w)$), and vibrational ($E_{vib}^{gas}(w)$) from the gas species that have not yet adsorbed on, or have already desorbed from the lattice. Mathematically, it can be written as follows.

$$\mathcal{E}(w) = E(w) + E_{vib}(w) + E^{gas}(w) + E_{transl}^{gas}(w) + E_{rot}^{gas}(w) + E_{vib}^{gas}(w) \quad (2.32)$$

Now the population of states $P^{eq}(w, t)$ can be expressed in terms of Boltzmann distribution:

$$P^{eq}(w) \sim \exp\left(-\frac{\mathcal{E}(w)}{k_B T}\right) \quad (2.33)$$

Therefore, transition rate constants which satisfy the detailed balance principle can be expressed as Boltzmann population ratio:

$$\frac{k_{w \rightarrow w'}}{k_{w' \rightarrow w}} = \exp\left(-\frac{\mathcal{E}(w) - \mathcal{E}(w')}{k_B T}\right) \quad (2.34)$$

Moreover, such equation can be also written in terms of electronic energy of the system and partition functions,

$$\frac{k_{w \rightarrow w'}}{k_{w' \rightarrow w}} = \frac{q_w}{q_{w'}} \exp\left(-\frac{\Delta E_{rxn}^{w \rightarrow w'}}{k_B T}\right) \quad (2.35)$$

$$\frac{k_{w \rightarrow w'}}{k_{w' \rightarrow w}} = \frac{q_w}{q_{w'}} \exp\left(-\frac{E(w', t) - E(w, t)}{k_B T}\right) \quad (2.36)$$

where q_w and $q_{w'}$ denote the partition function of product and reactant, respectively.

2.2.2 Cluster Expansion Hamiltonian

Calculating the electronic energy for every specific state in the system is non-trivial task. One alternative is to use brute force by performing first principle calculation method as DFT. However, considering the many possible structure of each state, direct calculation using DFT demands tremendous computational expenses. Therefore, in order to capture lattice energetics in more efficient way, one can employ the cluster expansion (CE) framework which can be used to obtain energy of any structure once the required basis set already known.

In the concept of CE introduced by Sanchez, a complete basis set is constructed using Chebysev polynomials $\Theta_n(\sigma)$ to describe a single lattice site with state variable $\sigma = 0, \pm 1, \pm 2, \dots$, the product of which is referred as clusters [41]. Then a function $\Phi_{\alpha s}(\sigma)$ for cluster α containing lattice sites $\{p, p', p''\}$ can be expressed as the following product:

$$\Phi_{\alpha s}(\sigma) = \Theta_n(\sigma_p) \cdot \Theta_{n'}(\sigma_{p'}) \cdot \dots \cdot \Theta_{n''}(\sigma_{p''}) \quad (2.37)$$

where s denotes a collection of indices n (i.e. $s = n, n', \dots, n''$) and the configurational variable $\sigma = (\sigma_1, \sigma_2, \dots, \sigma_{N_L})$ expresses the occupation of all sites. The lattice energy thus can be represented by the linear combination of the basis

set as follows:

$$E(w) = E(\sigma, N_{gas}) = \sum_{\alpha} \sum_s E_{\alpha s}^{Lat} \cdot \Phi_{\alpha s}(\sigma) \quad (2.38)$$

where α ranges over all clusters and s ranges over all indexes specifying Chebyshev polynomials. In a more intuitive formulation, the total energy of the lattice can be decomposed into the contribution of point, pair, and many body interactions of clusters, as mathematically written as follows[42]:

$$E(w) = \sum_k \frac{n_k^c(w)}{m_k} ECI_k \quad (2.39)$$

where ECI_k is the effective cluster interaction of cluster k (i.e. the energy contribution of the cluster to total energy), n_k^c is the number of detected clusters k in the current configuration, and m_k is the graph-multiplicity of cluster k (i.e. the number of times the exact same figure will be counted in a given lattice configuration).

2.2.3 Kinetics of Elementary Events

The rate constants of microscopic events (e.g. adsorption, diffusion, desorption, and elementary reactions) can be calculated from TST as first proposed by Eyring [43]. The main idea of this theory is treating the barrier crossing as a one-dimensional problem along the reaction coordinate, and averaging over all other degree of freedom. These ideas lead to the following expression for the rate constant of an elementary event [44].

$$k_{TST} = \kappa \cdot \frac{k_B \cdot T}{h} \cdot \frac{q}{q_{reac}} \cdot \exp\left(-\frac{E}{k_B \cdot T}\right) \quad (2.40)$$

where κ is a correction factor accounting for trajectories that do not lead to product formation due to the re-crossing the barrier (i.e. transmission coefficient); k_B denotes Boltzmann's constant; h Planck's constant; T the temperature; q and q_{reac} denotes the quasi-partition functions of transition state and reactants, containing translational, rotational, and vibrational contributions, E the activation energy of the event (the electronic energy of the transition state minus that of the reactants).

Based on the principle of the microscopic reversibility, every forward reaction must have a corresponding reverse reaction. The rate of the reverse reaction

obeying the microscopic reversibility then can be written as follow:

$$\frac{k_{TST}^{fwd}}{k_{TST}^{rev}} = \frac{q_{prod}}{q_{react}} \cdot \exp\left(\frac{\Delta E_{rxn}}{k_B \cdot T}\right) \quad (2.41)$$

$$= \frac{q_{prod}}{q_{react}} \cdot \exp\left(-\frac{E_{fwd} - E_{rev}}{k_B \cdot T}\right) \quad (2.42)$$

assuming that the transmission coefficients for the forward and reverse events are equal.

Further, the activation energy can be expressed in term of the energy change for the elementary event ΔE_{rxn} by assuming a linear relationship between those two, as originally proposed by Bronsted, Evans, and Polanyi [45]:

$$E_{fwd} = \alpha \cdot \Delta E_{rxn} + \beta \quad (2.43)$$

$$E_{rev} = (\alpha - 1) \cdot \Delta E_{rxn} + \beta \quad (2.44)$$

where the constants α and β can be found by fitting the first principles data into the above equations. A parametrization that relates these constants with the activation and reaction energies in the zero-coverage limit ($E_{fwd,0}$ or $E_{rev,0}$ and $(\Delta E_{rxn,0})$, respectively) as well as the 'proximity factor' ω of the reaction (i.e. the proximity of transition state to either initial or final state, ranging from 0 to 1) has been recently implemented in KMC by Nielsen et al. [42]:

$$\alpha = \omega \quad (2.45)$$

$$\beta = E_{fwd,0} - \omega \cdot \Delta E_{rxn,0} = E_{rev,0} - (\omega - 1) \cdot \Delta E_{rxn,0} \quad (2.46)$$

The predictions of the barriers from these equations are of course limited by how well the linear functions fit the first principle data, and recent studies that have implemented this methodology shows errors of about 0.2 eV at most (which is within the acceptable DFT error range of a few tens of an eV) [46].

Given a set of elementary events and their corresponding kinetic constants, the random waiting times for the occurrence of these events can be generated. Such times follow the distribution:

$$p_{\tau}^j(\tau|t, w) = k_{TST}^j(w, t + \tau) \cdot \exp\left(-\int_0^{\tau} k_{TST}^j(w, t + \tau') d\tau'\right). \quad (2.47)$$

The above equation expresses the probability density that elementary event j will occur at time $t + \tau$, given that the system is at state w at time t . In the case that the rate constant is time independent, this probability density can be simplified to the exponential distribution:

$$p_{\tau}^j(\tau|t, w) = k_{TST}^j(w, t + \tau) \cdot \exp\left(-k_{TST}^j(w) \cdot \tau\right) \quad (2.48)$$

The samples from this distributions can be generated by appropriately mapping uniformly distributed variables. One alternative is to use the inversion generating method which require to solve a linear equation:

$$-\int_0^{\tau} k_{TST}^j(w, t + \tau') d\tau' = -\ln(1 - u) \quad (2.49)$$

where u is a uniform random number and τ_j the waiting time. In the case of time independent rate constant the above equation simplifies to

$$\tau_j = -\frac{1}{k_{TST}^j(w)} \cdot \ln(1 - u) \quad (2.50)$$

2.2.4 Computational Implementation of KMC

The basic of KMC simulation involves the scheduling and random selection of elementary events governed by the statistic of the master equation. Implementation of this idea into computational practice requires the use of pseudo-random numbers for determining what and when the elementary process is executed. Despite of many variants of the algorithms, all KMC simulation follow a basic structure of backbone [47] as shown in the figure 3.1.

The general KMC algorithm is initialized by specifying the simulation setup and parameters, such as: operating condition (e.g. temperature, pressure, gas phase), lattice structure, energetics model, reaction mechanism, and initial configuration. Then the simulation enters a loop in which a process is selected and executed. This process is followed by the update of the clock time and system's state storing. The loop is terminated when the $t \geq t_{final}$, where t_{final} is the specified maximum simulation time.

At least there are three types of KMC algorithm has been developed. These algorithms are the null-event method, the first reaction method, and the direct method.

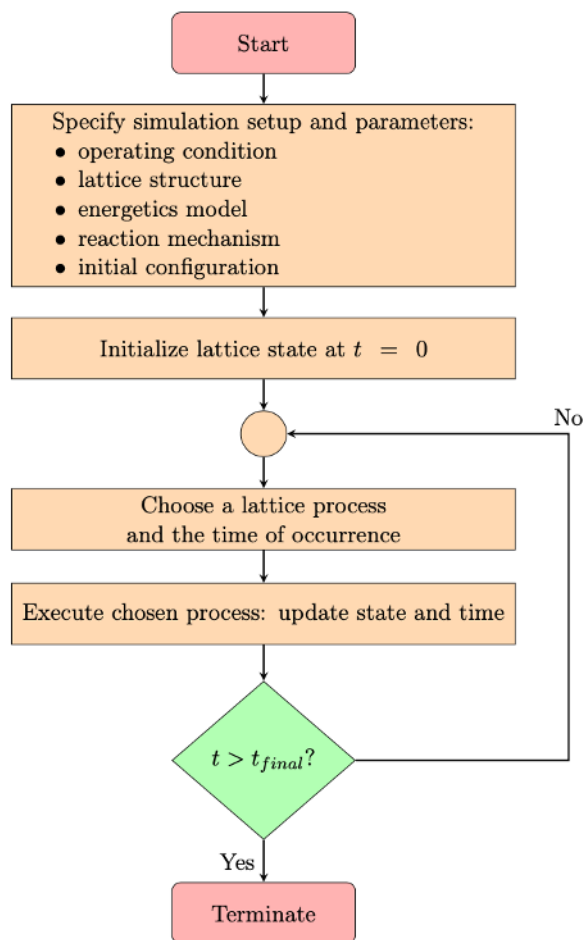


Figure 2.2: The flowchart of KMC algorithm.

2.2.5 The null event method

Null event method or random selection method is one of the earliest-employed KMC algorithms. In this algorithm, a site S_{exe} is first randomly selected among all sites of the lattice where they have an equal probability of being chosen. Subsequently, an elementary event is selected from the list that have been defined before. In this process, the probability of choosing event is equal to its normalized rate constant, thus events with higher kinetic constants have a higher probability of being chosen. However, since the selection of the site does not take into account of its current state, the selection process might lead to a non-realizable event to be selected. This event is called 'null-event' and will be rejected (i.e. the clock of KMC will be advanced, but the state of the system will remain the same). Because of this, the efficiency of the null-event algorithm depends on the probability attempting to realize such null-events. When this probability is low, the null-event algorithm may be very efficient. On the other hand, as the systems become more complex, the probability of

selecting null events increases and reduce the efficiency of the algorithm by wasting the random numbers generated.

2.2.6 Direct method

To avoid the selection of non-realizable events, a different class of algorithm called direct method (or variable step size method) is developed. This method requires the generation of two random numbers: the first number represents the time for the occurrence of any lattice process, whereas the second number indicates which process j_{exe} will be executed, an is chosen such that the following inequality holds:

$$\sum_{j=1}^{j_{exe}-1} k_{TST}^j(w, t + \tau) < u_2 \cdot \sum_{j=1}^{N_{proc}} k_{TST}^j(w, t + \tau) \leq \sum_{j=1}^{j_{exe}} k_{TST}^j(w, t + \tau) \quad (2.51)$$

2.2.7 The first-reaction method

One of more sophisticated method of KMC algorithm is called the first reaction method. Such method based on the generation of random times for all possible lattice process and subsequently executed the one with shortest waiting time:

$$j_{exe} = \underset{j=1,2,\dots,N_{proc}}{\operatorname{argmin}} (\tau_{TST}^j) \quad (2.52)$$

In the case of independent processes, such as those involving species further from the maximum lateral interaction length, the absolute time $t + \tau_{TST}^j$ in which process j will be executed can be computed, and kept intact until either of following occurs: (i) process j is simulated; (ii) another process takes place that consumes any of one reactants of process j (in which case process j can no longer happen); (iii) the rate constant k_{TST}^j changes due to the lateral interaction emerging as a result of another lattice process being executed within the vicinity of j (in which case τ_{TST}^j needs to be updated). This kind of algorithm can lead to parallelization of KMC simulation by dividing the whole system into several local 'box' in which the selection process can be performed independently as long as the three conditions mentioned before as satisfied.

2.3 Machine Learning Molecular Dynamics

Molecular Dynamics (MD) is an indispensable technique in material simulation which enables to compute the trajectory of atoms in the many-body system. MD simulation can effectively represent the actual experiment due to the efficiency of computing large models and measuring quantities that are similar in the experimental approach. In practice, the nuclear motion of the atoms in the system is assumed to follow the laws of classical mechanics, and thus the two key steps in MD are solving the equation of motion and obtaining the force of the atoms.

2.3.1 Equation of Motion

Equation of motion needs to be solved to obtain the position $r(t)$ and velocity of the atom $v(t)$ at every time step $\Delta(t)$. One of the simplest algorithm that can be used is called Verlet algorithm [48], and is derived as following.

The position of the atom around time t given the atomic mass m and the atomic force $f(t)$ can be described using Taylor expansion as the following.

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!}\ddot{r} + O(\Delta t^4) \quad (2.53)$$

$$r(t - \Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\ddot{r} + O(\Delta t^4) \quad (2.54)$$

Summing the two equations, the new position of the atoms can be obtained as follow.

$$r(t + \Delta t) \approx 2r(t) - r(t - \Delta t) + \frac{f(t)}{m}\Delta t^2 \quad (2.55)$$

As shown in the above equation, the future position of the atom is expressed as a function of the present and old positions, as well as the force of the atom. The force is obtained from the inter-atomic potential or force-field which is discussed in the following subsection.

2.3.2 Machine Learning Force-field

In the emergence of data science, the force-field with the accuracy near DFT level can be obtained by performing machine-learning to the data-points (i.e.,

atomic structure) labelled with energy and the associated atomic forces. The two most popular techniques used for this purpose are neural network [49] and Gaussian Process (GP) [50]. The works in this study (see Chapter 4 and Chapter 5) employ the GP to obtain the force-field used in the MD simulation, resulting in a new framework called Machine Learning Molecular Dynamics (MLMD). This sub-chapter is then intended to present (i) the formalism of the GP in the context of regression and (ii) the application of the GP to generate the force-field.

Gaussian Process Regression

To derive the formulation of the gaussian process for regression, first let us define the model $y(\mathbf{x})$ as a linear combination of feature vector:

$$y(\mathbf{x}) = \mathbf{w}^T \boldsymbol{\phi}(\mathbf{x}) \quad (2.56)$$

where $\mathbf{x}$, $\mathbf{w}$, and $\boldsymbol{\phi}(\mathbf{x})$ are the input vector, weight vector, and the feature vector, respectively. The $\boldsymbol{\phi}(\mathbf{x})$ maps the D – dimensional input vector $\mathbf{x}$ into M – dimensional feature vector that consists of M basis functions. Accordingly, the weight vector $\mathbf{w}$ is also a M – dimensional vector. The prior distribution over $\mathbf{w}$ is given by an isotropic Gaussian of the form:

$$p(\mathbf{w}) = \mathcal{N}(\mathbf{w} | \mathbf{0}, \alpha^{-1} \mathbf{I}) \quad (2.57)$$

where the α^{-1} represents the variance of the distribution. The function values for the N inputs then can be represented by N -dimensional vector $\mathbf{y}$ (i.e., $y_n = y(\mathbf{x}_n)$). This vector can be expressed as the multiplication of design matrix $\boldsymbol{\Phi}$ and weight vector $\mathbf{w}$:

$$\mathbf{y} = \boldsymbol{\Phi} \mathbf{w} \quad (2.58)$$

Each element of matrix $\boldsymbol{\Phi}$ corresponds to a basis function of a particular input (i.e., $\Phi_{nk} = \phi_k(\mathbf{x}_n)$). Since $\mathbf{w}$ is Gaussian distributed variables, the $\mathbf{y}$ is also governed by Gaussian distribution with the following mean and covariance:

$$\mathbb{E}[\mathbf{y}] = \boldsymbol{\Phi} \mathbb{E}[\mathbf{w}] = \mathbf{0} \quad (2.59)$$

$$cov[\mathbf{y}] = \mathbb{E}[\mathbf{y} \mathbf{y}^T] = \boldsymbol{\Phi} [\mathbf{w} \mathbf{w}^T] \boldsymbol{\Phi}^T = \frac{1}{\alpha} \boldsymbol{\Phi} \boldsymbol{\Phi}^T = \mathbf{K} \quad (2.60)$$

where $\mathbf{K}$ is Gram matrix whose elements is given by a kernel $k(\mathbf{x}_n, \mathbf{x}_m)$

$$K_{nm} = k(\mathbf{x}_n, \mathbf{x}_m) = \frac{1}{\alpha} \boldsymbol{\phi}(\mathbf{x}_n)^T \boldsymbol{\phi}(\mathbf{x}_m) \quad (2.61)$$

Similarly, it can also be shown that the covariance of $y(\mathbf{x})$ evaluated at any pair of $\mathbf{x}$ is given by the kernel function:

$$\mathbb{E}[y(\mathbf{x}_n)y(\mathbf{x}_m)] = \boldsymbol{\phi}^T(\mathbf{x}_n)[\mathbf{w}\mathbf{w}^T]\boldsymbol{\phi}(\mathbf{x}_m) = \frac{1}{\alpha} \boldsymbol{\phi}^T(\mathbf{x}_n)\boldsymbol{\phi}(\mathbf{x}_m) = k(\mathbf{x}_n, \mathbf{x}_m) \quad (2.62)$$

That is, the covariance between the outputs can be expressed as the covariance between the inputs. This implies that similar inputs will likely give similar output. The kernel then acts as a function that measures the degree of similarity between the two. The high value of kernel indicates a strong correlation between the input, and vice versa.

The kernel can be expressed indirectly through the choice of basis function or directly by choosing a specific function of kernel. One of widely used kernel is the squared exponential kernel that can be expressed as:

$$k(\mathbf{x}_n, \mathbf{x}_m) = \sigma_s^2 \exp\left(-\frac{\|\mathbf{x}_n - \mathbf{x}_m\|^2}{2l^2}\right) \quad (2.63)$$

The term σ_s^2 and l embedded in the kernel represent the signal variance and the length scale hyperparameters, respectively. The former controls the amplitude of the kernel while the latter control the resolution or the sensitivity of the kernel given different inputs.

In GP regression, the observed values t_n for each observation n is assumed to differ from a function value y_n by additive noise ϵ_n

$$t_n = y_n + \epsilon_n \quad (2.64)$$

By assuming the ϵ_n is drawn independently from a Gaussian distribution with variance β^{-1} , the distribution of the observed values conditioned on the function value is given by:

$$p(t_n|y_n) = \mathcal{N}(t_n|y_n, \beta^{-1}) \quad (2.65)$$

Since the noise of each data is assumed to be independent, the joint distribution of the observed values $\mathbf{t} = (t_1, t_2, \dots, t_N)^T$ conditioned on the function

values $\mathbf{y} = (y_1, y_2, \dots, y_N)^T$ is given by

$$p(\mathbf{t}|\mathbf{y}) = \mathcal{N}(\mathbf{t}|\mathbf{y}, \beta^{-1}\mathbf{I}_N) \quad (2.66)$$

where $\mathbf{I}_N$ is a unit matrix with size $N \times N$. The distribution $p(\mathbf{y})$ before seeing any data is a Gaussian distribution with zero mean and covariance is given by the Gram matrix $\mathbf{K}$.

$$p(\mathbf{y}) = \mathcal{N}(\mathbf{y}|\mathbf{0}, \mathbf{K}) \quad (2.67)$$

The marginal distribution $p(\mathbf{t})$ is then given by:

$$p(\mathbf{t}) = \int p(\mathbf{t}|\mathbf{y})p(\mathbf{y})d\mathbf{y} = \mathcal{N}(\mathbf{t}|\mathbf{0}, \mathbf{C}) \quad (2.68)$$

The matrix $\mathbf{C}$ is the covariance matrix whose element is given by:

$$C(\mathbf{x}_n, \mathbf{x}_m) = k(\mathbf{x}_n, \mathbf{x}_m) + \beta^{-1}\delta_{nm} \quad (2.69)$$

The joint distribution including the new data t_{N+1} is then given by:

$$p(\mathbf{t}_{N+1}) = \mathcal{N}(\mathbf{t}_{N+1}|\mathbf{0}, \mathbf{C}_{N+1}) \quad (2.70)$$

where now $\mathbf{C}_N$ is $(N + 1) \times (N + 1)$ matrix can be expressed as partition matrix in the form:

$$\mathbf{C}_{N+1} = \begin{bmatrix} \mathbf{C}_N & \mathbf{k} \\ \mathbf{k}^T & c \end{bmatrix} \quad (2.71)$$

$\mathbf{C}_N$ denotes the $N \times N$ covariance matrix, while scalar c is given by:

$$c = k(\mathbf{x}_{N+1}, \mathbf{x}_{N+1}) + \beta^{-1} \quad (2.72)$$

The vector $\mathbf{k}$ denotes the vector of kernels between each input in database and the new input (i.e., $k_n = k(\mathbf{x}_n, \mathbf{x}_{N+1})$). Given the Gaussian joint distribution $p(\mathbf{t}_{N+1})$, the conditional distribution $p(t_{N+1}|\mathbf{t})$ used to make prediction is also a Gaussian distribution whose mean and covariance is given by:

$$m(\mathbf{x}_{N+1}) = \mathbf{k}^T \mathbf{C}_N^{-1} \mathbf{t} \quad (2.73)$$

$$\sigma^2(\mathbf{x}_{N+1}) = c - \mathbf{k}^T \mathbf{C}_N^{-1} \mathbf{k} \quad (2.74)$$

The mean and covariance of $p(t_{N+1}|\mathbf{t})$ are taken as the predicted value and its associated uncertainty, respectively. This uncertainty play important role in the *active and on-the-fly* learning scheme as it can be used to measure how

well the prediction is. The low uncertainty value corresponds to the low representation of a particular data in the database and therefore should be included in the database.

Gaussian Process Force Field

Given the knowledge on how to make prediction using GP regression, the next problem is to determine the shape of the kernel function which can reliably compares two atomic structures. This task can be simplified by assuming the total energy of a particular structure can be decomposed into local contribution of its constituent atom in the form of atomic energy E_i , mathematically written as,

$$E_{tot} = \sum_i^{N_{atom}} E_i \quad (2.75)$$

This atomic energy then can be further assumed to depends only on small atomic clusters found in a local environment defined within a cutoff radius r_{cut} . The contribution of each cluster, denoted as ϵ , are uniquely described by the species of the constituent atoms and the interatomic distances within the clusters. Thus, the atomic energy can be expressed as:

$$E_i = \sum_{b=2}^B \sum_{i_{b-1} > \dots > i_1 \in \rho_i^{(b)}} \epsilon_{\mathbf{s}_{i,i_1,\dots,i_{b-1}}}(\mathbf{d}_{i,i_1,\dots,i_{b-1}}) \quad (2.76)$$

where $\mathbf{s}_{i,i_1,\dots,i_{b-1}}$ denotes the vector of species in a cluster and $\mathbf{d}_{i,i_1,\dots,i_{b-1}}$ denotes the corresponding interatomic distance within the cluster. For instance, in the case of a dimer, the vector $\mathbf{d}_{i,i_1}$ is only contain an element (i.e., the vector reduces to scalar). In the case of trimer, the vector $\mathbf{d}_{i,i_1,i_2}$ is a 3-dimensional vector consists of every pair distance between the trimer. Note that different cutoff radius can be introduced for each b -interactions, resulting the dependence of atomic environment ρ to the number of considered interactions (i.e., $\rho_i^{(b)}$).

The local energy kernel that compares two atomic environments $k(\rho_i, \rho_j)$ is expressed as [51]:

$$k(\rho_i, \rho_j) = \sum_{b=2}^B \sum_{i_{b-1} > \dots > i_1 \in \rho_i^{(b)}} \sum_{j_{b-1} > \dots > j_1 \in \rho_j^{(b)}} \delta_{\mathbf{s}_{i,i_1,\dots,i_{b-1}}, \mathbf{P}_b \mathbf{s}_{j,j_1,\dots,j_{b-1}}} k_b(\mathbf{d}_{i,i_1,\dots,i_{b-1}}, \mathbf{P}_b \mathbf{d}_{j,j_1,\dots,j_{b-1}}) \quad (2.77)$$

where the squared exponential kernels can be used as b -body kernels. For 2-body and 3-body cases, the kernel are written as:

$$k_2(r_{i,i_1}, r_{j,j_1}) = \sigma_{s,2}^2 \exp \left(-\frac{(r_{i,i_1} - r_{j,j_1})^2}{2l_2^2} \right) f_{cut}(r_{i,i_1}, r_{j,j_1}) \quad (2.78)$$

$$k_3(\mathbf{d}_{i,i_1,i_2}, \mathbf{d}_{j,j_1,j_2}) = \sigma_{s,3}^2 \exp \left(-\frac{\|\mathbf{d}_{i,i_1,i_2} - \mathbf{d}_{j,j_1,j_2}\|^2}{2l_3^2} \right) f_{cut}(\mathbf{d}_{i,i_1,i_2}, \mathbf{d}_{j,j_1,j_2}) \quad (2.79)$$

where $\sigma_{s,b}^2$ and l_b are the signal variance and length-scale for each b -body clusters, respectively. f_{cut} is used to ensure the smoothness of the model at the region near the cutoff.

To learn the atomic forces from the local environment, the forces kernel to describe the covariance between the force components α and β for atom i and j is necessary. This kernel can be obtained by differentiation of the local energy kernel with respect to the central atoms of each environment.

$$k_{\alpha,\beta}(\rho_i, \rho_j) = \frac{\partial k(\rho_i, \rho_j)}{\partial r_{i\alpha} \partial r_{j\beta}} \quad (2.80)$$

Given the kernels and the database, the prediction can be made by following the standard formulation in the GP regression discussed earlier. The prediction of α -component of atomic forces acting on atom i and the associated uncertainty are written as follows.

$$f_{i\alpha} = \mathbf{k}_{i\alpha} (\mathbf{K} + \sigma_n^2 \mathbf{I})^{-1} \mathbf{t} \quad (2.81)$$

$$\sigma_{i\alpha}^2 = k_{\alpha,\alpha}(\rho_i, \rho_i) - \mathbf{k}_{i\alpha}^T (\mathbf{K} + \sigma_n^2 \mathbf{I})^{-1} \mathbf{k}_{i\alpha} \quad (2.82)$$

The vector $\mathbf{k}_{i\alpha}$ denotes the vector of kernels comparing the atomic environment ρ_i and the other ones in the database (i.e., $k_{i\alpha,j\beta} = k_{\alpha,\beta}(\rho_i, \rho_j)$). The matrix $\mathbf{K}$ is the Gram matrix whose (m, n) element is given by $k_{\alpha,\beta}(\rho_m, \rho_n)$ in the database. The vector $\mathbf{t}$ is the forces of atomic environment j in β -direction, whose order in the vector should be consistent with the environments in $\mathbf{k}_{i\alpha}$.

2.3.3 Active and On-the-fly Learning

Due to uncertainty quantities provided by GP, the active learning scheme can be implemented in which the high uncertainty value is used as the criterion for an atomic environment to be included in the database. This learning scheme thus ensures each data point is sufficiently different from each other, resulting in a compact and low-correlated database. Further, on-the-fly learning scheme can be implemented by employing the force-field in dynamic simulation to generate more high-uncertainty data that can be used to improve the force-field continuously. The implementation of these learning schemes is schematically in the Figure 2.3.

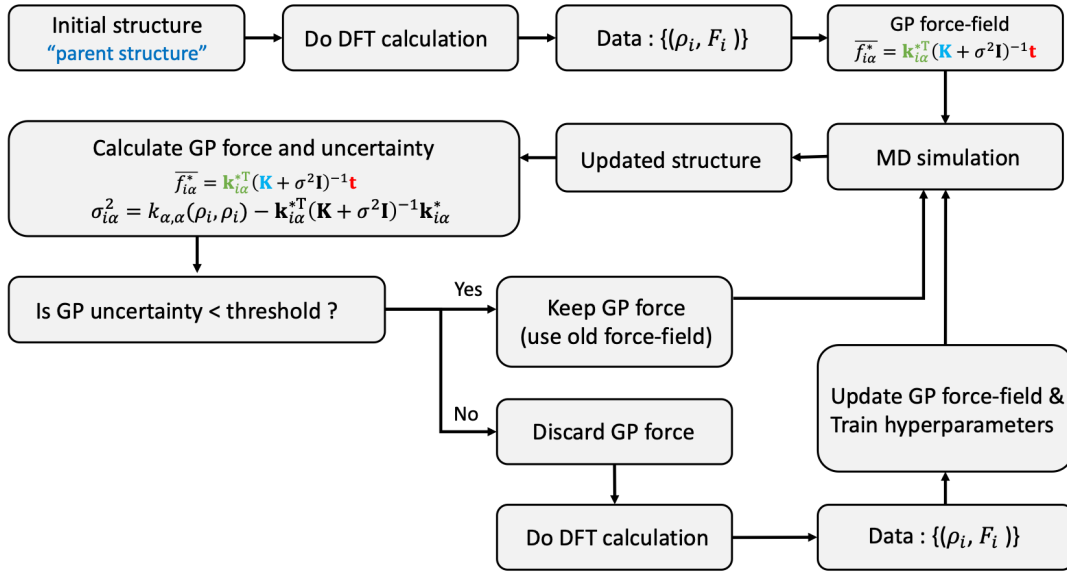


Figure 2.3: The flowchart of active and on-the-fly algorithm.

First, the initial structures that resemble the typical or expected morphology encountered in MD simulations are prepared. The DFT calculations are then performed for each structure to obtain the atomic forces which are included in the database. This database is not necessarily complete as more structures will be added in the subsequent steps. The GP regression is then applied to provide atomic forces that are necessary to run the MD simulation.

As the MD simulation running, more structures are generated. The atomic uncertainty of these structures are evaluated at every time step to ensure the reliability of the simulation. If the uncertainty is smaller than a specified threshold, then the old force-field is kept and be used again in the MD simulation. However, if the uncertainty is high, the predicted atomic forces are discarded and the DFT calculation of the current structure is performed to generate the DFT forces. The atomic environment and the DFT forces then

are added as a new data point in the database. The GP force-field is then re-train on the new database and be used again in the MD simulation. This process is repeated until no high-uncertainty structures are found within a sufficiently long time interval.

Chapter 3

Investigation on Atomic Scale Mechanisms of Step Fluctuations on the Cu(111) Surface

3.1 Introduction

Despite the high complexity of events that occur during the non-equilibrium states, they can be untangled into several elementary processes, of prime importance is surface diffusion [52, 53]. This diffusion can be calculated theoretically by using Density Functional Theory (DFT) and later interplayed by Kinetic Monte Carlo (KMC). Even though there have been many DFT-KMC studies concerning surface diffusion for various metal NPs, they have not yet included the general energetic descriptions of all structures that are possibly formed during catalytic reactions [54–57]. Such shortcomings might lead to the oversight of unique active sites emerged due to catalytic process. Fortunately, recent advancement in KMC simulation by Stamatakis et al. enables to include explicitly the energetics of all possible structures by employing Cluster Expansion (CE) framework. This method has been implemented in KMC simulation package, Zacros [42]. Due to the graph representation of the clusters occupying the lattices, this method is also called the Graph Theoretical KMC (i.e., GTKMC).

As a starting point, I study the diffusion of Cu adatoms on Cu(111) surface by using DFT-KMC simulation tools. There are three reasons why I begin with this model. First, Cu holds primary importance in catalysis as the active metal for chemical reactions such as water gas shift reaction (i.e. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) [10–12] and reverse water gas shift reaction (i.e. $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) [13–15]. Both of these reactions are attractive in the context of

green energy as the former reaction produces the H_2 and the latter utilizes the green-house gas CO_2 . Second, the investigation on Cu surfaces can be considered as prerequisite in the active site elucidation of Cu/ZnO/ Al_2O_3 for methanol synthesis, especially in terms of stacking faults formation that might be the origin of the catalyst's high activity [6, 58]. Third, this study might be used to investigate the effect of Cu surface defects to the overall catalyst activity in more realistic way by including dynamic of surface defects and general description of all structures that possibly formed during practical condition. Various studies have shown that steps and kinks on Cu surfaces have non-negligible effect to the catalyst activity. For instances, Behrens et al. have shown experimentally that the intrinsic activity of Cu for methanol synthesis is proportional to the probability of stacking faults (including steps and kinks) [6]. Theoretical studies also showed that the steps and kinks on Cu surfaces can alter the thermodynamic and kinetic of intermediates during methanol synthesis from CO_2 , resulting in different adsorption state, reaction pathway and the product yield [21, 22].

Based on these reasons, I performed DFT-KMC simulation employed with CE to elucidate the microscopic mechanisms of Cu surface diffusions related with defects such as steps and kinks. Fortunately, there are many previous studies on homoepitaxial growth and dynamic of Cu catalyst that can be used as guidance and comparison to this work [23, 24, 59–64]. One of the important studies is the time correlation function, from which the dominant atomic diffusion process can be identified [65].

The rest of this chapter is organized in the following manner. In subchapter 3.2, I provide the computational details on the DFT, KMC and CE method that I used. In subchapter 3.3, I present and discuss the results on the elementary processes of adatom diffusion, clusters used in CE framework, various diffusion events, and time correlation functions obtained from KMC simulations. Finally, in subchapter 3.5, I summarize and conclude the findings.

3.2 Computational Details

3.2.1 Density Functional Theory Calculations

I used DFT calculations to obtain the binding energies of various Cu clusters and activation energies of diffusion events. All DFT calculations were performed using the STATE code [66, 67]. I took into account the van der Waals

(vdW) interactions by applying exchange correlation functional optB86b-vdW [68], as implemented [69] in the STATE code. Such functional is a modern variant of vdW functionals [70] and has been proved to give Cu bulk lattice constant and molecular reactions on Cu(111), including CO₂ and NO, that are in good agreement with experiment [22, 71]. Cut off energies for the wavefunctions and augmented charge density are 36 Ry and 400 Ry, respectively. The electron-ion interaction was described by ultrasoft pseudopotentials [72]. I modelled the Cu(111) surface by using p(5 × 5) unit cell which were sampled using a uniform grid of 4x4x1 k-points. The unit cell consists of four-layers thick slab of which two upper-most layers are relaxed and two-bottom most are kept fixed. The calculated lattice constant of Cu (fcc) is 3.6102 Å. In addition, I inserted a vacuum region of more than 30 Å to separate two neighboring slabs. The convergence thresholds for energy and force are 10⁻⁹ Ha/atom and 10⁻³ Ha/Bohr, respectively.

I also compared the result of reaction and activation energies obtained from CE with direct DFT calculations. Therefore, aside from the flat surface I used four additional surfaces which incorporate step and kink sites on the surface. These surfaces include two types of step edges that can be found on Cu(111), namely step A with the ledge of (100)-type orientation and step B with the ledge of (111)-type orientation. Figure 3.1 shows the illustration of all surfaces with their corresponding unit cells that I used in the DFT calculations.

The binding energies of clusters consisting of n Cu atoms, denoted as E_b , are computed according to the following equation.

$$E_b = E_{tot}^{cluster+slab} - E_{tot}^{slab} - nE_{tot}^{Cubulk} \quad (3.1)$$

Finally, the Climbing Image-Nudged Elastic Band (CI-NEB) as implemented in STATE code is used to calculate the activation energies of adatom diffusions.

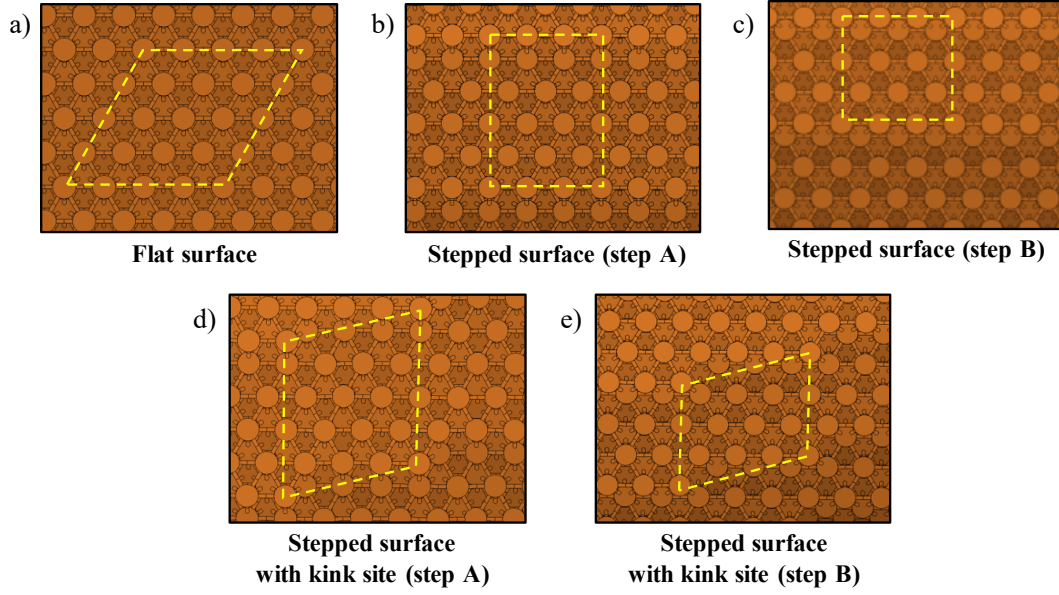


Figure 3.1: Models of Cu surfaces used in DFT calculations. a) represents the flat Cu(111) surface, b) represents Cu(111)-terrace with step edge type A, c) represents Cu(111)-terrace with step edge type B, d) represents Cu(111)-terrace with kink and step edge type A, and e) represents Cu(111)-terrace with kink and step edge type B. The area inside the dashed boundary are the unit cell used in the calculations.

3.2.2 Cluster Expansion Hamiltonian and Bronsted-Evans-Polanyi Principle

The total energy of any Cu adisland configurations can be calculated by CE method which is implemented in the graph-theoretical KMC framework [37]. The Hamiltonian of the system or the total energy of a lattice configuration, denoted as $H(\sigma)$, is given by

$$H(\sigma) = \sum_{k=1}^{N_c} \frac{ECI_k}{GM_k} NCE_k(\sigma) \quad (3.2)$$

where ECI_k is the effective cluster interaction of cluster k (i.e. the energy contribution of the cluster to the total energy), GM_k is the graph-multiplicity of cluster k (i.e. the number of times the exact same cluster will be counted in a given configuration), and NCE_k is the number of detected clusters k in the current configuration. In total there are 48 number of clusters calculated including fcc, hcp, and fcc-hcp clusters. All those clusters are presented in Appendix A. The ECI of a cluster is calculated by subtracting the binding energy with the ECI of its subclusters (e.g., the cluster with fewer components), where the ECI of the smallest cluster (i.e. monomer) is specified equal to its binding energy.

3.2. Computational Details

Given the energy of initial and final configurations, the forward and reverse activation energies of any diffusion events can be computed by applying Brønsted-Evans-Polanyi principle [45, 46]:

$$E_{act}^{fwd}(\sigma) = \max(0, \Delta E(\sigma), E_{act}^{fwd,0}(\sigma) + \omega \cdot (\Delta E(\sigma) - \Delta E^0(\sigma))) \quad (3.3)$$

$$E_{act}^{fwd}(\sigma) = \max(-\Delta E(\sigma), 0, E_{act}^{rev,0}(\sigma) - (1 - \omega) \cdot (\Delta E(\sigma) - \Delta E^0(\sigma))) \quad (3.4)$$

The E_{act}^{fwd} and E_{act}^{rev} in the equations above represent the forward and reverse activation energies, respectively while ΔE represents the reaction energy or the difference between the final and the initial states. The reaction and activation energies with additional superscript '0' correspond to the zero-coverage limit condition which are obtained by means of DFT calculations. The symbol ω represents the proximity factor or the proximity of the transition state to the initial or final states of the reaction, ranging from 0 to 1 [73].

3.2.3 Kinetic Monte Carlo Simulation

I performed Kinetic Monte Carlo Simulation within graph-theoretical framework, as implemented in Zacros version 2.0 developed by Stamatakis et al [42]. This framework performs MC simulation based on the energies obtained by CE. In this work, I simulated Cu adatoms diffusion at three different temperatures (300 K, 400 K, 500 K) where all the adatoms were initially deposited without the possibility of desorption, thereby the pressure and gas phase composition become irrelevant. For the elementary reaction, I used a reversible reaction of adatom hopping between one fcc site to the adjacent hcp site. The prefactor was approximated to be 10^{12} s^{-1} as suggested by previous studies [74–77]. I specified the surface model as a collection of fcc and hcp lattice sites in 42×42 supercell to capture the stable structure of the adatoms. The periodic boundary condition was implemented in both x and y axis.

In the initial structure, I used stripe-like island of which step edges are already equilibrated. This type of model contains 4 important parts: The step A with the ledge of (100)-type orientation, step B with the ledge of (111)-type, kink sites, and the terrace of Cu(111). I have made sure that the number of rows separating the two steps are large enough to avoid interaction. Before

starting the production run of the simulation, I performed the KMC simulation of a pre-initial structure (shown schematically in Figure 3.2) for a certain amount of time until no significant change in the structure and energy was detected.

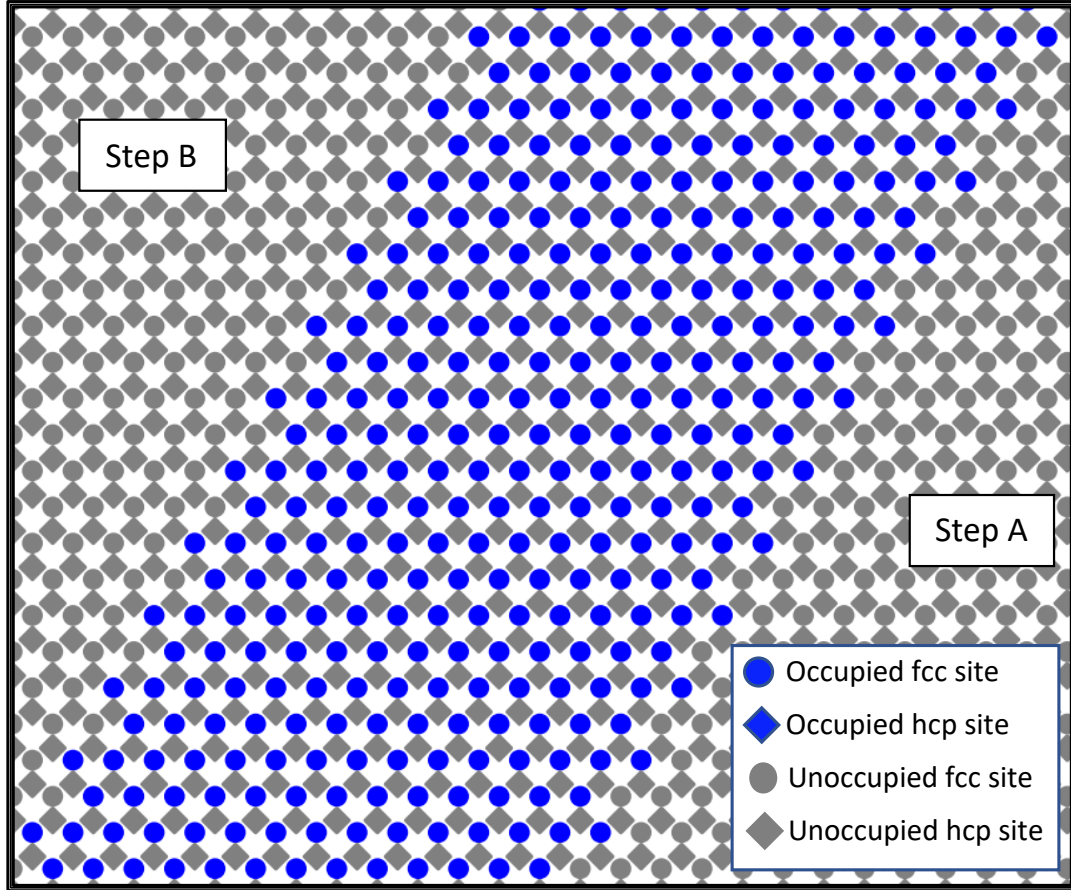


Figure 3.2: The pre-initial configuration used in KMC simulation. The blue circles and diamonds denote the occupied fcc and hcp sites, respectively. Whereas the grey circles and diamonds denote the unoccupied fcc and hcp sites, respectively. The step A and step B are located at the right and left sides of the stripe, respectively.

3.3 Results and Discussion

3.3.1 DFT Calculation of Elementary Diffusion Process and Cluster's ECI

In this work, I consider the adatom diffusion from fcc to hcp sites on the Cu(111) surface as the only reversible elementary reaction where the proximity factor equals to 0.5. The activation and reaction energies of this reaction are 0.055 eV and -0.011 eV, respectively. This finding is in good agreement with previous DFT calculations in which the activation and reaction energies

are 50 meV and -6 meV, respectively [77]. The concerted motion, namely the diffusion of dimers or larger clusters at once is not included since such processes result in the high activation energies and smaller prefactors [57].

I used a collection of fcc, hcp, and fcc-hcp clusters as a basis set in the CE Hamiltonian. To keep a practical number of DFT calculations, I only consider limited range of interactions. Those interactions among adatoms are then modeled by two body, three body, and four body interactions. All the clusters with their corresponding ECI and multiplicity included in the simulation are reported in the Appendix A. Figure 3.3 shows the fcc clusters that are used in this framework.

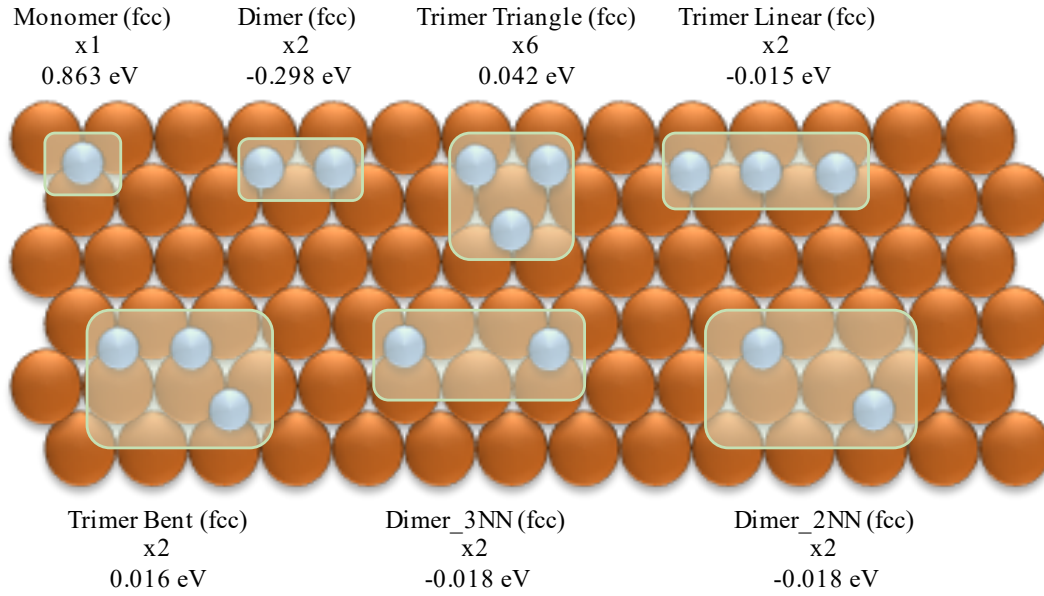


Figure 3.3: All fcc clusters used within CE framework ranging from monomer (point-cluster) to trimer (three-body cluster). The number after ‘x’ symbol denotes the graph-multiplicity of the cluster, GM_k . The number below the multiplicity denotes the ECI of the cluster.

3.3.2 Diffusion of Adatoms in the CE Approach

To examine the reliability of the CE model, I compared the reaction and activation energies obtained from CE with direct DFT calculations by investigating 13 diffusion process that might occur at step A and step B (Table 3.1).

Table 3.1: The 13 diffusion events that I investigated at step A and B. Superscript (*) indicates the change in number of bonding between final and initial state: 2. Superscript (**) indicates in number of bonding between final and initial state: 3.

Index	Diffusion Events	Figure Index
1	Detachment of adatom out of step edge	Figure 3.6
2	Attachment of adatom to a straight step	Figure 3.7
3	Diffusion of adatom along the step edge	Figure 3.8
4	Detachment of adatom in the presence of monoatomic kink site	Figure 3.9
5	Detachment of adatom from the step edge	Figure 3.10
6	Diffusion of adatom through exchange mechanism (part I)	Figure 3.11
7	Diffusion of adatom through exchange mechanism (part II)	Figure 3.12
8	Adatom emission from corner kink site, parallel to the step edge	Figure 3.13
9	Adatom emission from corner kink site, perpendicular to the step edge*	Figure 3.14
10	Adatom emission from corner kink site, perpendicular to the step edge**	Figure 3.15
11	Adatom attachment to corner kink site, parallel to the step edge	Figure 3.16
12	Adatom attachment to corner kink site, perpendicular to the step edge*	Figure 3.17
13	Adatom attachment to corner kink site, perpendicular to the step edge**	Figure 3.18

The results are shown in Figure 3.4 for reaction energies and Figure 3.5 for activation energies. Based on the calculations, the reaction energies obtained from CE and DFT are in good agreement, indicated by no more than 0.10 eV difference for both step A and step B. However, in the case of activation energies I found difference up to 0.11 eV for several process on step A: process 1 (i.e. detachment of adatom from a straight step), process 7 (i.e. adatom diffusion through exchange process), and process 12 (attachment of adatom to corner kink site). In the case of step B, I found one process that has different up to 0.13 eV: process 4 (i.e. the detachment of adatom in the presence of monoatomic kink site), while the rest of the process has no more than 0.10 eV

3.3. Results and Discussion

difference. I consider such errors acceptable since they are also within typical DFT errors [78]. The discrepancy between the CE and DFT are attributed to the limited size of the clusters that I used and the effect of atomic-relaxation from DFT calculations.

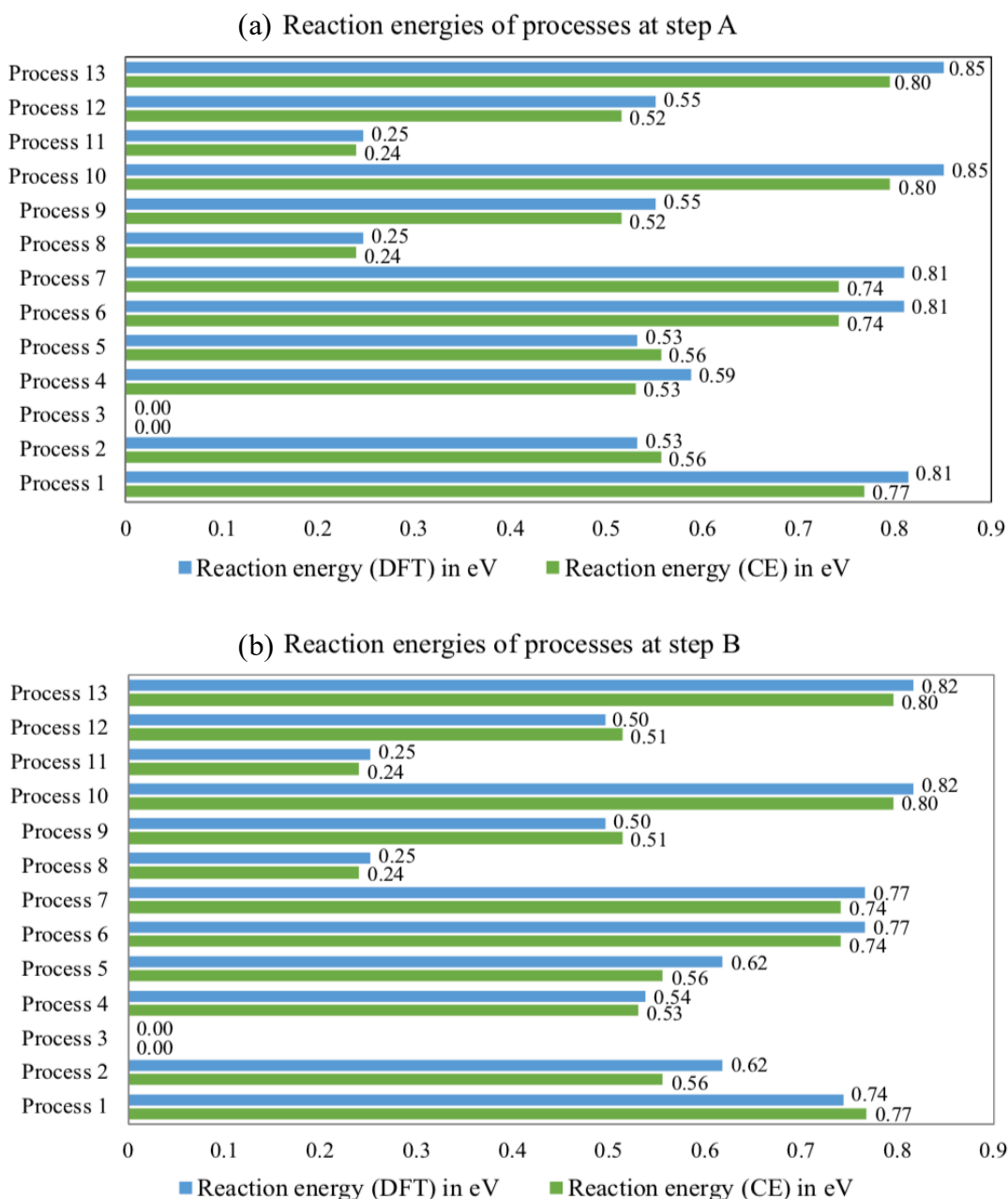


Figure 3.4: The activation energies of various processes obtained from direct DFT calculations (blue bars) and CE framework (green bars) for step A and step B. These 13 events will be discussed in more detailed in the following section.

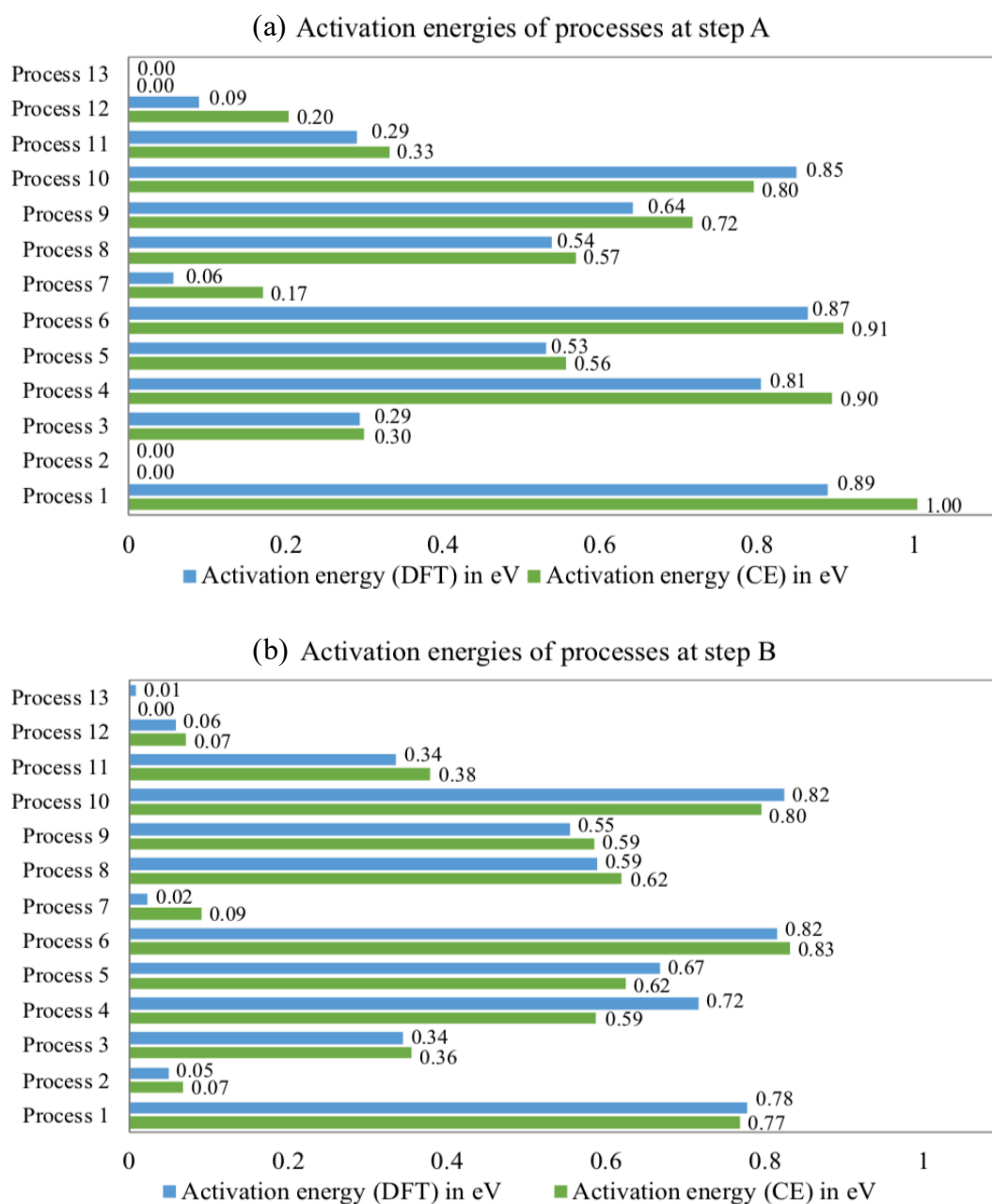


Figure 3.5: The absolute values of reaction energies for various processes obtained from direct DFT calculations (blue bars) and CE framework (green bars) for step A and step B. These 13 events will be discussed in more detailed in the following section.

In the following subsections, the discussion on the investigated diffusion events are divided based on the shape of the initial steps: straight step, straight step with monoatomic kink site, and straight step with corner kink site as shown in Figure 3.6 to Figure 3.18. These figures depict the top view of Cu(111) surfaces. The black and grey circles correspond to the Cu adatoms and first layer Cu atoms, respectively while small blue circles and diamonds

correspond to the fcc and hcp sites, respectively.

Straight Step

The least probable diffusion events for step A and step B is expected to be the detachment of adatom out of straight step, as indicated in Figure 3.6. The activation energies for such process are very high: 1.00 eV for step A and 0.77 eV for step B. For comparison, the calculations using EMT (Effective Medium Theory) method (without distinction between step A and step B) result in activation and reaction energies equal to 0.77 and 0.66 eV, respectively [59]. Due to the high activation energy, it is expected that the fluctuation of the upper terrace's adatom is unlikely to happen once it forms a straight step.

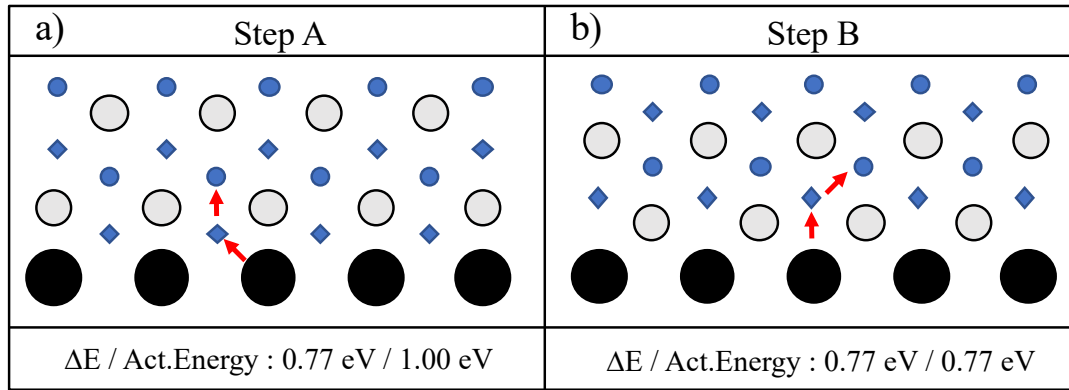


Figure 3.6: [Process 1]. (a) The detachment of adatom out of straight step A. (b) The detachment of adatom out of straight step B.

On the other hand, the formation of monoatomic kink site by attachment of a wandering adatom on the lower terrace has no barrier for step A and 68 meV for step B, as shown in Figure 3.7. In real experiment, the wandering adatoms might be originated from the atomic deposition. The EAM (Embedded Atom Method) calculation of activation energies for the same process by Marinica et al. are in good agreement with the present calculations : 0.6 meV and 19 meV for step A and step B, respectively [64].

Step edge with monoatomic kink site

Aside from attachment of wandering adatoms, diffusion along the step edge through hopping mechanism (Figure 3.8) is found to have the lowest activation energy: 0.30 eV for step A and 0.36 eV for step B. These values are in agreement with Scanning Tunneling Microscopy (STM) measurement by Giesen et al. that found the barriers of such diffusion to be about 0.30 eV

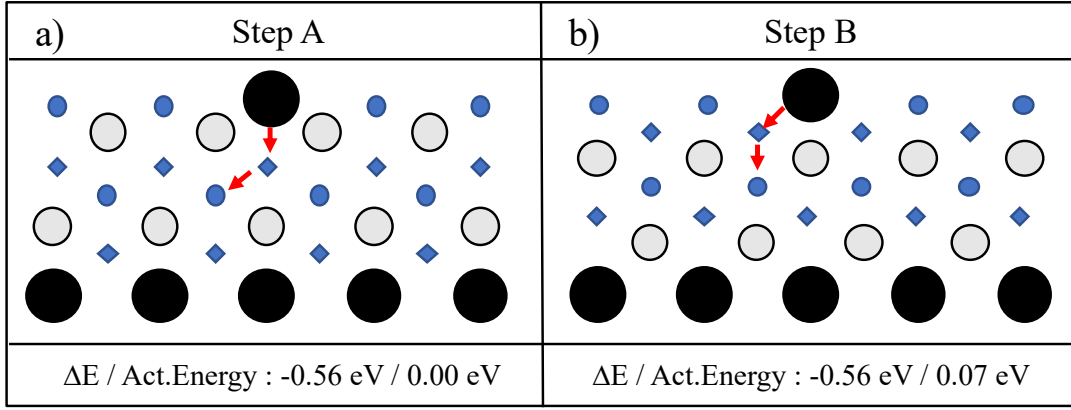


Figure 3.7: Process 2]. (a) The attachment of adatom to straight step A. (b) The attachment of adatom to straight step B.

for both types of step [24]. In regards to the theoretical study, the present results are consistent with EAM which obtained the barriers equal to 0.25 eV and 0.31 eV for step A and step B, respectively [64]. Based on the activation energy, I consider adatom diffusion along the step edge as the most probable event during the step fluctuation in the case of no atomic deposition producing wandering adatoms. This process for step A is expected to be faster than step B since the activation energy of the latter is higher by 55 meV, consistent with previous EAM study which obtained the difference to be 65 meV.⁴⁰ The STM measurements of Cu island on Cu(111) by Giesen et al [23] implied that the diffusion along Cu(111) steps should effectively have the same energy barrier for diffusion along both step A and B since no preferred island edge orientation was observed.

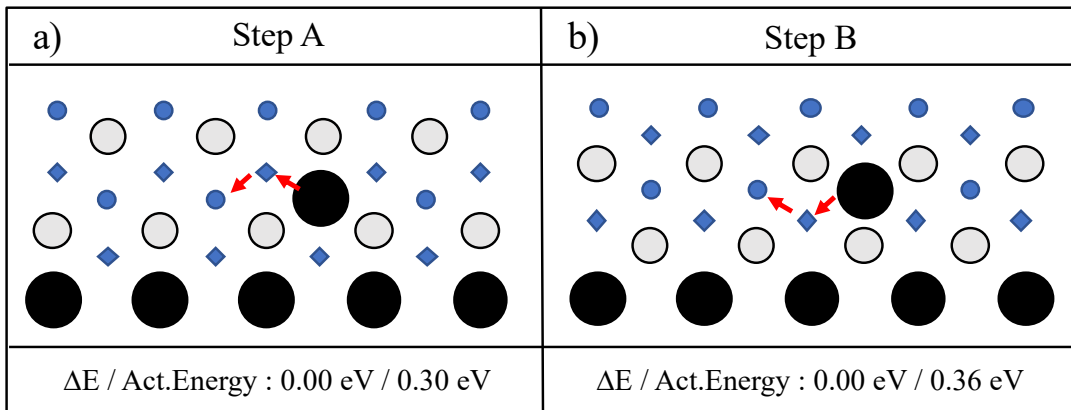


Figure 3.8: [Process 3]. (a) The diffusion of adatom along the edge of step A. The diffusion of adatom along the edge of step B.

In the presence of monoatomic kink site, the barrier of adatom detachment from the straight step (Figure 3.9) is reduced to 0.90 eV and 0.59 eV for step A

and step B, respectively. This is because the final state is stabilized by bonding formation between the diffusing adatom with the existing monoatomic kink site. For comparison, the EAM calculations on the edge of adisland on Cu(111): 0.73 eV and 0.65 meV for step A and step B, respectively.⁴⁰ The barrier at step B that I calculated using CE is relatively close to the EAM studies, while it is much higher for the step A.

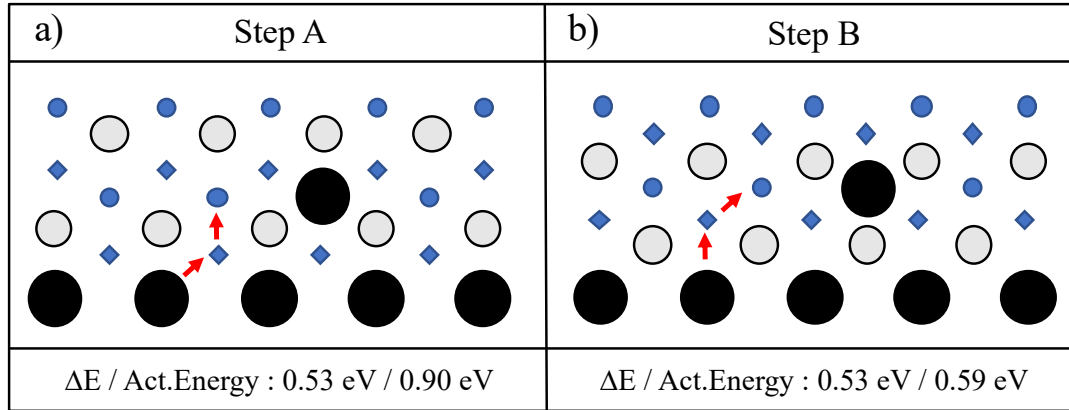


Figure 3.9: [Process 4]. (a) The detachment of adatom from straight step A in the presence of monoatomic kink site. (b) The detachment of adatom from straight step B in the presence of monoatomic kink site.

Another event that can happen in relation with monoatomic kink site is the formation of straight step by detachment of adatom from the step edge (Figure 3.10). The activation energies calculated from CE are 0.56 eV and 0.62 eV for step A and step B, respectively. Consistently, the EAM calculation on the same process at the step of an adisland result in the activation energies equal to 0.66 eV and 0.68 eV for step A and step B, respectively.⁴⁰ With respect to attachment of wandering adatom (Figure 3.7), I found the adatoms attachment is much easier than the detachments. Consequently, the system tends to agglomerate into bigger island by capturing the wandering atoms near the step edge.

Aside from hopping mechanism, diffusion along the step edge can also be achieved through exchange mechanism (Figure 3.11). The relaxed pathway obtained from NEB calculation shows that the exchange process proceeds by the detachment of adatom out of a step and followed by the attachment of the other adatom to occupy back the vacant site. However, the diffusion through this mechanism has very high energy barrier: 0.91 eV for step A and 0.83 eV for step B. In the case of low temperature, it is expected that the diffusion along the step edge is dominated by hopping mechanism.

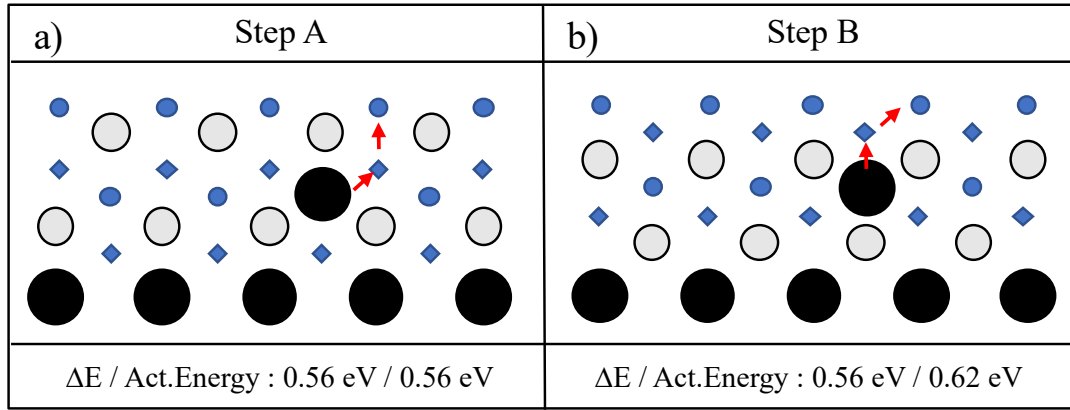


Figure 3.10: [Process 5]. The formation of straight step by detachment of adatom from step A. The formation of straight step by detachment of adatom from step B.

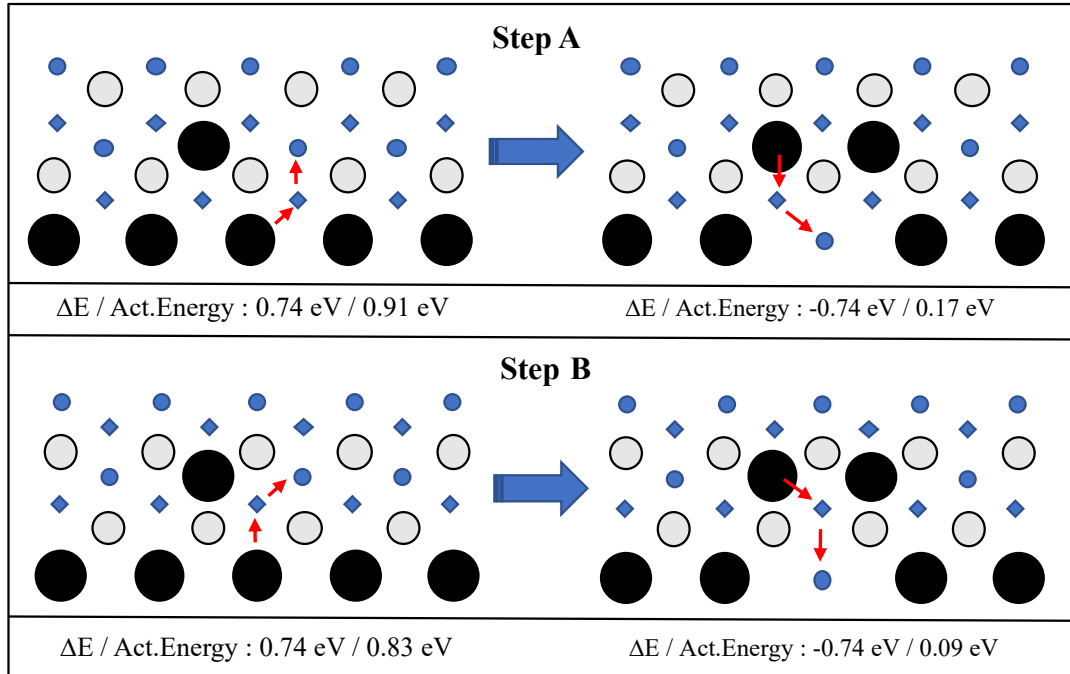


Figure 3.11: The initial and final state of adatom diffusion through exchange mechanism for step A (top figure) and step B (bottom figure). The initial and final states correspond to [process 6] and [process 7], respectively.

Step edge with corner kink site

Various events might occur in the presence of corner kink site. Based on calculation, it is found that the energy barrier of adatom emission from the corner site depends on its direction and the number of changes in bonding. The first case is the emission of adatom parallel to the step edge (Figure 3.12), of which the final state has one less bonding than the initial. The activation energies for this process are 0.57 eV and 0.62 eV for step A and step B, respectively. These values are rather close to the result of EAM calculations

where the activation energies are 0.51 eV and 0.56 eV for step A and step B, respectively [64].

The second case is the adatom emission perpendicular to the step edge, of which the final state has two less bonding than the initial (Figure 3.13). The activation energies for this process are 0.72 eV and 0.59 eV for step A and step B, respectively. Relatively close, the results of EAM calculations show the activation energies for step A and step B are 0.68 eV and 0.60 eV, respectively [64].

The third case is the adatom emission perpendicular to the step, of which the final state has three less bonding than the initial (Figure 3.14). Such case creates adatom on the terrace. The activation energy of this process is 0.80 eV for both step A and step B. However, the activation energies from EAM calculations are higher: about 0.95 eV for step A and step B. Based on temperature-dependent analysis of island decay, Giesen et al. found the sum of the adatom formation energy from kink sites onto the terrace and the terrace diffusion barrier are 0.76 eV [60]. In the present calculation, I found the sum of terrace's adatom reaction energy (0.80 eV) and terrace diffusion barrier (0.05 eV) to be 0.85 eV for both step A and B. In the case of step A, since the activation energy of the first case is lower than the second case and the third case, it is very likely that the emission will be followed by the diffusion along the step edge. It is also worthy of note that the trend in activation energy for step A is proportional to the changes in bonding, but not for step B. This indicates that bond-counting approximation to determine the activation energy is not always sufficient, thus highlighting the significance of more complete description on environmental condition.

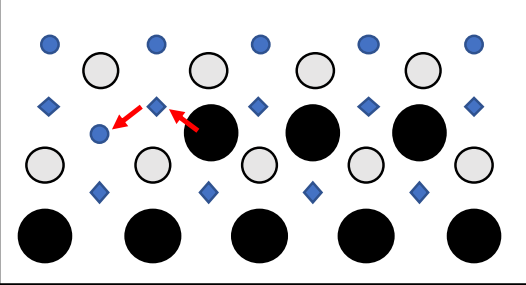
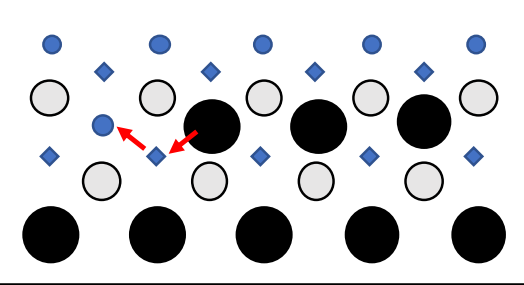
a) Step A	b) Step B
	
$\Delta E / \text{Act. Energy} : 0.24 \text{ eV} / 0.57 \text{ eV}$	$\Delta E / \text{Act. Energy} : 0.24 \text{ eV} / 0.62 \text{ eV}$

Figure 3.12: [Process 8]. (a) Adatom emission parallel to the step edge type A. (b) Adatom emission parallel to the step edge type B. The final state has one less bonding compared to initial state.

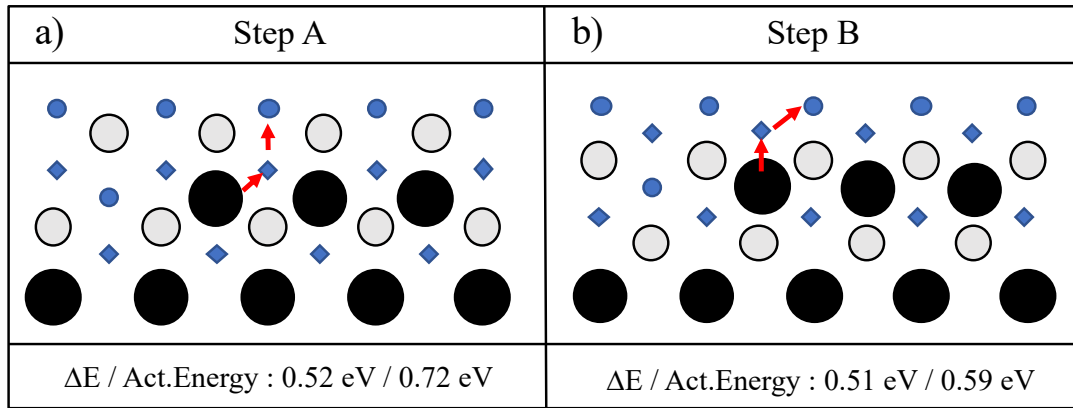


Figure 3.13: [Process 9]. (a) Adatom emission perpendicular to the step edge type A. (b) Adatom emission perpendicular to the step edge type B. The final state has two less bonding compared to the initial state.

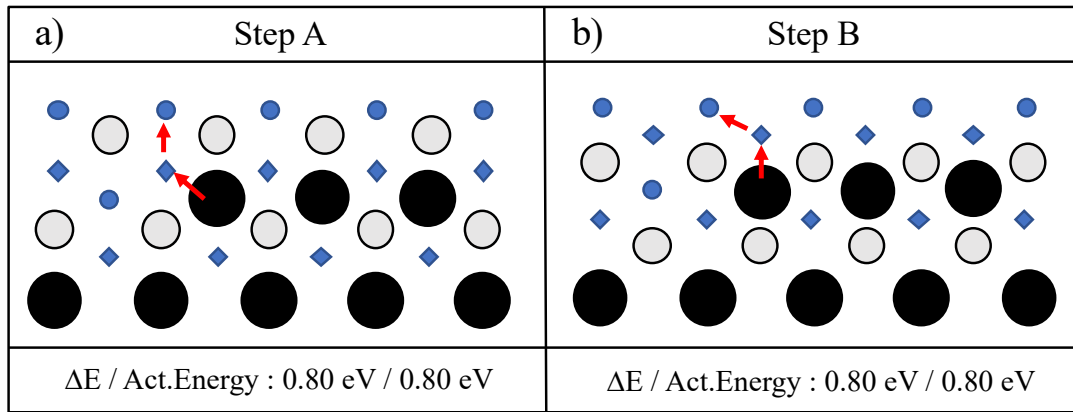


Figure 3.14: [Process 10]. (a) Adatom emission perpendicular to the step edge type A. (b) Adatom emission perpendicular to the step edge type B. The final state has three less bonding compared to the initial state, resulting in a wandering adatom on the terrace.

Similarly, the attachment of adatom to the corner kink site can be divided into three different cases. These attachment processes are basically the reverse of the detachment one. In contrast with the detachment, the trend of activation energy is proportional with the number of changes in bonding for both step A and step B. The first case is the attachment of adatom with parallel direction to the step edge, of which the number of bonding increases by one (Figure 3.15). The activation energies obtained are 0.33 eV and 0.38 eV for step A and step B, respectively. The EAM calculations of the same process result in lower values: 0.22 eV and 0.27 eV for step A and step B, respectively. The second case is the attachment of adatom perpendicular to the step edge, of which the number of bonding increases by two (Figure 3.16). According to CE calculation, I found the activation energies to be 0.20 eV and 0.07 eV

for step A and step B, respectively. However, the EAM studies show lower activation energies: 86 meV and 8 meV, respectively. The third case is the attachment of adatom perpendicular to the step edge, of which the number of bonding increases by three (Figure 3.17). The activation energies found by CE are zero for both step A and step B, similar with the result EAM calculations [64].

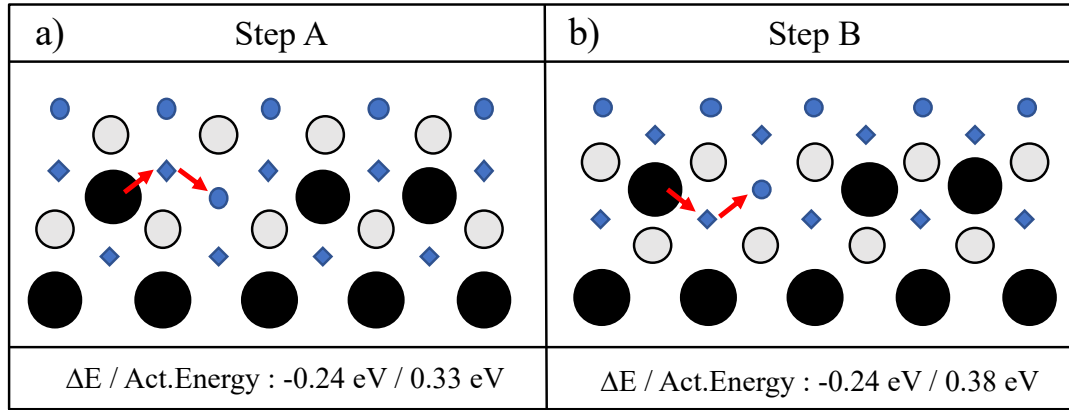


Figure 3.15: [Process 11]. (a) The attachment of adatom to corner kink site parallel to the step edge type A. (b) The attachment of adatom to corner kink site parallel to the step edge type B. The final state has one more bonding than the initial state.

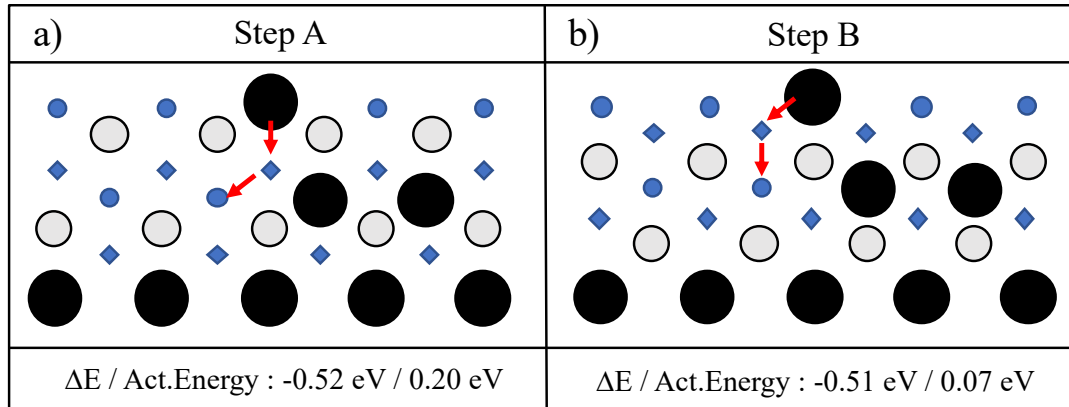


Figure 3.16: [Process 12]. (a) The attachment of adatom to corner kink site perpendicular to the step edge type A. (b) The attachment of adatom to corner kink site perpendicular to the step edge type B. The final state has two more bonding than the initial state.

1-Dimensional Ehrlich Schwoebel barrier

The energy diagram of an adatom moving across 1-D Ehrlich Schwoebel (ES) barrier obtained from CE and DFT calculations is shown in Figure 3.18. In the case of step A, the CE calculations on the energies of first transition state (TS-1), meta-stable state (MS state), second transition state (TS-2), and final state

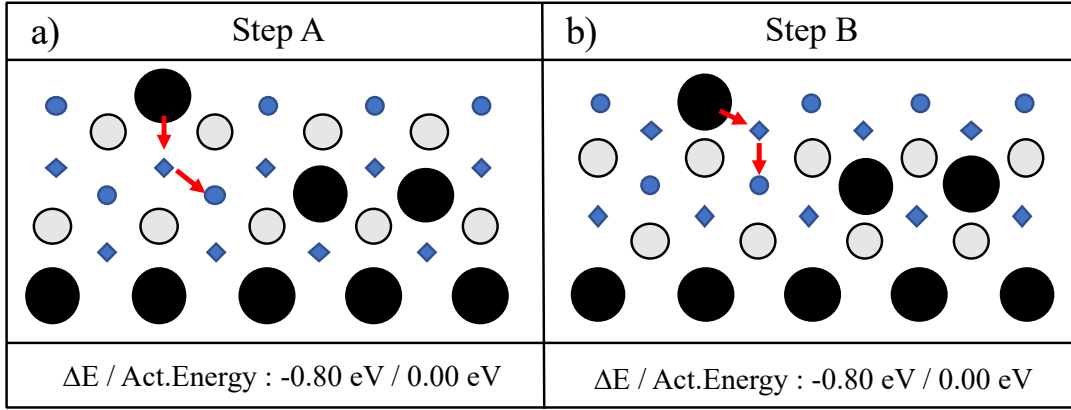


Figure 3.17: [Process 13]. (a) The attachment of adatom to corner kink site perpendicular to the step edge type A. (b) The attachment of adatom to corner kink site perpendicular to the step edge type B. The final state has three more bonding than the initial state.

relative to initial state are 0.32 eV, 0.26 eV, 0.46 eV, and -0.26 eV, respectively. While in the case of step B, the energies of TS-1, MS state, TS-2, and final state relative to the initial state are 0.45 eV, 0.26 eV, 0.33 eV, and -0.26 eV. In the CE model, the reaction energy and the energy difference between MS and final state are the same for both step A and step B. Further, the highest energy barrier of this process has almost similar value for both steps (0.46 eV for step A and 0.45 eV for step B), though the former is found at TS-2 while the latter is found at TS-1. For step A, the DFT energy calculations on TS-1, MS state, TS-2, and final state relative to the initial state are 0.35 eV, 0.26 eV, 0.35 eV, and -0.29 eV, respectively. While for step B, the DFT energy calculations on TS-1, MS state, TS-2, and final state relative to the initial state are 0.36 eV, 0.24 eV, 0.30 eV, and -0.25 eV, respectively. The 1-D ES barrier were also studied by means of EAM studies.⁴⁰ The energies of TS-1, MS state, TS-2, and final state relative to the initial state are: 328 meV, 308 meV, 393 meV, and -0.287 meV for step A; and 419 meV, 308 meV, 313 meV, and -287 meV for step B. I consider the present results to be reasonably similar to the EAM studies [64].

I found rather high energy difference between CE and DFT at TS-2 for step A and TS-1 for step B. The energy difference is 0.11 eV for the former and 0.08 eV for the latter. I attributed this error due to the relaxation effect in DFT calculations which is more severe at TS-2 for step A and at TS-1 at step B: the moving adatom and atom at corner kink site will repel each other at those sites, thus adding more distance between the corresponding atoms.

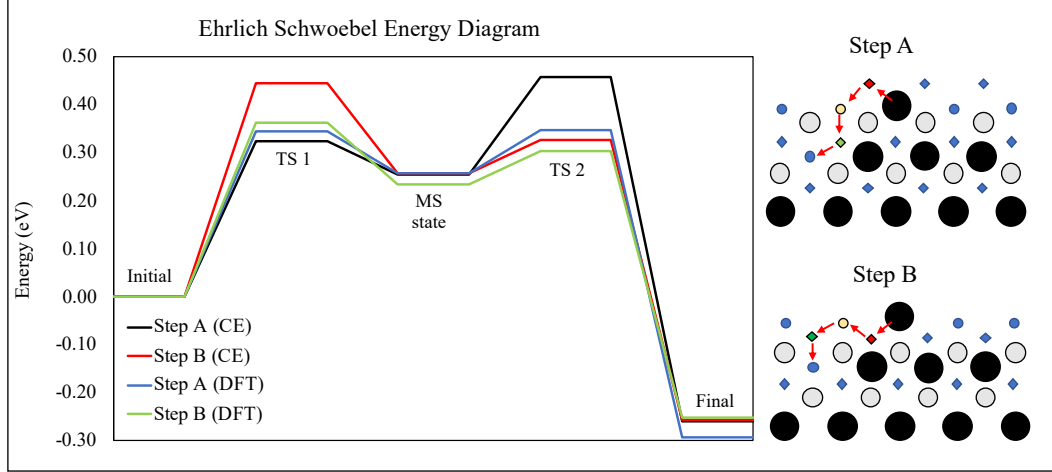


Figure 3.18: Potential energy surface of one-dimensional Ehrlich-Schwobel barrier for step A and step B. The red diamond, yellow circle, and green diamond represent the first transition state at hcp site (TS-1), meta-stable state at fcc site (MS state), and second transition state at hcp site (TS-2).

3.3.3 Step Parameters and Time Correlation Function of Step Fluctuations

Based on the energetics obtained from CE, several step parameters such as kink formation energy (ϵ) and kink density per site (P_k) can also be obtained. By taking the energy difference between system with 4 kinks (Figure 3.19) and system with perfect step then divide it by 4, I obtained ϵ equals to 0.145 eV for both step A and step B. This finding is a little bit higher than the ϵ obtained from the STM observation of islands on Cu(111) which are 0.113 ± 0.007 eV and 0.121 ± 0.007 eV for step A and step B, respectively [62]. Further, at $k_B T \ll \epsilon$ the kink concentration can be approximated as $P_k \approx 2 \exp(-\epsilon/k_B T)$ [79], from which I obtained P_k equals to 0.007, 0.030, and 0.070 for temperature 300 K, 400 K, and 500 K, respectively. Note that because the kink formation energies are the same for step A and step B, the kink concentrations calculated are also the same for both steps.

I can also obtain P_k by directly counting the number of kinks from the KMC results. These values are presented in Table 2. I found that the observed P_k at 300 K and 400 K deviate from the calculated values while at 500 K the values are in good agreement. The deviations come from the relatively short step (42 atomic units) within the unit cell and the ‘forced’ kinks which arise from the fluctuation of adatoms along such step edge. At the equilibrium, the step bumps that I introduced in the initial configuration tend to combine to form one long step bumps at each step A and B as shown in Figure 3.20. Such

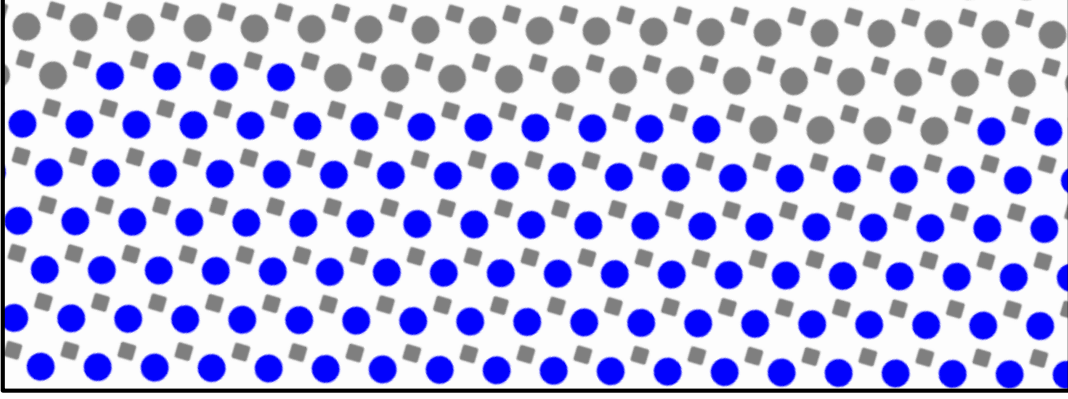


Figure 3.19: Step with 4 kinks obtained by moving set of adatoms out of the step.

Table 3.2: The kink concentration (P_k) at different temperatures. The calculated P_k are approximated as $P_k \approx 2 \exp(-\epsilon/k_B T)$ and are the same for both step A and step B due to the similar ϵ . The observed P_k are obtained by directly counting the number of kinks inside the unit cell.

Temp. (K)	P_k (calc.)	P_k (obs.) at Step A	P_k (obs.) at Step B
300	0.007	0.048	0.048
400	0.030	0.053	0.053
500	0.070	0.073	0.071

condition will limit the lower bound of possible number of kinks to 2 and consequently the minimum possible value of kink density will be $2/42$ (or 0.047619).

The snapshots of typical equilibrium step profile based on the KMC simulations at different temperatures are presented in Figure 3.20, Figure 3.21, and Figure 3.22. At 300 K, it is found that the number of kinks at the edge is minimum for both step A and B due to the effect of low temperature. I also observe that the locations of corner sites at each step change over time, indicating that the adatoms are emitted from the corner sites and move alternately between the two corners at the same step. Since no adatoms migrating on the terrace are found, I expect such event proceeds through the diffusion along the step edge. At 400 K, the number of kinks found at the step is higher, mainly due to the formation of several local step bumps as shown in the snapshot. This process is the indication of consecutive adatom emissions from the corner sites since such processes are more accessible at this temperature. However, these local steps might combine again at the later time due to the dynamics of the adatoms. At 500 K, the number of kinks is increased

3.3. Results and Discussion

and the bumps at the steps are more pronounced since the high-energy processes such as emissions of adatom from the corner perpendicularly to the step edge are now more accessible.

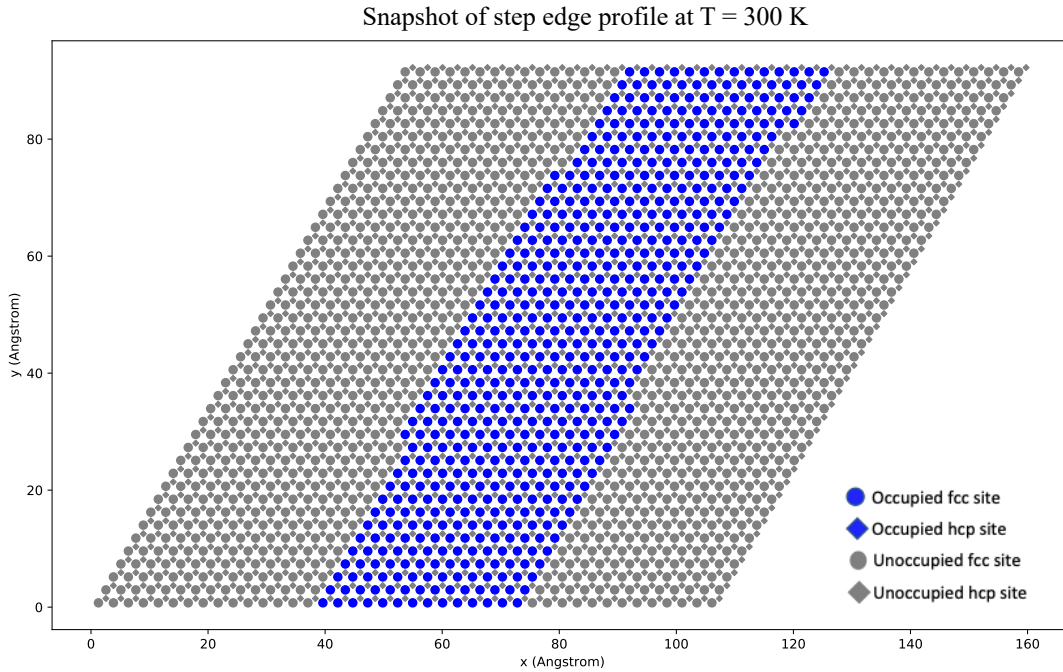


Figure 3.20: Snapshot of typical step edge profile at temperature 300 K that shows the minimum number of kinks which are equal to 2 for each step.

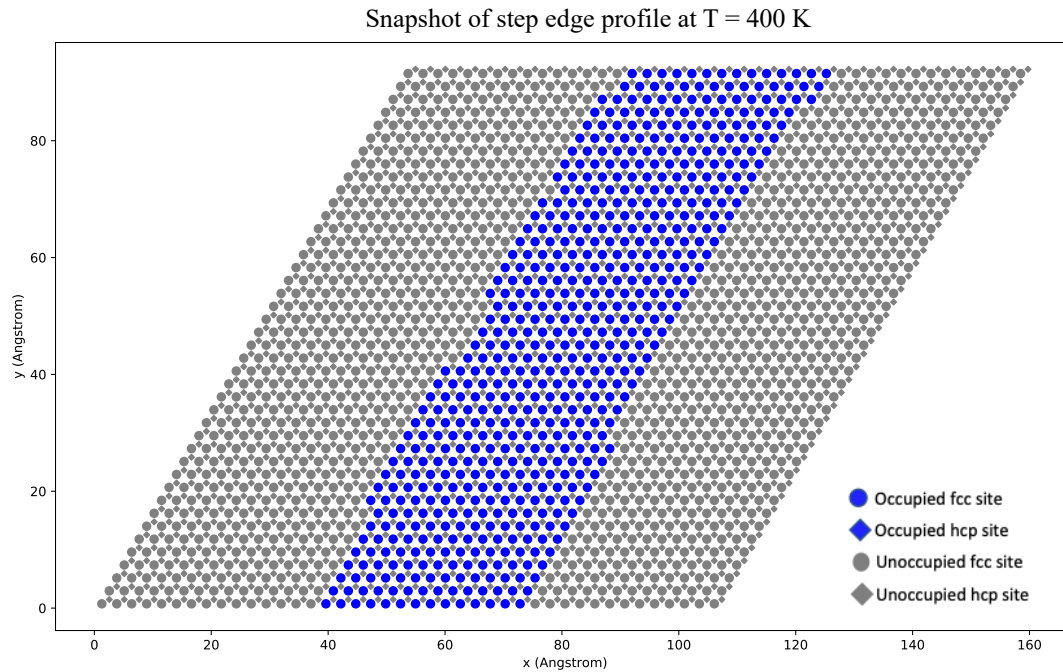


Figure 3.21: Snapshot of typical step edge profile at temperature 400 K. The formation of local step bumps that increase the number of kinks is shown at the step B.

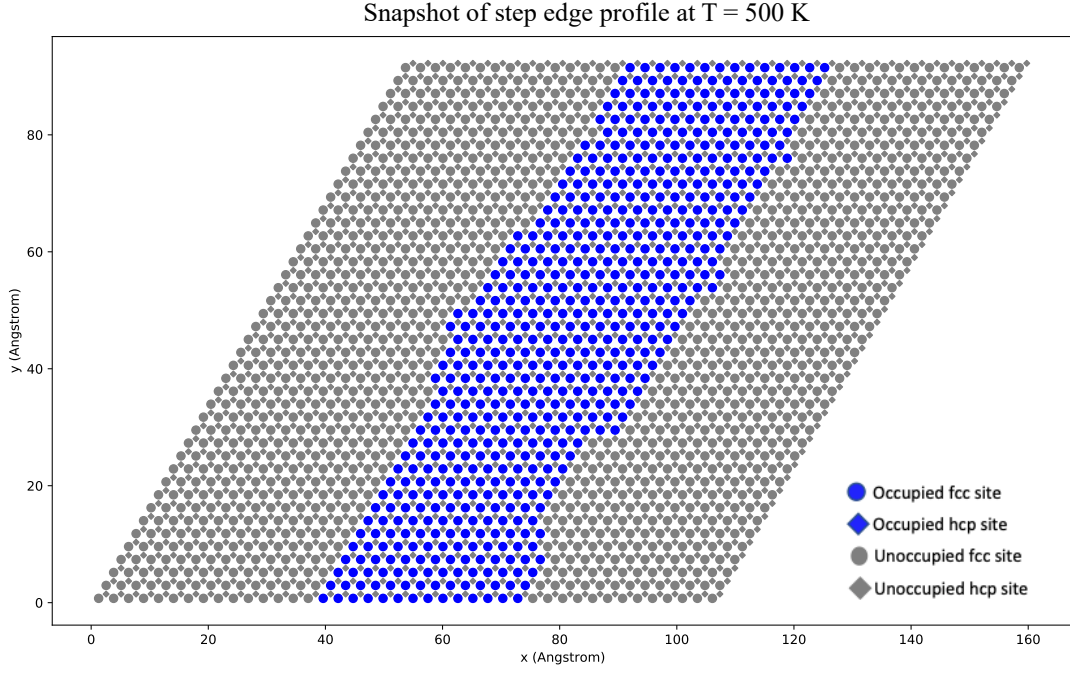


Figure 3.22: Snapshot of typical step edge profile at temperature 500 K. At this temperature, the step bumps are more pronounced and the number of kinks increases.

A quantitative way to analyze the equilibrium step fluctuations is by measuring the time correlation function, denoted as $G(t)$ [24, 80–82]. This function is computed by taking the ensembles average of the squared distance between adatom position at the step edge at different time [24], which mathematically written as:

$$G(t) = \langle [x(y, t) - x(y, t_0)]^2 \rangle \quad (3.5)$$

where x and y are spatial axis in the direction perpendicular and parallel to the step, respectively. Since the model is basically a collection of discrete sites, I can regard x as column and y as row. One sample to be averaged is defined as the squared distance between x values of step edge at time t and the x values of step edge at the reference time t_0 . Both values of $x(t)$ and $x(t_0)$ are obtained at the fixed values of y . In the KMC model, all the result of $G(t)$ for every possible values of y are averaged together with the other samples obtained with different Monte Carlo random seed.

According to the continuum theory, the dominant process of mass transport involved in the step fluctuation can be extracted from the functional form of $G(t)$ [23, 24, 65, 83]. To obtain such functional, the partial differential

equation, namely the Langevin equation, has to be solved [24, 83]:

$$\frac{\partial x}{\partial t} = -\frac{\Gamma_a}{k_B T} \frac{\delta H}{\delta x} + \eta(y, t) \quad (3.6)$$

The term Γ_a denotes the friction coefficient which depends on the dominant mass transport process, while the term H and η denote the effective Hamiltonian and the noise term that allows thermal fluctuation, respectively. The various functional forms of $G(t)$ and the corresponding dominant mass transport scenarios derived from the Langevin equation have been well summarized by Giesen [24]. It is expected that the $G(t)$ should be proportional to $t^{1/4}$ when the diffusions along the step edge become the dominant mass transport [23]. To compute $G(t)$ as in equation (5) from the KMC simulations, a home-made python-based program is written to identify the change of adatoms position at the step edge. Further, to obtain more uncorrelated samples for the ensembles average, up to 20 different random seeds are used for each temperature during the KMC simulation. The number of samples averaged in the formulation is different at each temperature. For simulation at 300K, 400K, and 500K, the numbers of samples to average at every time in time correlation function are around 10,000; 6,000; and 3,000 samples, respectively. The log-log plot of time correlation function obtained from KMC simulation is presented in Figure 3.23.

By comparing the result of $G(t)$, a comparison between continuum theory, experimental observation, and the KMC model can be made. The experimental result, consistent with continuum theory, suggested that the time correlation functions of step fluctuations on vicinal Cu(111) surfaces are closely proportional to $t^{1/4}$, indicating that the mass transport is dominated by adatom diffusion along the step edge.^{35,38} However, as shown in the log-log plot, the time correlation functions that I obtained still do not fit perfectly the expected value. At 300 K, I found $G(t) \propto t^{0.54}$ and $G(t) \propto t^{0.46}$ for step A and step B, respectively. At 400 K, I found $G(t) \propto t^{0.47}$ and $G(t) \propto t^{0.33}$ for step A and step B, respectively. And at 500 K, I found $G(t) \propto t^{0.26}$ and $G(t) \propto t^{0.11}$ for step A and step B, respectively. Moreover, the shape of the time correlation functions is still rough, which indicates that the samples are still not statistically enough, thereby they still suffer from large uncertainty.

I considered two possible origins of the inconsistency in the time exponent of the correlation function: the insufficiency of samples and the finite size effect. In the report of STM measurement of step and island dynamics by

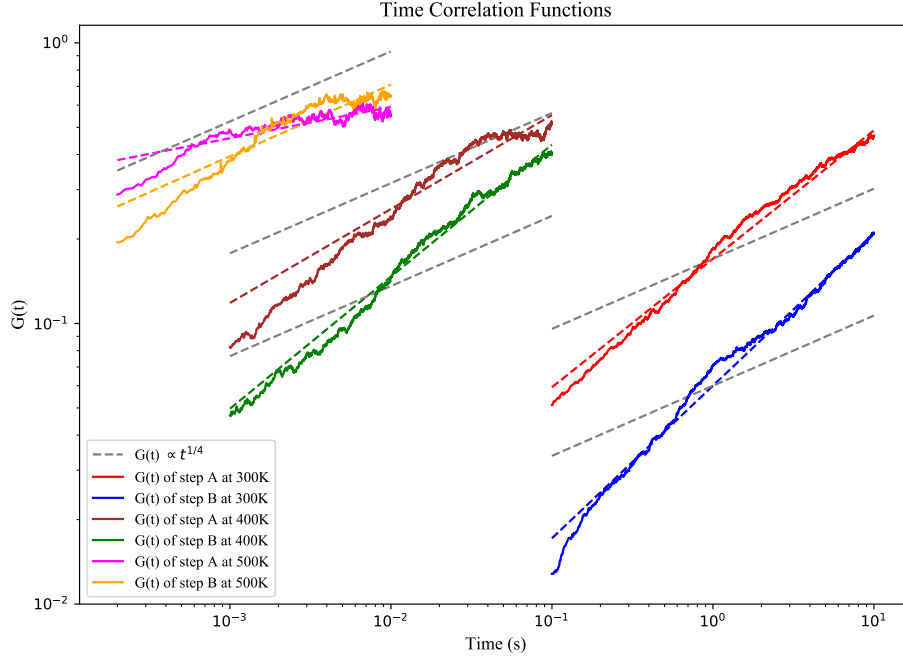


Figure 3.23: The log-log plot of time correlation functions of step A and step B at various temperatures. The colored solid lines represent the time correlation functions obtained from KMC simulations at specific temperatures, while the dashed line with same color represent the corresponding power fitting. The grey dashed lines represent the expected power law behavior, in which the $G(t)$ is proportional to $t^{1/4}$.

Giesen [24], she emphasized that statistically relevant experimental data on time correlation function require very large dataset. Further, the finite size effect or short length of step in the simulation will inhibit the variations in the kink density. Such low variations produce large errors in the step correlation function since realistically the kink density should vary in different surface area. As a rule of thumb, it is suggested to analyze up to several μm long step to obtain statistically relevant data on the step correlation function [24]. Unfortunately, the length of the model of the step analyzed in each unit cell is just around $0.01 \mu\text{m}$, which is far from the rule of thumb. Moreover, as also discussed in the earlier paragraph, the finite size of the length step introduces the deviation in the kink density which eventually affects the time correlation function as well. In the present simulation, the choice of step length is based on the consideration of the computational cost, since bigger model needs more expensive computational cost.

Aside from the limitation of the present KMC model, I also consider the possibility of the error from DFT and CE to be the source of deviations in the

measurement of time correlation function. However, I think that such error will not lead to the significant error such as altering the dominant mass transport. In the KMC algorithm, the process with higher rate (or lower activation energy) will always be given higher chance to be executed. Based on the calculations of the activation energy, the lowest activation energies are owned by the processes involving the detachment by adatom, specifically from the adatom at the terrace as shown in Figure 3.7. However, such generation of detached adatom requires high activation energies thus is considered as random event especially in the equilibrium condition. The next process with lowest activation energy is owned by the diffusion of the adatom along the step edge which then should become the dominant mass transport process.

3.4 Conclusion

In this study, first principles calculations and kinetic modelling are combined in the form of DFT-KMC simulation to investigate the equilibrium fluctuations of steps on Cu(111). A model stripe-like Cu islands which consist of step A, step B, and terrace of Cu(111) are used. In order to include explicitly all possible structures generated during simulation, a CE framework is implemented by including various fcc and hcp clusters as a basis set.

Based on investigation on 13 different diffusion events that might occur during the step fluctuations, I found that the energetics obtained from CE framework reasonably agree with direct DFT calculations. The results of activation energy calculations show that the diffusion of adatom along the step edge has considerably low barrier, thus can be expected to be dominant in the mass transport process during step fluctuations. I also found that the trend of activation energy in the case of adatom emission from the corner is proportional to the number of changes in bonding for step A, but not for step B. On the other hand, the trend of activation energy in the case of adatom attachment to the corner kink site is proportional to the number of changes in bonding for both step A and step B. Additionally, I investigated the diffusion of adatom through exchange mechanism and the diffusion related to one dimensional Ehrlich-Schwobel barrier.

Finally, I have calculated the time correlation functions of equilibrium step fluctuations at 300 K, 400 K, and 500 K. However, the results show that the time correlation functions still do not fit the $t^{1/4}$ as suggested from the theory.

The two main reasons are the insufficient number of samples and the low variation in kink density caused by the short length of the step.

Chapter 4

Elucidation of Cu-Zn Surface Alloying on the Cu(997) Surface

4.1 Introduction

The catalysts based on metal-alloys are well recognized in the world of heterogeneous catalysis considering the emerging of unique properties upon alloying [84, 85]. Given the optimal composition and environment, these catalysts can offer high catalytic performance that outperform their alloy constituents. There have been notorious examples on the application of metal-alloy based catalysts in heterogeneous catalysis [86–89]. In the present study, I focus on Cu-Zn surface alloy which has been reported to be very active for methanol synthesis by hydrogenation of CO₂ [6, 90]. Experimental studies have shown that the deposition of Zn on Cu(111) promotes the activity of methanol production by an order of magnitude at Zn coverage of 0.197 [16]. In addition, the Cu-Zn alloy has been reported as a good model of Cu/ZnO/Al₂O₃ (CZA) [6, 17], the industrial catalyst used to synthesize methanol by hydrogenation of CO₂ [5]. Thus, this alloy has been extensively involved in the investigation of the true active site of CZA which remains under controversy [6–9, 17–20].

In many previous computational studies, the Cu-step surface decorated with Zn atoms were assumed as the surface model and became part of the rationalization of the experimental results [6, 7, 18, 91, 92]. The introduction of the surface defects (e.g., steps and kinks) in the computational model is based on previous computational and experimental studies which found that they play critical role in improving the catalytic activity [6, 93, 94]. Meanwhile, the addition of Zn to the Cu-steps also gives improvement in the catalytic activity as suggested by calculations [6, 18], however, the basis of assuming

attached Zn at the rigid step edge has not been clearly justified due to the challenge in capturing the true surface property under reaction condition. In fact, the STM experiments by Sano et al. indicated that most of Zn atoms are eventually substituted homogenously into the terrace instead of localized at the step edge under vacuum condition [95]. Further, it is well known that the Cu step-adatom migrates intensively along the step edge, resulting in step fluctuation even at room temperature [23, 24]. The assumption of the perfect step edge will also become invalid if the presence of adsorbates induce the reconstruction of the surface, the phenomenon that has been evidenced by various studies [25, 96–100]. Therefore, the understanding of the realistic catalyst's surface is essential to provide good assumption of the surface model and better interpretation of experimental data.

Another motivation of the present study is to rationalize the formation of the Cu-Zn alloy. Experimentally, it was clearly shown that the alloying is initiated at the upper terrace near the step edge before distributed randomly at the middle terrace [95]. The mechanism to allow Zn propagation from upper to middle terrace was proposed to be the local-exchange between Zn and neighboring Cu atoms. However, the confirmation of such proposal (i.e., the occurrence of local-exchange) have remained elusive due to the challenge in capturing the fast and rare atomic events during the alloying. In fact, based on DFT calculations, I found that such local-exchange should be impractical even with the condition of high temperature, as it is required to overcome barrier of more than 2 eV (see Section C.4). Therefore, I am motivated to revise the existing proposal and improve the current knowledge of the alloying process.

The atomic-level observation of the surface alloying in principle can be achieved through dynamic simulation of surface under relevant working conditions. Given the active development of machine-learning in material science [49], it is now possible to construct machine-learned force-field with first-principles accuracy in exchange of computationally demanding ab-initio molecular dynamics. Some of the works have been successfully applied in the dynamic simulation of Cu-based catalysts [101–104]. In this framework, it is highly desirable to obtain the accurate force-field with minimum number of costly first-principles calculations. Thus, strategies called active-learning and on-the-fly learning has been progressing in recent years [105]. The active-learning (or self-learning) framework allows the model itself to automatically selects the datapoint to be included in the database while the

on-the-fly learning allows the iterative improvement of the model during simulation. These strategies are often coupled to obtain accurate force-field based on compact database containing only the most representative structures. For instance, the Stochastic Surface Walking (SSW) global optimization, which can efficiently locate the structures in Transition State (TS) region, is used to generate important datapoints to be appended in the database, thereby allow to improve the NN potential iteratively during training [106–108]. This framework has successfully treated the complex PES involving high energy barrier such as catalytic reactions and phase transitions. Another implementation is achieved by means of Query by Committee (QbC) framework, in which multiple NN models are combined to seek for the disagreement that is used to give error estimate of the prediction [109]. The structures that have highest disagreement are then treated as important datapoints to be included in the database. Alternatively, the reliable uncertainty estimation can be directly calculated within the Gaussian Process (GP) framework in the form of standard deviation (σ). This uncertainty is an intrinsic part of the framework and can be readily used with on-the-fly and active learning schemes. The GP-based framework has been successfully applied to build efficient force-field for investigating melting points⁴¹, phase transition of hybrid perovskites [110] and atomistic rare events [51].

Recently, it was reported that by coupling Molecular Dynamics (MD), active-learning, and automated event detection, Lim et al. have successfully reveal the restructuring mechanisms of Pd deposited on Ag [111, 112]. By adopting similar methodologies, I performed MD simulation of Zn depositions on Cu(997) surface to explicitly capture the mechanisms that are responsible to the Cu-Zn surface alloying. The MD simulations were implemented based on force-field that was trained by means of Gaussian Process (GP). The database, containing information of atomic forces acting on various environments, were obtained from DFT calculations. The task of training was done by using Fast Learning of Atomistic Rare Events (FLARE) code which utilizes the uncertainty information from GP, together with active on-the-fly learning scheme to build the force-field efficiently [51].

The rest of this chapter is organized in the following manner. In Section 4.2, I provide the computational details on the DFT, GP and MD method that I used. In section 4.3, I present and discuss the results on the database used to build GP force-field, the structures and the time evolution of the alloy as obtained by MD. In section 4.4, I discuss the mechanistic analysis of surface

reconstruction. Finally, in section 4.5, I summarize and conclude the findings.

4.2 Computational Details

I used DFT calculations to provide forces of the central atom on each atomic environment. All DFT calculations were performed using the STATE code [66, 67]. The electron-ion interaction was described by ultrasoft pseudopotentials [72]. The convergence threshold for energy is set to 10^{-9} Ha/atom. I took into account the van der Waals (vdW) interactions by applying optB86b-vdW exchange correlation functional [68] as implemented in the STATE code [69]. The lattice constant and surface energy of Cu(111) are calculated to be 3.6102 Å and 1.88 J/m², respectively. These values are in good agreement with experimental values of Cu lattice constant (i.e., 3.6149 Å) [113] and surface energy of Cu(111) (i.e., 1.83 J/m²) [114], thus confirming the reliability of the chosen functional. Detail on surface energy calculation can be found in the Section 1 of Appendix B.

To construct GP force-field, I used FLARE code with two- and three-body multi-species kernels [51]. The interaction cutoffs for two- and three-body kernels are set to 7.0 Å and 4.5 Å, respectively. The hyperparameters embedded to these kernels, namely two-body signal variances ($\sigma_{s,2}$), two-body length scale (l_2), three-body signal variances ($\sigma_{s,3}$), three-body length scale (l_3), and noise hyperparameter (σ_n) was optimized by maximizing the log marginal likelihood using BFGS algorithm as implemented in SciPy [115] used inside the FLARE code. The database is constructed by employing active and on-the-fly learning scheme that update the database based on uncertainty information calculated by GP. In order to provide new atomic environments to be candidate for the database, MD code internal to FLARE is used to evolve atomic structures with 1 fs timestep within canonical (NVT) ensemble. The temperature is set up at 700 K with all atoms are allowed to move. To obtain more diverse atomic environments, I manually changed the initial structure after certain MD steps during the on-the-fly learning when no significance improvement in the Mean Absolute Error (MAE) was found. The details of this procedure and the resulting database are reported in the next section. When the GP database is completed, the two- and three-body mean predictions are mapped onto cubic spline models using Mapped Gaussian Process (MGP) method [116] with uniform 64 control points and 20 x 20 x 20 grid of control points for the two-body mean function and the three-body

mean function, respectively. The resulting MGP potential is then used as pair-style in large-scale MD simulation code, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [117], by which I performed MD simulations within NVT ensemble with timestep 5 fs.

The analysis of MD simulations to extract the non-equilibrium information is built using combination of home-made Python code [empty citation], Ovito [118], and Atomic Simulation Environment (ASE) [119]. Clamping the atoms to the particular sites are necessary to ease the analysis process by removing the thermal noise [111, 112]. Thus, in this study, I clamped all the atoms to the nearest fcc sites based on the structure of Cu. All the MD images shown in this work were already clamped to aid the understanding of the alloyed structure. The images depicting Cu and Zn atoms were generated using Ovito.

4.3 Results and Discussion

4.3.1 Construction and Evaluation of Training Database

I constructed the database using active and on-the-fly learning scheme as implemented in FLARE code. Each data-point in the database is a local atomic environment with corresponding atomic forces. Specifically, an atomic environment constitutes all two-body and three-body clusters found within certain cutoff radius from a central atom, which I specified to be 7 Å and 4.5 Å for two-body and three-body cutoff, respectively. Within active and on-the-fly learning scheme, the new data containing local atomic environment and the associated force is appended to the database whenever the uncertainty is higher than a specified threshold. The new atomic environments are continuously generated from the MD simulations based on the iterative updating of GP force-field. In more detail, the procedure to construct the database is as follow.

- (i) First, I constructed four layers of Cu(111) surface (Figure 4.1a) which represents the most common environment in the Cu(997) surface. The atomic forces of this structure are then calculated by DFT and some atomic environments are randomly selected to populate the empty database.
- (ii) Next, the resulting database is used in the GP framework to construct the temporary force-field used in MD simulation. The MD within NVT ensemble is used to generate new trajectories at temperature 700 K based on Cu(111) as

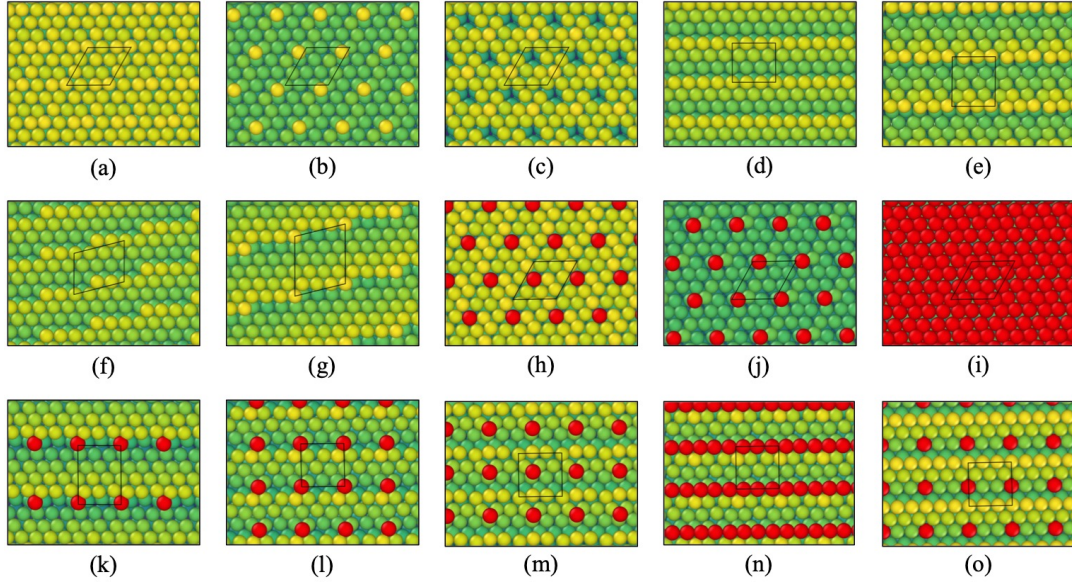


Figure 4.1: . The parent structures used in the simulation: (a) Cu(111), (b) Cu(111) with Cu adatoms, (c) Cu (111) with vacancies, (d) Cu(221), (e) Cu(211), (f) Cu(111) with kinked step edge of (100) microfacet, (g) Cu(111) with kinked step edge of (111) microfacet, (h) Cu (111) with substituted Zn atoms, (i) Cu(111) with Zn adatom, (j) Cu(111) with Zn overlayer, (k) Cu(211) with Zn adatom attached to step edge, (l) Cu (221) with Zn adatom attached to step edge, (m) Cu(221) with diffusing Zn adatom at upper terrace, (n) Cu(221) with Zn step adatoms, (o) Cu(221) with Zn adatom incorporated near step edge. The green to yellow color indicates Cu atom while red color indicates Zn atom. The black box shown in each figure depicts the unit cell of the structure.

the initial structure. Such initial structure is what I call parent structure since it is used to generate additional structures as candidate for the database.

(iii) At each MD step, all the atomic environments found in the trajectory are examined. If the uncertainty of the environment is higher than the noise hyperparameter (σ_n), the DFT calculation is performed and such environment with the corresponding atomic forces is appended to the database. Otherwise, the database is not updated and the MD step continues. All the hyperparameters embedded in the kernel (i.e., $\sigma_{s,2}, l_2$, $\sigma_{s,3}, l_3$, and σ_n) are re-optimized whenever the database is updated. This routine is implemented in the FLARE code. More detail on the equations used to calculate force and uncertainty, updating hyperparameters, and the description of the data-points include in the database can be found in the reference [51] and also in Chapter 2.

(iv) Since the MD simulation of the Cu(111) is not sufficient to capture the vast variation of the environment in the target structure (i.e., Zn-Cu(997) surface), I gradually increase the complexity of the parent structure with

features such as steps, kinks, and Zn atoms. All the structures consist of four layers with at least 30 Å vacuum region between two neighboring slabs in z-direction. The top view and the corresponding unit cell of the parent structures are depicted in order in Figure 4.1. The training is performed sequentially through all these parent structures. For instance, after no high-uncertainty structure is found using the first parent structure (i.e., Cu(111) surface), then the parent structure is replaced with the more complex one (i.e., Cu(111) surface with adatom) and then stage (ii) and (iii) are repeated. In total the training data consisting of 301 environments that have passed 15 parent structures in Figure 4.1 are obtained.

(v) To further search for the local environment that possibly appear during Zn alloying on Cu(997), I significantly enlarge the size of parent structure to four layers Cu(221) surface with five step edges and 15 atoms in every row per unit cell, as shown in Figure 4.2(a-c). This model is chosen since it has denser steps, thereby allowing more step-edge related events to happen. I then deposited Zn on top of the surface and let the system evolve within NVT ensemble at 700 K for 300 ps. The evolution of this structure is shown in Figure 4.2(d-f). The environments of the moving atom in the resulting trajectories are sampled and their uncertainties are calculated. I then manually added 25 more environments with highest uncertainty to the database. Each of these new environments has 7 Å cutoff radius from the central atom. Due to the expensive cost of DFT calculation, I could not perform DFT calculation on this large system. Instead, I sliced the region near the central atom of the atomic environment to obtain smaller unit cell (15.32 Å x 15.32 Å x 30 Å) and do the DFT calculation based on this small cell.

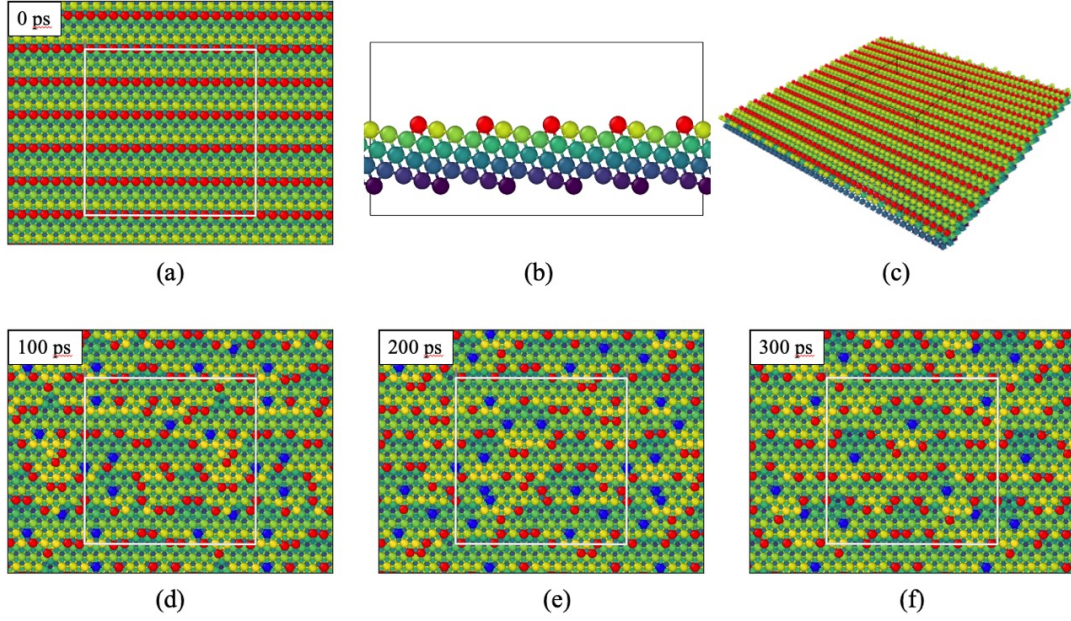


Figure 4.2: (a) Top view of Cu(221), (b) Side view of Cu(221), (c) Perspective view of Cu(221), (d-f) Snapshots of MD simulation at 100 ps, 200 ps, and 300 ps of Zn-deposited on Cu(221) within NVT ensemble at 700 K. The green to yellow atom indicates the Cu atoms, the red atom indicates Zn as adatom, and blue atom indicates substituted Zn atom. The box shown in each figure depicts the unit cell of the structure.

In the end of training, the final database consists of 326 atomic environments. The final optimized GP hyperparameters are $0.125 \text{ eV}/\text{\AA}$ for two-body signal variances ($\sigma_{s,2}$), $0.001 \text{ eV}/\text{\AA}$ for three-body signal variances ($\sigma_{s,3}$), $0.750 \text{\AA}$ for two-body length scale (l_2), $1.068 \text{\AA}$ for three-body length scale (l_3), and $0.037 \text{ eV}/\text{\AA}$ for the noise hyperparameter (σ_n).

To evaluate the accuracy of the force-field, I compared the GP vs DFT barriers of various elementary events including pop out and vacancy insertion, step crossing, direct exchange, indirect-exchange, and local exchange mechanism as defined in Table B.1-B.5 of the Appendix B. The comparison between DFT and GP barriers are shown in Figure 4.3. The MAE of barriers of elementary events involving Cu as active atom (indicated by black indices in Figure 4.3) and elementary events involving Zn as the active atom (indicated by red indices in Figure 4.3) are calculated to be 70 meV and 88 meV, respectively. I noted that in the active and on-the-fly learning employed in this work, I do not explicitly search for the TS region. The main principle of the learning scheme employed in this work is to selectively include the structures with high uncertainty that is calculated within the GP framework (see equation (2) in Appendix B). In the case of more complicated PES such as in phase

4.3. Results and Discussion

transition and chemical reactions, method such as Stochastic Surface Walking (SSW) can be used to sample the PES efficiently at the TS region, thus help to improve the consistency of the barrier between DFT and the force-field [106–108]. Aside from the barrier, I also calculated the MAE of the force in the transition states structures and found the MAE to be 14 meV/Å, as shown by the parity plot at the middle bottom of Figure 4.3.

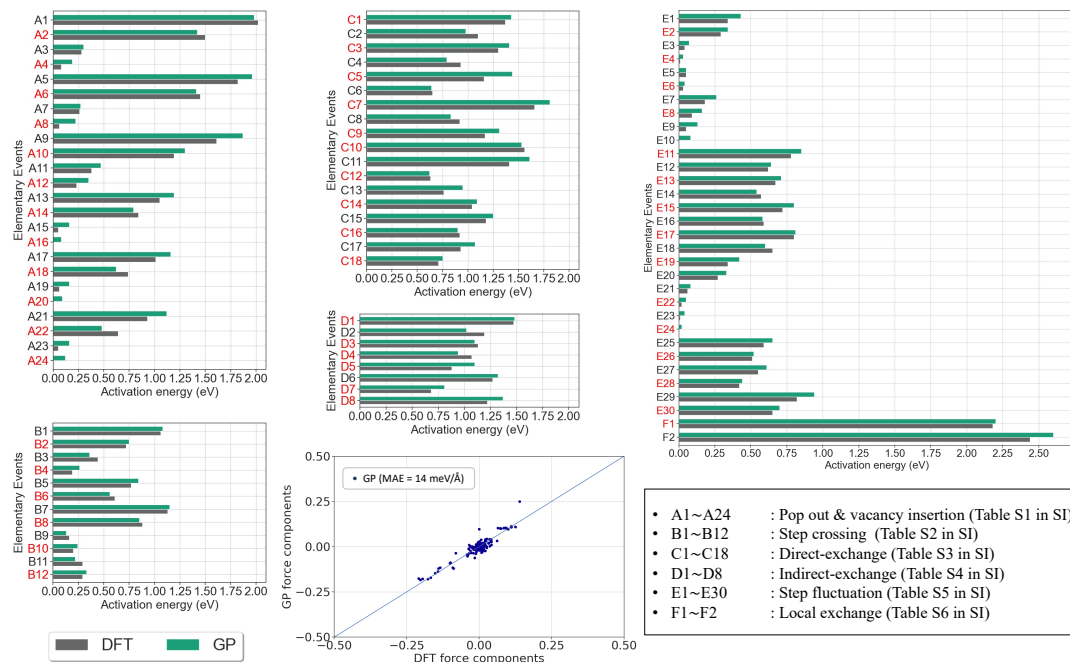


Figure 4.3: Activation energies obtained from DFT and GP for elementary events Cu atom (indicated by black indices) and Zn atom (indicated by red indices). The parity plot presented in the middle bottom shows the comparison between DFT and GP forces of the transition state structures in each investigated elementary event.

In addition, I calculated the force component's MAE of 357 environments with highest uncertainty found in 2 μ s MD simulations of more realistic Zn-deposited Cu(997) surface. The Cu(997) structure has six layers and consists of 2352 atoms with two step edges and 20 atoms in every row per unit cell. The top and side views of such surface are shown in Figure 4.4a and Figure 4.4b, respectively. The three bottom-most layers are fixed with the lattice constant obtained from DFT calculation (i.e., 3.6102 Å), which is in good agreement with the experimental lattice constant of Cu (i.e., 3.6149 Å) [113]. To provide the DFT forces, I again sliced the original unit cell of Cu(997) near each central atom to obtain smaller cells containing the environments with the highest uncertainty. These smaller cells then are used in the DFT calculations with periodic boundary condition. I obtained the resulted MAE to be 89 meV/Å. The parity plots are presented in Figure 4.4c.

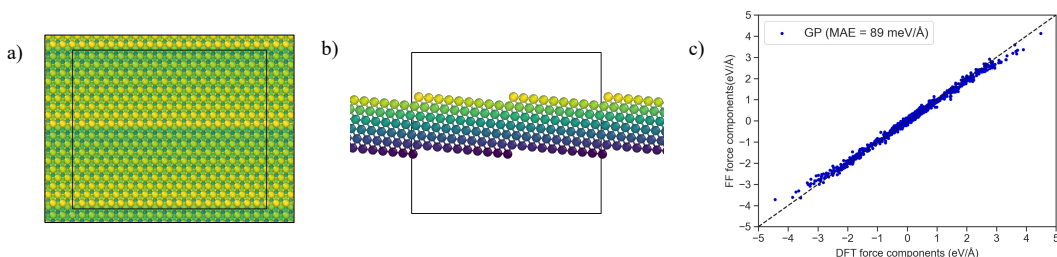


Figure 4.4: (a) The top view of the Cu(997), (b) The side view of the Cu(997), (c) The parity plot showing the GP and DFT atomic forces of the center atoms in the environments with the highest uncertainties. The validation set consists of 1071 data points which correspond to x, y, and z force component of each center atom in the 357 environments with highest uncertainty found in 2 μ s MD simulations of more realistic Zn-deposited Cu(997) surface.

4.3.2 The Evolution of Deposited Zn atoms on Cu(997)

Preparation of the Surface

In order to observe the formation process of Cu-Zn surface alloy, I performed MD simulations of Cu(997) surface with 0.19 coverage of deposited Zn atoms. Such Zn coverage has been observed in experiment to give optimum Turn Over Frequency (TOF) for methanol synthesis [16, 90]. There are two terraces and two step edges for each unit cell as indicated in Figure 4.5a. The Zn atoms are then deposited randomly on top of the surface at 300 K (Figure 4.5b). After the equilibration for several ns, I found that the randomly distributed Zn atoms either attach to the step edges or form Zn islands on the upper terrace (Figure 4.5c). Such structure is in good agreement with the STM observation that suggested the localization of Zn atoms around the

step and the formation of small Zn islands on the terraces after Zn deposition [95]. After that, I raised the temperature into 550 K and again equilibrate the surface for 20 ns. The island of Zn atoms is then collapse and majority of the Zn atoms now attach to the step edge though some others, in the form of diffusing atoms, still can be found at the terrace (Figure 4.6a). This surface structure was then used to observe the Cu-Zn surface alloying process at 700 K.

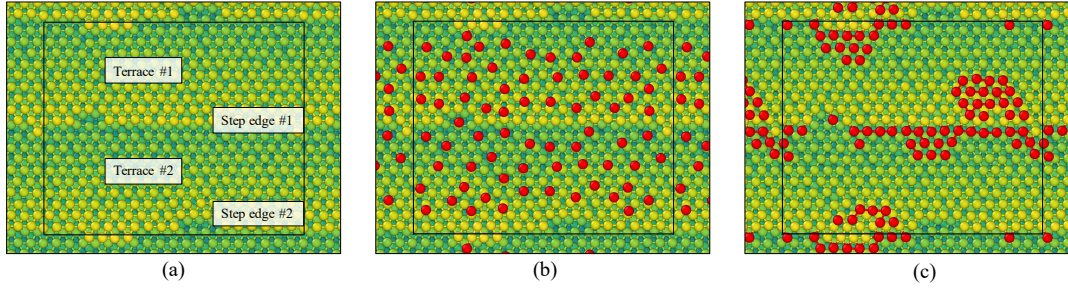


Figure 4.5: The preparation of the Zn-deposited Cu surface. The green to yellow atom indicates Cu atom while the red atom indicates Zn atom. (a) The clean Cu(997) surface with the step and kink features obtained after annealing. (b) The Zn atoms are randomly deposited on the clean surface at 300 K. (c) Some of the Zn atoms attach to the step edge while some others agglomerate into small islands at the upper terrace.

Surface Profile (MD Frames)

To observe the alloying process of Cu-Zn, I performed MD simulations within NVT ensemble at temperature 700 K for up to $6.25 \mu s$. Figure 4.6(a-f) shows the evolution of deposited Zn atoms on Cu(997) until the Cu-Zn surface alloy is formed. To clearly observed the number of Zn atoms that substituted at the terrace, I also plotted the composition of Cu and Zn atoms as a function of rows for every certain timesteps. Such plots accompany each MD snapshots in Figure 4.6(a-f). The snapshots of the MD simulation are also presented as video in the Appendix B.

In the beginning (Figure 4.6a), the Zn atoms are found to localize at the step edge, covering the original Cu step adatoms. The profile of boundary between Cu and Zn is still fairly linear. After $1.25 \mu s$, some of the Zn atoms are incorporated at the upper and lower terrace near the step edge (Figure 4.6b). At this stage, almost no Zn atoms are incorporated at the middle terrace. I also noticed Zn atoms are dominantly incorporated to the upper terrace whereas only few incorporated Zn atoms found at the lower terrace. After

2.5 μs (Figure 4.6c), the distribution of the Zn on the surface and the number of incorporated Zn atom are still relatively similar.

The change in the percentage of Zn adatom vs Zn incorporated over time is shown in Figure 4.7a. Shortly after the deposition, almost all Zn atoms are in the state of adatom as indicated by the contrast percentage between Zn adatom and incorporated Zn at the early time. The Zn atoms then incorporate the Cu surface over time, decreasing the percentage of Zn adatom until nearly half of the original number. The change in percentage is shown to be saturated around 2 μs but the fluctuation is clearly observed in the following time. This indicates that the interchange between Zn adatom and incorporated Zn still actively occur during the simulation.

I found shallow incorporation of Zn to the subsurface layer, for instance, at time 1.25 μs (Figure 4.6b) and at time 3.75 μs (Figure 4.6d). However, the subsurface incorporated Zn cannot penetrate further to the bulk and eventually they transform back into adatom or surface atom as indicated by succeeding snapshots. This is consistent with the experimental finding in which no dissolution of Zn to the bulk was observed [95]. At 6.25 μs , finally I found some of Zn atoms are incorporated at the middle terrace (Figure 4.6f). The trend observed in this simulation thus suggests the alloying is initiated at the upper and lower terrace near the step edge, before taking place at the middle terrace at the later time. At the end of simulation, 2 out of 72 Zn atoms (2.78 %) are desorbed from the surface.

To see the distribution of incorporated Zn atom more clearly, I show in Figure 4.7b the distance of the incorporated Zn atoms relative to the step edge at 6.25 μs . As shown in the figure, most of the Zn incorporates the surface at the region near the step edge, which indicate that the alloying dominantly occurs near the step-edge and thus the step-edge plays important role in the alloying. Sano et al. observed that the alloying of Cu-Zn at or above 523 K leads to the homogenous distribution of Zn into the Cu(111) surface layer [95]. However, since the MD simulation requires short time step, it is infeasible to simulate the alloying at the time scale longer than what I have performed (i.e., 6.25 μs). Thus, I was not able to reproduce the homogenous distribution of the Zn into the Cu surface. The simulation with longer timescale can be achieved, for instance, with Kinetic Monte Carlo (KMC) simulation [37]. Nevertheless, I managed to observed the incorporation of Zn atoms and elucidate the corresponding mechanisms. I also list DFT barriers of various elementary events (see Section 3 of Appendix B) that contribute to the alloying,

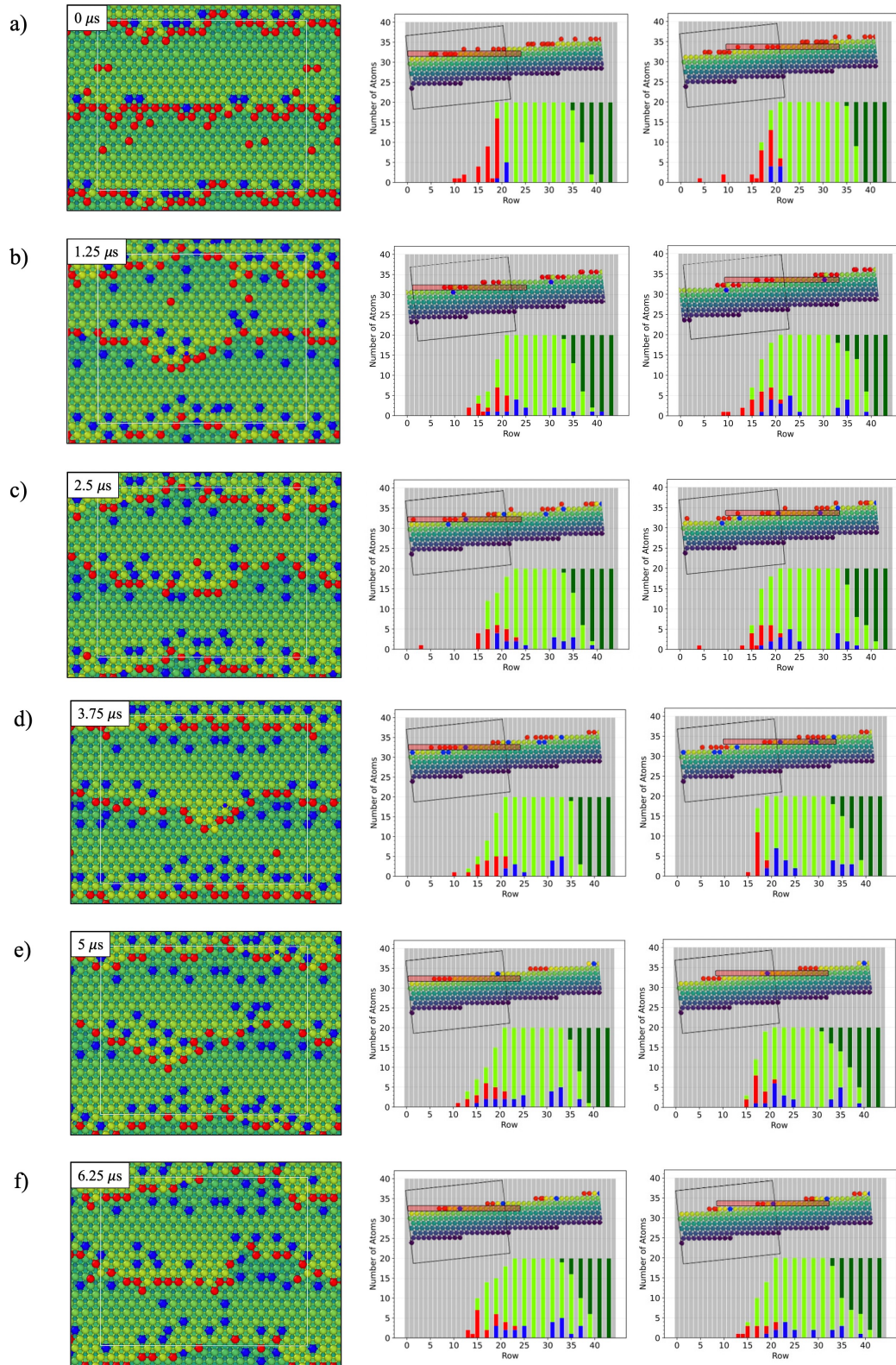


Figure 4.6: The snapshots of MD simulations showing the evolution of deposited Zn atoms on Cu(997) at 700K. The green to yellow atom indicates the Cu atom, the red atom indicates Zn as adatom, and blue atom indicates substituted Zn atom. The two plots accompanied each snapshot show the composition of atom as a function of row. In each plot, the red, blue, light green, and dark green bars indicate the number of Zn as adatom, Zn as incorporated atom, Cu as surface atom, and Cu atom which is covered by additional Cu or Zn layer.

which can be used as parameters in the KMC. More detail discussion on the mechanistic aspect of the alloying and the role of step edge are presented in the next section.

The distribution of the Zn coordination number at 6.25 μs , accounting all the Zn bonding with other Cu and Zn neighboring atoms, is shown in Figure 4.7c. Almost all the incorporated Zn atoms have nine coordination number which indicate that they stay at the surface. Few of the Zn atoms have coordination number of ten and eleven, which means that they are almost buried by the surface atoms. On the other hand, the coordination number of Zn adatom varies from three to eight as they are distributed along the wavy step edge. Figure 4.7d shows the coordination number of Zn atoms at the 6.25 μs , but accounting only the Zn-Zn coordinations. The histogram depicted in the figure shows that the Zn is mostly surrounded by the Cu atoms and thus there is no significant Zn-Zn interaction in the resulting alloy, consistent with the analysis from STM observation [95].

4.4 Alloying Mechanism

In this section, I discuss in detail the alloying schemes of Zn that was observed during MD simulation. These schemes describe how the Zn in the form of adatoms turn into incorporated atoms, thus ‘alloyed’ into the surface. I categorize the schemes based on three regions where the incorporation occurs: upper terrace, lower terrace, and middle terrace. I also show examples of each in-operation scheme that were observed during simulation.

Alloying at Upper Terrace

Alloying at the upper terrace is dominant in the early stage of alloying, which is mainly caused by two factors: the localization of Zn at the step edge after the deposition and the fluctuation of the step adatoms. The observation of Zn alloying at upper terrace as the initial alloying stage was also reported by Sano et al. by means of STM observations [95]. Based on the simulation, I found three schemes responsible to the alloying at this region: (i) vacancy-insertion at upper terrace, (ii) exchange-descend, and (iii) confinement by other step adatoms. The characteristics of these schemes are described as follow.

(i) Vacancy insertion at upper terrace

Vacancies at upper terrace might be formed by means of detachment of step

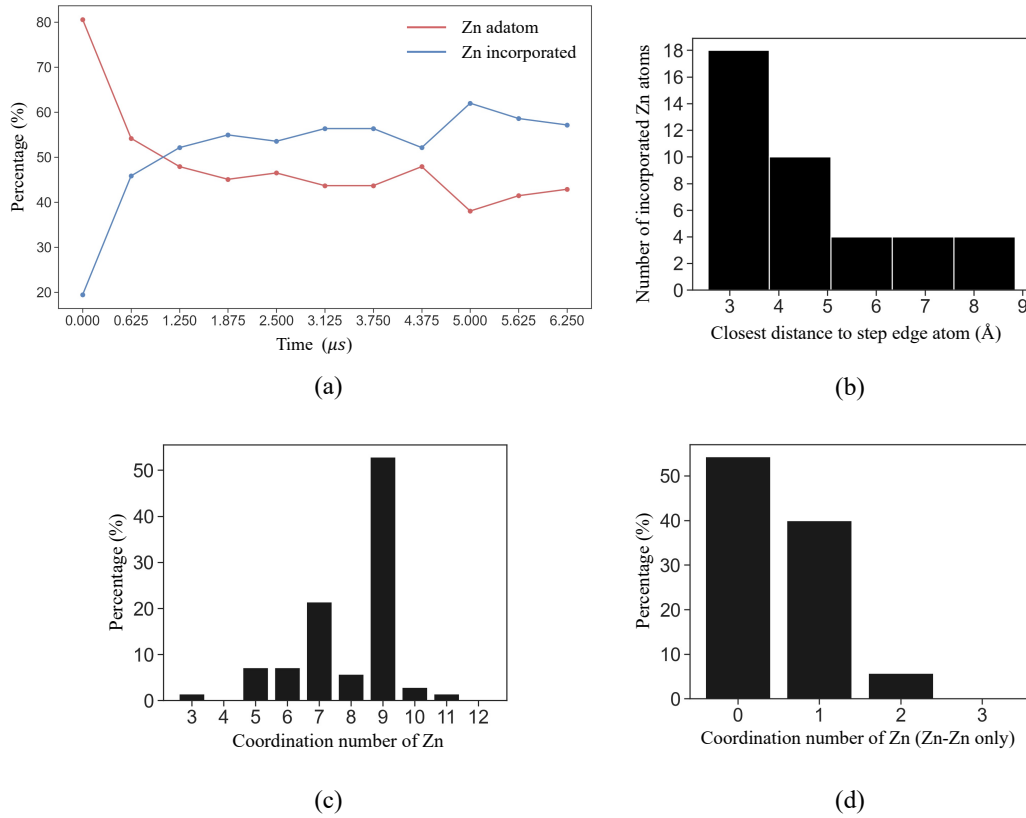


Figure 4.7: The analysis of the structure of Cu-Zn surface. (a) The change in percentage of Zn adatom vs Zn incorporated over time. (b) Histogram of the relative distance between incorporated Zn atoms and the step edge. (c) The distribution of the Zn coordination number, accounting the Zn bonding with other Cu and Zn neighboring atoms. (d) The coordination number of Zn atoms but accounting only the Zn-Zn coordinations.

adatom or the pop out of surface atom. Such vacancy may occasionally preserve for certain time period and attract the nearby Zn adatom. By using simplified model, I calculated the barrier of the vacancy formation by detachment of Cu and Zn adatom from the step edge to be 0.80 eV (event No. E17 in Table B.5) and 0.65 eV (event No. E18 in Table B.5), respectively. Meanwhile, the barriers to form the vacancy through the atom pop out at upper terrace are higher, as I found more than 1 eV barrier for both Cu and Zn pop out (event No. A5 and A6 in Table B.1).

I observed that there are several ways for Zn atom to occupy the vacancy: lateral-exchange, vacancy hopping-descend/simple-vacancy insertion, and vacancy exchange-descend. In lateral-exchange, the step adatom diffuses away toward the lower terrace, subsequently leaves a vacancy which is then occupied by the nearby Zn step adatom (Figure 4.8a). In contrast with lateral-exchange, the vacancy hopping-descend (Figure 4.8b) and vacancy

exchange-descend (Figure 4.8c), requires the diffusing Zn adatom on upper terrace. The source of this terrace-adatom can be varied, for instance: Zn hopping ascend (event No. B2 in Table B.2), Zn exchange ascend (event No. 6 in Table B.2), and detachment of Zn step adatom from higher step edge (event No. E14 in Table B.5). Such mechanisms have barrier of 0.72 eV, 0.61 eV, and 0.57 eV, respectively. The Zn terrace-adatom is very unlikely to be formed by atomic pop out from upper terrace (event No. A6 in Table B.1) or middle terrace (event No. A2 in Table B.1) considering more than 1 eV barrier for both cases. The barrier of the vacancy insertion by Zn is typically small, thus, the energy cost of this scheme mainly comes from the formation of vacancy at upper terrace or diffusing terrace-adatom.

(ii) Exchange-descend

In this scheme, the Zn terrace-adatom near descending step edge pushes step-adatom underneath toward the lower terrace and then take its position (Figure 4.8d). The Zn exchange descend has modest barrier of 0.20 eV (event No. B10 in Table B.2) in the presence of straight edge, and slightly higher in the presence of kinked edge as I found barrier of 0.30 eV (event No. B12 in Table B.2). Despite the modest barrier, the exchange-descend also requires the Zn adatom to be on the upper terrace, similar with vacancy hopping-descend and vacancy exchange-descend.

(iii) Confinement by other step adatoms

Another alloying scheme at upper terrace is the confinement of Zn step adatom by the other Cu or Zn step adatoms (Figure 4.8e). It is well known that the Cu step-adatom migrates intensively along the step edge, resulting in step fluctuation even at room temperature [23, 24]. In addition, the previous STM observation also reported the increasing of density and waviness of step after the deposition of Zn [95]. By calculating the barrier of elementary events of step edge fluctuations (i.e., attachment and detachment of adatom to/from step edge), I found all the elementary events involving Zn atom (all events in Table B.5) have lower barrier than the pure Cu system, suggesting Zn atoms enhance the step edge fluctuations.

I identified 75 alloying events that take place at the upper terrace and counted the occurrence of the first and second schemes to be 12 and 44 events, respectively. Additionally, in all 75 alloying events, I found that the Zn atoms are eventually confined by more step adatoms for certain period of time, considering the high intensity of step fluctuation. Thus, I considered the third scheme (i.e., confinement by other step adatoms) as the dominant scheme for

the alloying at the upper terrace. The smaller percentage of the first and second schemes are attributed to the high barrier for the formation of vacancy and terrace-adatom on the upper terrace. Despite the high frequency, the third alloying scheme only results in the shallow Zn incorporation to the upper terrace, thus the alloyed Zn can easily transform back into step adatom when the confining atoms move away.

The alloying at upper terrace which is induced by step fluctuation and vacancy diffusion was found in the case of Mn alloying on Cu(100), suggested by STM images and Monte Carlo simulation [120, 121]. However, in contrast to Mn/Cu(100), alloying of Zn by the step fluctuation is not accompanied by the frequent alloying vacancy diffusions as evidenced by the low frequency of alloying by means of vacancy insertion at the upper terrace. I noticed that the Zn can be incorporated simply through confinement by fluctuating adatoms as shown in Figure 4.8e.

Alloying at Lower Terrace

The alloying of Zn at the lower terrace was found by means of STM observations by Bikaljevic et al. in the form of roughened area, which was interpreted as the intermixing region between Cu and Zn [122]. Similarly, I also observed the formation of alloy together with the associated alloying scheme at this region. I found three dominant alloying schemes for this case: (i) step-assisted direct exchange, (ii) vacancy insertion at lower terrace, and (iii) indirect-exchange mechanism. The characteristics of this scheme are described as follow.

(i) Step-assisted direct exchange

In this scheme, the Zn step atom kicks out the surface atom at the lower terrace and takes its position (Figure 4.9a). The kicked atom then might diffuse away or attach to the step edge. By DFT calculations, I examined three types of step-assisted direct-exchange. Type 1 is direct-exchange which is initiated by the Zn step adatom, resulting in the formation of Cu terrace adatom. Type 2 is direct-exchange which is initiated by Zn terrace adatom, resulting in the formation of Cu step adatom. Type 3 is direct-exchange which is initiated by Zn step adatom, resulting in Cu step adatom. The barriers of direct-exchange type 1, type 2, and type 3 (event No. C11, C13, C15 in Table B.3) are 1.41 eV, 0.76 eV, and 1.14 eV, respectively. Even though type 2 has the lowest barrier,

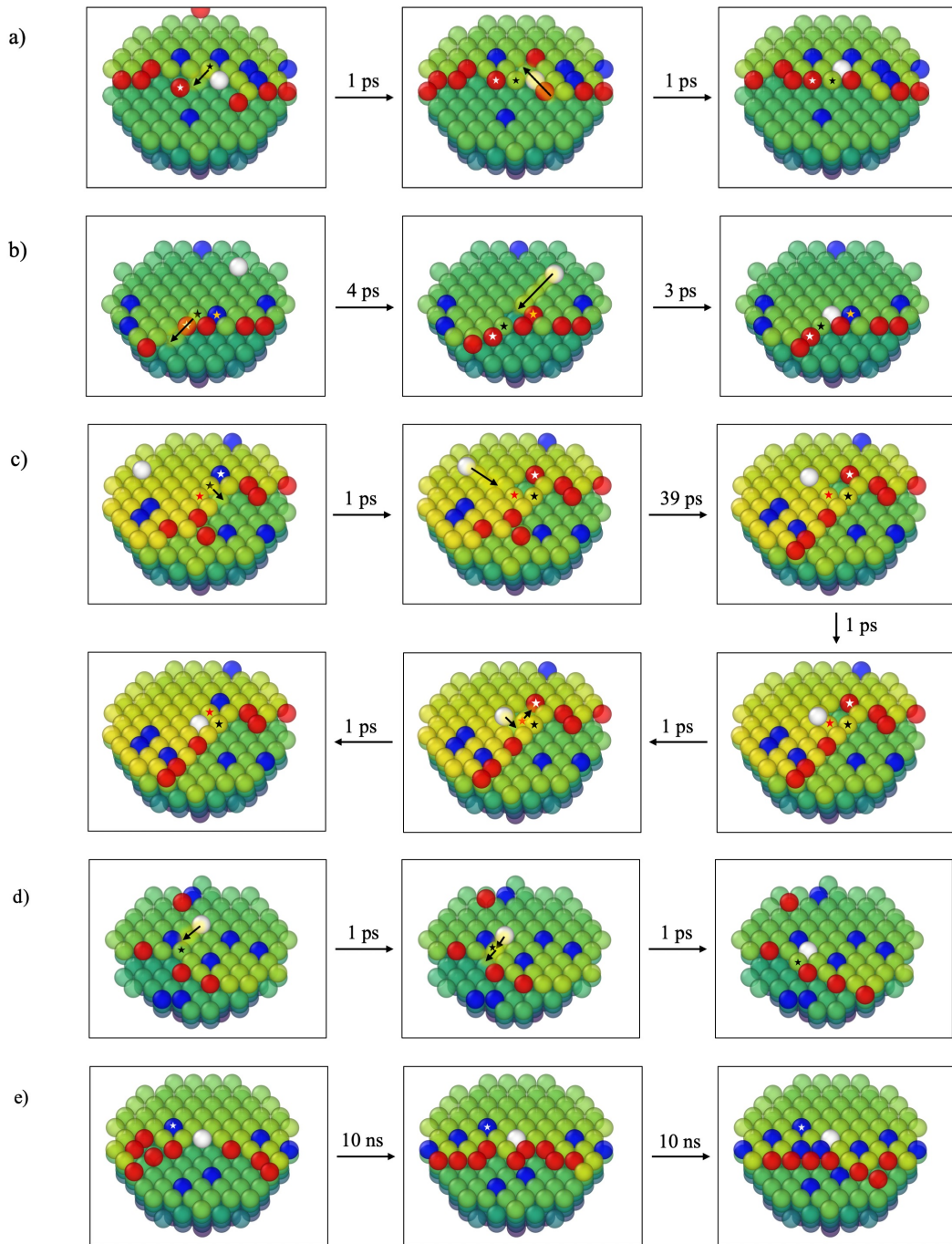


Figure 4.8: The alloying scheme at the upper terrace. (a) The temporary vacancy formed by detaching Cu step adatom is then occupied by nearby Zn step adatom. (b) The Zn atom fills the vacancy at the upper terrace by hopping descend. (c) The Zn atom fills the vacancy at the upper terrace by exchange descend. (d) The Zn atom descending the step edge by kicking another step adatom. (e) The Zn step adatom is confined by other step adatoms.

the requirement of Zn terrace adatom suppresses its occurrence since additional barrier to form Zn terrace adatom is necessary. In fact, all the step-assisted direct-exchange scheme that I found are closer to type 3 in which the

kicked Cu atom subsequently attaches to the step edge. I also observed the positive contribution of kink site to this scheme as I found the barrier reduces to 0.93 eV (event No. C17 in Table B.3). In previous study of the Pd-Ag alloy, the step-assisted direct-exchange scheme was found to predominantly occurs in the early stage of restructuring, in connection with small barrier of 0.29 eV of which the final state is more stable by around 1 eV for the mechanism at the lower terrace near the kink site [112]. In contrast, in the case of Cu-Zn surface alloying, the similar mechanism near the kink site has much higher barrier of 0.93 eV with the final state is less stable by 0.22 eV. This trend is in agreement with the cohesive energy of Cu and Ag, in which the Ag has lower cohesive energy (2.95 eV/atom) compared to Cu (3.49 eV/atom) [123].

(ii) Vacancy insertion at lower terrace

This scheme is initiated by the vacancy generated by the pop out of surface atom at the lower terrace. Once the vacancy is generated, the nearby Zn adatom at the step edge then fills the vacancy and hence alloyed into the surface (Figure 4.9b). In the case of straight edge, the barrier for Cu pop out (event No. 9 in Table B.1) and Zn pop out (event No. 10 in table B.1) from the lower terrace are very high: 1.61 eV and 1.19 eV, respectively. However, in the presence of the kinked edge, such barriers are significantly reduced to 1.05 eV and 0.84 eV for Cu (event No. A13 in Table B.1) and Zn (event No. A14 in Table B.1), respectively. This indicates the positive contribution of kink sites toward vacancy generations at lower terrace, mainly by stabilizing the final state of the popped atom. In addition, I found the Cu or Zn atom nearby other substituted Zn atoms has smaller pop out barrier to overcome. In the presence of two neighboring Zn atoms, the Cu and Zn pop out barrier (No. A21 and event No. A22 in Table B.1) are reduced to 0.93 and 0.64 eV, respectively.

(iii) Indirect-exchange

In this scheme, the Zn adatom influence the surface atom underneath to push adjacent surface atom out of the surface (Figure 4.9c). This scheme involves three atoms: one ‘initiator’ adatom and two ‘passive’ surface atoms. To estimate the barrier of this scheme, I performed DFT calculations using simplified structure as presented in Table B.4. Treating the diffusing adatom as the initiator and one pre-substituted Zn atom at the lower terrace, I found the activation energies to be 0.67 eV and 1.20 eV for forward (event No. 7 in Table B.4) and reverse (event No. D8 in Table B.4) processes, respectively.

By observing 60 alloying events at lower terrace within 5 μ s MD simulation,

I found the percentage of first, second, and third scheme to be 74%, 22%, and 5%, respectively. I also note that the scheme of step-assisted direct-exchange and vacancy insertion at lower terrace might have high similarity when the vacancy is formed near the active atom. Thus, I distinguished those schemes by the lifetime of the vacancy: if the lifetime of the vacancy is within 1 ps, I classified the scheme to step-assisted direct exchange; otherwise, I classified the scheme to vacancy insertion at lower terrace. In addition, I also found the incorporated atom at the lower terrace is buried by the fluctuating step adatoms, thus transformed into subsurface atom for a certain time period (Figure 4.9d).

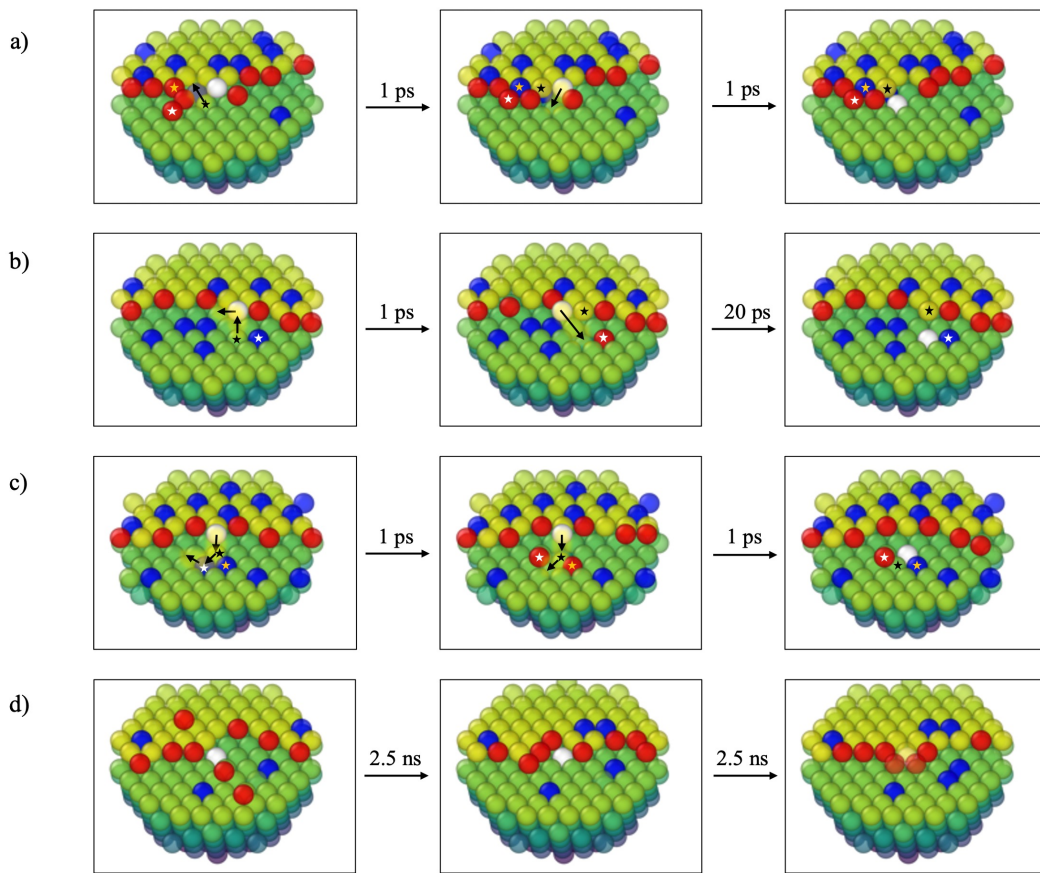


Figure 4.9: The alloying scheme at the lower terrace. (a) The Zn atom kicks out and takes the position of the Cu adatom underneath. (b) The Zn step adatom fills the vacancy at the lower terrace. (c) The Zn adatom influences the Cu adatom underneath to push adjacent Zn substituted atom. (d) The incorporated Zn atom at lower terrace is buried by other step adatoms.

Alloying at Middle Terrace

The homogenous substitution of Zn into the Cu surface after annealing at 560 K was reported by Sano et al. by means of STM observation [95]. I have performed the MD simulation for up to several μs but unfortunately, I could not reproduce such homogenous substitutions due to the slow process of the alloying. Even so, I still observed few incorporation of Zn atoms at the middle terrace and investigate the responsible scheme of the alloying. I found there are four schemes that contribute to the alloying at the middle terrace: (i) vacancy insertion at the middle terrace, (ii) wave deposition mechanism, (iii) confinement by other step adatoms, and (iv) indirect-exchange. The characteristics of these schemes are described as follow.

(i) **Vacancy insertion at the middle terrace** This scheme is similar with the other schemes of vacancy insertion at the upper and lower terrace, except that the vacancy is found at the middle terrace (Figure 4.10a). The DFT calculations indicate that the vacancy formation by atom hopping at middle terrace has very high barrier: 2.02 eV and 1.74 eV for Cu pop out (event No. A1 in Table B.1) and Zn pop out (event No. A2 in Table B.1), respectively. Therefore, the vacancy found in the middle terrace may result from the lower and upper terrace at which the vacancy generation is easier (event No. A5, A6, A9, A10, A13, and A14 in Table B.1).

(ii) **Wave deposition mechanism** In this scheme, the Zn atom was originally formed at the lower terrace through the step-assisted direct exchange or vacancy insertion at the lower terrace. However, at the later time the step or kink sites which previously assisted the mechanism disappear due to the step fluctuation, leaving the Zn atom incorporated at the middle terrace (Figure 4.10b). Thus, the step fluctuation acts like a wave which move back and forth, similar with the behavior of the sea wave that deposit the material at the sea shore.

(iii) **Confinement by other step adatoms** This scheme is similar with the confinement of Zn step adatom at the upper terrace, except that in this case the Zn adatom are confined deeper to the terrace (Figure 4.10c).

(iv) **Indirect exchange** The last scheme is the indirect-exchange mechanism which is similar with the one occurring at the lower terrace (Figure 4.10d). Using simplified structure, the DFT activation energy is calculated to be 1.07 eV (event No. D4 in Table B.4). In the case of no pre-substituted Zn, the

activation energy is increased to be 1.39 eV (event No. D1 in Table B.4), indicating the role of pre-substituted Zn in the process to lower the activation energy by 0.3 eV.

Based on observation of 46 alloying events at middle terrace, the percentage for the first, second, third, and fourth schemes are found to be 13%, 39%, 33%, and 15%, respectively. Even though the alloying scheme at the middle terrace is dominated by the second and third schemes, the incorporated Zn atom resulted from this scheme are close to the step edge and can easily transformed back to step adatom due to the high intensity of the step fluctuation. On the other hand, the incorporated Zn atoms farther from the step edge are more stable and stay incorporated longer.

Complete scenario of Cu-Zn Surface Alloying

Summarizing all the alloying schemes that I found, I then devise the Cu-Zn surface alloying based on the simulation. Initially, the randomly deposited Zn atoms will localize at the step edge. At room temperature, the Zn islands might be formed through bindings between Zn adatoms on the terrace (Figure 4.5c). However, such islands are not stable and readily collapse when the temperature is raised to 550 K. Most of the Zn atoms then attach to the step edge or diffuse as adatom on the terrace (Figure 4.6a). At 700 K, the alloying at upper terrace occurs, mainly due to confinement of Zn by other step adatoms and the exchange descend of diffusing Zn adatom on the upper terrace. The alloying at the lower terrace occurs slightly later than the alloying at the upper terrace. The main mechanism of the alloying at this region is the direct exchange between Zn step adatom and surface atom underneath. Finally, the alloying at the middle terrace occurs at the later stage, of which the main mechanism is found to be wave deposition and deep confinement by the other step adatoms. I noted that the Zn alloyed at the middle and lower terrace has not been included in the previous DFT studies of the methanol synthesis by CO₂ hydrogenation on Cu-Zn surface results [6, 7, 18, 91, 92]. In such catalytic reaction, it was suggested that Zn stabilizes the adsorbates that bind through O atom and destabilizes the ones that bind through C atom. Thus, the presence of Zn atoms at the lower and middle terrace may also affect the catalytic reactions to some extent. The surface alloying is also accompanied by the formation of wavy step edge with high kink density, much different with the model of rigid step edge used in the previous DFT studies.

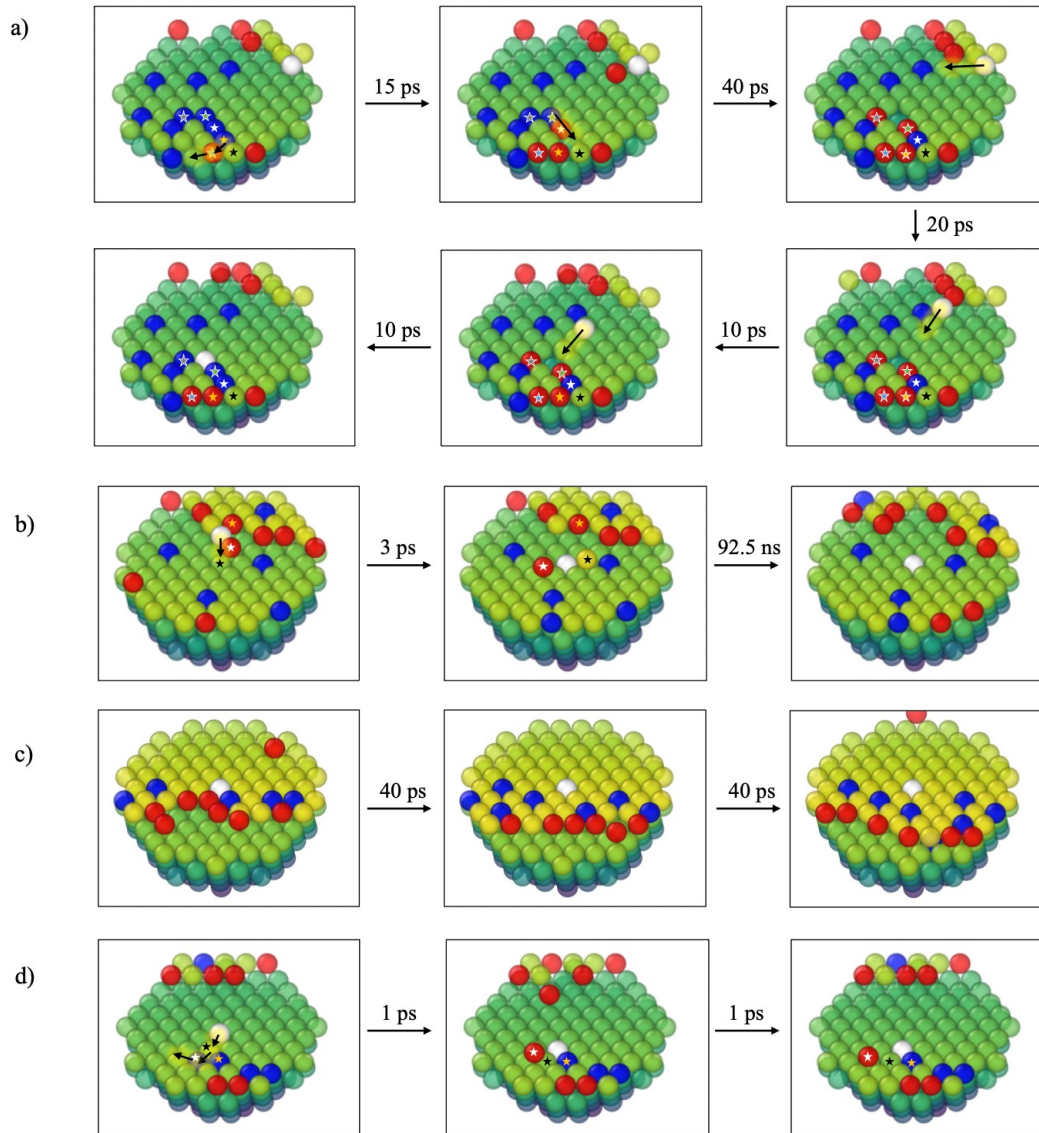


Figure 4.10: The alloying scheme at the middle terrace. (a) The diffusing Zn adatom fills in the vacancy in the middle terrace. (b) The direct exchange between the Zn step adatom and Cu surface atom occurs, then the step adatom moves back while the substituted Zn atom stays. (c) Deep confinement of Zn atom by other step adatoms. (d) Indirect-exchange at middle terrace.

The possible mechanism for the alloy formation has also been proposed based on previous STM observation [95]. Since it was observed that Zn incorporate the surface from step into the terrace without long-distance Zn migration, it was suggested that the alloying mechanism occurs through so called local-exchange between Zn and the neighboring Cu atoms (Figure 4.11). This mechanism is initiated by hopping ascend of Zn step adatom followed by Zn exchange descend. Once the Zn atom is incorporated at the upper terrace, the

Zn atom then performs sequence of pop out and exchange descend mechanisms to propagate to the middle terrace. In the case of alloying at the upper terrace, the local-exchange mechanisms were also found in the present simulation in the form of sequence of hopping-ascend and exchange-descend as mentioned in the previous subsection. However, I could not find such mechanism in operate to form the alloy at the middle terrace or the region far from the edge. In addition, by performing the DFT calculations using simplified structure, I found that the local exchange has barrier of more than 2 eV (event F1 and F2 in Table B.6) at the middle terrace. Therefore, I consider such mechanism is unlikely to be responsible for the alloying at the middle terrace or any part of surface which is far from the step edge.

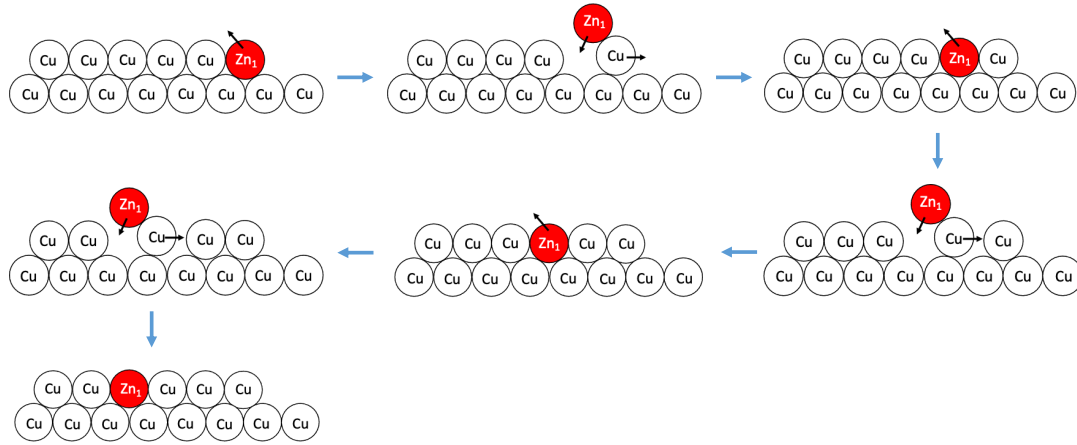


Figure 4.11: The transformation of Zn step adatom into incorporated Zn atom at middle terrace by means of local exchange mechanism.

Interestingly, a kind of propagation of Zn atom from upper and lower terrace to middle terraces are found in the present simulation, which is achieved through the indirect-exchange as discussed in previous section. Such propagation is essentially different with the one suggested by Sano et al., since in the case of indirect-exchange mechanism, the Zn at the initial and final states is different atom. In addition, the indirect-exchange mechanism found in the present study requires the diffusing Zn terrace-adatom, which mainly comes from the detachment of Zn step adatom (Figure 4.12).

It was reported that the long jump of Zn atom was not observed in previous STM observation, thus the migration of Zn incorporated atom occurs locally in the form of short propagation. Considering the moderate barrier of adatom formation by detachment or the step-climbing of Zn step adatom, I think that the Zn adatom diffusing on the terrace should exist in the experiment. To investigate this idea, I calculated the histogram of the adatom's

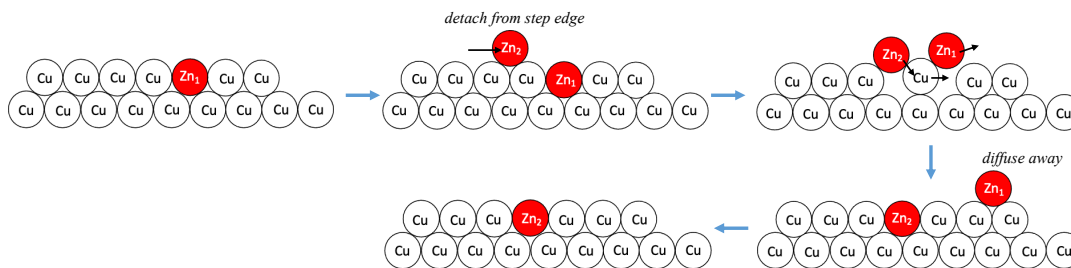


Figure 4.12: The migration of incorporated Zn at the middle terrace by means of leverage mechanism.

life time based on the simulation as shown in Figure 4.13. The histogram shows that the majority of adatoms have very short lifetime, with 0.5 ns at the longest. By fitting exponential function to the histogram, I obtained very short time constant (τ) of 34.498 ps. Given the low frequency of adatom with long lifetime, it is very reasonable that they are invisible in experiment. The reason behind the apparent short propagation of Zn incorporated atom observed in experiment is that the pre-substituted atom contributes in lowering the barrier of the indirect-exchange as shown in event D1 D3 in Table B.4. Therefore, the indirect-exchange mechanism would tend to happen nearby another incorporated Zn atom, which in experiment might be considered as short or local propagation.

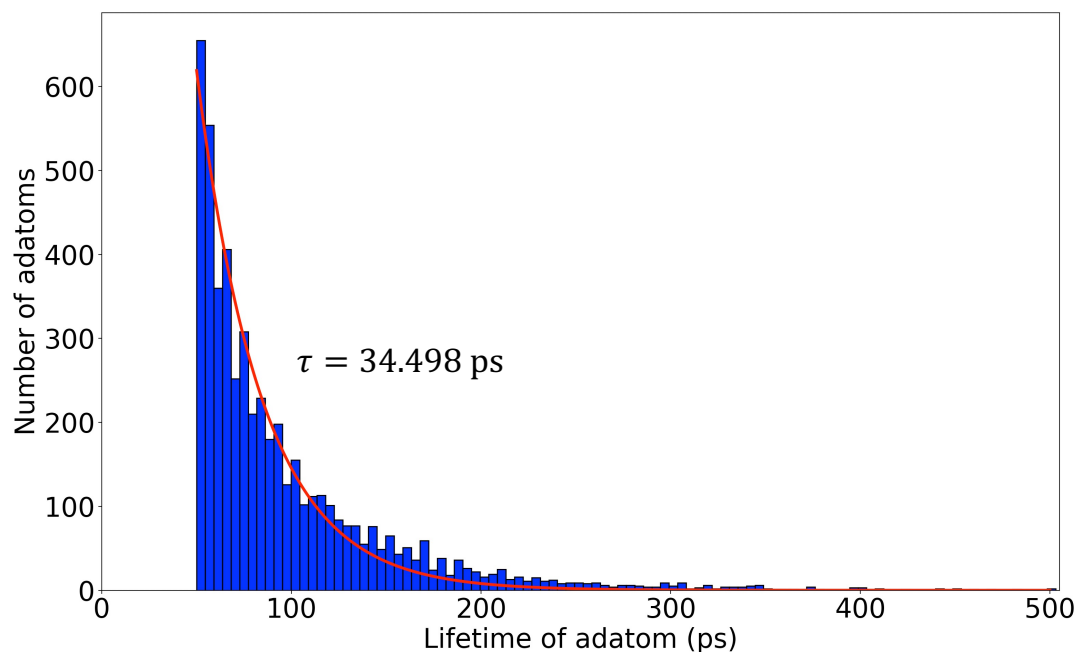


Figure 4.13: The histogram of adatom lifetime.

Before attempting to revise the possible scenario of the Cu-Zn surface alloying, I would like to highlight an important difference between the present

simulation and actual experiment. Naturally, the Zn atom must overcome barrier to climb the step edge (i.e., hopping-ascend or exchange-ascend barrier). However, due to the periodic boundary condition employed in this simulation, the Zn atoms that were in the bottom-most terrace can go directly to the top-most terrace just by crossing the boundary of the unit cell. Such circumstance would result in the constant presence of Zn atoms diffusing on the higher terrace as long as they have not been incorporated to the surface. This is obviously not the case in the experiment. Therefore, given the condition where the number of diffusing Zn adatom on the higher terrace is limited, the source of adatom in experiment would come mainly through hopping-ascend or exchange-ascend of Zn step adatom.

4.4.1 Migration Rate and Activation Energy

I estimated the Zn migration rate $\nu(s^{-1})$ at constant temperature by using the Poisson statistics [95, 124]:

$$\ln \frac{n(t)}{n_0} = -\nu t \quad (4.1)$$

where $n(t)/n_0$ is the fraction of Zn atoms that had not moved within a time interval t . The migration rate is thus obtained by plotting the logarithm of $n(t)/n_0$ against the time interval t and then taking the slope. The resulting Poisson statistics of Zn migrations at 550 K, 700 K, and 1000 K are shown in Figure 4.14 (a-c). At each temperature, the resulting migration rate is expressed as average residence time τ (s) which equals to the inverse of the migration rate. The residence time for temperature 550 K, 700 K, and 1000 K are calculated to be 3.87 μs , 1.26 μs , and 25 ns, respectively. By using Arrhenius law, I thus estimated the activation energy of the Zn migrations to be 0.52 eV. The Arrhenius plot is shown in Figure 4.14d.

Based on STM observation, Sano et.al. has derived the activation energy to be 0.25 eV [95], which is much lower than the result obtained in this study. One possible origin of this discrepancy is the influence of STM tip used in the simulation. It has been reported that the STM tip can induce motion of adatom, enhance the vacancy formation and even move the embedded atom [125–128]. To give more detail to this, I calculated simple elementary events under the influence of STM tip and measured the change of the barriers due to the influence of the tip. The tip is modelled as isolated (100) surface of

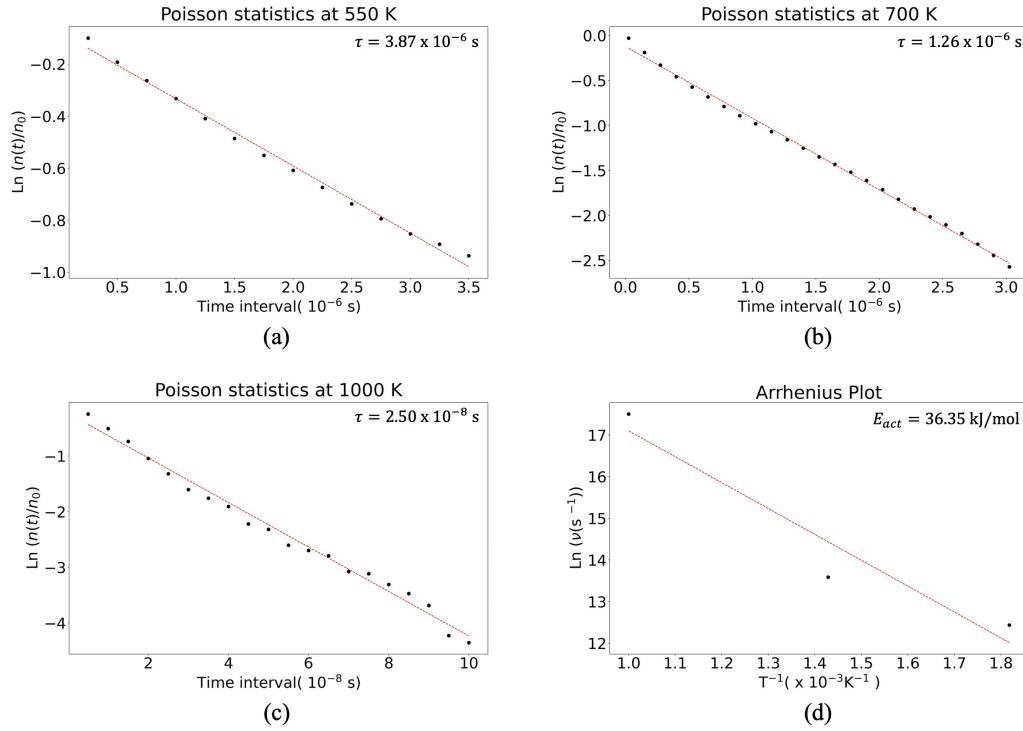


Figure 4.14: The Poisson statistics at (a) 550 K, (b) 700 K, and (c) 1000 K. (d) The Arrhenius plot.

tungsten, similar element with the tip used in the previous STM measurements [95]. The detail of the model and calculation can be found in the Section 3 of Appendix B. As discussed in the previous section, the barriers of Cu pop out and Zn pop out without the influence of the tip are 2.02 eV and 1.50 eV, respectively. Interestingly, I found these barriers of pop out reduce significantly under STM tip to be 0.88 eV (tip-surface distance is 4.1 Å) and 0.67 eV (tip-surface distance is 4.5 Å) for Cu and Zn, respectively (Figure 4.15). In the case of direct exchange between Zn adatom and Cu surface atom, the barrier of Zn kicks Cu is reduced from 1.37 eV to 0.96 eV with tip-surface distance of 3.7 Å (Figure 4.16). In addition, I found very large reduction of around 1 eV for the barrier of hypothetical local exchange under STM tip. In the case of local exchange initiated by Zn pop out (with tip surface distance of 4.3 Å), the barrier is reduced from 2.18 eV to 1.08 eV (Figure 4.17). Similarly, the barrier of local exchange initiated by Cu pop out (with tip distance of 4.5 Å) is also reduced from 2.44 eV to 1.41 eV (Figure 4.18). This suggest that the STM tip may accelerate the alloying at the middle terrace by assisting vacancy formation and direct exchange between Zn and Cu. Under the influence of STM tip, the local exchange might be also possible as a rare process given the significant reduction in the barrier. More detail study on

the alloying mechanisms under the influence of STM tip will be the topic for further studies.

4.4. Alloying Mechanism

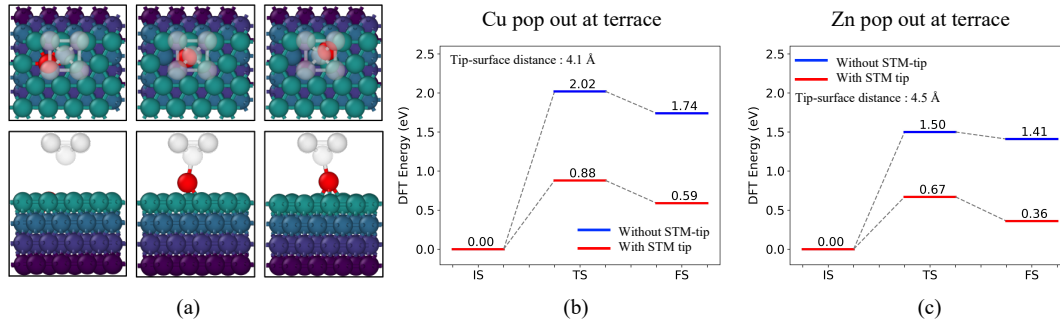


Figure 4.15: The influence of STM tip to pop out and vacancy insertion event.

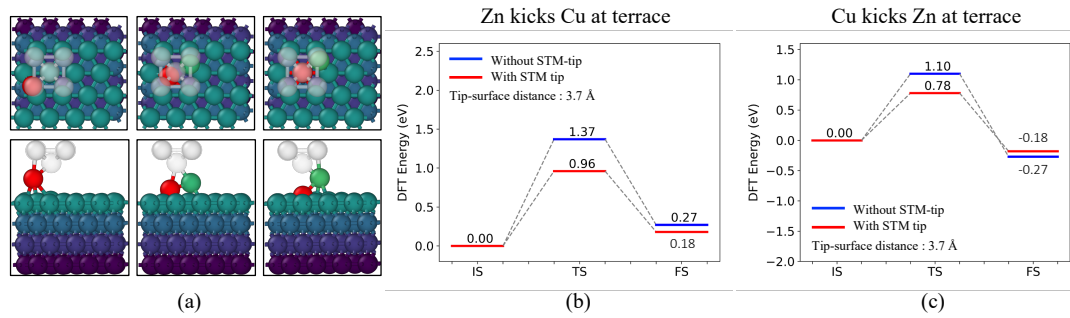


Figure 4.16: The influence of STM tip to direct-exchange event.

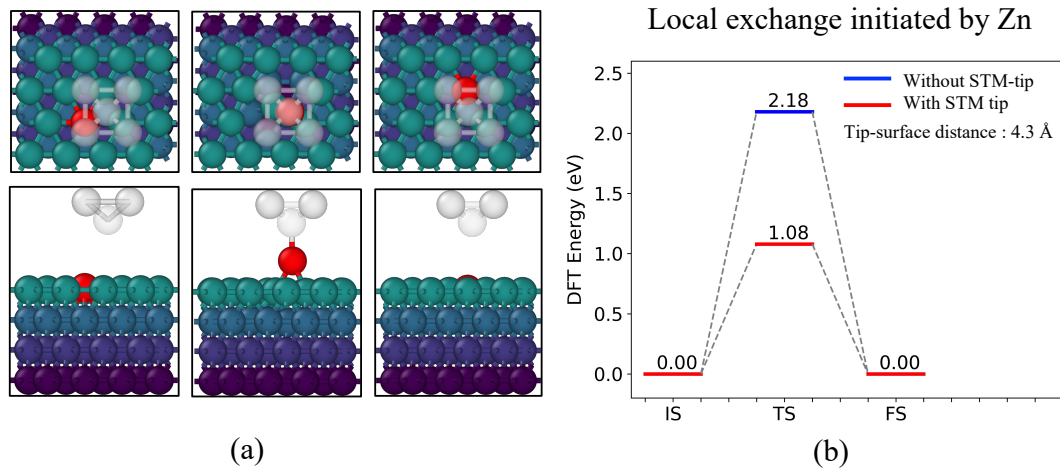


Figure 4.17: The influence of STM tip to local exchange initiated by Zn pop out.

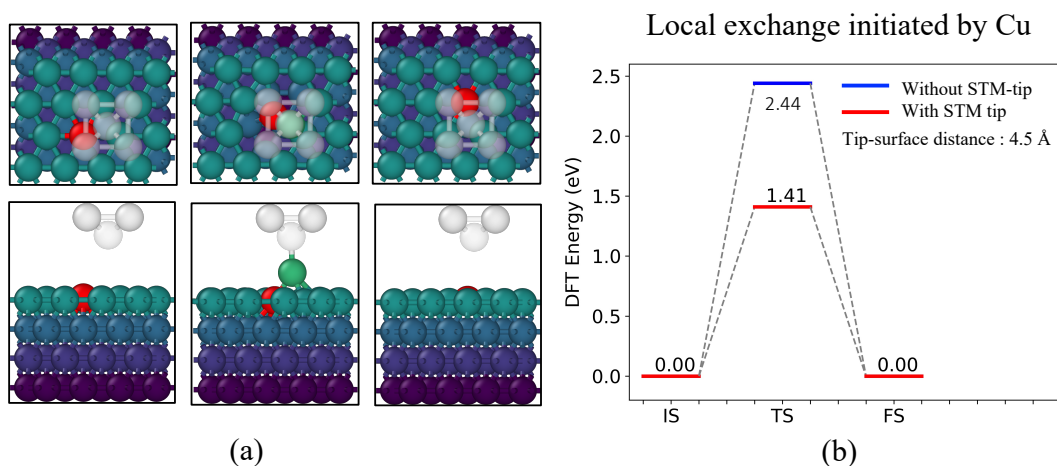


Figure 4.18: The influence of STM tip to local exchange initiated by Cu pop out.

4.5 Conclusion

In the present study, I investigated the structure and the formation process of Cu-Zn surface alloy on Cu(997) by machine-learning molecular dynamics. Gaussian Process (GP) regression aided with on-the-fly learning scheme were employed to build force-field based on data of first principles calculations. The resulting force-field is validated by comparing the DFT and GP calculated barriers of various elementary events, the atomic forces of the transition states structures, and the forces of the atomic environments with the highest uncertainty found during simulation.

The simulation reveals atomistic details of the alloying process, i.e., the incorporation of deposited Zn adatoms to the Cu substrate. I found the Zn incorporate the surface not only at upper terrace, but also at lower and middle terraces which have not been considered in the previous DFT studies of methanol synthesis on Cu-Zn surface. The surface alloying is also accompanied by the formation of wavy step edge with high kink density, much different with the model of rigid step edge used in the previous DFT studies. By calculating the barrier of elementary events of step edge fluctuations (i.e., attachment and detachment of adatom to/from step edge), I found all the elementary events involving Zn atom have lower barrier than the pure Cu system, suggesting Zn atoms enhance the step edge fluctuations.

The time evolution of the surface shows the alloying is initiated at upper and lower terraces near the step edge, giving emphasis to the role of steps and kinks in the surface alloying which lower the barriers of elementary events such as vacancy generation and direct-exchange. The alloyed Zn was found

at the middle terrace at the later stage of the simulation. I found the alloying at the upper terrace is dominated by the confinement of Zn step adatom by other step adatoms which migrates heavily along the step edge, highlighting the importance of step fluctuation in the alloying which is also enhanced by the presence of Zn. Meanwhile, the alloying at the lower terrace is dominated by the direct exchange between Zn step adatom and Cu surface atom underneath. In the case of alloying at middle terrace, the alloying is dominated by the wave deposition and deep confinement of Zn adatom.

The short propagation of alloyed Zn in the middle terrace was observed to occur by means of indirect-exchange mechanism instead of local exchange as proposed in the previous STM observation. The comparison of migration rate and activation energies to the result of STM observation is also made. Based on Arrhenius plot, I calculated the activation energy to be 0.52 eV which is around two times higher than the experimental activation energy measured by experiment. I explained such discrepancy as the result of the STM tip influence to the surface. In addition, I have found that, at certain distance from the surface, the STM tip significantly affects the elementary events such as vacancy formation and direct exchange.

Chapter 5

Unveiling CO-driven Clusters Formations of Cu(111) Surface

5.1 Introduction

Active sites, defined as specific area where the catalytic reactions take place, are the crucial part that determines the activity and selectivity of the catalyst. Considering the atomic size and dynamics of active sites, it is often non-trivial to identify the active sites of heterogeneous catalyst [129]. The challenge to understand the nature of active sites lies in the elusive interplay between surface and chemical adsorbates at operating condition. A well-known example is the controversy in the active site identification of industrial catalyst for methanol synthesis, Cu/ZnO/Al₂O₃ [4]. Methanol synthesis has been well established in industry but the active sites of the catalyst are still debatable: Cu-Zn metallic [6, 90] vs the Cu-ZnO [7] synergy. Aside from the atomic species of the active sites, the morphology of the active sites is an important factor that cannot be neglected. Theoretical calculations have shown that the flat Cu-Zn and stepped Cu-Zn exhibits different activity in synthesizing methanol, of which only the latter gives significant promotional effect [6]. Further, it has been observed that the turn over frequency of methanol is increased along with the number of stacking faults such as steps and kinks [6]. Even though the typical profile of the Cu surface is expected to be flat due to the high stability of the low index facets (e.g., (111) and (100) facets), it is possible that the surface reconstruction alters the structure and concentration of the active sites during operating condition. In fact, the high-pressure scanning tunneling microscopy (HPSTM) and ambient pressure x-ray photoelectron spectroscopy (APXPS) have shown that the Cu(111) surface is decomposed into small nanoclusters when exposed to CO

molecules [25]. The CO-induced surface reconstruction on other Cu facets have also been reported [26–28].

Considering CO is a part of the feed gas in methanol synthesis (i.e., CO/CO₂/H₂) [130, 131], we are motivated to elucidate the mechanism of these cluster formations that contributes to the increasing of concentration of steps and kinks on the surface. In order to observe the formation of the clusters at the atomic level, we performed a set of machine-learning molecular dynamics (MLMD) simulations in which the molecular dynamics (MD) is driven by the force-field obtained by fitting the function to the data of density functional theory (DFT) calculations. MLMD method offers higher accuracy compared to classical potentials and higher efficiency compared to expensive ab-initio molecular dynamics (AIMD). We used the machine-learning technique called gaussian process (GP) regression which is able to provide the uncertainty of prediction based on the database itself [50]. This enables the learning scheme called active learning in which the high uncertainty value is used as the criterion for an atomic environment to be included in the database. This learning scheme thus ensures each data is sufficiently different from each other, resulting in a compact and low-correlated database. Further, on-the-fly learning scheme can be implemented by employing the force-field in dynamic simulation to generate more high-uncertainty data that can be used to improve the force-field continuously.

To provide atomic level description on the cluster formation, the MLMD simulations were performed at three different temperatures: 350 K, 450 K, and 550 K. The system involves CO molecules and Cu island deposited on Cu(111) surface. We let the CO molecules to freely adsorb and desorb on the Cu surface. The evolution of the system is analyzed and the information of non-equilibrium states such as clusters' size, number of occurrence of the clusters, clusters' lifetime, as well as the mechanistic insight to the CO-induced cluster formation can be obtained.

The rest of this chapter is organized in the following manner. In section 5.2, we provide the technical details on the DFT, machine-learning, and MD methods that we used. In section 5.3, we present and discuss the results on the behavior of CO adsorption on flat and stepped Cu(111) surfaces, the training and validation of the GP force-field, CO diffusion and desorption on Cu surfaces, the structures and the time evolution of the cluster formation, and mechanistic analysis to the formation of the clusters. Finally, in section 5.4, we summarize and conclude the findings.

5.2 Computational Details

A set of MD simulations were performed to observe the interplay between CO and Cu surface at the atomic level. The MDs are driven by machine learning force-field that is trained based on various atomic environments labelled with the associated forces. The implementation of this framework thus requires integration of three different methods: DFT, machine-learning, and MD. The computational details of these methods are described as follows.

DFT calculations, as employed in Quantum ESPRESSO code [132–134], were performed to provide the forces of atoms within various configurations of CO and Cu surfaces. The electron-ion interaction is described by ultrasoft pseudopotentials [72]. We took into account the van der Waals (vdW) interactions by employing vdW-DF exchange-correlation functional [70, 135–138]. Since the invention of the vdW-DF, this functional has been applied for various applications related to the molecule adsorption on metals. For instance, this functional gives adsorption energy of 1,4-benzenediamine (BDA) on Au(111) and azobenzene on Ag(111) consistent with the experiment [139]. Study on the adsorption of n-butene on Cu(100), Cu(111), Au(111), and Pt(111) also evidenced that the adsorption energies calculated using vdW-DF are in good agreement with experiment [140]. More importantly, the improvement of the vdW-DF non-local correlation to the CO adsorption on metal surface has also been discussed extensively in the previous studies [141, 142]. We set the cutoff energy for wave-functions and charge density to 60 Ry and 480 Ry, respectively. The convergence threshold for energy is set to 10^{-8} Ry. The optimized lattice constant of Cu(111) is calculated to be 3.692 Å. These values are in good agreement with the experimental measurement of Cu lattice constant (i.e., 3.615 Å) [113]. To find the barrier of atomic detachments and attachments from step edges, we also performed nudged elastic band (NEB) calculations and climbing-image nudged elastic band (CI-NEB). The NEB calculation is terminated when the norm of the force orthogonal to the path is smaller than 0.05 eV/Å.

The force field is constructed by using machine-learning technique called GP regression as employed in FLARE code [51]. Gaussian process is kernel-based technique which not only provide the prediction but also the uncertainty. This uncertainty is used to drive the on-the-fly learning scheme of

which the new data is obtained by taking only the structure with high uncertainty value. The kernel contains several hyperparameters, namely, two-body signal-variances σ_s^2 , two-body length-scale l_2 , three-body signal variances σ_s^3 , three-body length scale l_3 , and noise hyperparameter σ_n . For better distinction of the atomic interactions in the kernel, we set different hyperparameters of signal variances and length scale for interaction between Cu atoms and the interaction between Cu atom and the other elements (i.e., C and O). In total, there are nine hyperparameters embedded in the kernel which we list in Table C.2 of the Appendix C. The mathematical details on the kernels as well as how the force prediction and uncertainty are calculated, are provided in the sub-chapter 2.3.2. To be used efficiently as a pair style in the MD code, the final GP model is mapped into tabulated spline models using mapped gaussian process (MGP) method [116] with 128 grid of control points and 64x64x64 grid of control points for two and three-body mean predictions, respectively.

Once reliable MGP force field is obtained, MD simulations are performed to provide direct observation to the CO-induced formation of Cu clusters at different temperatures. Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [117] is employed to perform dynamic simulations within NVT ensemble. The timestep of 1 fs is used in the simulations. The analysis of MD trajectories to extract the non-equilibrium information has been done using two Python libraries, namely Atomic Simulation Environment (ASE) [119] and Ovito [118]. The images depicting Cu and CO atoms were generated using Ovito [118].

5.3 Results and Discussion

5.3.1 CO Adsorptions on Flat and Stepped Cu(111) Surfaces

Before proceeding to the construction of machine-learning force-field, we examined the accuracy of DFT calculations in describing CO adsorptions on Cu surface. The adsorption energy of CO molecule on various sites of flat and stepped Cu(111) surfaces are presented in Figure 5.1. On the flat Cu(111) surface, the calculations employing vdW-DF functional show that CO is favorably adsorbed on top site with adsorption energy of -0.51 eV, while other sites (i.e., bridge, fcc, and hcp sites) give relatively similar adsorption energy. The CO adsorption energy on fcc-hollow (site a2) and hcp-hollow (site a3) are expected to be similar since the geometries of both adsorption sites are

rather similar (i.e., three-fold symmetry). Seemingly, the adsorption energy on bridge sites (a4) is exactly identical with the hollow sites, but given higher precision, it is actually more positive by 0.004 eV. We note that CO binds to Cu surface through the carbon atom for all adsorption sites. The result of adsorption energy and the site preference is in agreement with experiments that shows CO is adsorbed on top sites of Cu(111)-based surface at low coverage with adsorption energy of -0.49 eV [143]. We also examined the outcome of other functional and found that vdW-DF gives the closest adsorption energy as well as consistent site preference to experiment (Table C.1 of Appendix C), thereby motivates the use of vdW-DF functional in this study.

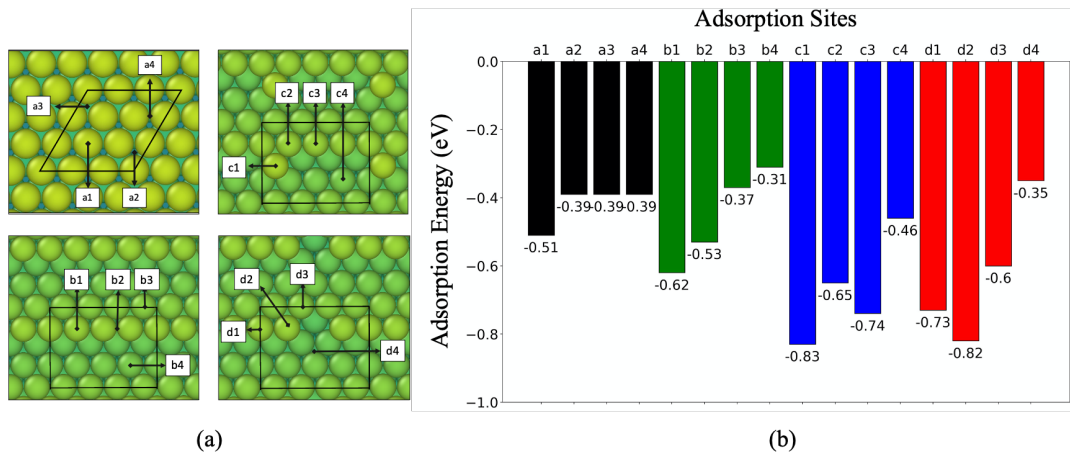


Figure 5.1: (a) Various adsorption sites of CO on flat Cu(111) (top-left), perfect step-B (bottom-left), step-B with step-adatom (top-right), and step-B with kink-atoms (bottom-right). Step-B is type of step-edge with (111) microfacet. The unit cell is indicated by the black frame in each figure. (b) The adsorption energy of various sites depicted in (a).

Compared to the top site of flat Cu(111) surface (site a1), CO on top site of the step-edge (site b1) has more negative adsorption energy (i.e., -0.62 eV), consistent with the previous experiments [143, 144]. We found the strongest adsorption on top of step-adatom which gives -0.83 eV adsorption energy (site c1). Weakening of adsorption is observed when CO moves further from the step edge as indicated by more positive adsorption energy at site b3. Discrepancy of 0.1 eV is observed between top site (site b1) and bridge site (site b2) near the step edge. The calculations also show the preference of CO to adsorb at upper terrace near the step edge, whereas the adsorption at lower terrace (e.g., site c4 and site d4) shows significantly more positive (weaker) adsorption energies. The high energy differences in the CO adsorption near the non-flat region of the surface (e.g., sites b1-b4, c1-c4, and d1-d4). mainly come from the contribution of the geometry of its environment. That is, the

large fluctuation is caused by the difference in the coordination number of the surrounding Cu atoms. In general, the trend in the adsorption energies on the top sites suggest the strong preference of CO adsorption on the low coordinated atom as also reported in previous computational studies [145–147].

5.3.2 Training and Validation

A training point in the database is defined as a local atomic environment labelled with the associated forces. An atomic environment constitutes all two-body and three-body clusters found within certain cutoff radius from the center atom, which we specified to be 7 Å and 4.5 Å for two-body and three-body cutoffs, respectively. The database to train the force-field was built based on active and on-the-fly learning as implemented in the FLARE code [51]. This learning scheme (drawn schematically in Figure 2.3) employs the MD simulations to generate diverse atomic environments. Thus, some structures called ‘parent structures’ are required to serve as the initial structures in such MD simulations. These structures, shown in Figure 5.2, consist of varying number of adsorbed and desorbed CO on flat Cu(111), adatoms and clusters on Cu(111), as well as Cu surface with step edges and kinks. The new training points which have low correlation with the existing training data are then included in the database. The selection of low correlation training points is based on the uncertainty of prediction provided by GP framework. That is, the new data is added only when the calculated uncertainty of the particular structure is higher than the threshold, which we specified to the value of noise hyperparameters σ . More detail information on the procedure to generate the training set is provided in Section 2.3.3. The final database consists of 2,997 atomic environments.

The machine-learned force-field was validated using 144 structures which were independent from the training set. These validation set is a collection of system of CO interacting with various geometries of Cu surface, namely, Cu(111), Cu(111) + 1 adatom, Cu(111) + 3 adatoms, Cu(111) + 7 adatoms, Cu(221), and Cu(211). In total, these 144 structures consist of 1418 C atoms, 1418 O atoms, and 13,086 Cu atoms. We also provided some pictures depicting the validation structures in Figure C.1. The details on these structures are provided in section 3 of the Appendix C. By using this validation set, we obtained mean absolute errors of 0.04 eV/Å, 0.08 meV/Å, and 0.06 meV/Å for the environments of Cu, C, and O atoms, respectively. We noted that

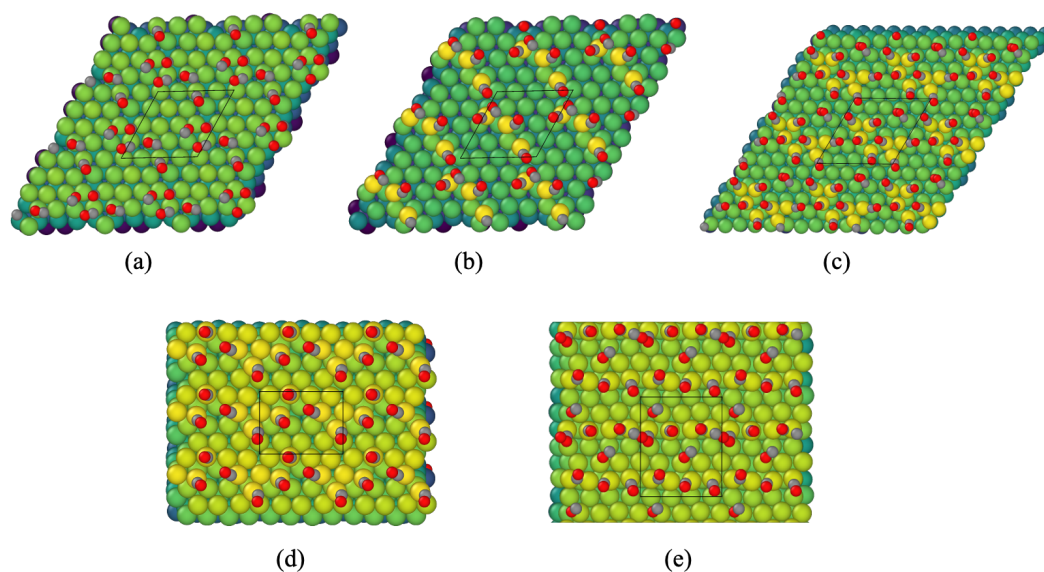


Figure 5.2: Various geometry of Cu and CO system included in the database: (a) CO molecules on flat Cu(111) surface, (b) CO molecules on Cu(111) with adatoms, CO molecules on Cu(111) with small Cu clusters, (d) CO molecules on Cu(221), and (e) CO molecules on Cu(211).

the predictions are resulted from the MGP force-field which is the final form of force-field used in the MD simulations presented in this study. All the calculated uncertainties of the validation structures, expressed as standard deviation of the prediction, are found below the noise standard deviation of $0.09 \text{ eV}/\text{\AA}$. The parity plot (obtained using this validation set) as well as the distribution of uncertainty for each atomic species are shown in Figure 5.3.

Though we only used atomic forces for training, the force-field can also reproduce the DFT energy barriers quite well. We compared the results of DFT and MGP force-field for calculating the barriers of various attachment and detachment of atoms from step edge as shown in Table reftab:C4-reftab:C6. The resulting MAE is 0.04 eV with 0.14 eV at the highest.

5.3.3 The Evolution of CO Molecules on Cu Surfaces

CO diffusion and desorption on Cu surfaces

Aside from the mean absolute error of the force predictions, we also confirm the reliability of the force-field in terms of two important elementary events of CO dynamics on Cu surface, namely CO diffusion and CO desorption. We investigated the behavior of the diffusion by measuring the mean squared displacement (MSD) of Cu, CO, and $\text{Cu}_1(\text{CO})_1$ on the Cu(111) surface. In

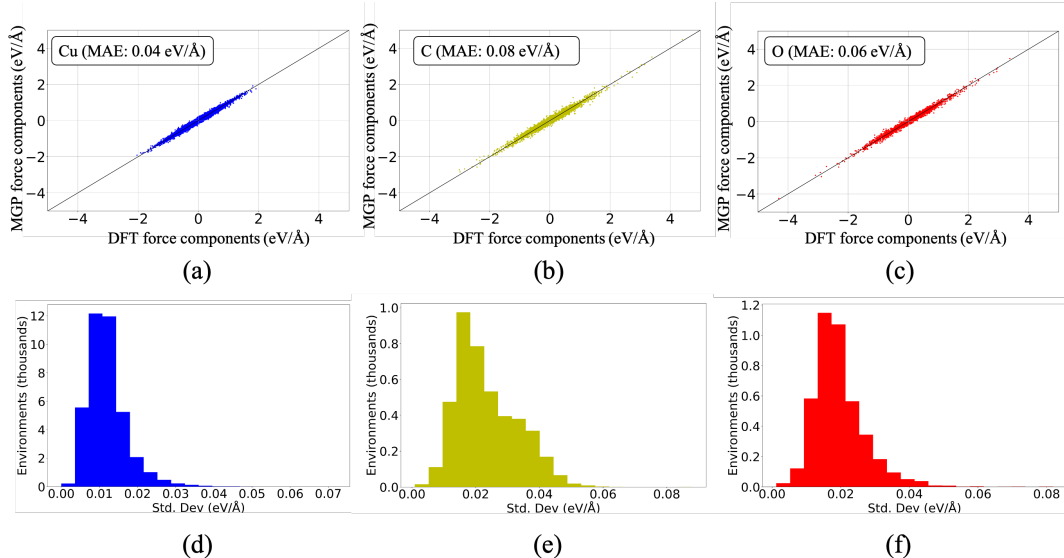


Figure 5.3: Parity plot of the forces predictions using the validation set for (a) Cu atoms with MAE of 0.04 eV/Å, (b) C atoms with MAE of 0.08 eV/Å, and (c) O atoms with MAE of 0.06 eV/Å. The histograms of the standard deviation that represents the uncertainty of the prediction for Cu, C, and O atoms are shown in figure (d), (e), and (f) respectively. All the standard deviations of the prediction are found below 0.09 eV/Å

the adsorbed state, the travelling of CO across the surface can be achieved by two mechanisms: (i) direct diffusion in which the adsorbed CO hopping from one site to another site, and (ii) adatom-mediated diffusion in which the CO rides the diffusing Cu adatom in the form of $\text{Cu}_1(\text{CO})_1$. Table C.3 shows the results of the diffusion constant D extracted from the MSD measurements at different temperatures. We then plugged in the diffusion constants to Arrhenius plot (Figure 5.4a) to obtain the barriers for diffusion: 35, 49, and 34 meV for Cu, CO, and $\text{Cu}(\text{CO})_1$ diffusions, respectively. The results of NEB calculations for the diffusion barriers of Cu, CO, and $\text{Cu}(\text{CO})_1$ are 36, 120, and 39 meV, respectively. Thus, the barriers extracted from Arrhenius plot are consistent with DFT calculations with the discrepancy lower than 0.1 eV.

We noticed that the MSD measurements underestimate the barrier of CO diffusion by 0.07 eV compared to NEB calculation. We attributed this discrepancy due to the assumption of diffusion path in the NEB calculation. We noted that the 0.12 eV barrier of CO diffusion from the NEB calculation assumes that the diffusion path is simple hopping from one top site to the other nearest top site via top-bridge-top diffusion path (where the bridge site in the middle could be substituted by fcc or hcp hollow sites since their corresponding adsorption energies are very similar).

However, in actual dynamics simulation, diffusion path other than short hopping might occur. Especially given rather small energy difference between the top site and the other sites. By sampling some trajectories of CO diffusions from the MD simulation, we found that the CO can diffuse from one top site to another top site through the path “top-fcc-bridge-hcp-top”. The CO that goes through this path will experience almost no barrier in the middle (e.g., the fcc-bridge-hcp) due to the similarity in the adsorption energies of bridge, fcc, and hcp sites. That is, the diffusion of CO on Cu(111) does not only involve the short hopping from top to fcc/bridge/hcp sites with barrier of 0.12 eV, but also the diffusion from non-top site to another non-top site (e.g., fcc to bridge, hcp to bridge, etc.) which has lower barrier. Therefore, it is reasonable that the MSD calculation underestimate the barrier of CO diffusion. In the case of Cu and Cu₁(CO)₁ diffusion, the Cu adatom on top of the surface is very unstable. Therefore, the diffusion path is more homogenous (i.e., fcc-bridge-hcp) and the assumption of NEB calculation on the short hopping is reliable.

Nevertheless, we don’t think the behavior of CO diffusion will significantly affect the behavior of clusters’ formation since the MD simulations to observe the clusters’ formation would be performed above 350 K. The experimental desorption temperature of CO on Cu(111) (at which the desorption rate reaches maximum) measured by thermal desorption spectroscopy is rather low (i.e., below room temperature) [143]. Therefore, even though the CO diffusion barrier is small, since it will already desorb at high temperature, the direct CO diffusion on surface is hindered. Considering strong CO adsorption on Cu adatom, it is expected that the travelling of CO by adatom-mediated diffusion is more preferred at high temperature.

We also compared the desorption rate of CO on different Cu facets, namely Cu(111), Cu(211), and Cu(221) surfaces. The detail of the calculation is presented in section 5 of the Supporting Information. To minimize lateral interactions between adjacent molecules, CO are deposited regularly at low coverage on the Cu surface as shown in Figure C.2. The system is then equilibrated at temperatures: 150 K, 200 K, and 250 K for Cu(111) surface and 500, 600, and 700 K for Cu stepped surfaces. The re-adsorption of CO is prevented by annihilating the desorbed CO which are already far from the surface. The rate of desorption is then obtained as the change of coverage over time (Figure C.3-C.5). The results of the desorption rate as well as the Arrhenius plot is shown in Figure 5.4b, where the desorption energy (E_{des}) is estimated to be

0.45 eV, 0.65 eV, and 0.66 eV for Cu(111), Cu(211), and Cu(221) surfaces, respectively. These values are consistent with thermal desorption spectroscopy (TDS) experiment that shows the desorption energy of 0.49 eV, 0.60 eV, and 0.61 eV for Cu(111), Cu(221), and Cu(211) surfaces, respectively [143].

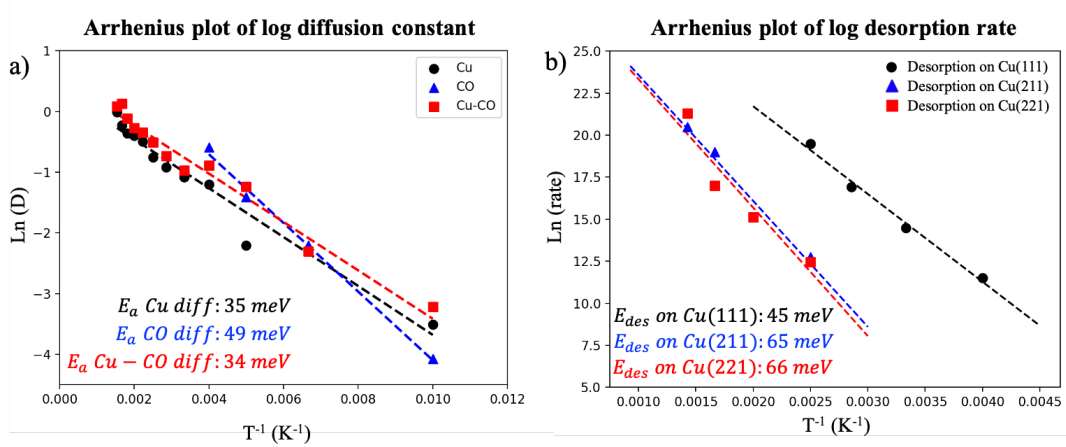


Figure 5.4: (a) Arrhenius plot of the $\ln$ diffusion constant D for Cu, CO, and $\text{Cu}_1(\text{CO})_1$ on Cu(111). The slope of the fitted line indicates the barrier of diffusion (E_a). The E_a of the Cu, CO, and $\text{Cu}_1(\text{CO})_1$ obtained from the fitting are 0.035 eV, 0.049 eV, and 0.034 eV, respectively. (b) Arrhenius plot of the $\ln$ CO desorption rates on Cu(111), Cu(211), and Cu(221) surfaces. The slope of the fitted line indicates the desorption energy (E_{des}). The E_{des} of CO on Cu(111), Cu(211), and Cu(221) are calculated to be 0.045 eV, 0.065 eV, and 0.066 eV, respectively.

CO-induced Cu(111) decomposition into small clusters

After confirming the accuracy of the diffusion and desorption of CO on Cu surfaces using the MD simulations, we performed another set of MD simulations at constant temperature to observe the decomposition of Cu surface into small clusters. To observe the events within the time scale of MD simulation, small island deposited on wide terrace is used. Figure 5.5a shows the snapshot of this initial structure without CO exposure. The kink sites provided by the island accelerate the restructuring process by exposing Cu atoms with lower coordination number which are more mobile than the atoms at the perfect step edge. The wide terrace is necessary to give space for the detached adatoms to do random walk before attaching back to the island. We note that the small terrace will hinder the formation of the clusters due to the interaction of adatoms with the neighboring island. Before starting the production run at constant temperatures for 100 ns, we equilibrated the system by ramping up the temperature from 10 K to the target temperature (i.e., 350 K, 450 K, and 550 K) with low heating rate of at most 0.05 K / ps.

In the case of Cu surface interacted with CO, we initially deposited the CO on top and bottom of the four layers slab and let them to freely adsorb and desorb in a vacuum with height of 16.25 Å. The periodic boundary condition is applied to the surface in x, y, and z directions.

We would like to note that even though we only used 4 atomic layers as the surface model, the atoms at the third layers are fixed/clamped to their bulk positions. Thus, the first and second layers effectively represent the surface and subsurface atoms on top of the bulk, respectively. We don't freeze the position of atoms at the fourth layer since they are used to model a wall which catch or reflect the CO once they desorb from the surface (note that the periodic boundary condition is also applied in z-direction). We should also note that we only investigate the atoms above the surface (1st layers and above), so even though the atoms at fourth layer slightly deviate from the bulk positions, it will not affect the dynamics of the surface atoms.

The CO is initially deposited with high coverage (i.e., $\theta_{CO} = 0.5$) with no CO initially exist in the gas phase. Since the number of CO are kept fixed during this simulation, the coverage will decrease when the simulation starts due to the desorption of CO that fill the vacuum region. Thus, the initial high coverage is chosen in order to have substantial amount of adsorbed CO even when part of the molecules desorb at high temperature. Further, we applied temperature of 350 K, 450 K, and 550 K to accelerate the movement of Cu atoms on the surface and to represent the operating temperature of catalysis. If the coverage is too low and the number of CO in the system is too small, then most of the CO will stay in the gas phase and consequently the events of CO-induced Cu clusters will happen very rarely. In such case, it will be inefficient for the MD simulations to simulate very long physical time since most of the event is just the dynamic of CO gas.

Figure 5.5b and Figure 5.5c show the top and side views of the CO-exposed Cu surface. In the cluster analysis, we define a group of atoms as cluster if the atomic distance is 3.0 Å with each other and have a life time of at least 10 ps. The number of clusters with various sizes are counted by sampling the MD trajectory at every 10 ps.

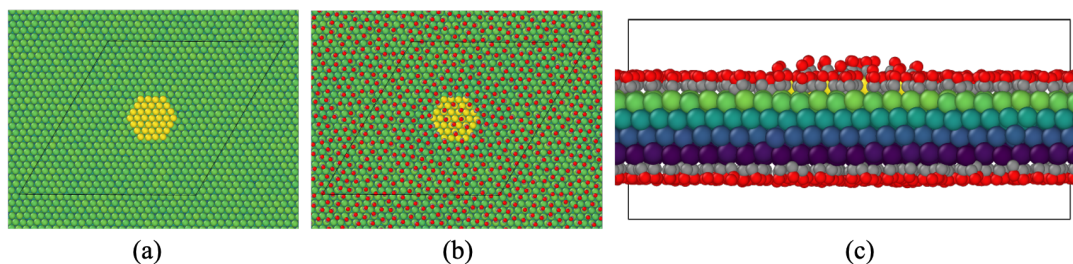


Figure 5.5: The initial structures used in MD simulations. (a) Cu island on Cu(111) surface without CO exposure (top-view). (b) Cu island on Cu(111) surface with CO exposure (top-view). (c) Side view of figure (b).

Figure 5.6a shows the snapshot of the Cu island on Cu(111) without CO exposure. The shape of the island fluctuates over the time due to the thermal mobility of step and kink-atoms. Even at temperature of 550 K, no cluster formation is observed within 100 ns though some monomers (i.e., Cu₁) at around 20 ns of the simulation are detected (Figure 5.7a).

In all set of simulations of CO-exposed Cu surface, we observed the diffusion of CO to the edge of the island or the low-coordinated atoms (Figure 5.6b, 5.6c, 5.6d). No dissociative adsorption was observed. The preference of CO adsorption on atom with low coordination number (CN) is supported by the DFT calculations as presented in Figure 5.1. In more detail, the adsorption energy on top site of flat (CN = 9), step-atom (CN = 7), and step-adatom (CN = 5) are calculated to be -0.51 eV, -0.62 eV, and -0.83 eV, respectively. Based on these calculations, it is clear that the adsorption becomes stronger when the CN decreases. The preference to the low-coordinated atom are also reported in the previous computational studies that show much stronger adsorption on step and kink compared to the flat Cu(111) [145]. Similar trend has also been reported for the CO adsorptions on other metal surfaces, such as Pt(111) [148].

For each temperature, we show some snapshots of MD simulations to qualitatively describe the behavior of the system. We also show the quantitative results in term of the clusters' size, number, and lifetime. All of them are discussed in detail in the following.

A snapshot of the 350 K simulation is shown in Figure 5.6b. At this relatively low temperature, only monomers (i.e., Cu₁(CO)₁) are detected diffusing on the terrace and no cluster formation is observed during 100 ns of simulation. Figure 5.7b indicates that the number of detected Cu₁(CO)₁ is never bigger than one. This means the formation of monomer is scarce and it attaches

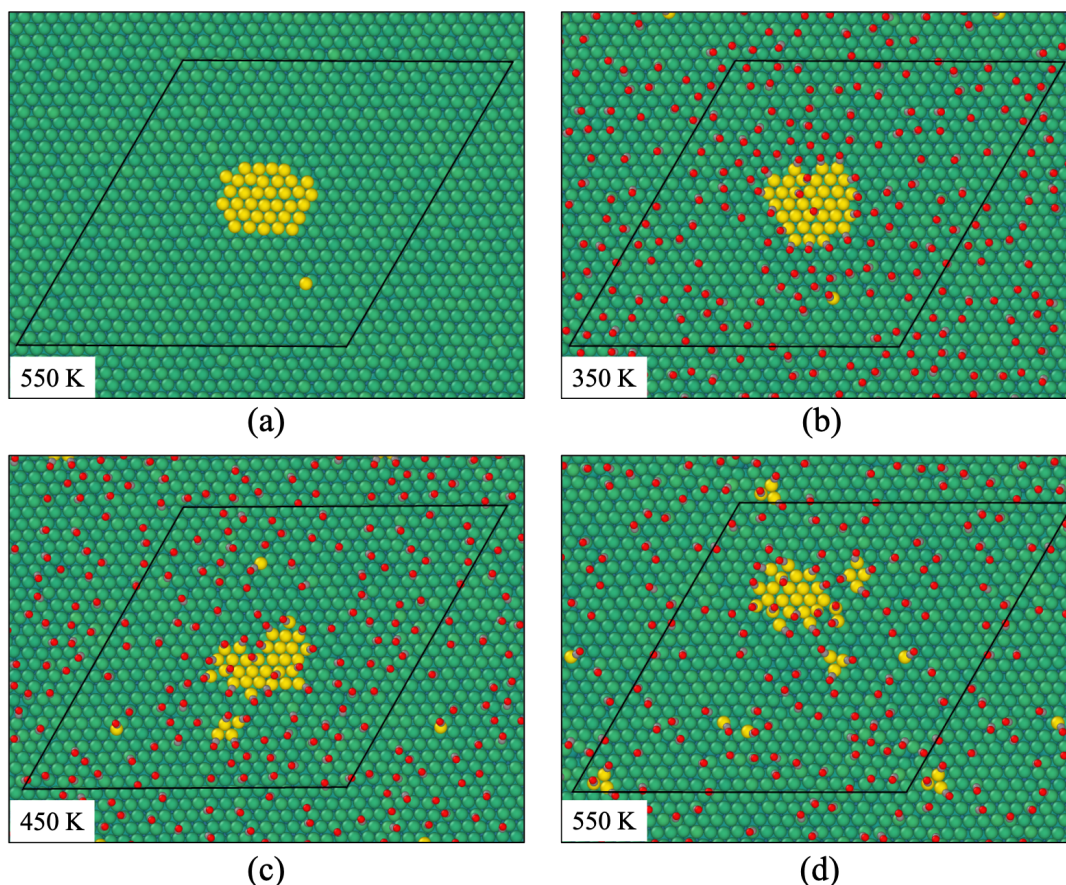


Figure 5.6: (a) Snapshots of the MD simulations of Cu island on Cu(111) with the following conditions: (a) at 550 K without exposure to CO, (b) at 350 K with CO exposure, (c) at 450 K with CO exposure, and (d) at 550 K with CO exposure. The images of CO molecules in the gas phase are hidden to clearly reveal the change in the shape of the Cu island as well as the clusters formation.

back to the island before the new one is formed. Nevertheless, the frequency of monomer formation under CO exposure at 350 K is still higher compared to the one without CO exposure even at 550 K.

A snapshot of the 450 K simulation, which depicts a tetramer and some monomers diffusing on the terrace is shown in Figure 5.6c. Quantitatively, the number of detected monomers and various size of the clusters are shown in Figure 5.8a. Monomers are found to dominate as they are detected at almost every ns of the simulation. At this temperature, we detected various size of clusters ranging from dimer to hexamer within 100 ns as well as the significant increase of the monomers. The histogram of the clusters' lifetime is shown in Figure 5.8b. The decay of the clusters' lifetime is fitted to the exponential function where number of clusters is proportional to $\exp -t/\lambda$, from which we can obtain λ as the mean lifetime of the cluster. The lifetime

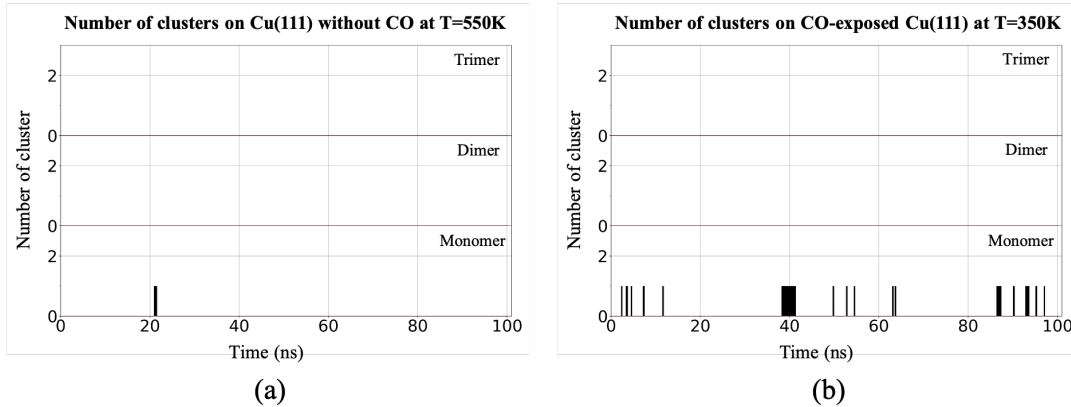


Figure 5.7: (a) Number of clusters on Cu(111) without CO exposure at 550 K. Only monomers are found at around 20 ns of simulation. (b) Number of clusters on Cu(111) with CO exposure at 350 K. More monomers are observed within 100 ns of simulation.

of dimers, trimers, tetramers, and the pentamers & above are found to be 0.094 ns, 0.126 ns, 0.067 ns, and 0.081 ns, respectively. We found the trimer has longer lifetime than a dimer which implies the former is more stable.

A snapshot of the 550 K simulation, which depicts trimers and monomers diffusing on the terrace, is shown in Figure 5.6d. As indicated in Figure 5.9a, the frequency and the numbers of detected monomers and clusters on the terrace is clearly much higher than the case of 350 K and 450 K. We also observed the formation of heptamer which is not found in the simulations with lower temperature. The histogram of the clusters' lifetime is shown in Figure 5.9b. The mean lifetime of the dimers, trimers, tetramers, and pentamers & above are found to be 0.030 ns, 0.036 ns, 0.023 ns, and 0.028 ns, respectively. Similar to the case of 450 K, the trimer has longer lifetime than the dimers. We also observed that the mean lifetimes of the clusters are shorter compared to 450 K. Thus, raising the temperature increases the frequency of the clusters' formation but at the same time shortens their lifetimes.

As shown in Figure 5.8a and Figure 5.9a the formation of monomers is clearly shown to precede the formation of larger clusters at the beginning of the simulation. This indicates that at the early stage of the simulation, the formation of clusters is initiated by the formation of monomers. More detail analysis on such mechanism is provided in the next section. Over the time, the number of monomer or large clusters shows the appearance and disappearance of peaks, which indicate their dynamics on the surface. In the middle of simulation, the formation and decomposition of the clusters of different sizes might happen simultaneously. Thus, the preceding of the monomer's

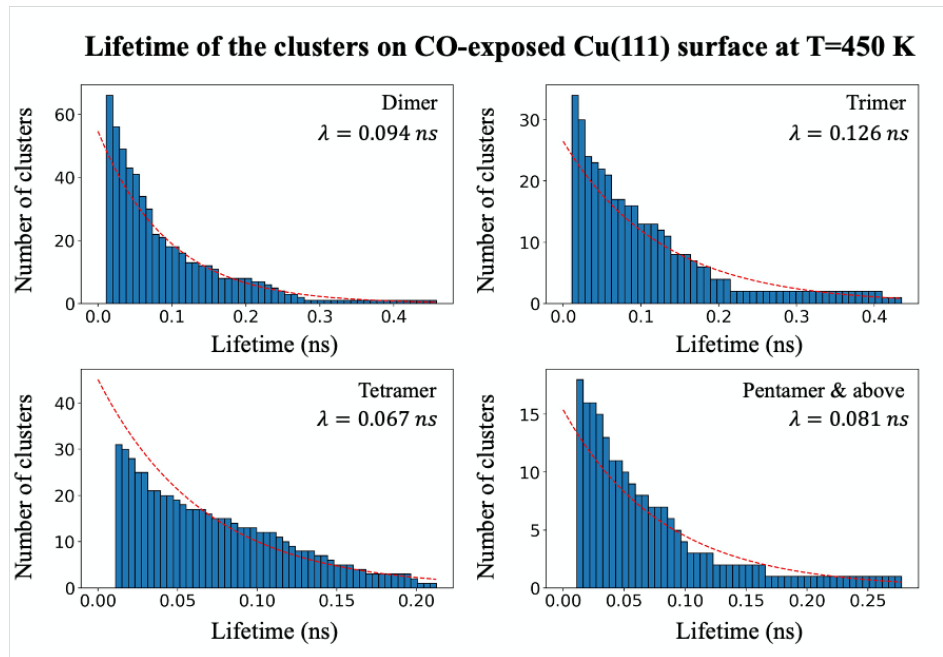
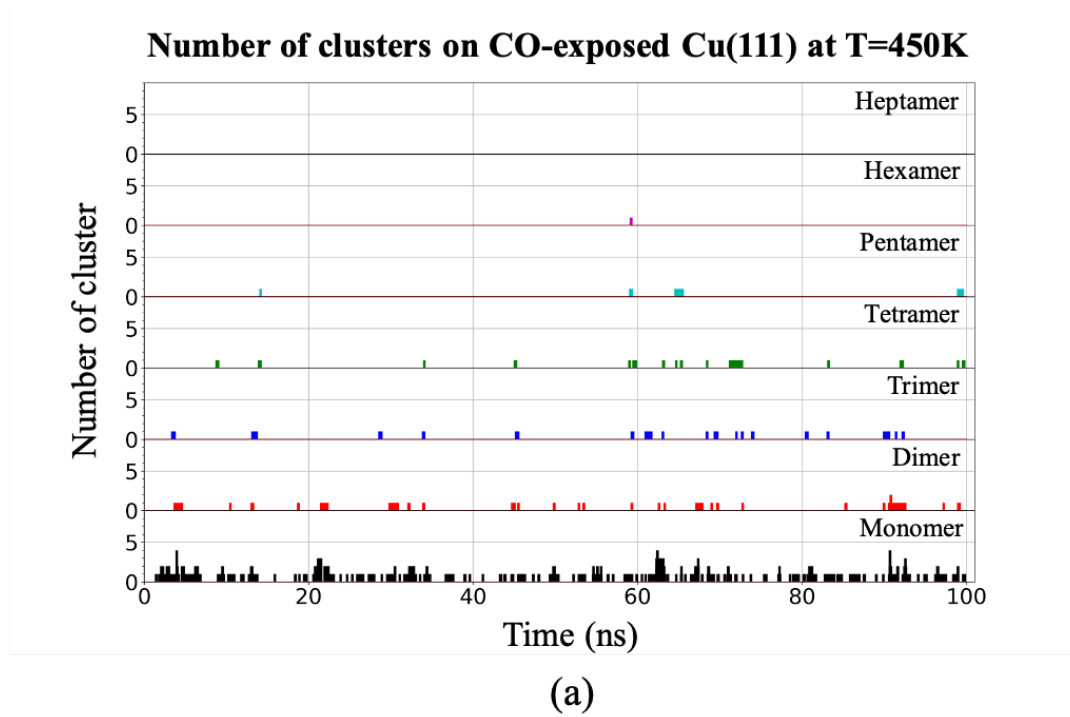


Figure 5.8: (a) Plot of number of clusters detected within 100 ns of simulation at 450 K. (b) The histogram of the clusters' lifetime in the simulation at 450 K.

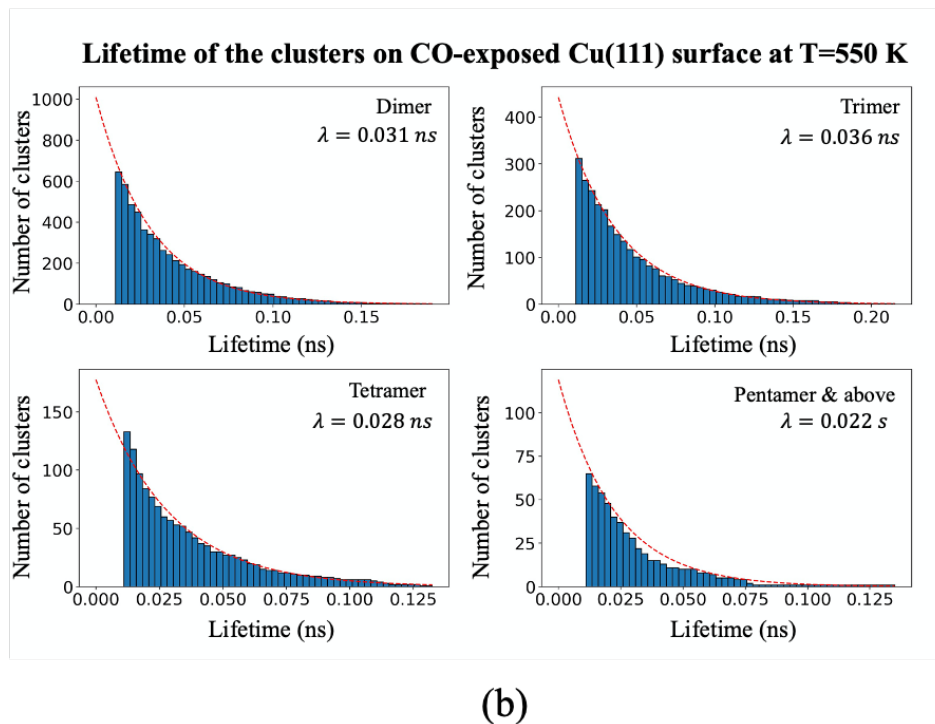
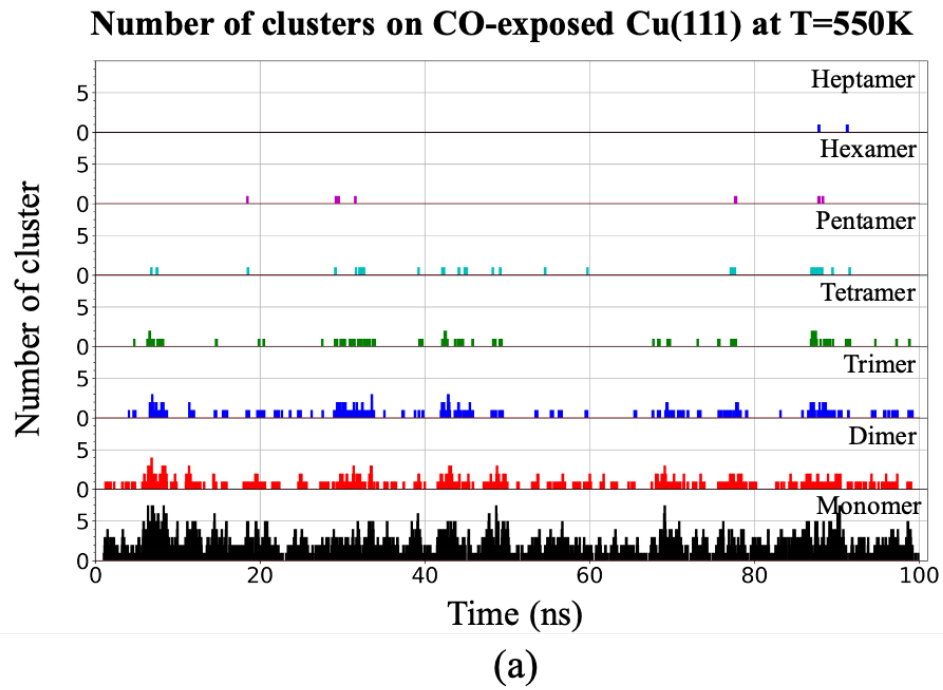


Figure 5.9: (a) Plot of number of clusters detected within 100 ns of simulation at 550 K. (b) The histogram of the clusters' lifetime in the simulation at 550 K.

peak before the cluster's peak (as observed in the beginning of simulation) is not necessarily observed in the middle of simulation. For instance, when some of monomers aggregate to form bigger cluster, additional monomers can be formed directly by detachment from the island or by dissociation of big cluster, thereby preventing the peak of monomer to disappear. Moreover, the cluster can be formed directly from the island without the involvement of monomer which cause the peak of the particular cluster to be independent from the peak of monomer.

By comparing the occurrences of clusters on the Cu surface with and without CO exposure at 550 K (Figure 5.7a and Figure 5.9a), it is clear that CO plays important role in driving the formation of clusters. Qualitatively, the CO induced the stabilization of the Cu island at the step edge, thereby accelerating the detachment of adatom or clusters from the island. Raising the temperature further promotes this process since more energy are available to overcome the detachment barrier. Further, the high temperature induces the high fluctuation of the step edge, which expose more kink atoms that have high mobility.

The typical shape of clusters observed in the MD simulations are shown in Figure 5.10. In all sizes, we found the CO adsorb on the edge of the cluster which corresponds to the low coordinated atoms as also suggested by the DFT calculations in this study (see section 3.A). Due to the repulsive lateral interactions, the CO adsorbed geometry is tilted outward the cluster, which was also reported in the experiment [25]. We noticed that no CO adsorption in the center atom of close-packed shape of hexamer and heptamer as shown in Figure 5.10g and Figure 5.10h, respectively. This is due to the CO adsorption on that particular atom is weaker than those on the edge atoms. Previous DFT study also found that the CO adsorption on the center of heptamer is less stable by 0.36 eV compared the edge [147]. However, due to the dynamic nature of the clusters, the shape of the cluster changes over time and might form more open shape of the cluster (Figure 5.10f) which can accommodate more CO adsorptions.

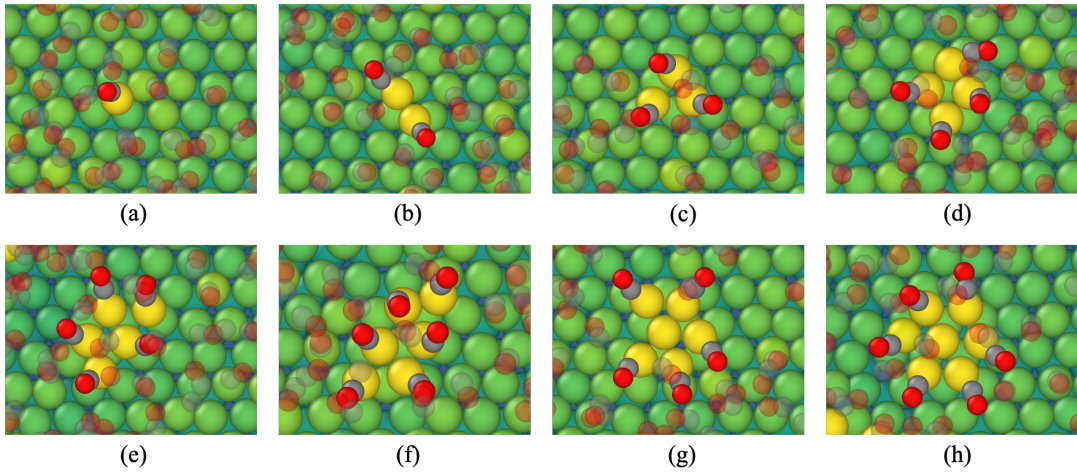


Figure 5.10: The snapshot of different size of clusters with different size: (a) monomer, (b) dimer, (c) trimer, (d) tetramer, (e) pentamer, (f) hexamer, (g) closed-packed hexamer, and (h) closed-packed heptamer as observed in the MD simulations at 550 K. In these figures, the CO molecules that are not directly connected to the clusters are made semi-transparent.

The stability of the clusters can be inferred from the dissociation energy E_d , defined as the energy required to dissociate a monomer from the cluster. The formula to obtain E_d for clean and CO-decorated Cu clusters are written in Eq. (5.1) and Eq. (5.2), respectively.

$$E_d^{(slab+Cu_N)} = E_{form}^{(slab+Cu_{N-1})} + E_{form}^{(slab+Cu_1)} - (E_{form}^{(slab+Cu_N)}) \quad (5.1)$$

$$E_d^{(slab+Cu_N(CO)_M)} = E_{form}^{(slab+Cu_{N-1}(CO)_{M-1})} + E_{form}^{(slab+Cu_1)} - (E_{form}^{(slab+Cu_N(CO)_{M-1})}) \quad (5.2)$$

$$E_{form}^{(slab+Cu_N(CO)_M)} = E_{tot}^{(slab+Cu_N(CO)_M)} + E_{tot}^{slab} - NE_{bulk}^{Cu} - M\mu_{CO} \quad (5.3)$$

N and M represent the number of adatoms in the cluster and the number of adsorbed CO, respectively. The formation energy E_{form} for the corresponding cluster then can be obtained from Eq. (5.3), written as follows [25, 26].

The $E_{tot}^{(slab+Cu_N(CO)_M)}$, E_{tot}^{slab} , E_{bulk}^{Cu} , and μ_{CO} are the total energy of the cluster deposited on the slab, total energy of the slab, bulk atomic energy of Cu, and chemical potential of CO, respectively. M equals to zero in the case of clean Cu cluster. The μ_{CO} is calculated from $E_{tot}^{CO(g)} + E_{ads}^{CO}$, in which the first and second terms represent the total energy of isolated CO and adsorption energy of CO on Cu(111) surface.

We then applied the Eq. (5.1) to Eq. (5.3) to the closed-packed clusters that we found in the MD simulations. The optimized structures of the clusters (i.e., $Cu(CO)_1$, $Cu_2(CO)_2$, $Cu_3(CO)_3$, $Cu_4(CO)_4$, $Cu_5(CO)_5$, $Cu_6(CO)_5$, and $Cu_7(CO)_6$) are shown in Figure C.6. As shown in Figure 5.11a, the formation energies of clean cluster are much more positive than the CO-decorated cluster, which implies the promotional effect of the CO adsorptions to the cluster formation.

We also found that the formation energy of the Cu clusters gets higher as the size of the cluster increases. This is reasonable since forming the clean Cu clusters requires energy for the bond-breaking of the Cu atoms, and more bond-breaking are involved as the size of Cu cluster increases. Due to CO adsorption(s), the bond-breaking becomes easier, resulting in the lower formation energy of Cu-CO cluster. As observed in Figure 5.11a, the reduction of the formation energy of Cu clusters due to CO adsorptions gets higher as the cluster size increases. In other words, the more CO adsorbed to the Cu cluster, the easier the bond- breaking to occur.

By means of DFT with PBE+U approximation, the previous study also shows the reduced formation energy of the Cu cluster upon the CO adsorption [25]. For instance, the formation energy of Cu_3 is reduced from 1.64 eV to 0.26 eV when the $Cu_3(CO)_3$ is formed. The trend of increasing formation energy of clean Cu cluster when the clusters get bigger is also shown in the literature

[25]. Though the sizes of the calculated clusters are different, this trend is also suggested by results of this study. Additionally, the reference6 also shows that the discrepancy of the formation energy of Cu and Cu-CO clusters gets higher when the size of the cluster increases. This indicates that the reduction of formation energy due to CO adsorption gets higher when the clusters get bigger.

Following Eq. (5.1), the calculated dissociation energy is shown Figure 5.11b. We should note that the CO-decorated hexamer (i.e., $\text{Cu}_6(\text{CO})_5$) and heptamer (i.e., $\text{Cu}_7(\text{CO})_6$) have number of adsorbed CO smaller than the Cu adatoms. Thus, the products of the dissociated $\text{Cu}_6(\text{CO})_5$ are $\text{Cu}_5(\text{CO})_4$ and $\text{Cu}(\text{CO})_1$ as shown in Figure C.6. The calculated dissociation energy show that the CO-decorated clusters have lower dissociation energy, which implies that CO adsorptions also facilitate the dissociation of the clusters. Both the case of clean cluster and CO-decorated cluster show the highest dissociation energy at heptamer which implies its high stability as also reported in previous studies [149, 150].

As shown in Figure 5.11b, there is a significant increase of dissociation energy when going from dimer to trimer. This indicates that dissociating the trimer would be more difficult, hence such cluster is more stable and has longer lifetime compared to dimer. Further, we also observed that the mean lifetime of trimer is longer compared to the group of “pentamer & above”. In the case of large clusters, the entropy effect caused by the individual movement of each constituent atoms might play important role. Since the larger clusters correspond to more constituent atoms, such clusters can dissociate faster than the trimer even though the dissociation energy is higher.

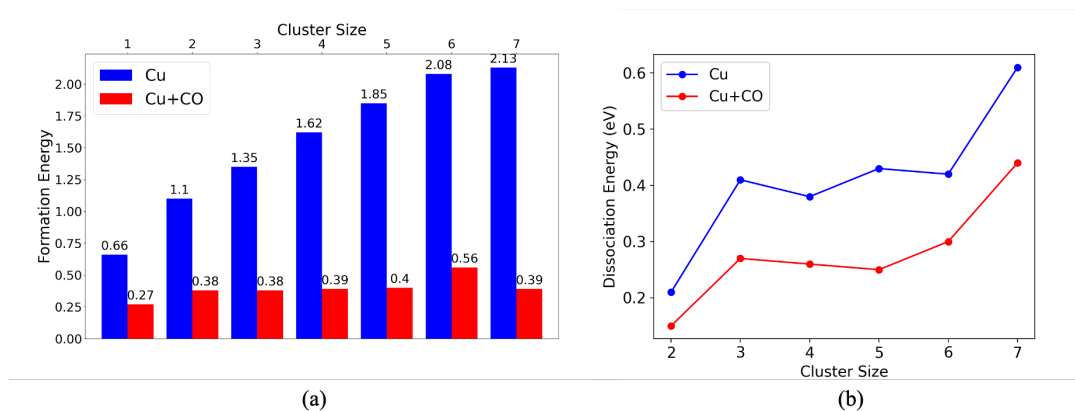


Figure 5.11: (a) The formation energy and (b) dissociation energy of the closed-packed clusters as observed in MD simulations at 550 K. The structures used in the calculations are the optimized closed-packed clusters shown in Figure C.6.

5.3.4 Mechanistic Insight to the CO-driven Formation of Cu Clusters

Given the result of the number, size, and occurrence time of the detected clusters, we can track the mechanisms of these clusters' formation. In general, there are two ways the clusters can be formed: (i) by the breaking some part of the island and (ii) by aggregation of monomers or smaller clusters that are already diffusing on the terrace. The present simulations show that both of them can occur at high temperature. We discuss each of them in the following. The formation of the cluster by the first mechanism is shown in (Figure 5.12). Due to the temperature, the step edge of the clusters fluctuates and at some point, form a kind of 'neck' or protrusion. This protrusion exposes Cu atoms with smaller coordination number which are subsequently occupied by the CO. Next, the concerted detachment of cluster decorated with CO is occurred. This clusters can diffuse on the terrace or decompose producing smaller cluster or monomers.

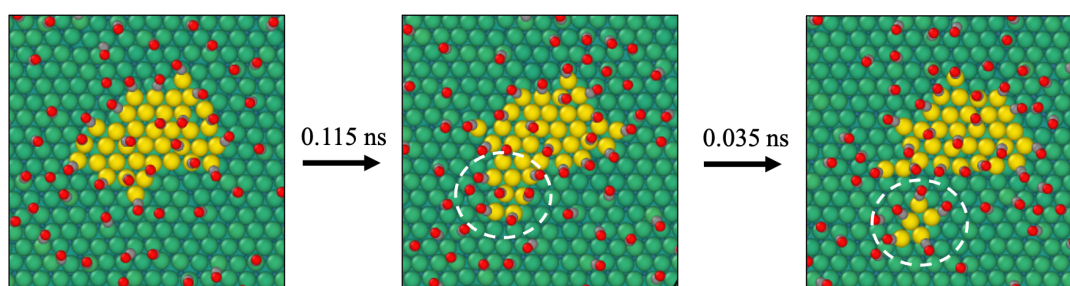


Figure 5.12: The direct formation of Cu cluster in which the cluster is formed instantaneously from the source (Cu island). The images of CO in the gas phase are hidden to clearly reveal the change in the shape of the Cu island as well as the clusters formation. The time intervals between the snapshot are shown in the figure.

The second mechanism is shown in Figure 5.13. Initially, the Cu step and kink atoms that adsorb the CO detach from the island and do random walk on the terrace. This wandering single Cu-CO complexes then collide with each other and form dimer, trimer, or even larger clusters. By counting and classifying the mechanisms by which the clusters are formed (Figure C.7 - C.12), we found that $\text{Cu}(\text{CO})_1$ is significantly involved in the formation and decomposition of the clusters, resulting in the preference of the indirect mechanism. The high frequency of aggregations and detachments of this complex implies their high mobility on the surface.

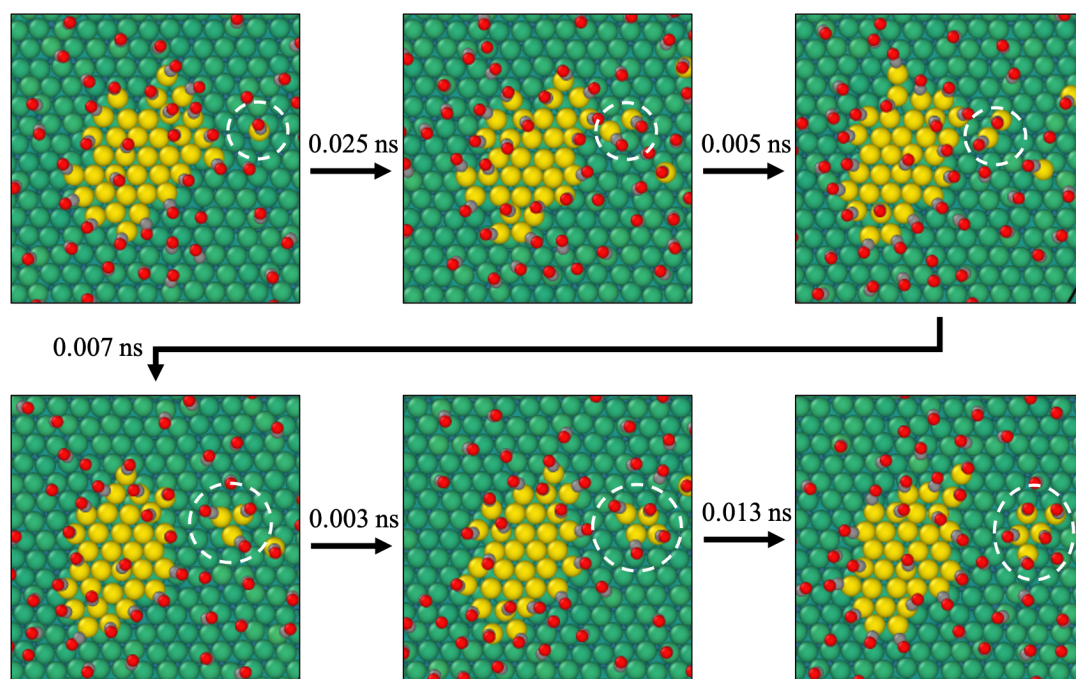
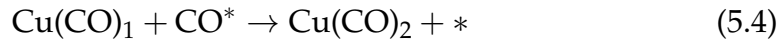


Figure 5.13: The indirect formation of Cu cluster in which the cluster is formed by agglomeration of diffusing monomer or smaller clusters on the terrace. The images of CO in the gas phase are hidden to clearly reveal the change in the shape of the Cu island as well as the clusters formation. The time intervals between the snapshot are shown in the figure.

As also indicated in Figure 5.8a and Figure 5.9a, The $\text{Cu}_1(\text{CO})_1$ are dominating because mechanically the formation of this complex is easier compared to formation of larger cluster. For instance, in the case of indirect mechanism, the formation of $\text{Cu}_1(\text{CO})_1$ does not require any prerequisite component, in contrast to the formation of larger cluster that has to wait until sufficient components are satisfied. In addition, due to the high temperature, dissociations that form $\text{Cu}_1(\text{CO})_1$ happen frequently which contribute to the high frequency of the detection of $\text{Cu}_1(\text{CO})_1$. However, we should note that the formation of the clusters at low temperature could not be efficiently observed

in the MD study due to the rare events. Thus, we emphasize that the dominance of $\text{Cu}_1(\text{CO})_1$ that we observe are for the given temperatures (350 K to 450 K). At low temperature, the cluster could be more dominant compared to the $\text{Cu}_1(\text{CO})_1$ since the dissociation of cluster will occur less frequent and their lifetime will be longer. However, due to the slow dynamics at low temperature, the observation of such events requires very long simulation time which might be not within the feasible time scale of MD. In the case of the direct mechanism, the formation of $\text{Cu}_1(\text{CO})_1$ is also the easiest since it requires the least bond-breaking. Larger cluster involves more atoms and obviously requires more bond-breaking to be formed by direct mechanism.

In contrast to the CO-induced cluster formation on Pt surface [151, 152], no dicarbonyl (i.e., $\text{Cu}(\text{CO})_2$) is observed on Cu surface even though we have included such structures in the database. We then calculated the reaction energy of the formation of dicarbonyl on Cu surface:



where the reaction energy is defined as:

$$\Delta E = E_{\text{tot}}^{\text{Cu}(\text{CO})_2} + E_{\text{slab}}^{\text{tot}} - E_{\text{tot}}^{\text{Cu}(\text{CO})_1} - E_{\text{tot}}^{\text{CO}^*}$$
 (5.5)

The $E_{\text{tot}}^{\text{Cu}(\text{CO})_2}$, $E_{\text{tot}}^{\text{Cu}(\text{CO})_1}$, $E_{\text{tot}}^{\text{CO}^*}$, $E_{\text{tot}}^{\text{slab}}$ represent the total energy of dicarbonyl, total energy of adsorbed CO on Cu monomer, total energy of adsorbed CO on flat surface, and total energy of the slab which consists of four layers of 4x4 Cu atoms. The value of the ΔE is calculated to be +0.10 eV which implies the endothermicity of the reaction and the preference of the decomposition of dicarbonyl to $\text{Cu}(\text{CO})_1$ and adsorbed CO on the terrace. The observation of dicarbonyl in the Pt surface might be the manifestation of the strong CO adsorption energy. Experimentally, Pt is shown to have more than -1.0 eV CO adsorption energy even on flat Pt(111) surface [153, 154], much stronger than CO adsorption energy on Cu(111) (i.e., -0.49 eV) [143]. Nevertheless, the present simulations show that clusters can be formed even without the formation of this dicarbonyl.

To find out the importance of CO adsorptions to the detachment of Cu atoms, we performed set of NEB calculations for different numbers and configurations of adsorbed CO on step with (100) microfacet (i.e., step-A) and step

with (111) microfacet (i.e., step-B). Based on the source of the atom, we categorized the detached Cu atom as step-atom, step-adatom, and kink-atom (Figure 5.14), the terminology of which follows the surface science literature [24]. The CO adsorb only on the atoms at the step edge. All the results of NEB calculation including the DFT barrier of detachment of Cu atom, the associated mechanisms, and the predicted barrier by machine-learning are provided in section 8 of Appendix C. We also provide the corresponding figures for each detachment/attachment mechanism in Figure C.13-C.18. Here we discuss the mechanisms of atom detachment and re-attachment which have the lowest DFT barrier for different number of CO per unit cell.

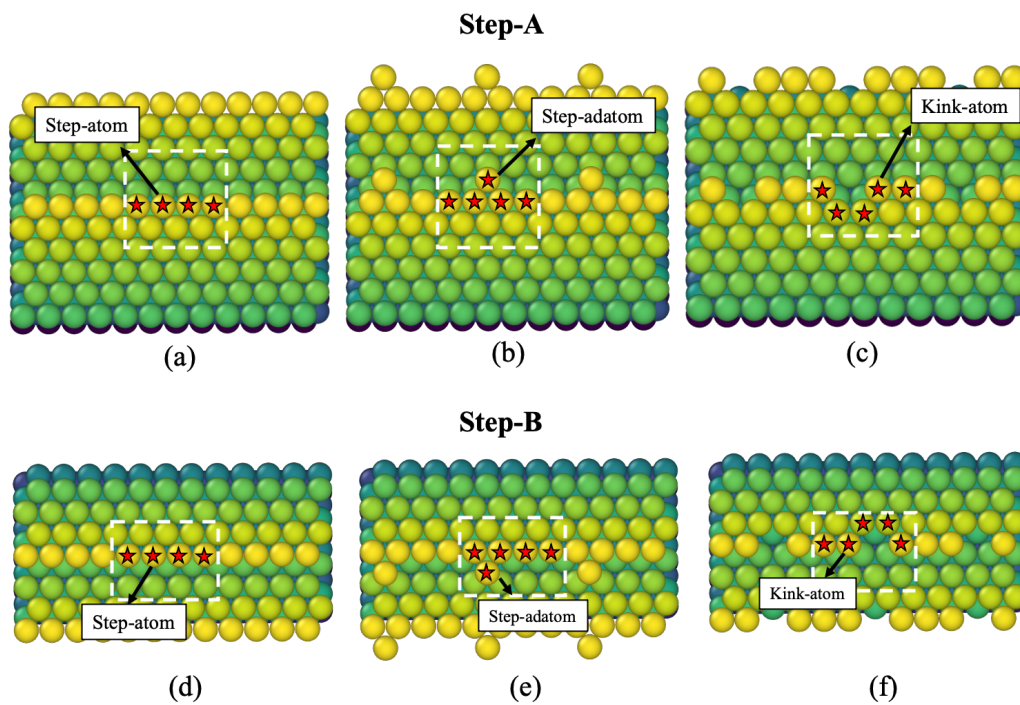


Figure 5.14: The categorization of Cu atoms into step-atom, step-adatom, and kink-atom on Cu stepped surfaces as pointed by the arrow in each sub-figure. The Cu stepped surfaces with (100) microfacet (i.e., step-A) are depicted in (a-c), while the Cu stepped surface with (111) (i.e., step-B) microfacet are depicted in (d-f). The atoms marked with the red-star symbols are used as the candidate of CO adsorption sites to get the results shown in Figure 5.15 and Figure 5.16.

The detachment (i.e., forward) and re-attachment (i.e., reverse) barriers of Cu step-atom, step-adatom, and kink-atom from step A are shown in Figure 5.15. Without CO adsorption, the detachment barriers of these atoms are calculated to be 0.73 eV, 0.45 eV, and 0.70 eV, respectively. The lower detachment barrier for step-adatom is expected due to the fewer bond-breaking upon detachment. In all cases, the adsorptions of CO results in lower detachment barrier compared to the case of no CO adsorption. The lowest barrier of around 0.2 eV is achieved when all the step-atoms are occupied by CO. We noticed the barrier slightly increases from 0.22 eV to 0.27 eV when the CO/unit cell changes from three to four in the case of step-adatom detachment. However, in general, the reduction of the barriers is linear with respect to the increasing number of adsorbed CO at step edge.

Interestingly, we found a steady increase of the re-attachment barrier of Cu step-atom along with the number of CO adsorption on the step edge. The increasing of the re- attachment barrier might be due to the repulsive interactions between the CO on the detached Cu atom and the remaining CO on the step edge. As shown in Figure 5.15a, with full occupation of step-atom at the perfect step-edge (No. of CO = 4), the re-attachment barrier is found to be 0.34 eV which is higher than the detachment barrier (i.e., 0.24 eV). This indicates that the full occupation of the step-atoms favors the detachment of step-atom. We noticed that once the step-atom carrying the CO detaches and leaves a vacant site, the remaining CO on step edge is tilted toward that particular site and thus blocking the re- attachment process. This might be the origin of such high-reattachment barrier since the incoming atom has to fit into a tight space and ‘push’ the nearby CO a little bit. In the case of step adatom (Figure 5.15b) and kink atom (Figure 5.15c), the full CO occupation of the step edge type A (i.e., No. of CO = 5) also raises the re-attachment barrier, though not as high as the re- attachment of the step-atom, since now there is wider space for the incoming atom. Unlike the case of step-atom in Figure 5.15a, the barriers of detachment of step-adatom and kink-atom are still higher than the barrier of re-attachment.

The detachment and re-attachment barriers of Cu step-atom, step-adatom, and kink-atom from step B are shown in Figure 5.16. Without CO adsorption, the detachment barriers of Cu step-atom, step-adatom, and kink-atom are calculated to be 0.72 eV, 0.55 eV, and 0.68 eV respectively. Similar with step A, the adsorptions of CO help to reduce the detachment barrier in all cases. Given full CO occupation at step edge (i.e., No. of CO = 4), the re-attachment

barrier of step-atom is higher than the detachment barrier in the case of detachment of step-atom though only 0.01 eV difference (Figure 5.16a). We noted that the detachment barrier of step-atom for step B (i.e., 0.12 eV) is much lower than in the case of step A (i.e., 0.24 eV). This indicates that, given full occupation of CO to the step edge, the Cu step-atom is easier to detach from step B compared to step A.

In the case of detachment of step-atom (Figure 5.16a) and kink-atom (Figure 5.16c), the lowest detachment barriers are achieved in the case of full CO occupation on the step edge in the case of step-atom and kink-atom detachments. On the other hand, the full occupation at the step edge raises the detachment barrier of step-adatom to 0.31 eV (Figure 5.16b), which is slightly higher than the barrier with fewer number of adsorbed CO. Nevertheless, in general, the CO adsorptions on the step edge promote the detachment of the atoms from the A and step B by lowering the detachment barrier and increasing the re-attachment one.

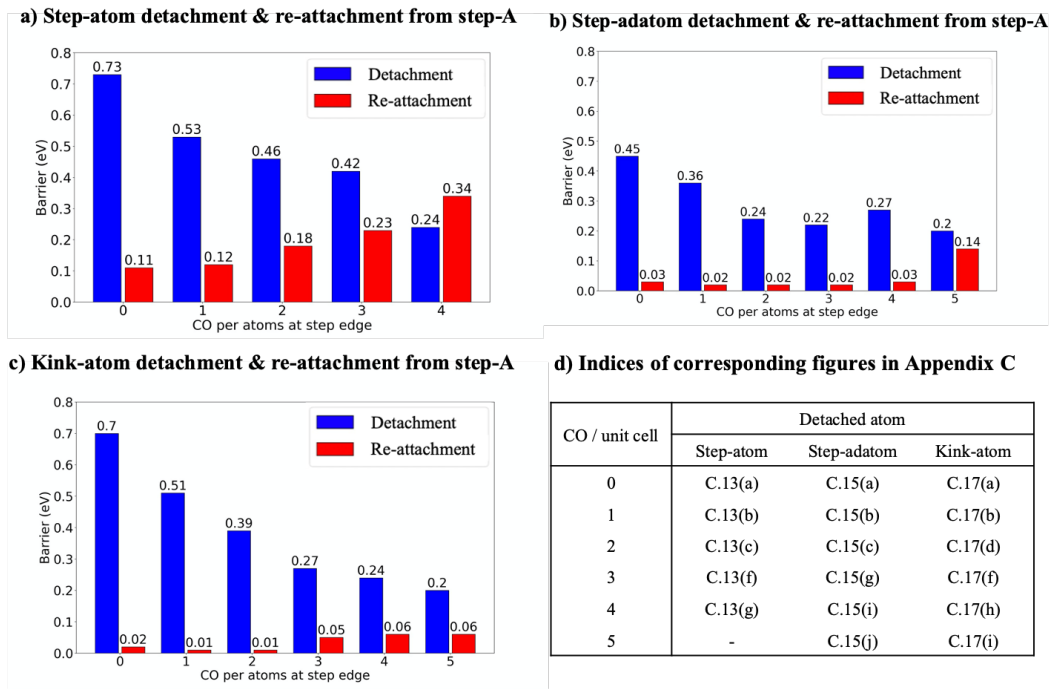


Figure 5.15: Energy barrier for detachment and re-attachment of Cu atom from step A (i.e, step with (100) microfacet). The definition of step-atom, step-adatom, and kink-atom as well as the adsorption sites can be seen in Figure 5.14 (a-c). (d) Table shows the indices of corresponding figures in Appendix C.

5.4. Conclusion

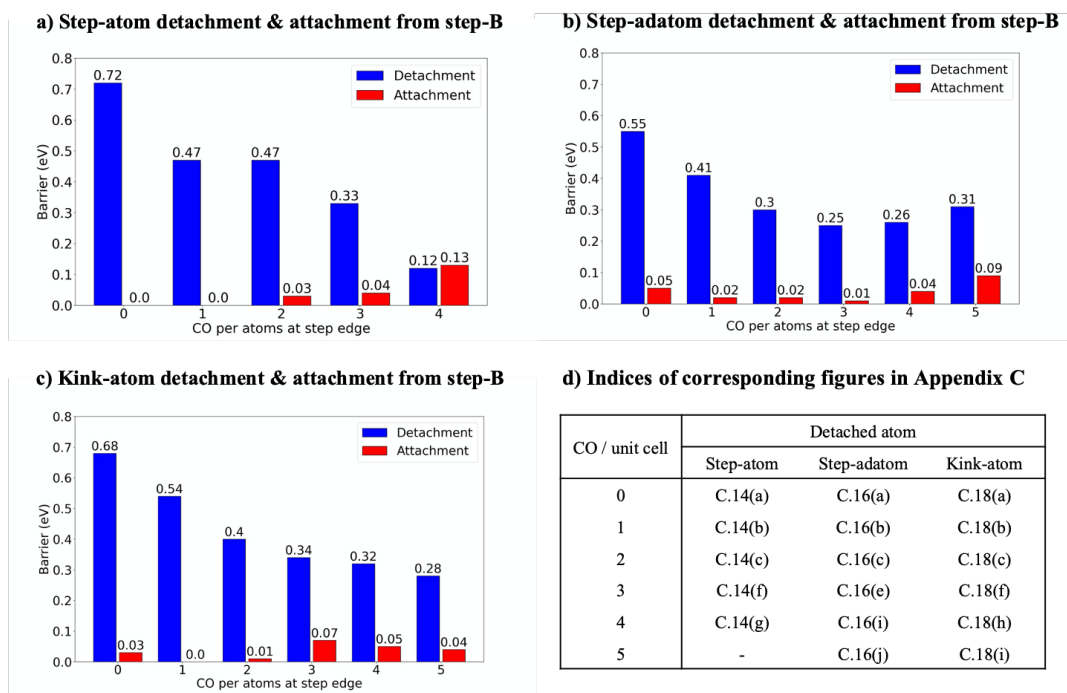


Figure 5.16: Energy barrier for detachment and re-attachment of Cu atom from step B (i.e, step with (111) microfacet). The definition of step-atom, step-adatom, and kink-atom as well as the adsorption sites can be seen in Figure 5.14 (a-c). (d) Table shows the indices of corresponding figures in Appendix C.

5.4 Conclusion

In the present study, we investigated the influence of CO to the formation of Cu clusters on Cu(111) surface by doing a set of MD simulations driven by machine-learning force-field. By using the Cu island deposited on the Cu surface as the model, the simulations show that the CO-decorated Cu clusters are formed within a hundred of ns at 450 K and 550 K given the exposure to CO molecules. On the other hand, no cluster is formed on clean Cu surface even at 550 K within the same time interval. The effect of temperature to the formation of cluster has also been investigated. CO-decorated Cu clusters ranging from dimer to hexamer are detected within a hundred of ns at 450 K. Lowering the temperature to 350 K doesn't result in the formation of clusters within a hundred ns due to the scarce detachments of adatom. Raising the temperature to 550 K results in the formation of bigger clusters, ranging from dimer to heptamer, but with shorter lifetime. At 450 K and 550 K, the CO-decorated trimer has the longest lifetime which comes from its high dissociation energy.

The clusters can be formed directly through simultaneous detachment of a group of step- atoms or indirectly by agglomeration of wandering $\text{Cu}_1(\text{CO})_1$

and smaller clusters on the surface terrace. By counting and classifying the mechanisms by which the clusters are formed, we found that $\text{Cu}_1(\text{CO})_1$ is significantly involved in the formation and decomposition of the clusters, resulting in the preference of the indirect mechanism. We have also shown that the $\text{Cu}_1(\text{CO})_1$ dominating on the surface at temperature of 450 K to 550 K. This behavior is expected since mechanically the formation of this complex is easier compared to formation of larger cluster, in contrast to the formation of larger cluster that has to wait until sufficient components are satisfied. In addition, due to the high temperature, dissociations that form $\text{Cu}_1(\text{CO})_1$ happen frequently which contribute to the high frequency of the detection of $\text{Cu}_1(\text{CO})_1$. In the case of the direct mechanism, the formation of $\text{Cu}_1(\text{CO})_1$ is also the easiest since it requires the least bond-breaking. Larger cluster involves more atoms and obviously requires more bond-breaking to be formed by direct mechanism.

By analyzing the formation energy of different shapes of cluster, we found that the discrepancy between the formation energy of Cu cluster and CO-decorated Cu cluster gets higher when the size of cluster increases since the CO adsorption on the cluster facilitates the bond-breaking of Cu clusters. We confirmed the influence of CO to the detachment of Cu atoms by conducting set of NEB calculations. The result of NEB shows the adsorption of CO at the step edge indeed promotes the detachment of Cu atoms by lowering their detachment barrier.

Chapter 6

Summary and Future Plan

6.1 Summary

In this dissertation, the multi-scale simulations have been applied to elucidate the non-equilibrium states of the Cu surface. These non-equilibrium states, in the increasing complexity, includes the step edge fluctuation of the Cu (111) surface, the surface alloying of Cu(997) with Zn, and the surface reconstructions of the Cu(111) induced by the CO adsorbates. The methods used involved the integration of DFT with higher-scale computational frameworks such as MD and KMC. The outcomes of these research are summarized as follow.

Chapter 3 presents the study on the step edge fluctuation of the Cu (111). The first principles calculations and kinetic modelling were combined in the form of DFT-KMC simulation to investigate the equilibrium fluctuations of steps on Cu(111). Based on investigation on 13 different diffusion events that might occur during the step fluctuations, the energetics obtained from CE framework reasonably agree with direct DFT calculations. The results of activation energy calculations show that the diffusion of adatom along the step edge has considerably low barrier, thus can be expected to be dominant in the mass transport process during step fluctuations. The time correlation functions of equilibrium step fluctuations at 300 K, 400 K, and 500 K have been calculated and compared with experiments and theoretical studies.

Chapter 4 presents the study on the surface alloying of Cu(997) with Zn to form CuZn catalyst which has been shown to exhibit high activity for methanol synthesis. The structure and the formation process of Cu-Zn surface alloy on Cu(997) by machine-learning molecular dynamics. Gaussian Process (GP) regression aided with on-the-fly learning scheme were employed to build force-field based on data of first principles calculations. The

simulation reveals atomistic details of the alloying process, i.e., the incorporation of deposited Zn adatoms to the Cu substrate. We found the Zn incorporate the surface not only at upper terrace, but also at lower and middle terraces which have not been considered in the previous DFT studies of methanol synthesis on Cu-Zn surface. The surface alloying is also accompanied by the formation of wavy step edge with high kink density, much different with the model of rigid step edge used in the previous DFT studies. By calculating the barrier of elementary events of step edge fluctuations (i.e., attachment and detachment of adatom to/from step edge), we found all the elementary events involving Zn atom have lower barrier than the pure Cu system, suggesting Zn atoms enhance the step edge fluctuations. The time evolution of the surface shows the alloying is initiated at upper and lower terraces near the step edge, giving emphasis to the role of steps and kinks in the surface alloying which lower the barriers of elementary events such as vacancy generation and direct-exchange.

Chapter 5 presents the study on the surface reconstruction of Cu surface induced by CO adsorbates. The influence of CO to the formation of Cu clusters on Cu(111) surface has been investigated by doing a set of MD simulations driven by machine-learning force-field. By using the Cu island deposited on the Cu surface as the model, the simulations show that the CO-decorated Cu clusters are formed within a hundred of ns at 450 K and 550 K given the exposure to CO molecules. On the other hand, no cluster is formed on clean Cu surface even at 550 K. The effect of temperature to the formation of cluster has also been investigated. CO-decorated Cu clusters ranging from dimer to hexamer are detected within a hundred of ns at 450 K. Lowering the temperature to 350 K does not result in the formation of clusters due to the scarce detachments of adatom. Raising the temperature to 550 K results in the formation of bigger clusters, ranging from dimer to heptamer, but with shorter lifetime. The clusters can be formed directly through simultaneous detachment of a group of step-atoms or indirectly by agglomeration of wandering $\text{Cu}(\text{CO})_1$ and smaller clusters on the surface terrace. The statistical analysis on the evolution of the clusters shows the $\text{Cu}(\text{CO})_1$ significantly involved in the formation and decomposition of the clusters due to their high mobility. A set of NEB calculations has been performed to confirm the adsorption of CO at the step edge promotes the detachment of Cu atoms by lowering the detachment barrier.

6.2 Future Plan

The ultimate goal of this study is to elucidate the non-equilibrium states of heterogeneous catalysis, in particular the catalytic reactions of methanol synthesis. Obviously, there are many parts of the non-equilibrium states of methanol synthesis that have not been covered in this dissertation. For instance, the inclusion of ZnO and the Al_2O_3 support to the Cu surface are necessary to better represent the CZA, the catalyst used in industrial application. In addition, the methanol synthesis involves various reactants and intermediate chemical species, including CO_2 , H_2 , HCOO , H_2COO , HCOOH , and many other species that might be elusive in experiments. The step fluctuations, Cu-Zn alloying, and the interplay between CO and Cu surface presented in this dissertation are just the very beginning in the research of the complex non-equilibrium states of methanol synthesis. Nevertheless, Here I show some of preliminary results of the multi-scale simulations involving the interactions of Cu surface with other adsorbates: H_2 , CO_2 , and the HCOO .

6.2.1 Preliminary Results

H-Induced Cu Surface Reconstruction

In this ongoing research, the surface reconstruction and the corresponding mechanism of the Cu surface due to the interaction with H will be elucidated. Hydrogen plays important role in methanol synthesis considering almost all the intermediate steps involve hydrogenation [73, 155]. By means of MLMD, the explicit interaction between hydrogen and Cu surface can be simulated and the mechanistic aspect of the surface evolution can be observed. Figure 6.1 shows the recombination of two hydrogen atoms on the Cu surface.

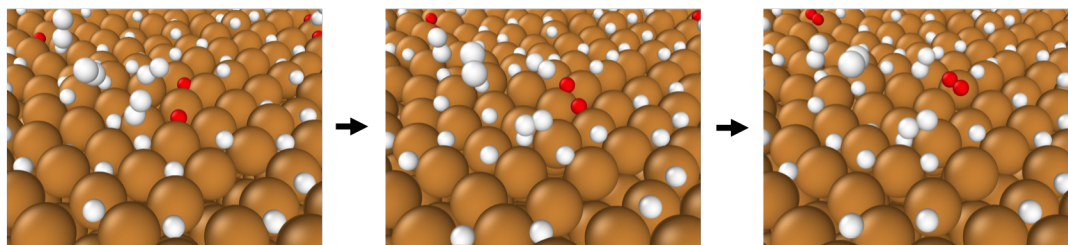


Figure 6.1: The snapshots of simulations at 500 K showing explicitly recombination of two hydrogen atoms (indicated by red atoms)

Vibration-driven Hydrogenation of CO₂ on Cu Surface

Based on the molecular beam experiment, it has been shown that the probability of successful hydrogenation of CO₂ to formate, which proceeds by means of Eley-Rideal mechanism, can be controlled by adjusting the translational and vibrational states of the molecular reactant [156]. However, the influence of the specific vibrational states of CO₂ can not be clearly understood as the molecular beam experiment can only measure the average of vibrational energy). To elucidate the role of each vibrational states, as well as other initial parameters of CO₂ (e.g., incident velocity and incident angle), the MLMD is performed and the probabilities of the hydrogenation with different initial conditions are measured.

Structure of co-adsorbed Formate on Cu Surface

I am also investigating the co-adsorption structure of the formate species which eventually form a kind of chain on Cu surface. The effect of this chain-like structure to the subsequent hydrogenations (to form formic acid or dioxymethylene) will be investigated. Figure 6.2 shows the formation of the chain from randomly co-adsorbed formate species.

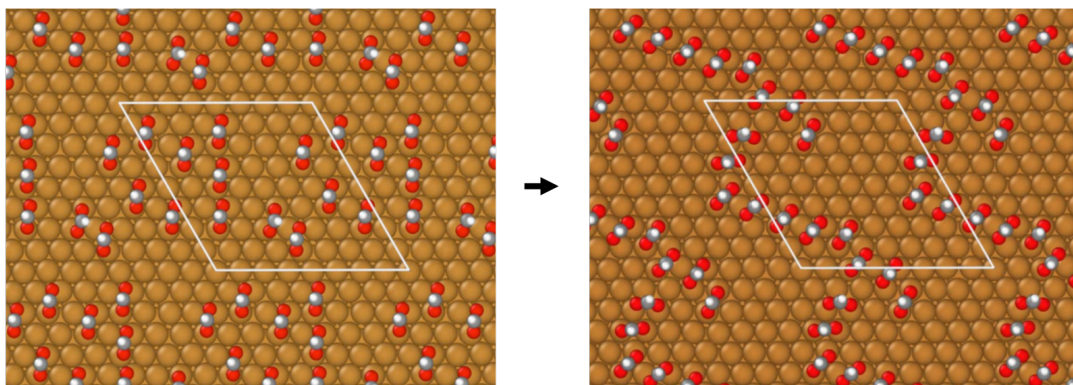


Figure 6.2: The snapshots of simulations at 300 K showing the formation of chain-like structures from the randomly co-adsorbed formate species on Cu surface.

Appendix A

Supporting Information on Step Fluctuations on Cu(111)

A.1 Cu Clusters Included in Cluster Expansion

This supporting information contains all the 48 clusters that we included in the cluster expansion framework. The associated graph multiplicity (represented by a value after the 'x' symbol) and the ECI are written below the name of each cluster. The blue and red circles represent the adatom adsorbed on the fcc and hcp lattices of Cu surface, respectively. Note that we assigned the value of 1.000 eV to the ECI of highly unstable clusters, whose structure cannot be relaxed to the particular configuration.

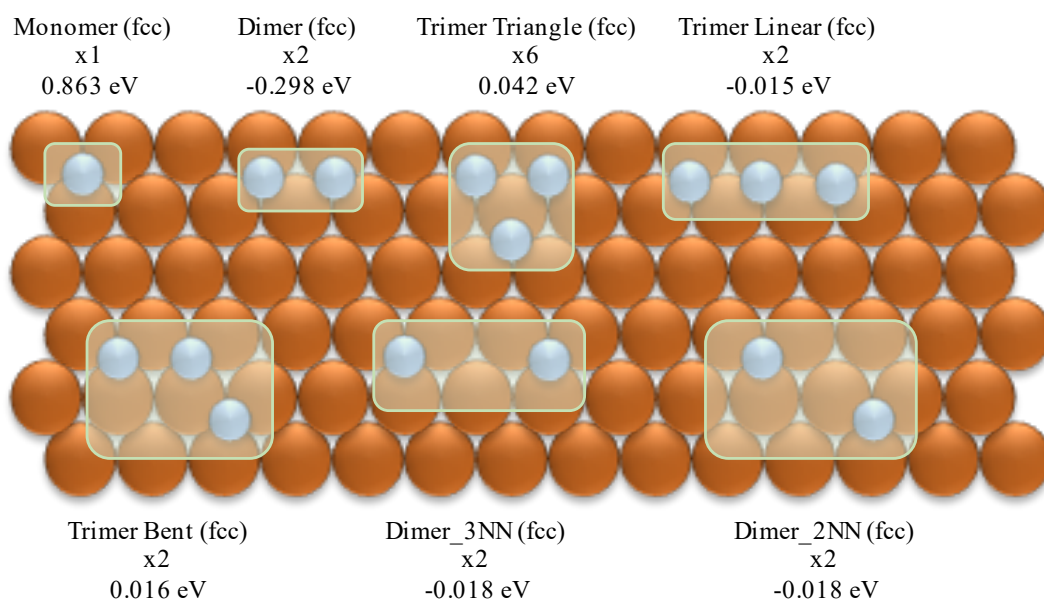


Figure A.1: FCC clusters included in the CE framework.

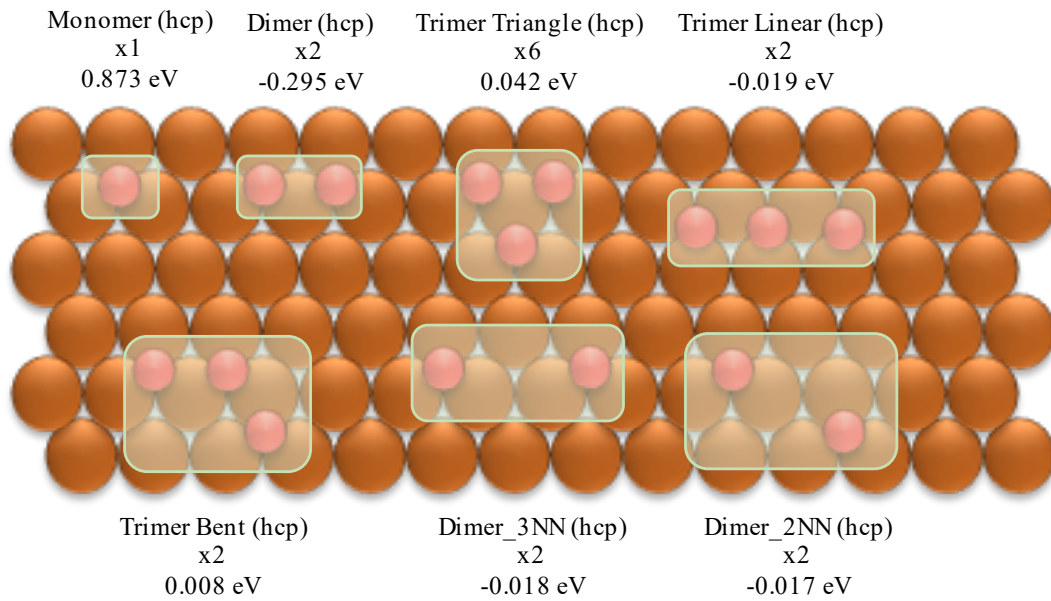


Figure A.2: HCP clusters included in the CE framework.

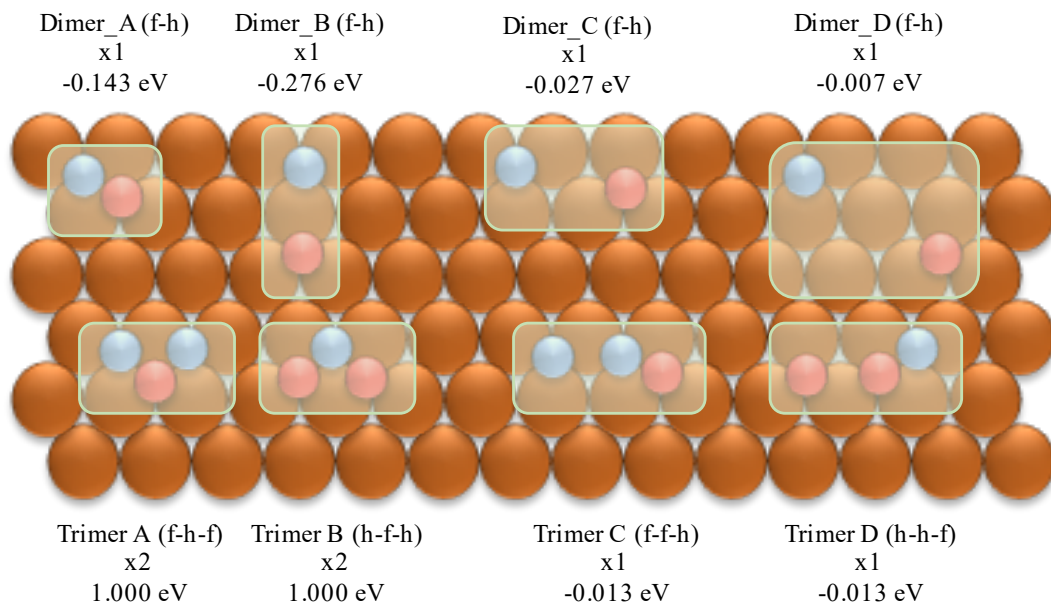


Figure A.3: FCC-HCP clusters included in the CE framework.

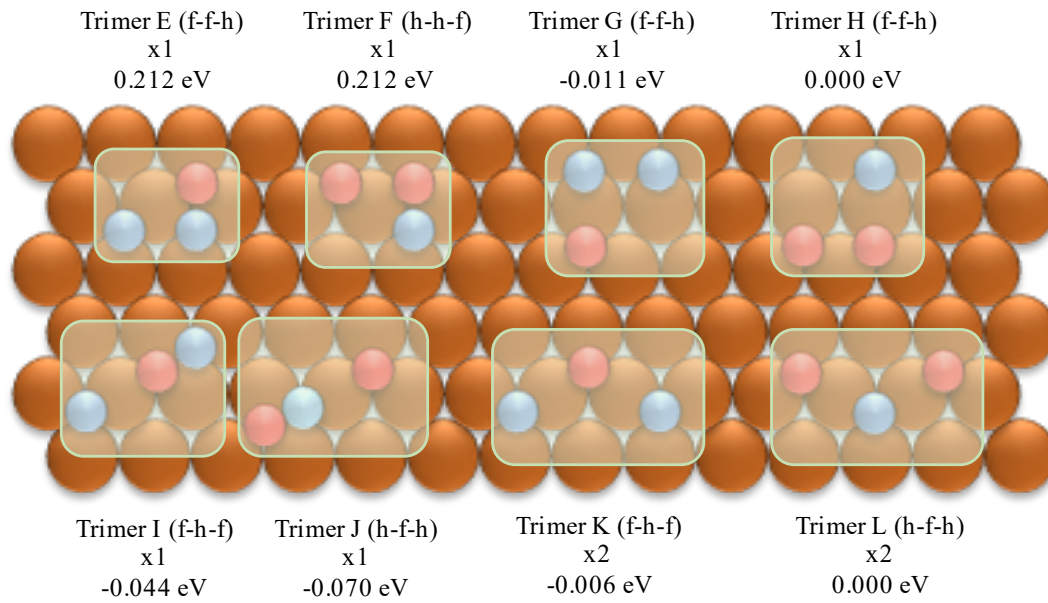


Figure A.4: FCC-HCP clusters included in the CE framework.

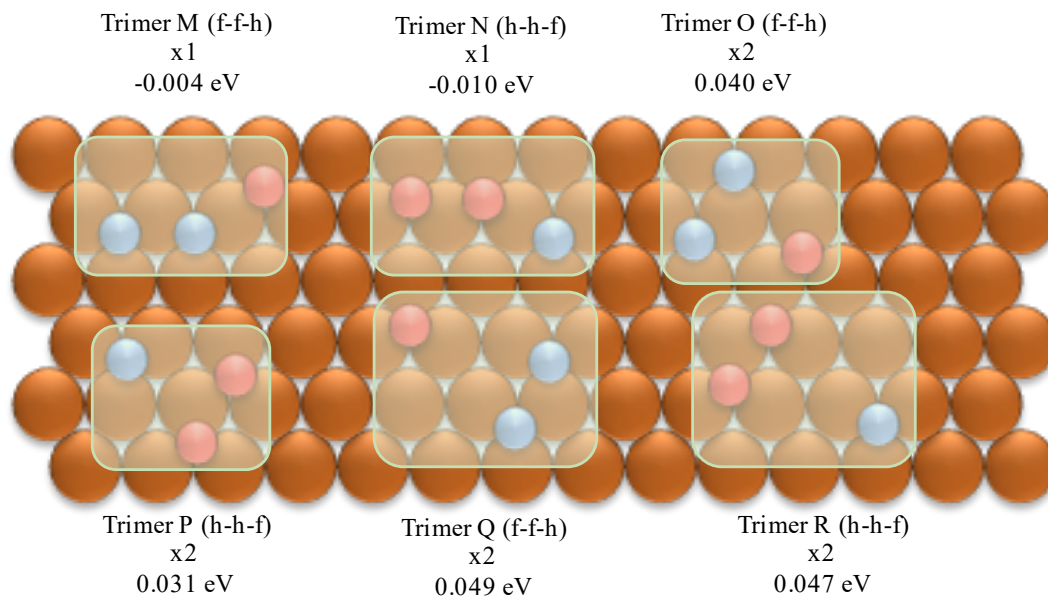


Figure A.5: FCC-HCP clusters included in the CE framework.

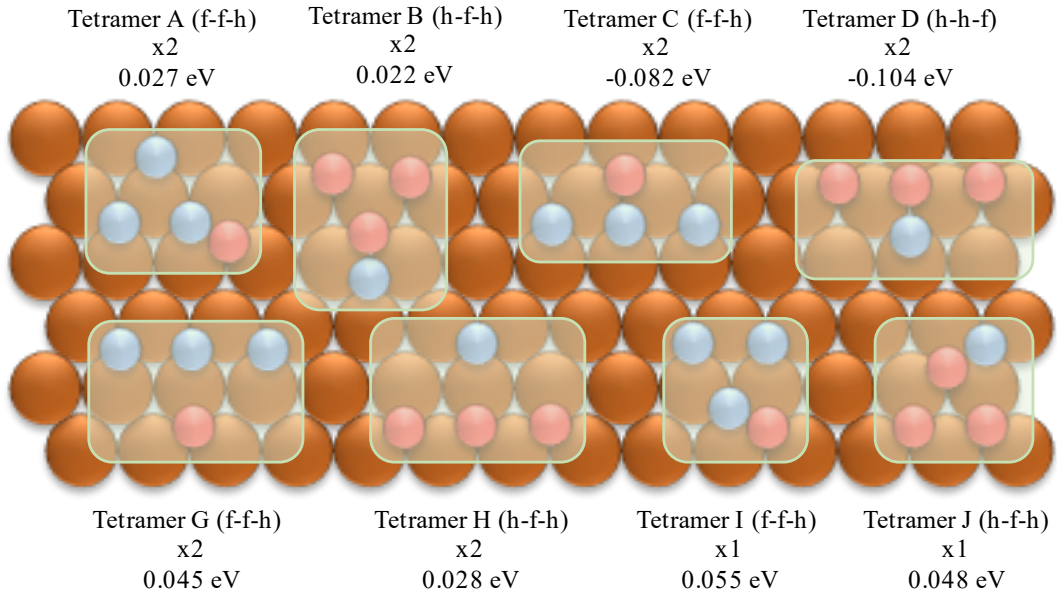


Figure A.6: FCC-HCP clusters included in the CE framework.

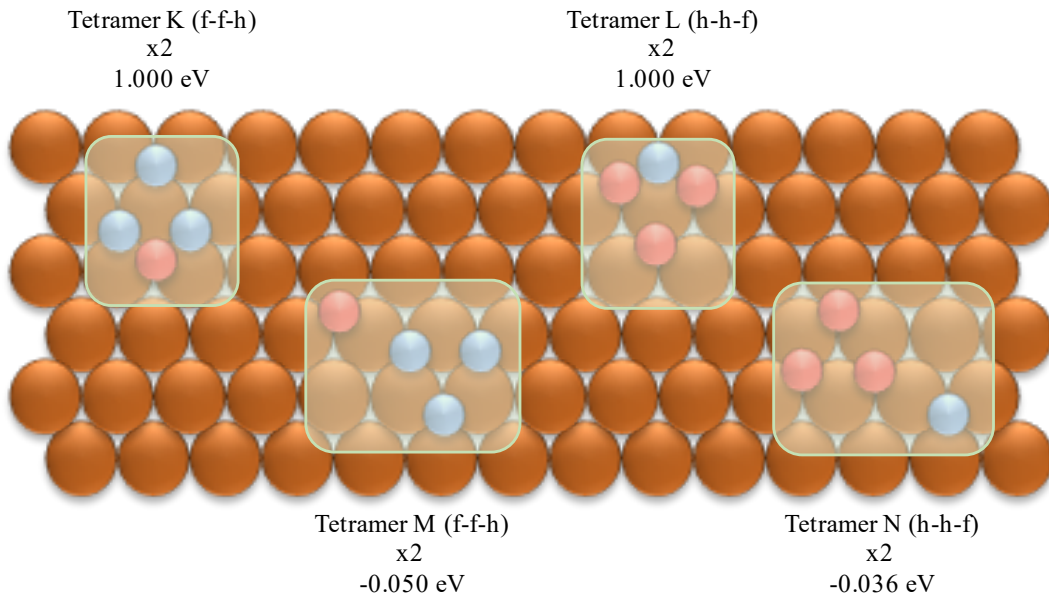


Figure A.7: FCC-HCP clusters included in the CE framework.

Appendix B

Supporting Information on CuZn Surface Alloy

B.1 Calculation of Surface Energy

I calculated surface energy of Cu(111) based on the following definition:

$$\sigma = \lim_{N \rightarrow \infty} \frac{1}{2} (E_{slab}^N - N E_{bulk}) \quad (B.1)$$

in which σ is the surface energy, E_{slab}^N is the total energy of N-layer slab, and E_{bulk} is the total energy of bulk. The bulk total energy is obtained by taking linear fitting to the slab total energy as a function of number of layers, as suggested by Fiorentini and Methfessel [157], to avoid the divergence of surface energy with respect to the slab thickness. The plot of surface energy vs number of layers is shown in Figure B.1, from which I obtained the bulk total energy by taking the slope of the plot. Plugging the bulk total energy to Equation B.1, I then plotted the surface energy vs the number of layers. The surface energy obtained for $N = 18$ is 0.66 eV/atom or 1.88 J/m², considering 3.6102 Å of calculated lattice constant.

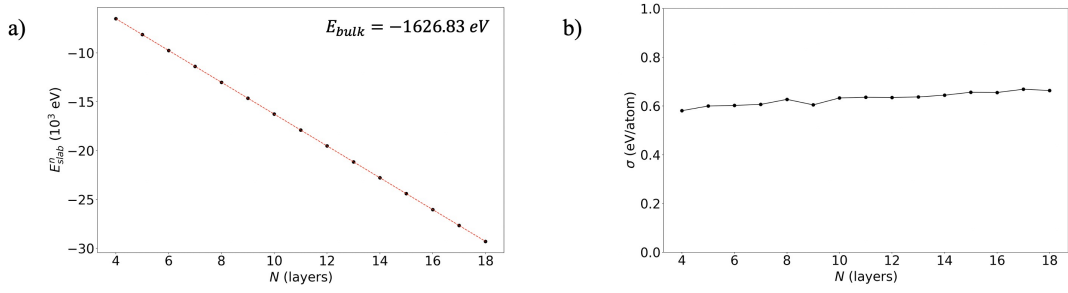


Figure B.1: (a) Plot of slab energy as a function of layers, from which the bulk energy is obtained by linear fitting and taking the slope. (b) The surface energy in eV/atom for different number of layers as obtained based on Eq. B.1

B.2 Classification of the alloying events

The alloying of Zn to the Cu surface can be separated into two categories: the one that involve the change in the z-position of the atom (e.g., the confinement of Zn atom by step adatoms) and the one that involve the change in the z-position (e.g., the direct and indirect exchange, the vacancy insertion, and exchange-descend mechanisms). The former category is identified by checking the change of the coordination number of the Zn atoms. If the coordination number increased to 9 to 12 and there is no change of the z-position, then the confinement of the atom has happened. On the other hand, the classification of the latter category is a bit more complicated. The classification of such alloying process is done based on the following schematic.

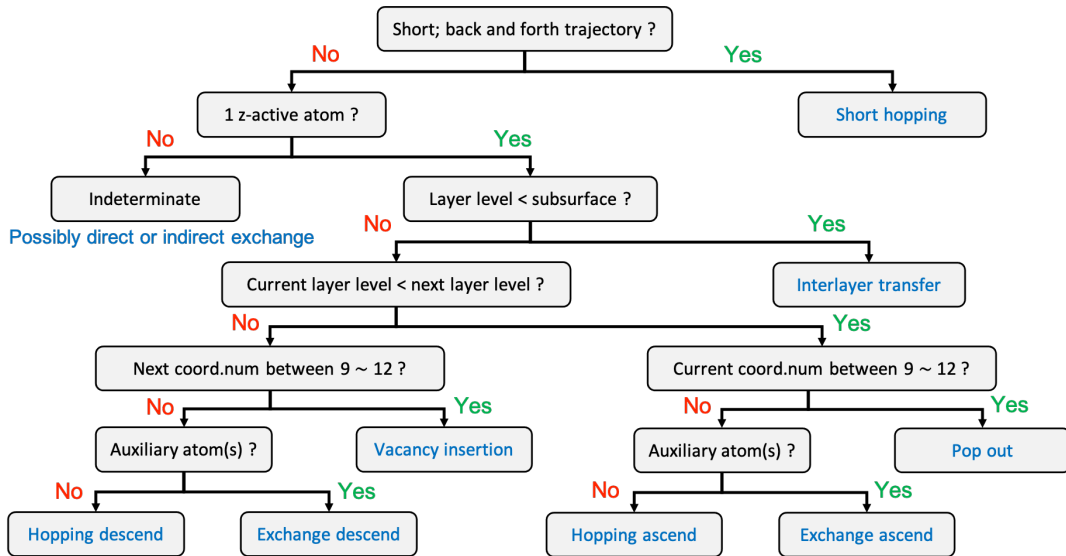


Figure B.2: The process of classifying the some of the alloying events.

First, the z-position of each atom is tracked at every time step. The next

task is to identify the atom that undergoes change in the z-position. The short and back-and-forth movement at high frequency is not particularly interested since it does not result in the alloying. After the back-and-forth movement is ignored, the z-positions of the surrounding atoms (up to second nearest neighbor) are checked. If other atoms also undergo change in the z-position, then most likely the direct and indirect-exchange has happened. The atom and its neighbors are then isolated and be classified manually. On the other hand, if the movement only involves one atom, then its current layer is checked. If the layer is below the subsurface, then the process happen at the bulk region and the event is considered as inter-layer transfer (though no such event is found in this study).

After confirming the event happens at above or equal to the sub-layer, the z-difference is evaluated (i.e., whether the atom going up or down). If the atom is going down, the coordination number is further checked. If the next coordination number is between 9 to 12, then the atom has undergoes vacancy insertion, and thus incorporated to the surface. If the next coordination number is not in that range, then the event happen at or near the step edge. Next, if the process involve the x or y movement of the neighboring atom (i.e., auxiliary atom) then the event is classified as exchange descend (i.e., the auxiliary atom pushes an atom to climb the step edge). If the process does not involve the auxiliary atom, then it means the atom simply descending (or hopping) to the lower terrace. Similar procedure can be applied when the atom is going up.

I should note that after the classifications are performed based on the described automatic procedure, all the resulting alloying event is re-checked manually to ensure the classifications are made correctly. In fact, there are some events that are wrongly classified and should be excluded. Nevertheless, the automatic scheme described earlier can be used to reduce the number of candidates to be evaluated manually. In addition, all the alloying events happen at the middle terrace are classified manually since the number of events are much scarce and can be feasibly classified by myself.

B.3 Event Energetics

I calculated the DFT activation energies (E_{act}) and reaction energies (ΔE) representing various events that occurs in the MD simulations of Zn-deposited on Cu(997). The three main features of Cu(997) (i.e., middle terrace, upper

terrace, and lower terrace) are considered. The middle terrace is modelled by Cu(111) surface. The upper and lower terrace are modelled by Cu(221) surface for the events involving straight step edge and Cu(965) for event involving kinked edge. All the models consist of four layers, of which the two bottom-most layers are fixed.

B.3.1 Pop Out and Vacancy Insertion

The calculated DFT E_{act} and reaction energies ΔE for atomic pop out and vacancy insertion at terrace, upper terrace, and lower terrace are presented in Table C.1. The mechanisms of each event are shown in Figure B.1.

B.3.2 Step Crossing

The calculated DFT E_{act} and ΔE for step crossing events including hopping ascend/descend and exchange ascend and descend are presented in Table C.2. The mechanisms of each event are shown in Figure B.4.

B.3.3 Direct Exchange

The calculated DFT E_{act} and ΔE for direct exchange between Cu and Zn at terrace, upper terrace, and lower terrace are presented in Table C.3. The mechanisms of each event are shown in Figure B.5.

B.3.4 Indirect-exchange Mechanism

The calculated DFT E_{act} and ΔE for indirect-exchange mechanisms at terrace and lower terrace are presented in Table C.4. The mechanisms of each event are shown in Figure B.6.

B.3.5 Event Related to Step Fluctuations

The calculated DFT activation energies (E_{act}) and reaction energies (ΔE) for events related to step fluctuations are presented in Table C.5. The activation reaction energies for event related to step fluctuation of Cu surface are taken from the previous study³. The mechanisms of each event are shown in Figure B.7.

B.3.6 Local Exchange at Terrace

The calculated DFT activation energies (E_{act}) and reaction energies (ΔE) for events related to local exchange at the terrace are presented in Table C.5. The mechanisms of each event are shown in Figure B.8.

B.4 STM-tip Dependency

DFT calculations were performed to investigate the effect of STM tip to the elementary events such as atomic pop out and direct exchange. The STM tip is modelled using a cluster of tungsten atoms with (100) surface as shown in Figure B.8. Initially, the four layers of W atoms were prepared. I then fixed the atoms in the base regions with the optimized lattice constant of 3.125 Å and relaxed the remaining atoms in the apex region. The base region and the apex region are represented by gray and red atoms in Figure B.9. After obtained the optimized geometry, I then took only the apex region, consists of two layers, to be used above the surface. During the calculation with surface, the first layers that consists of four W atoms are fixed whereas the single tip atom is allowed to move.

To find the tip-surface distance that gives the highest stabilization for the transition state of elementary events, I plotted the change of total energy of the transition state as a function of tip-surface distance as shown in Figure B.10. No relaxation is allowed for this kind of calculations. Five elementary events were investigated, including the Cu pop out at the terrace (Figure B.3a, left to right), Zn pop out at the terrace (Figure B.3a, left to right), Zn kicks Cu at terrace (Figure B.5a, left to right), Cu kicks Zn at the terrace (Figure B.5a, right to left), local exchange at terrace initiated by Zn pop out (Figure B.8a, left to right), and local exchange at terrace initiated by Cu pop out (Figure B.8b, left to right). As shown in Figure B.10a, the tip-surface distance that gives the lowest energy of the transition states of Cu pop out, Zn pop out, and direct exchange (i.e., Cu kicks Zn or Zn kicks Cu) at terrace are 4.1 Å, 4.5 Å, and 3.7 Å, respectively. As shown in Figure B.10b, the tip-surface distance that gives the lowest energy of transition states of local exchange initiated by Zn pop out and Cu pop out are 4.3 Å and 4.5 Å, respectively.

The tip-surface distances correspond to the most stable transition states were then used in the NEB calculation of the elementary events. The four base atoms of STM tip are fixed with the tip consisting single atom is allowed to relax.

Table B.1: DFT E_{act} and ΔE of pop out and vacancy insertion of Cu and Zn atom at terrace, upper terrace, and lower terrace.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
A1.	Cu pop out at terrace	2.02	1.74	(Figure B.3a, left to right)
A2.	Zn pop out at terrace	1.50	1.41	
A3.	Cu vacancy insertion at terrace	0.28	-1.74	(Figure B.3a, right to left)
A4.	Zn vacancy insertion at terrace	0.08	-1.41	
A5.	Cu pop out at upper terrace	1.82	1.56	(Figure B.3b, left to right)
A6.	Zn pop out at upper terrace	1.45	1.38	
A7.	Cu vacancy insertion at upper terrace	0.26	-1.56	(Figure B.3b, right to left)
A8.	Zn vacancy insertion at upper terrace	0.06	-1.38	
A9.	Cu pop out at lower terrace	1.61	1.23	(Figure B.3c, left to right)
A10.	Zn pop out at lower terrace	1.19	0.96	
A11.	Cu vacancy insertion at lower terrace	0.38	-1.23	(Figure B.3c, right to left)
A12.	Zn vacancy insertion at lower terrace	0.23	-0.96	

Table B.1: (cont) DFT E_{act} and ΔE of pop out and vacancy insertion of Cu and Zn atom at terrace, upper terrace, and lower terrace.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
A13.	Cu pop out at lower terrace (near kinked step edge) type 1	1.05	1.00	(Figure B.3d, left to right)
A14.	Zn pop out at lower terrace (near kinked step edge) type 1	0.84	0.83	
A15.	Cu vacancy insertion at lower terrace (near kinked step edge) type 1	0.05	-1.00	(Figure B.3d, right to left)
A16.	Zn vacancy insertion at lower terrace (near kinked step edge) type 1	0.01	-0.83	
A17.	Cu pop out at lower terrace (near kinked step edge) type 2	1.01	0.95	(Figure B.3e, left to right)
A18.	Zn pop out at lower terrace (near kinked step edge) type 2	0.74	0.73	
A19.	Cu vacancy insertion at lower terrace (near kinked step edge) type 2	0.06	-0.95	(Figure B.3e, right to left)
A20.	Zn vacancy insertion at lower terrace (near kinked step edge) type 2	0.01	-0.73	
A21.	Cu pop out at lower terrace (near kinked step edge) type 3	0.93	0.88	(Figure B.3f left to right)
A22.	Zn pop out at lower terrace (near kinked step edge) type 3	0.64	0.63	
A23.	Cu vacancy insertion at lower terrace (near kinked step edge) type 3	0.06	-0.88	(Figure B.3f, right to left)
A24.	Zn vacancy insertion at lower terrace (near kinked step edge) type 3	0.01	-0.63	

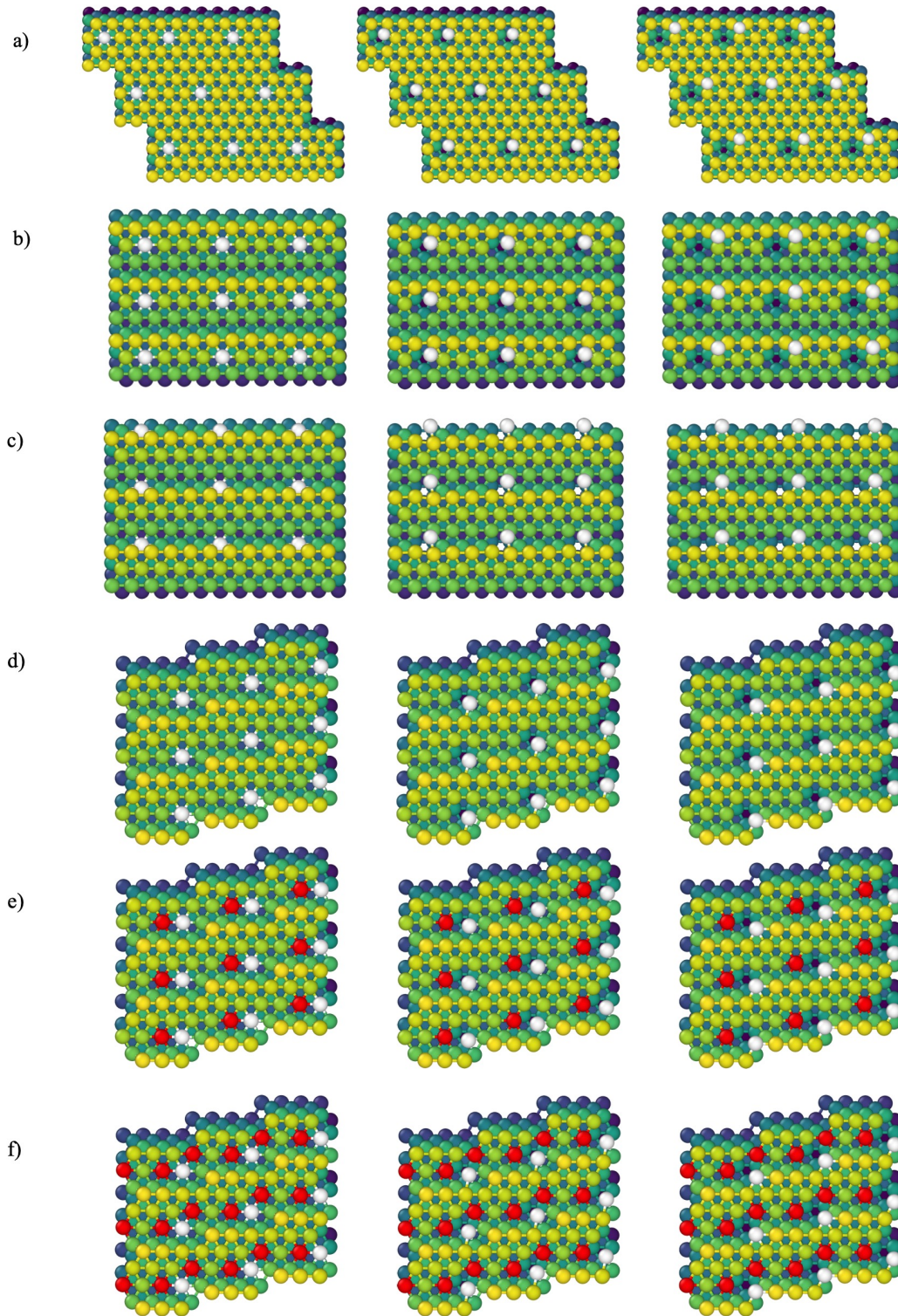


Figure B.3: Initial, transition, and final states of the events described in Table B.1. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.1. Figure (a) to (c) show the atomic pop out (left to right) and vacancy insertion (right to left) at the terrace, upper terrace, and lower terrace, respectively. Figure (d) to (f) shows the atomic pop out (left to right) and vacancy insertion (right to left) near the kinked edge with no preoccupied Zn atom, one preoccupied Zn atom, and two preoccupied Zn atoms, respectively.

Table B.2: DFT E_{act} and ΔE of Cu and Zn hopping ascend/descend, and exchange ascend/descend.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
B1.	Cu hopping ascend	1.06	0.61	(Figure B.4a, left to right)
B2.	Zn hopping ascend	0.72	0.53	
B3.	Cu hopping descend	0.44	0.61	(Figure B.4a, right to left)
B4.	Zn hopping descend	0.19	-0.53	
B5.	Cu exchange ascend	0.77	0.61	(Figure B.4b, left to right)
B6.	Zn exchange ascend	0.61	0.42	
B7.	Cu exchange ascend at kinked edge	1.13	0.84	(Figure B.4b, right to left)
B8.	Zn exchange ascend at kinked edge	0.89	0.59	
B9.	Cu exchange descend	0.16	-0.61	(Figure B.4c, left to right)
B10.	Zn exchange descend	0.20	-0.42	
B11.	Cu exchange descend at kinked edge	0.29	-0.84	(Figure B.4c, right to left)
B12.	Zn exchange descend at kinked edge	0.30	-0.59	

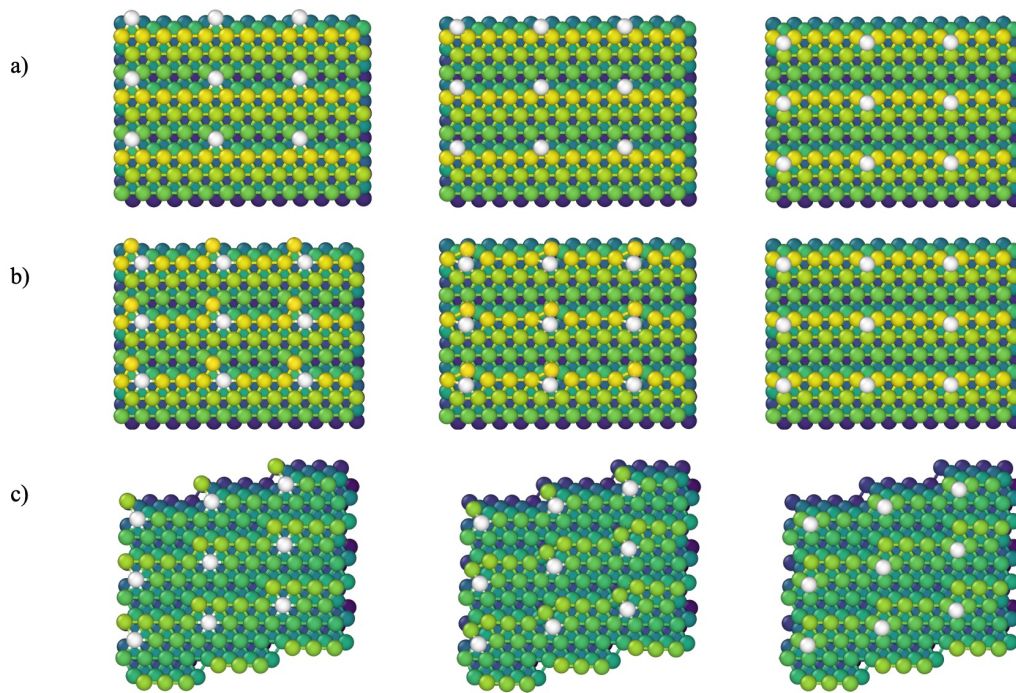


Figure B.4: Initial, transition, and final states of the events described in Table B.2. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.2. (a) Hopping ascend (left to right) and hopping descend (right to left). (b) Exchange ascend (left to right) and exchange descend (right to left). (c) Exchange ascend (left to right) and exchange descend (right to left) near kinked edge.

Table B.3: DFT E_{act} and ΔE of Cu and Zn direct exchange at terrace, upper terrace, and lower terrace.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
C1.	Zn kicks Cu at terrace (type 1)	1.37	0.27	(Figure B.5a, left to right)
C2.	Cu kicks Zn at terrace (type 1)	1.10	-0.27	
C3.	Zn kicks Cu at terrace (type 2)	1.29	0.37	(Figure B.5b, left to right)
C4.	Cu kicks Zn at terrace (type 2)	0.92	-0.37	
C5.	Zn kicks Cu at terrace (type 3)	1.16	0.51	(Figure B.5c, left to right)
C6.	Cu kicks Zn at terrace (type 3)	0.65	-0.51	
C7.	Zn kicks Cu at upper terrace (type 1)	1.66	0.75	(Figure B.5d, left to right)
C8.	Cu kicks Zn at upper terrace (type 2)	0.92	-0.75	
C9.	Zn kicks Cu at upper terrace (type 2)	1.17	-0.39	(Figure B.5e, left to right)
C10.	Cu kicks Zn at upper terrace (type 1)	1.56	0.39	
C11.	Zn kicks Cu at lower terrace (type 1)	1.41	0.78	(Figure B.5f, left to right)
C12.	Cu kicks Zn at lower terrace (type 2)	0.63	-0.78	

Table B.3: (cont) DFT E_{act} and ΔE of Cu and Zn direct exchange at terrace, upper terrace, and lower terrace.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
C13.	Zn kicks Cu at lower terrace (type 2)	0.76	-0.28	(Figure B.5g, left to right)
C14.	Cu kicks Zn at lower terrace (type 1)	1.04	0.28	
C15.	Zn kicks Cu at lower terrace (type 3)	1.14	0.26	(Figure B.5h, left to right)
C16.	Cu kicks Zn at lower terrace (type 3)	0.88	-0.26	
C17.	Zn kicks Cu at lower terrace near kink site (type 1)	0.93	0.22	(Figure B.5i, left to right)
C18.	Cu kicks Zn at lower terrace near kink site (type 1)	0.71	-0.22	

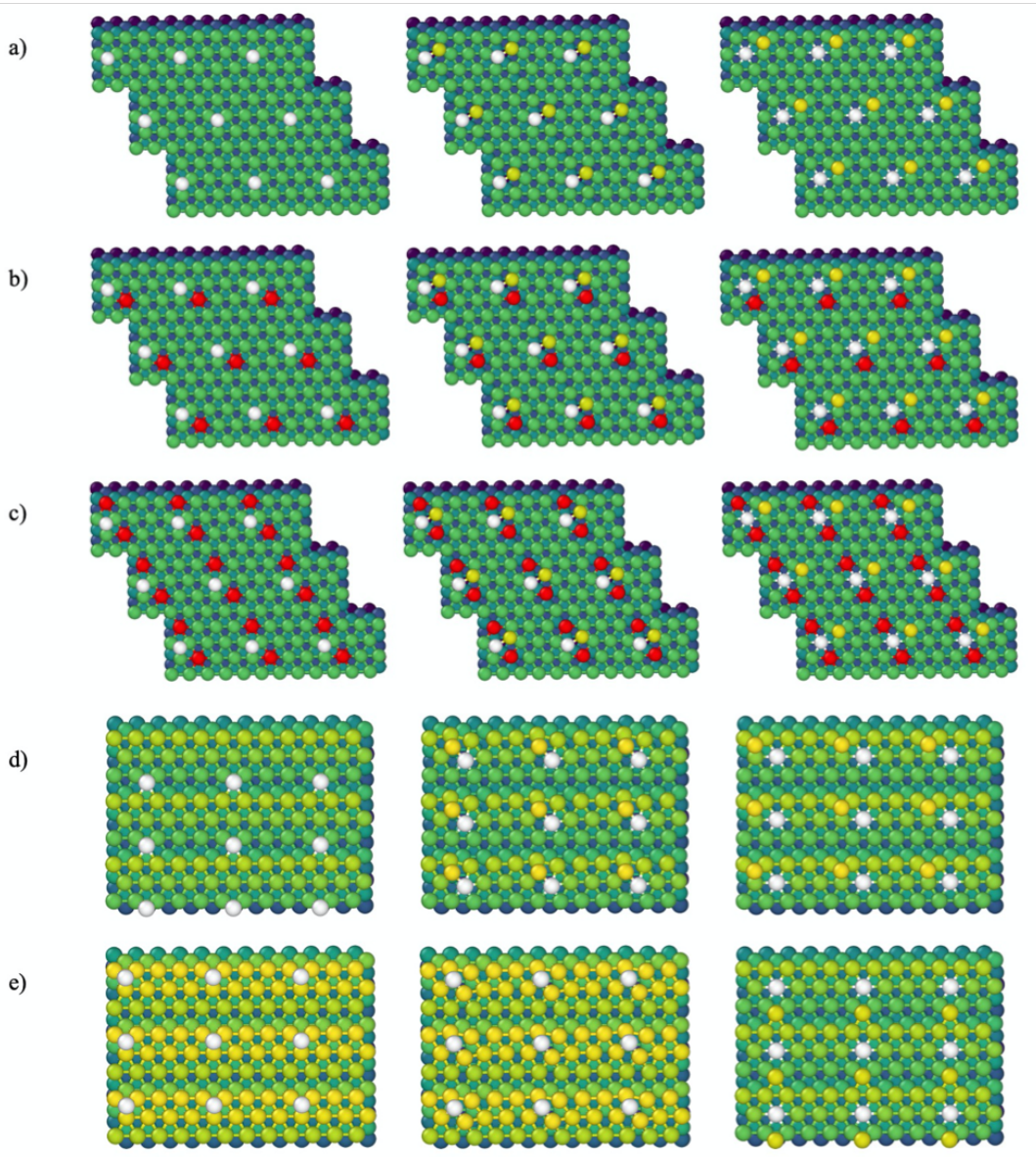


Figure B.5: Initial, transition, and final states of the events described in Table B.3. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.3. (a) The Zn atom kicks Cu event at terrace without pre-substituted Zn (left to right) and the Cu kicks Zn event at terrace with one pre-substituted Zn (right to left). (b) The Zn atom kicks Cu event at terrace with one pre-substituted Zn (left to right) and the Cu kicks Zn event at terrace with two pre-substituted Zn (right to left). (c) The Zn atom kicks Cu event at terrace with two pre-substituted Zn (left to right) and the Cu kicks Zn event at terrace with three pre-substituted Zn (right to left).

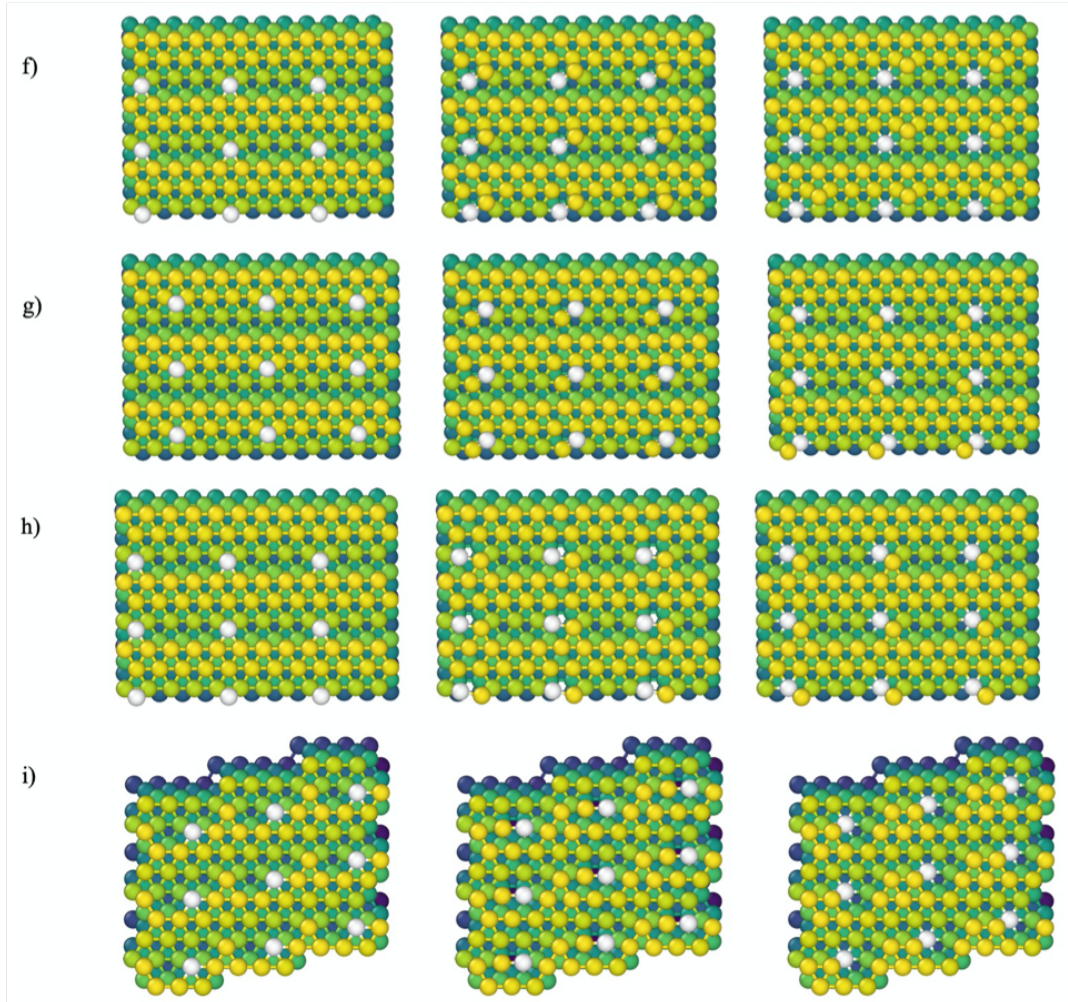


Figure B.5: (Cont.) Initial, transition, and final states of the events described in Table B.3. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.3. (d) The Zn kicks Cu event at upper terrace type 1 (left to right) and Cu kicks Zn event at upper terrace type 2 (right to left). (e) The Zn kicks Cu event at upper terrace type 2 (left to right) and the Cu kicks Zn event at upper terrace type 1 (right to left). (f) The Zn kicks Cu event at lower terrace type 1 (left to right) and Cu kicks Zn event at lower terrace type 2 (right to left). (g) The Zn kicks Cu event at lower terrace type 2 (left to right) and the Cu kicks Zn event at lower terrace type 1 (right to left). (h) The Zn kicks Cu event at lower terrace type 3 (left to right) and the Cu kicks Zn event at lower terrace type 3 (right to left). (i) The Zn kicks Cu event at lower terrace near the kink site (left to right) and the Cu kicks Zn at lower terrace near the kink site (right to left).

Table B.4: DFT E_{act} and ΔE of indirect-exchange mechanisms at terrace and lower terrace.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
D1.	Indirect-exchange at terrace initiated by Zn atom (type 1, forward)	1.39	0.27	(Figure B.6a, left to right)
D2.	Indirect-exchange at terrace initiated by Cu atom (type 1, reverse)	1.12	-0.27	
D3.	Indirect-exchange at terrace initiated by Zn atom (type 2)	1.13	0.00	(Figure B.6b, left to right)
D4.	Indirect-exchange at terrace initiated by Zn atom (type 3)	1.07	0.00	
D5.	Indirect-exchange at lower terrace initiated by Zn atom (type 1, forward)	0.87	-0.39	(Figure B.6d, left to right)
D6.	Indirect-exchange at lower terrace initiated by Cu atom (type 1, reverse)	1.26	0.39	
D7.	Indirect-exchange at lower terrace initiated by Zn atom (type 2, forward)	0.67	-0.53	(Figure B.6e, left to right)
D8.	Indirect-exchange at lower terrace initiated by Zn atom (type 2, reverse)	1.20	0.53	

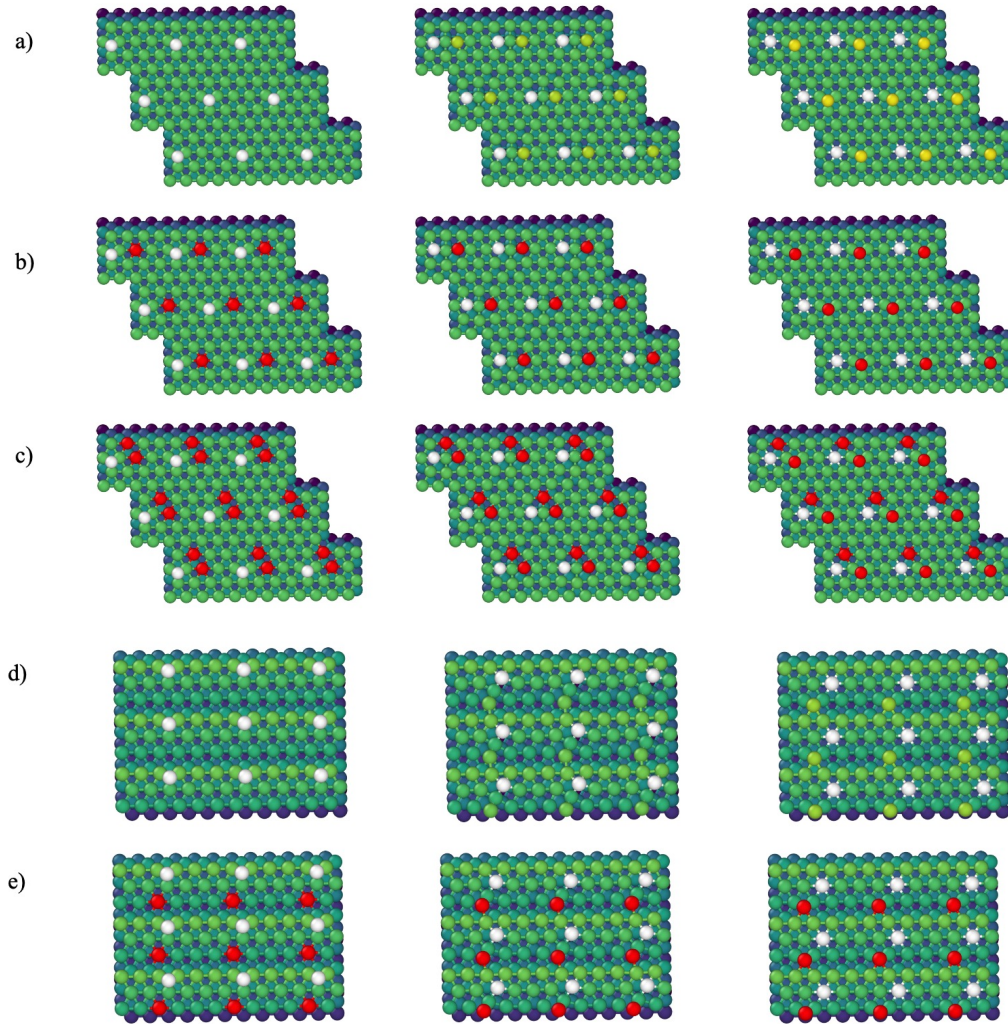


Figure B.6: Initial, transition, and final states of the events described in Table B.4. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.4. (a) The indirect-exchange mechanism at the terrace without pre-substituted Zn atom. (b) The indirect-exchange mechanism at the terrace with one pre-substituted Zn atom. (c) The indirect-exchange mechanism at the terrace with two pre-substituted Zn atoms. (d) The indirect-exchange mechanism at the lower terrace without pre-substituted Zn atom. (e) The indirect-exchange mechanism at the lower terrace with one pre-substituted Zn atom. Some atoms are marked with star-shaped symbol to ease the tracking of their positions.

Table B.5: DFT E_{act} and ΔE of various events related to step fluctuations.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
E1.	Cu diffusion along the step edge	0.34	0.00	(Figure B.7a, left to right)
E2.	Zn diffusion along the step edge	0.29	0.00	
E3.	Cu attachment to the step edge (type 1)	0.04	-0.74	(Figure B.7b, right to left)
E4.	Zn attachment to the step edge (type 1)	0.01	-0.61	
E5.	Cu attachment to the step edge (type 2)	0.05	-0.62	(Figure B.7c, right to left)
E6.	Zn attachment to the step edge (type 2)	0.03	-0.54	
E7.	Cu attachment to the step edge (type 3)	0.18	-0.54	(Figure B.7d, right to left)
E8.	Zn attachment to the step edge (type 3)	0.09	-0.50	
E9.	Cu attachment to the step edge (type 4)	0.05	-0.76	(Figure B.7e, right to left)
E10.	Zn attachment to the step edge (type 4)	0.00	-0.65	

Table B.5: (cont) DFT E_{act} and ΔE of various events related to step fluctuations.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
E11.	Cu detachment from step edge (type 1)	0.78	0.74	(Figure B.7b, left to right)
E12.	Zn detachment from step edge (type 1)	0.62	0.61	
E13.	Cu detachment from step edge (type 2)	0.67	0.62	(Figure B.7c, left to right)
E14.	Zn detachment from step edge (type 2)	0.57	0.54	
E15.	Cu detachment from step edge (type 3)	0.72	0.54	(Figure B.7d, left to right)
E16.	Zn detachment from step edge (type 3)	0.59	0.50	
E17.	Cu detachment from step edge (type 4)	0.80	0.76	(Figure B.7e, left to right)
E18.	Zn detachment from step edge (type 4)	0.65	0.65	
E19.	Cu attachment to kink site (type 1)	0.34	-0.25	(Figure B.7f, left to right)
E20.	Zn attachment to kink site (type 1)	0.27	-0.24	

Table B.5: (cont) DFT E_{act} and ΔE of various events related to step fluctuations.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
E21.	Cu attachment to kink site (type 2)	0.07	-0.50	(Figure B.7g, left to right)
E22.	Zn attachment to kink site (type 2)	0.02	-0.39	
E23.	Cu attachment to kink site (type 3)	0.01	-0.82	(Figure B.7h, left to right)
E24.	Zn attachment to kink site (type 3)	0.00	-0.65	
E25.	Cu detachment from kink site (type 1)	0.59	0.25	(Figure B.7f, right to left)
E26.	Zn detachment from kink site (type 1)	0.51	0.24	
E27.	Cu detachment from kink site (type 2)	0.57	0.50	(Figure B.7g, right to left)
E28.	Zn detachment from kink site (type 2)	0.42	0.39	
E29.	Cu detachment from kink site (type 3)	0.82	0.82	(Figure B.7h, right to left)
E30.	Zn detachment from kink site (type 3)	0.65	0.65	

Table B.6: DFT E_{act} and ΔE of local exchanges at the terrace.

No.	Event	DFT E_{act} (eV)	DFT ΔE (eV)	Figure index
F1.	Local exchange initiated by Zn pop out	2.18	0.00	(Figure B.8a, left to right)
F2.	Local exchange initiated by Cu pop out	2.44	0.00	(Figure B.8b, left to right)

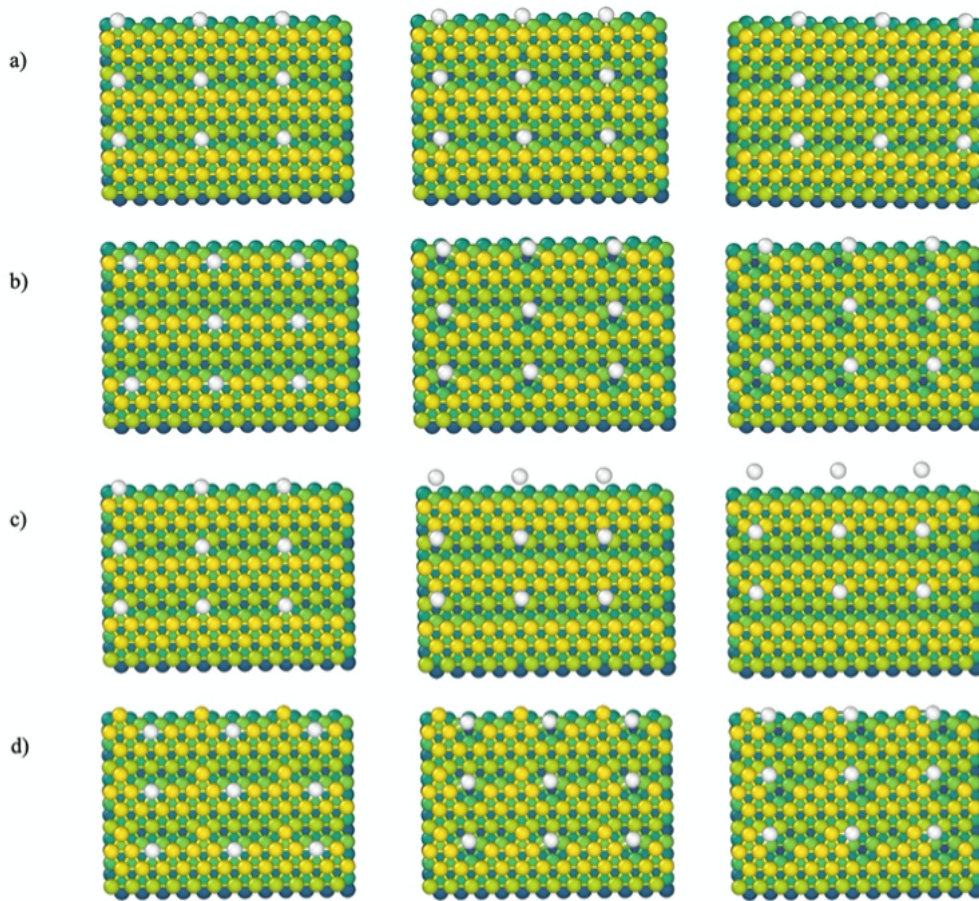


Figure B.7: Initial, transition, and final states of the events described in Table B.5. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.5. (a) Adatom diffusion along step edge. (b) Adatom detachment from step edge type 1 (left to right) and attachment to step edge type 1 (right to left). (c) Adatom detachment from step edge type 2 (left to right) and attachment to step edge type 2 (right to left). (d) Adatom detachment from step edge type 3 (left to right) and attachment to step edge type 3 (right to left).

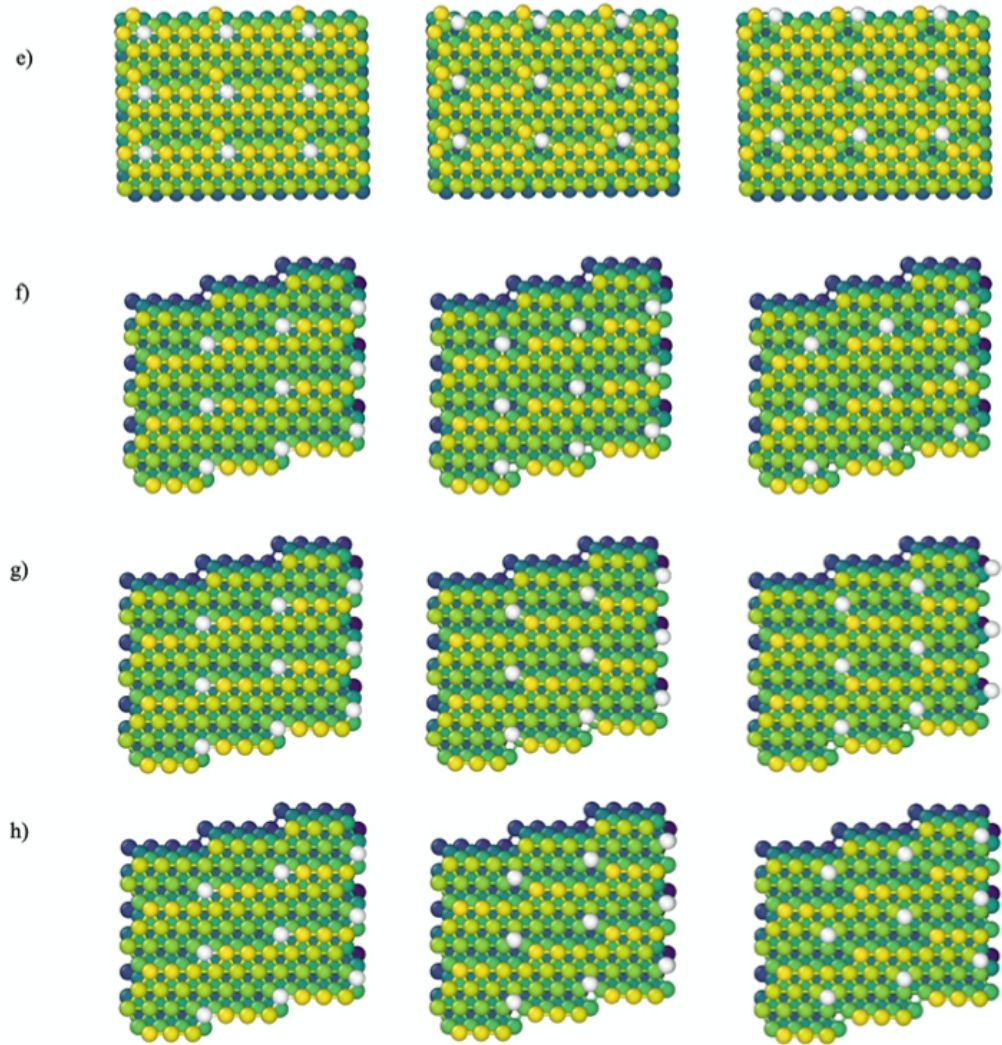


Figure B.7: (Cont.) Initial, transition, and final states of the events described in Table B.5. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table B.5. (e) Adatom detachment from step edge type 4 (left to right) and attachment to step edge type 4 (right to left). (f) Adatom detachment from kinked edge type 1(left to right) and attachment to kinked edge type 1 (right to left). (g) Adatom detachment from kinked edge type 2 (left to right) and attachment to kinked edge type 2 (right to left). (h) Adatom detachment from kinked edge type 3 (left to right) and attachment to kinked edge type 3 (right to left).

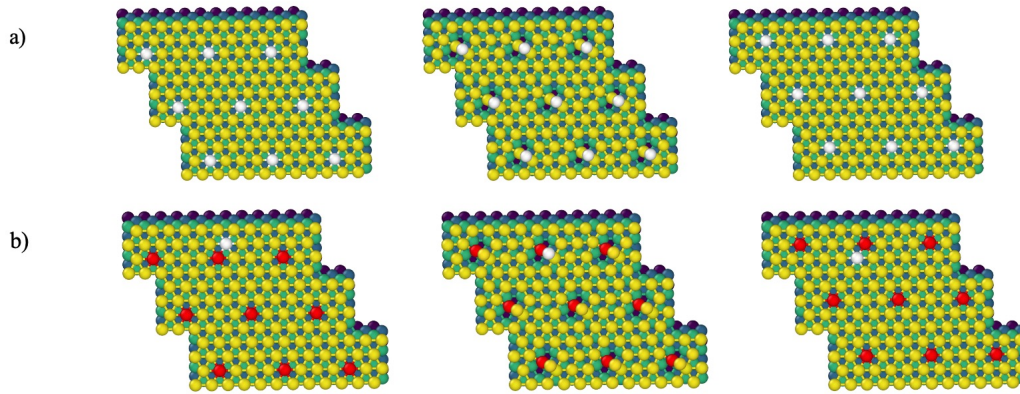


Figure B.8: Local exchange mechanism as proposed by Sano et al. [95] (a) The local exchange initiated by Zn pop out. (b) The local exchange initiated by Cu pop out. The green to yellow color indicates Cu atom while the red atom indicates Zn atom. The white atom indicates the atom on the move, which can be Cu or Zn depending on the event described in Table C.6.

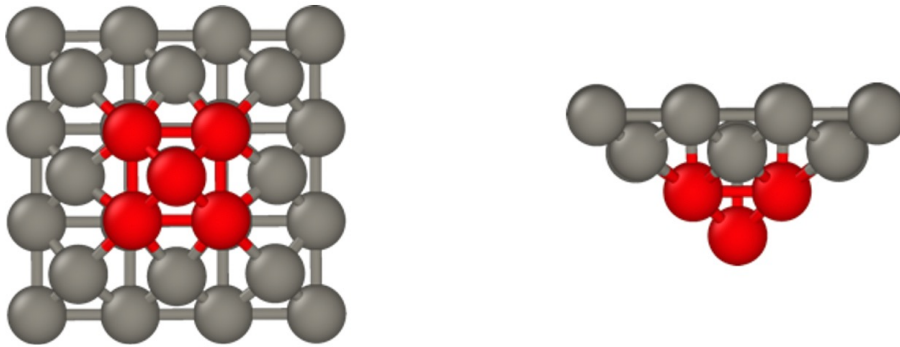


Figure B.9: Structure of W(100) used as STM tip.

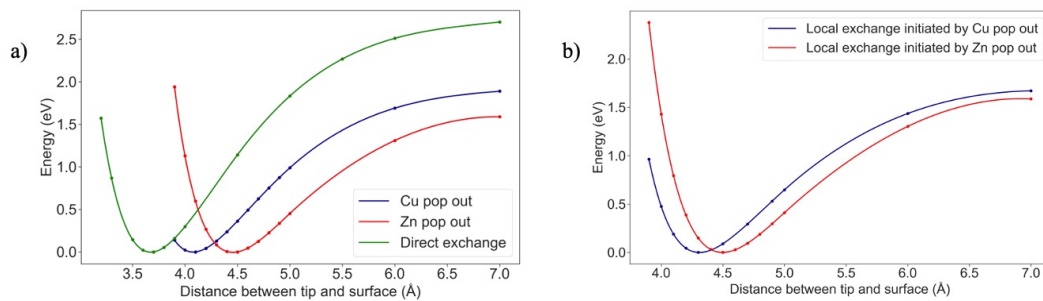


Figure B.10: (a) The total energy of static transition state structure as a function of distance between STM tip and surface for elementary events such as (a) Cu pop out, Zn pop out, direct-exchange, and (b) local exchange initiated by Cu pop out and Zn pop out.

Appendix C

Supporting Information on CO Interactions with Cu(111)

C.1 CO Adsorption Energy with Various Exchange Correlation Functionals

The list of CO adsorption energy on top, fcc, hcp, and bridge sites of Cu(111) using different functional is shown in Table C.1. I used slab consisting four layers with 9 Cu atoms per layer. The calculations show that the vdw-df functional gives the preference to the top site as well as the adsorption energy that are similar with the experiment [143].

Table C.1: CO adsorption energy on flat Cu(111) surface using various functionals.

	Adsorption Energy (eV)			
	top	fcc	hcp	bridge
GGA-PBE	-0.73	-0.80	-0.80	-0.74
optB86b-vdW	-0.90	-1.00	-0.99	-0.94
rev-vdw-df2	-0.84	-0.91	-0.91	-0.85
revpbe-d2	-0.84	-0.97	-0.95	-0.92
rev-pbe-d3	-0.81	-0.81	-0.80	-0.80
rpbe-d2	-0.72	-0.73	-0.72	-0.66
vdw-df	-0.51	-0.39	-0.39	-0.39

C.2 Kernels and Hyperparameters

The list of the optimized values of the hyperparameters used to generate the force-field for Cu-CO system is shown in Table C.2. The hyperparameters are separated based on the interacting elements. The $\sigma_{s,b}$ indicates the (square-root) of the signal variance for the b -body interactions. The l_b denotes the length scale of the b -body interactions. The σ_n indicate the noise hyperparameters acting on all interacted elements.

C.3 Validation Structures

The typical structures used to validate the force-field in terms of mean absolute error of the force prediction are presented in Figure C.1. I used structures of CO on flat Cu(111) (Figure C.1a), structures of CO on Cu(111) with single adatom (Figure C.1b), structures of CO on Cu(111) with three adatoms (Figure C.1c), and structures of CO on Cu(111) with seven adatoms (Figure C.1d). The slab on which the adatoms are deposited consists of four layers of 4x4 Cu atoms. Additionally, I used structures of CO on four layers of Cu(221) (Figure C.1e) and on four layers of Cu(211) (Figure C.1f). These representatives were then used in MD to generate more validation structures by sampling the trajectory. In total, I obtained 144 structures consisting 24 structures for each representative. These structures consist of 1418 C atoms, 1418 O atoms, and 13086 Cu atoms. After obtaining the forces of all the atoms through DFT, I then compared the values to the prediction of the MGP and construct the parity plot as shown in Figure 5.3 of the main text.

Table C.2: List of the hyperparameters embedded used in the GP framework

Hyperparameters	Interacting elements	Value
$\sigma_{s,2}$ l_2	[Cu, Cu]	0.011 eV/Å 0.470 Å
$\sigma_{s,2}$ l_2	All pairs except [Cu, Cu]	1.408 eV/Å 0.912 Å
$\sigma_{s,3}$ l_3	[Cu, Cu, Cu]	0.002 eV/Å 2.036 Å
$\sigma_{s,3}$ l_3	All triplets except [Cu, Cu, Cu]	0.005 eV/Å 0.592 Å
σ_n	All interacted elements	0.088 eV/ Å

C.4 Mean Squared Displacement Calculations of Cu, CO, and Cu-CO Complexes

I investigated the diffusivity of Cu, CO, and Cu-CO by letting them diffuse on 8x8 Cu(111) surface. The diffusion constant D , depends on temperature T , can be calculated through the Einstein equation [48],

$$\frac{\partial \langle r^2(t) \rangle}{\partial t} = 6D(T) \quad (C.1)$$

The $\langle r^2(t) \rangle$ in equation (6) is the mean squared displacement (MSD) which is obtainable from the MD simulation. Integrating both sides result in the following equation:

$$\langle r^2(t) \rangle = 6D(T)t + C \quad (C.2)$$

The slope of the line fitted to equation (7) then corresponds to the diffusion constant D . To find the barrier of diffusion E_a , I plugged in D to the Arrhenius equation [158],

$$D(T) = D_0 \exp \left(-\frac{E_a}{RT} \right) \quad (C.3)$$

The D_0 and E_a in the equation (8) corresponds to the pre-exponential factor

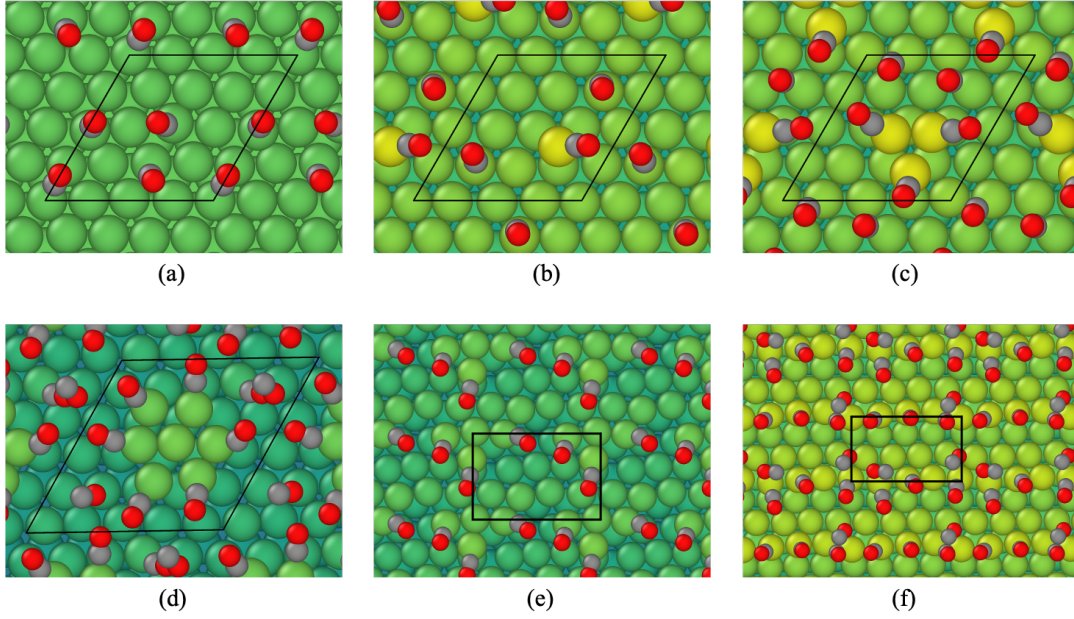


Figure C.1: Structures used as validation set. (a) CO on flat Cu(111), (b) CO on Cu(111) with adatom, (c) CO on Cu(111) with three adatoms, (d) CO on Cu(111) with seven adatoms, (e) CO on Cu(221), and CO on Cu(211). The unit cell is indicated by the black frame in each figure.

and the barrier of the diffusion, respectively. R is the universal gas constant. The result of diffusion constants obtained from the MD simulations is listed in the Figure C.13.

C.5 CO desorption rate on Cu(111), Cu(211), and Cu(221)

I used the first-order Redhead formula⁵ to calculate the desorption energy E_{des} as also implemented to determine the desorption energy in the thermal desorption spectroscopy (TSD) experiment of CO on Cu surfaces [143, 159].

$$\ln \left(-\frac{1}{\theta} \frac{d\theta}{dt} \right) = \ln v_n - \frac{E_{des}}{RT} \quad (\text{C.4})$$

The rate of the desorption equals to the term inside the logarithmic function at the left-hand side of the equation:

$$-\frac{1}{\theta} \frac{d\theta}{dt} = r \quad (\text{C.5})$$

Table C.3: The diffusion constant D at different temperatures for Cu, CO, and Cu-CO.

Temperature (K)	Diffusion Constant ($\text{\AA}^2/\text{ps}$)		
	Cu	CO	Cu-CO
100	0.02	0.01	0.03
150	0.08	0.07	0.13
200	0.15	0.30	0.18
250	0.21	0.48	0.30
300	0.30	N/A	0.40
350	0.45	N/A	0.50
400	0.53	N/A	0.59
450	0.62	N/A	0.69
500	0.71	N/A	0.75
550	0.75	N/A	1.03
600	0.91	N/A	0.91
650	1.03	N/A	1.04

I solved this ordinary differential equation by integrating both sides which leads to:

$$\int \frac{1}{\theta} d\theta = - \int r dt \quad (\text{C.6})$$

Solving the integrals result in the following linear equation:

$$\ln \theta = -rt + C \quad (\text{C.7})$$

Thus, the rate of desorption corresponds to the gradient of the line fitted to the equation. The evolution of coverage over the time upon desorption then can be obtained from molecular dynamics simulation. I set low CO coverage on the initial structure to reduce the intermolecular interaction: 0.100, 0.063, and 0.083 for Cu(111), Cu(221), and Cu(211) surfaces, respectively. The surface models used to evaluate CO desorption are shown in Figure C.2.

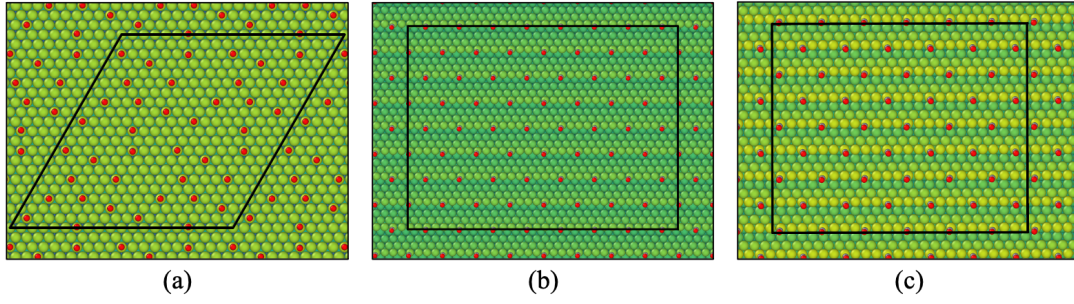


Figure C.2: The initial structures used in the measurement of CO desorption on different surfaces: (a) Cu(111), (b) Cu(221), and (c) Cu(211).

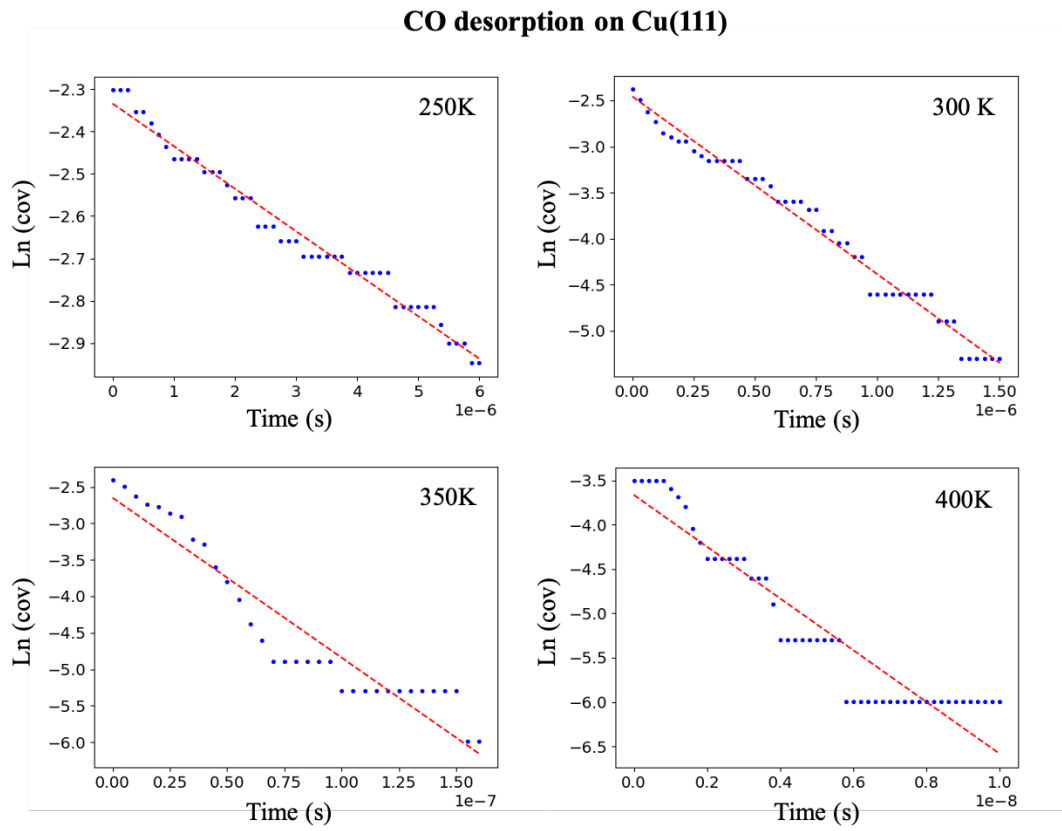


Figure C.3: CO desorption rate on Cu(111) at different temperatures

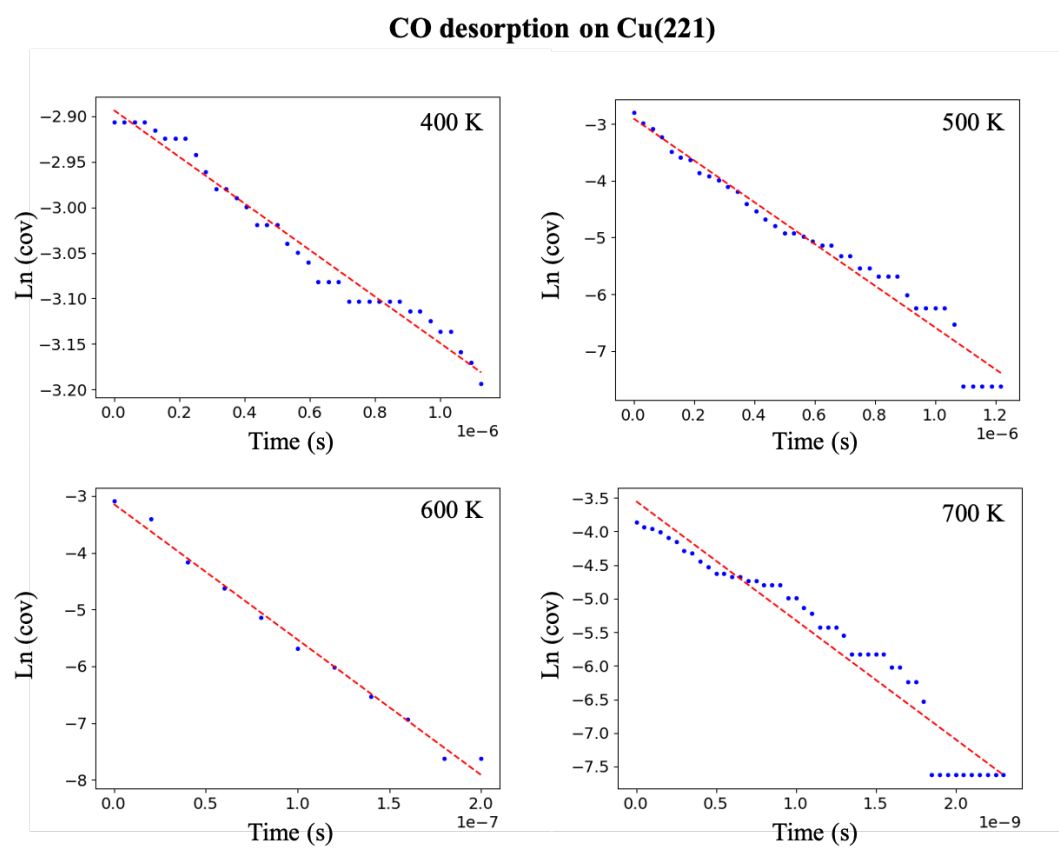


Figure C.4: CO desorption rate on Cu(221) at different temperatures

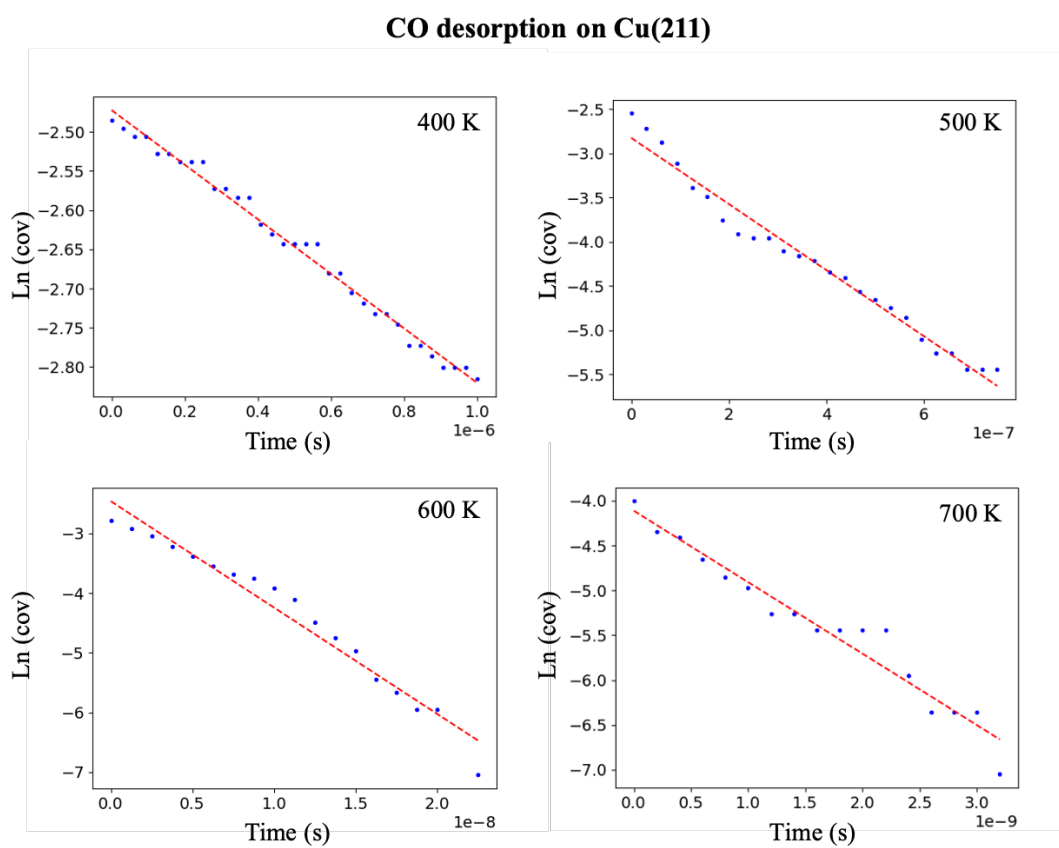


Figure C.5: CO desorption rate on Cu(211) at different temperatures

C.6 Formation energy calculations of closed-packed structure

The optimized structures of the closed-packed clusters (taken from the MD simulations at 550 K) used in the calculation of formation energies are shown in Figure C.6. The slab on which the clusters are deposited consists of four layers of 5x5 Cu atoms.

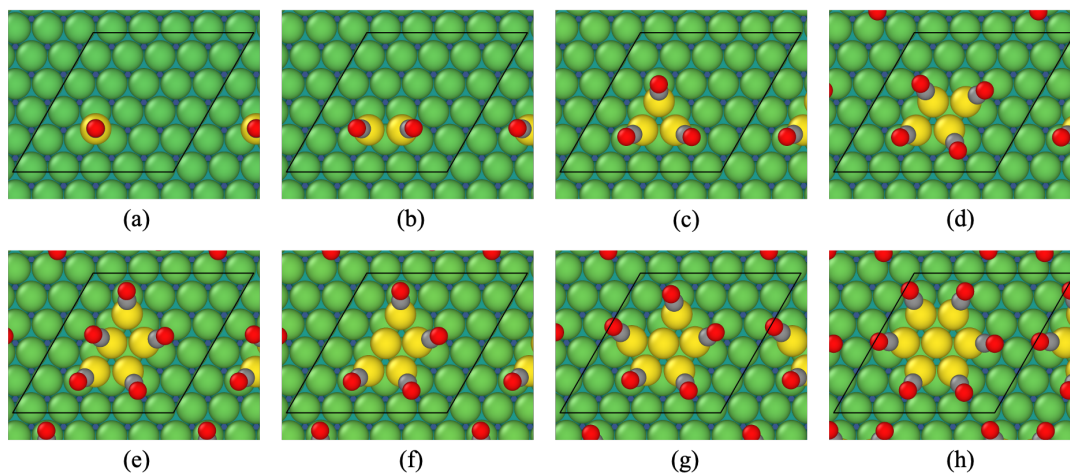


Figure C.6: The optimized structures of the closed-packed clusters taken from the MD simulations at 550 K: (a) $Cu_1(CO)_1$, (b) $Cu_2(CO)_2$, (c) $Cu_3(CO)_3$, (d) $Cu_4(CO)_4$, (e) $Cu_5(CO)_5$, (f) $Cu_5(CO)_4$, (g) $Cu_6(CO)_5$, (h) $Cu_7(CO)_6$.

C.7 Statistics of the formation and decomposition mechanism of clusters

The number of mechanisms by which each size of CO-decorated clusters is formed and decomposed is plotted in Figure C.7-C.12. The symbols Cu_n and Cu_X represent the CO-decorated cluster consists of n Cu atoms and the cluster with arbitrary size.

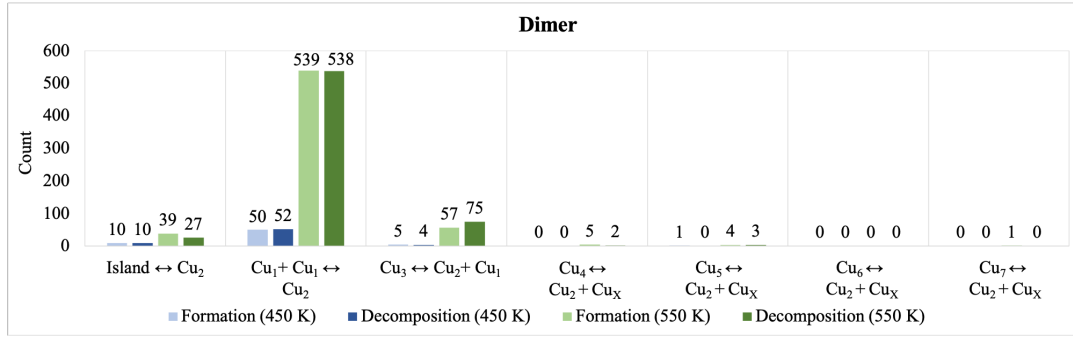


Figure C.7: Mechanisms of dimer formation and decomposition

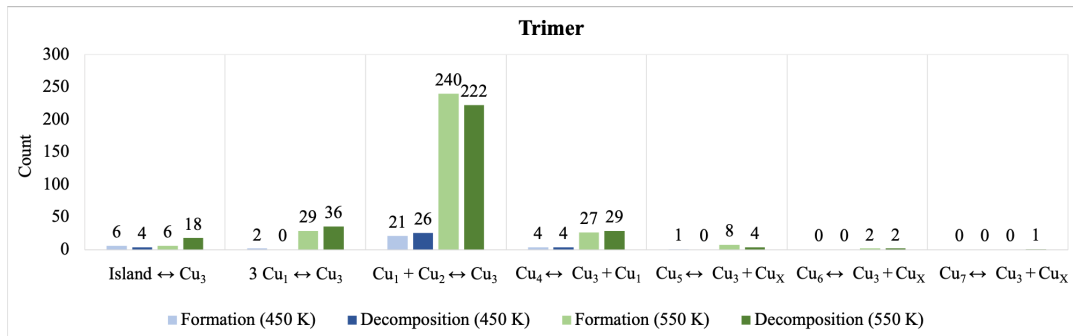


Figure C.8: Mechanisms of trimer formation and decomposition

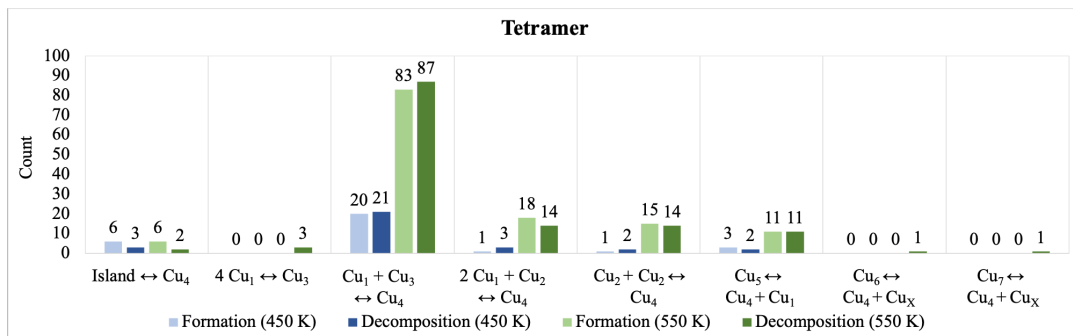


Figure C.9: Mechanisms of tetramer formation and decomposition

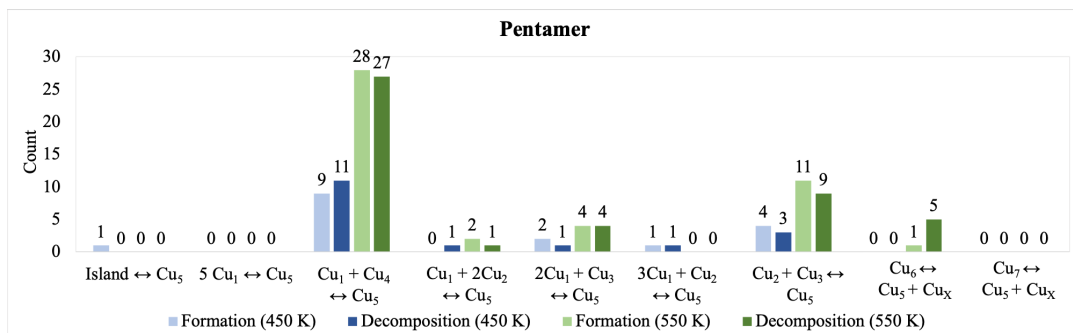


Figure C.10: Mechanisms of pentamer formation and decomposition

C.8. NEB Calculations of Atom Detachment and Attachment from the Step Edge

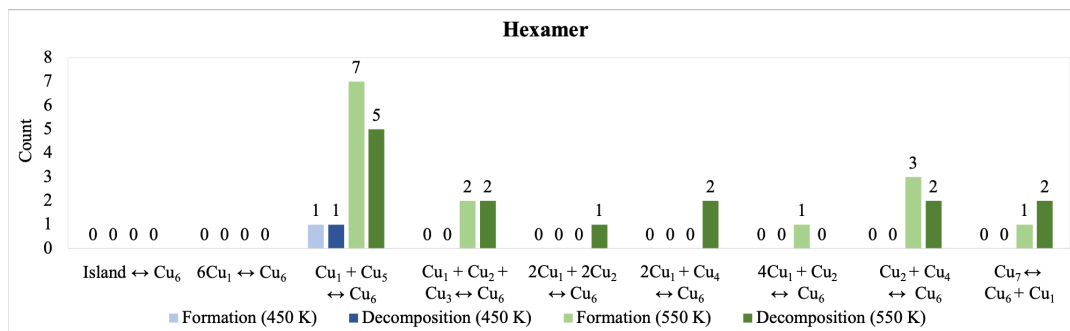


Figure C.11: Mechanisms of hexamer formation and decomposition

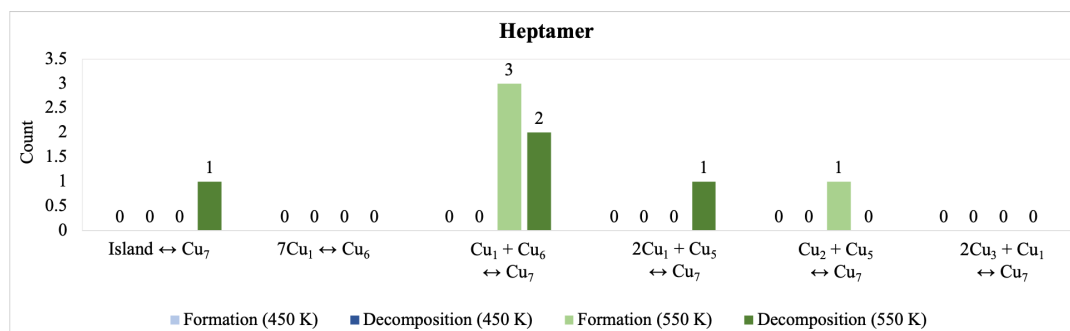


Figure C.12: Mechanisms of heptamer formation and decomposition

C.8 NEB Calculations of Atom Detachment and Attachment from the Step Edge

Set of NEB calculations were performed to obtain detachment and attachment barriers of Cu atom from the step edge given various configurations of CO adsorptions on step atoms. Two types of step edge were investigated, namely A-step (step with (100) microfacet) and B-step (step with (111) microfacet). The mechanisms of detachment and the associated barrier are shown in the following subsections.

C.8.1 Detachment of Cu step-atom from step edge

I investigated the barriers of step-atom detachment from perfect step edge given various configuration of adsorbed CO. The barriers and the associated figure index are shown in Table C.4. The mechanisms for each detachment are shown in Figure C.13 and Figure C.14 for step-A and step-B, respectively.

Table C.4: Forward and reverse barrier or activation energy of detached step-atom from perfect step-edge. The number in square bracket indicates the predicted value from machine-learning.

Figure Index	Step	CO / unit cell	Forward E_{act} (eV)	Reverse E_{act} (eV)
Figure C.13 (a)	A	0	0.73 [0.76]	0.11 [0.08]
Figure C.13 (b)	A	1	0.53 [0.52]	0.12 [0.07]
Figure C.13 (c)	A	2	0.46 [0.53]	0.18 [0.16]
Figure C.13 (d)	A	2	0.54 [0.55]	0.14 [0.09]
Figure C.13 (e)	A	3	0.49 [0.55]	0.23 [0.16]
Figure C.13 (f)	A	3	0.42 [0.45]	0.23 [0.16]
Figure C.13 (g)	A	4	0.24 [0.28]	0.34 [0.35]
Figure C.14 (a)	B	0	0.72 [0.81]	0.00 [0.00]
Figure C.14 (b)	B	1	0.47 [0.46]	0.00 [0.01]
Figure C.14 (c)	B	2	0.47 [0.53]	0.03 [0.01]
Figure C.14 (d)	B	2	0.48 [0.48]	0.01 [0.02]
Figure C.14 (e)	B	3	0.36 [0.42]	0.06 [0.05]
Figure C.14 (f)	B	3	0.33 [0.33]	0.04 [0.06]
Figure C.14 (g)	B	4	0.12 [0.13]	0.18 [0.13]

C.8.2 Detachment of Cu adatom from step edge

I investigated the barriers of detachment of step-adatom from the step edge given various configuration of adsorbed CO. The barriers and the associated figure index are shown in Table C.5. The mechanisms for each detachment are shown in Figure C.15 and Figure C.16 for A-step and B-step, respectively.

Table C.5: Forward and reverse barrier or activation energy of detached step-atom from step-edge. The number in square bracket indicates the predicted value from machine-learning.

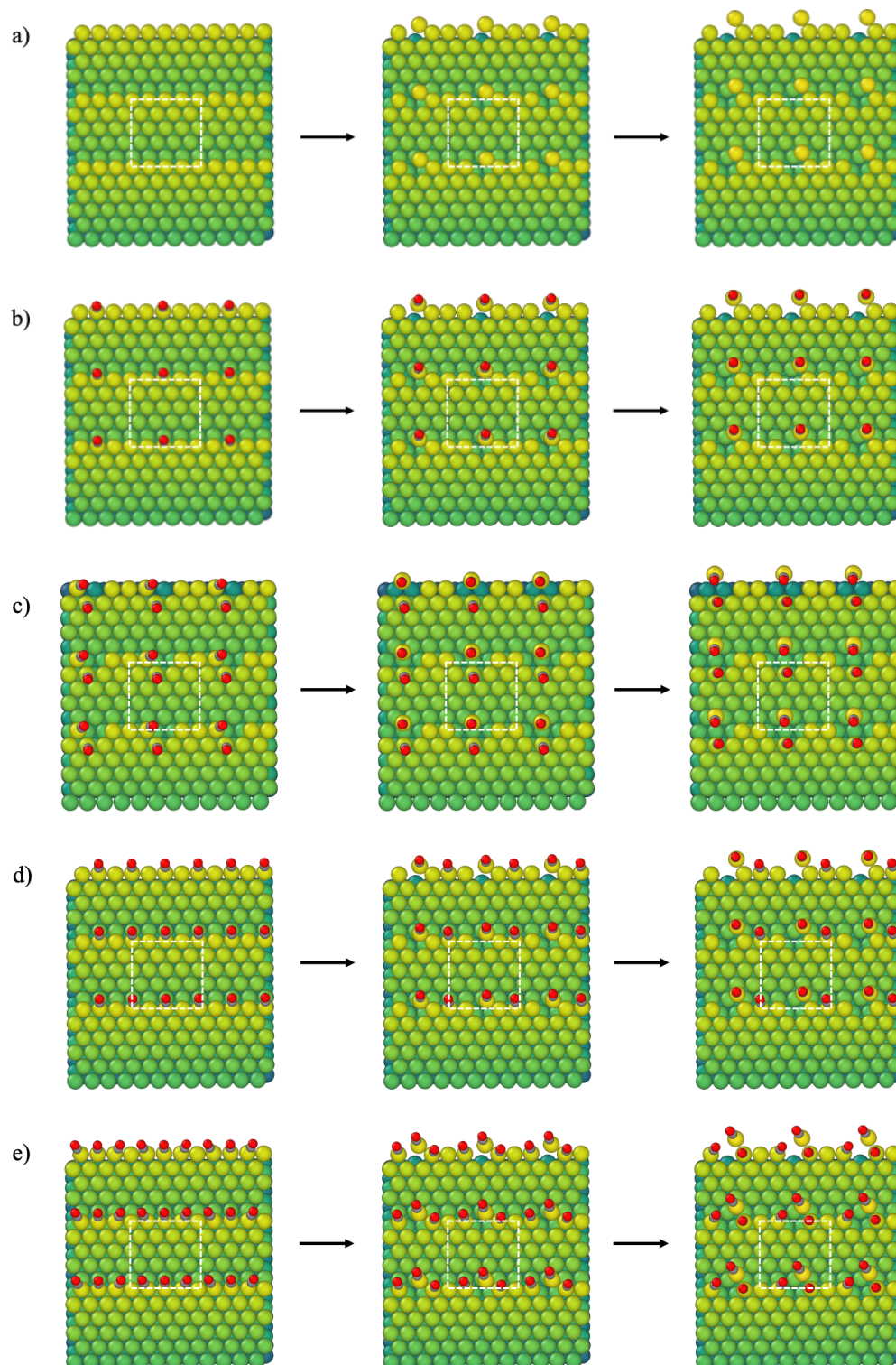
Figure Index	Step	CO / unit cell	Forward E_{act} (eV)	Reverse E_{act} (eV)
Figure C.15 (a)	A	0	0.45 [0.56]	0.03 [0.00]
Figure C.15 (b)	A	1	0.36 [0.44]	0.02 [0.00]
Figure C.15 (c)	A	2	0.24 [0.28]	0.02 [0.00]
Figure C.15 (d)	A	2	0.37 [0.43]	0.02 [0.00]
Figure C.15 (e)	A	3	0.23 [0.21]	0.05 [0.05]
Figure C.15 (f)	A	3	0.31 [0.36]	0.03 [0.00]
Figure C.15 (g)	A	3	0.22 [0.20]	0.02 [0.00]
Figure C.15 (h)	A	3	0.38 [0.41]	0.03 [0.01]
Figure C.15 (i)	A	4	0.27 [0.26]	0.03 [0.04]
Figure C.15 (j)	A	5	0.20 [0.18]	0.14 [0.06]
Figure C.16 (a)	B	0	0.55 [0.58]	0.05 [0.06]
Figure C.16 (b)	B	1	0.41 [0.43]	0.02 [0.04]
Figure C.16 (c)	B	2	0.30 [0.31]	0.02 [0.04]
Figure C.16 (d)	B	2	0.44 [0.47]	0.02 [0.03]
Figure C.16 (e)	B	3	0.25 [0.18]	0.01 [0.04]
Figure C.16 (f)	B	3	0.31 [0.30]	0.04 [0.06]
Figure C.16 (g)	B	3	0.28 [0.23]	0.02 [0.05]
Figure C.16 (h)	B	3	0.41 [0.47]	0.02 [0.05]
Figure C.16 (i)	B	4	0.26 [0.21]	0.04 [0.08]
Figure C.16 (j)	B	5	0.31 [0.34]	0.09 [0.12]

C.8.3 Detachment of kink-atom from the step edge

I investigated the barriers of detachment of kink-atom from the step edge given various configuration of adsorbed CO. The barriers and the associated figure index are shown in Table C.6. The mechanisms for each detachment are shown in Figure C.17 and Figure C.18 for A-step and B-step, respectively.

Table C.6: Forward and reverse barrier or activation energy of detached step-atom from step-edge. The number in square bracket indicates the predicted value from machine-learning.

Figure Index	Step	CO / unit cell	Forward E_{act} (eV)	Reverse E_{act} (eV)
Figure C.17 (a)	A	0	0.70 [0.81]	0.02 [0.02]
Figure C.17 (b)	A	1	0.51 [0.64]	0.01 [0.00]
Figure C.17 (c)	A	2	0.40 [0.42]	0.05 [0.02]
Figure C.17 (d)	A	2	0.39 [0.50]	0.01 [0.01]
Figure C.17 (e)	A	2	0.50 [0.62]	0.02 [0.00]
Figure C.17 (f)	A	3	0.27 [0.41]	0.05 [0.08]
Figure C.17 (g)	A	3	0.40 [0.51]	0.05 [0.04]
Figure C.17 (h)	A	4	0.24 [0.37]	0.06 [0.08]
Figure C.17 (i)	A	5	0.20 [0.25]	0.06 [0.10]
Figure C.18 (a)	B	0	0.68 [0.74]	0.03 [0.02]
Figure C.18 (b)	B	1	0.54 [0.55]	0.00 [0.00]
Figure C.18 (c)	B	2	0.40 [0.40]	0.01 [0.01]
Figure C.18 (d)	B	2	0.46 [0.57]	0.04 [0.06]
Figure C.18 (e)	B	2	0.53 [0.55]	0.00 [0.00]
Figure C.18 (f)	B	3	0.34 [0.44]	0.07 [0.09]
Figure C.18 (g)	B	3	0.54 [0.60]	0.00 [0.02]
Figure C.18 (h)	B	4	0.32 [0.38]	0.05 [0.05]
Figure C.18 (i)	B	5	0.28 [0.26]	0.04 [0.06]



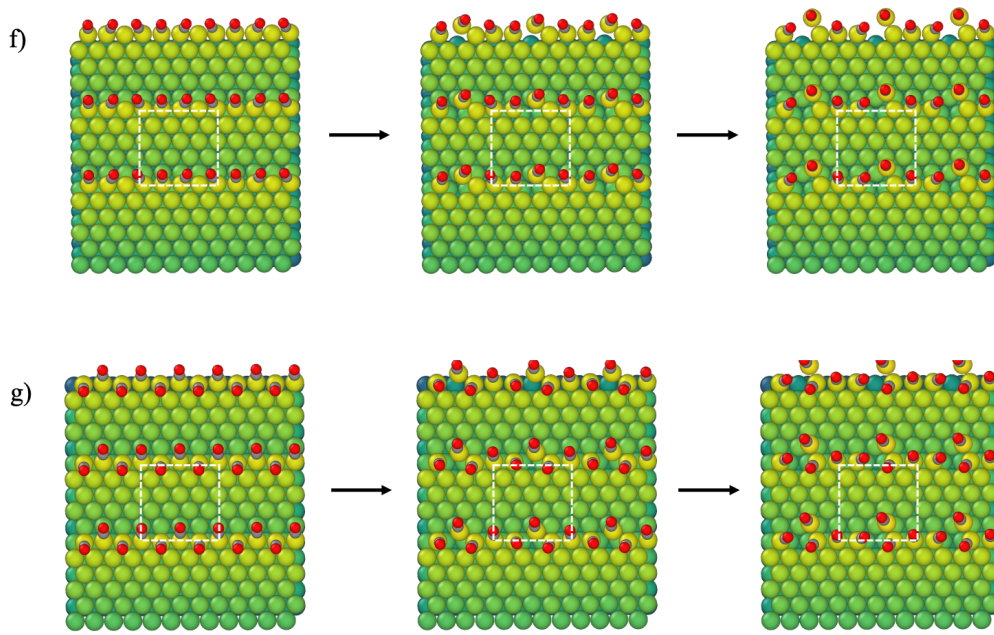
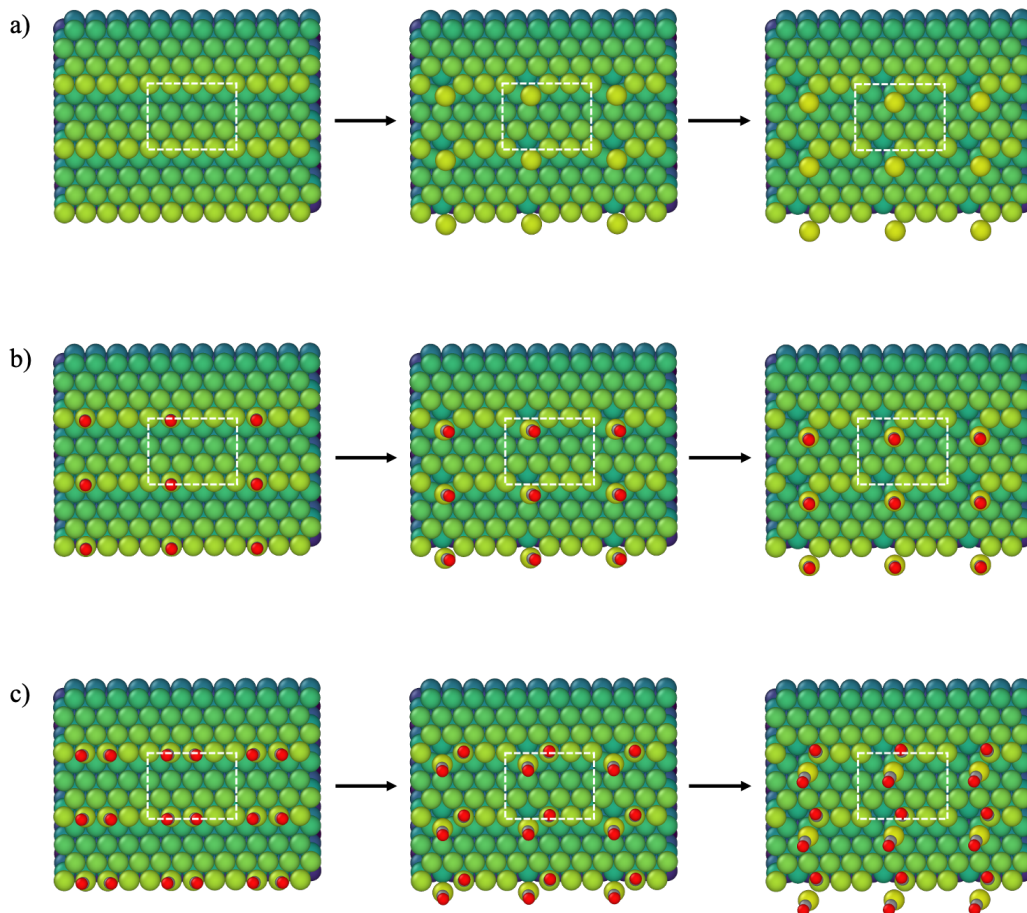


Figure C.13: Detachment of Cu step-atom from perfect A-step: (a) without CO adsorption, (b) with 1 adsorbed CO / unit cell, (c-d) with 2 adsorbed CO / unit cell, (e-f) with 3 adsorbed CO / unit cell, and (g) with 4 adsorbed CO / unit cell.



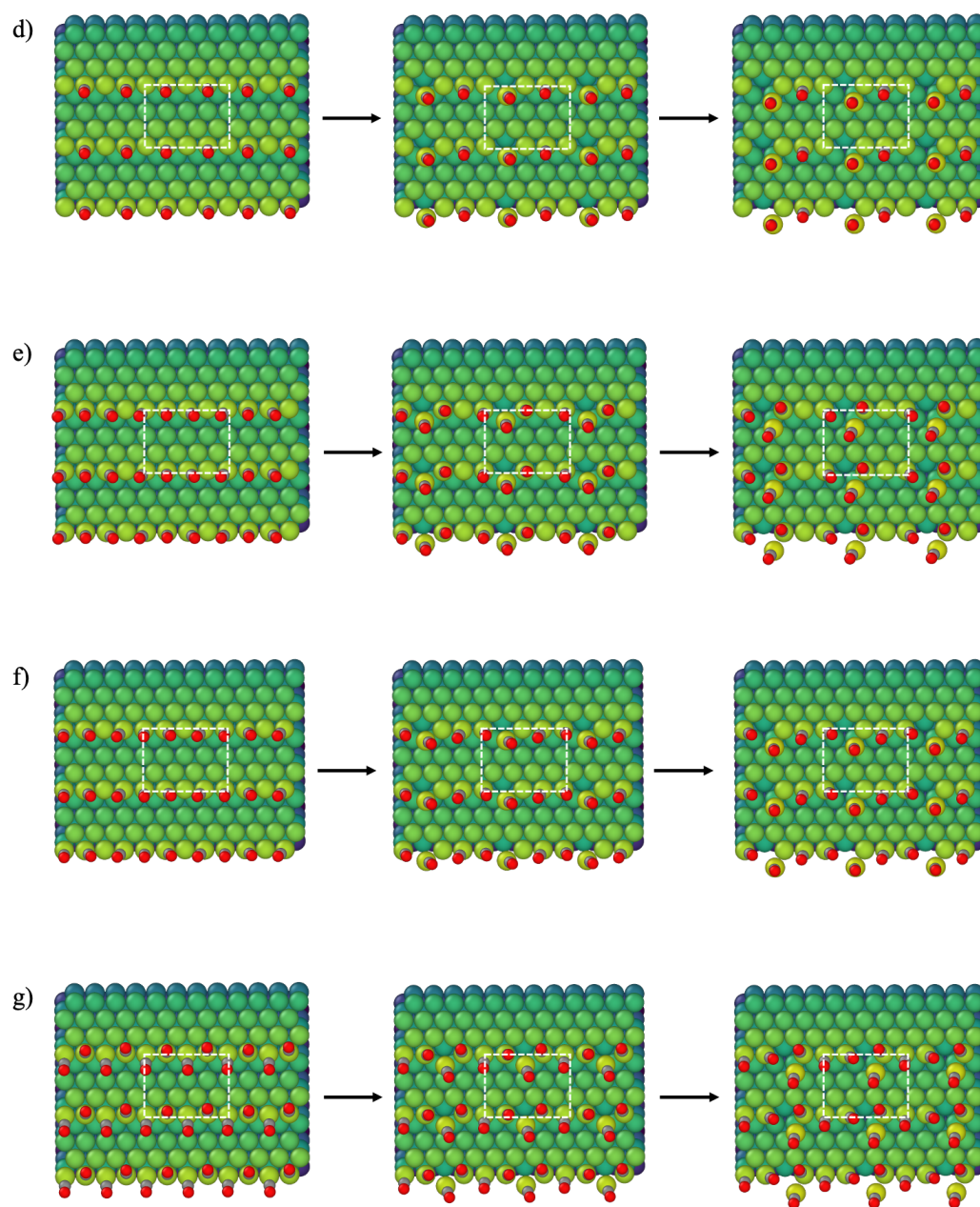
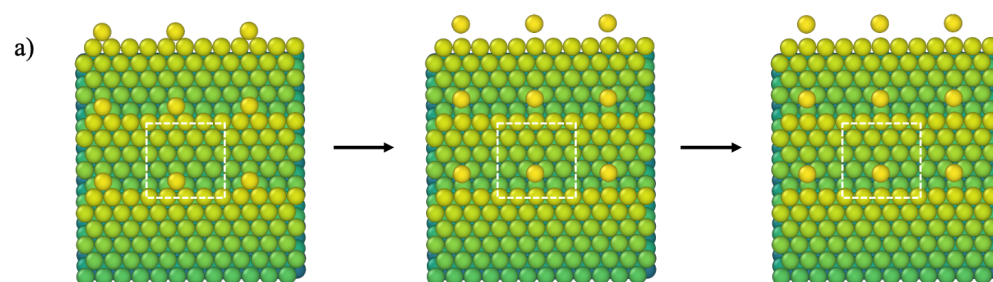
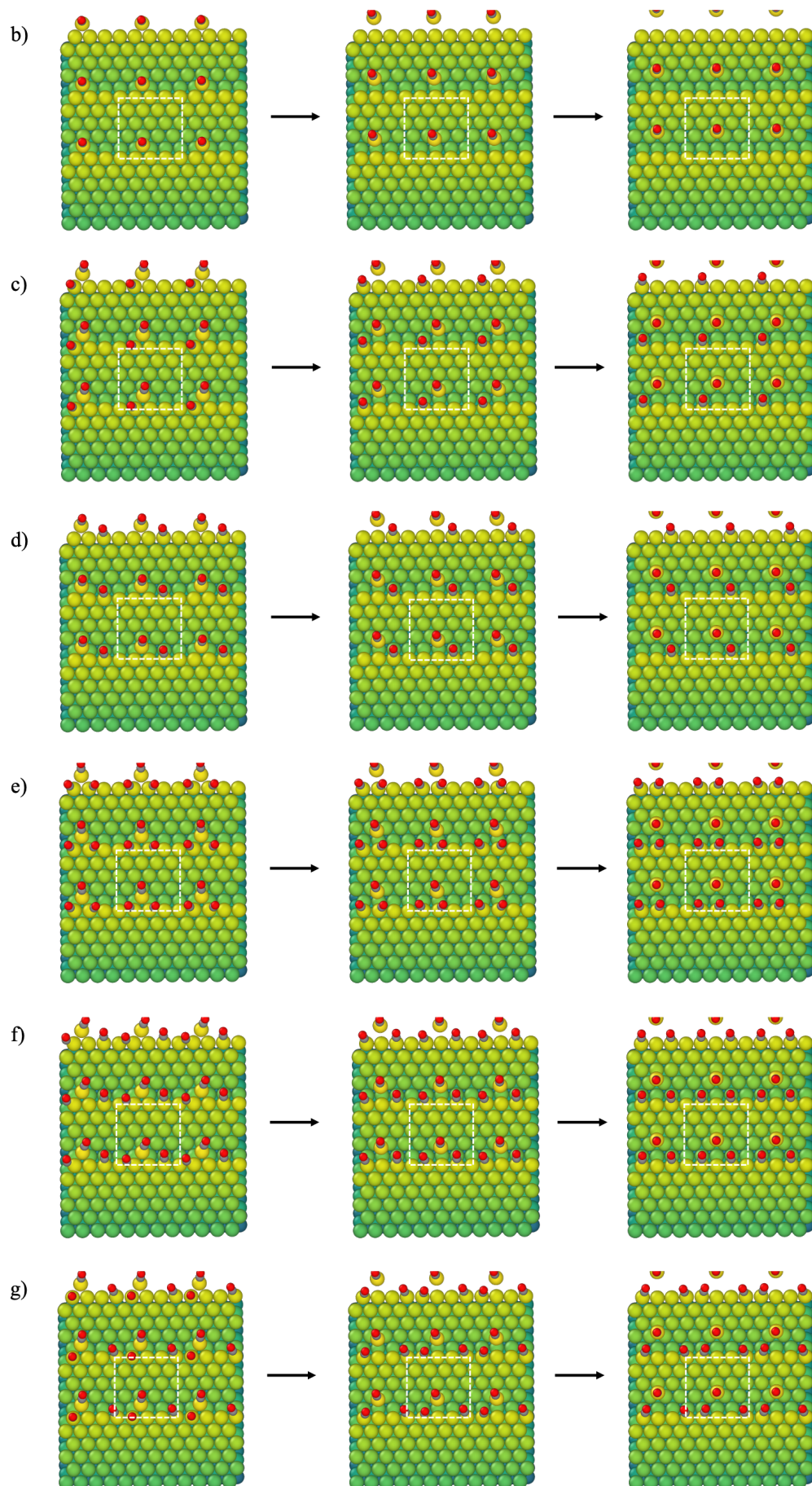


Figure C.14: Detachment of Cu step-atom from perfect B-step: (a) without CO adsorption, (b) with 1 adsorbed CO / unit cell, (c-d) with 2 adsorbed CO / unit cell, (e-f) with 3 adsorbed CO / unit cell, and (g) with 4 adsorbed CO / unit cell.





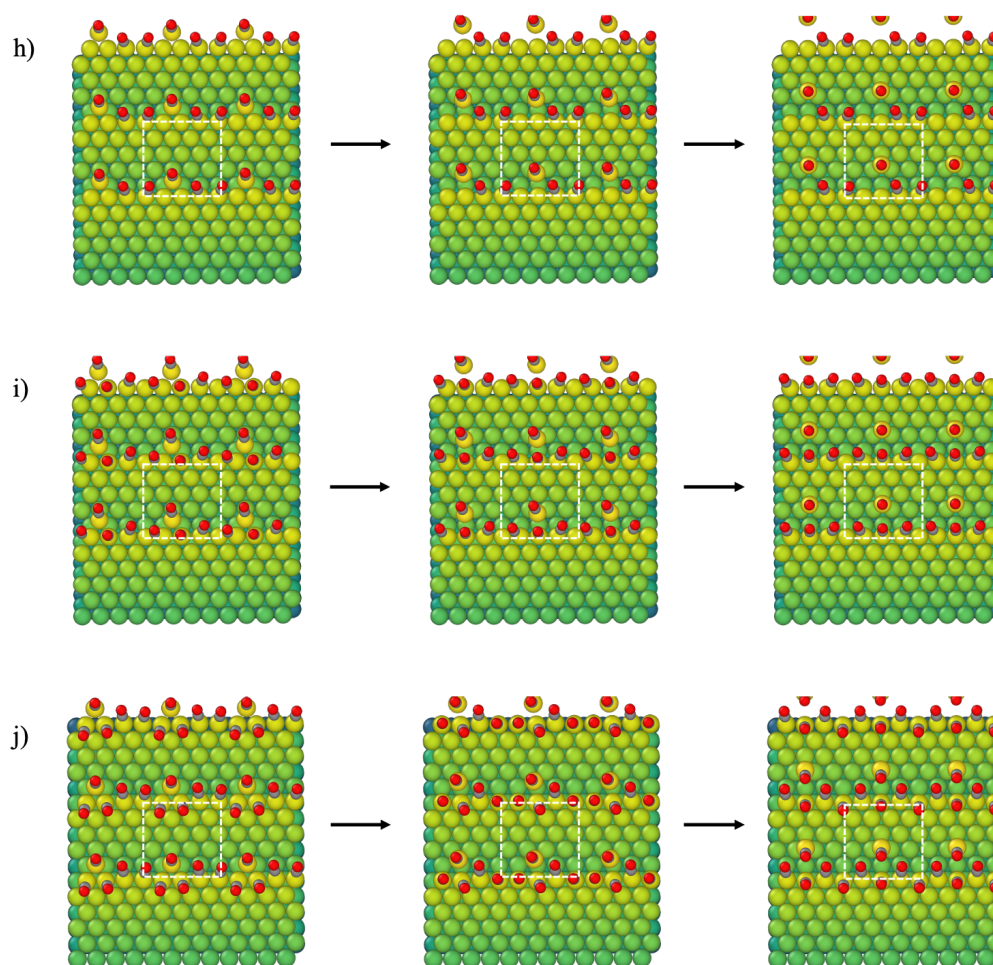
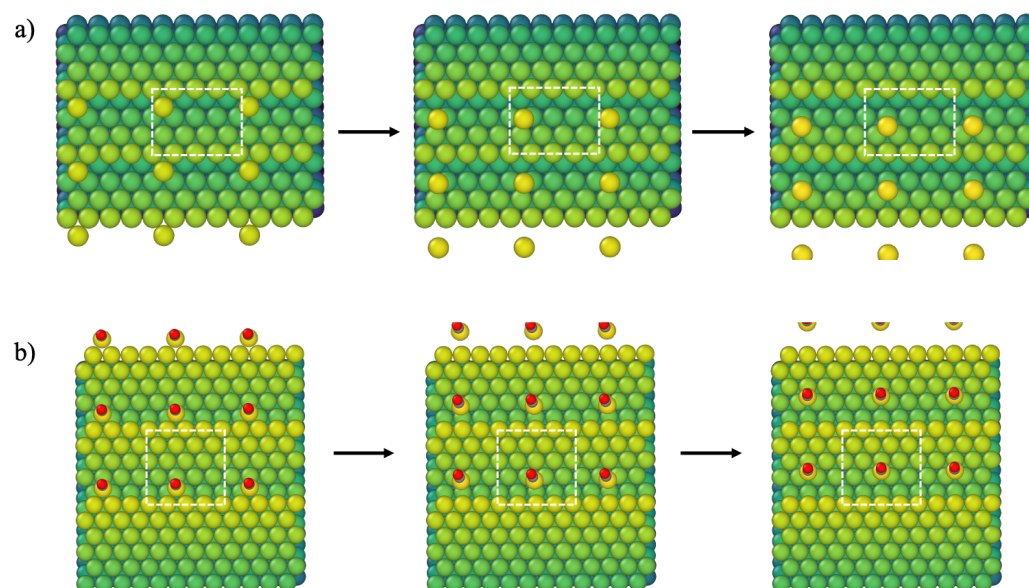
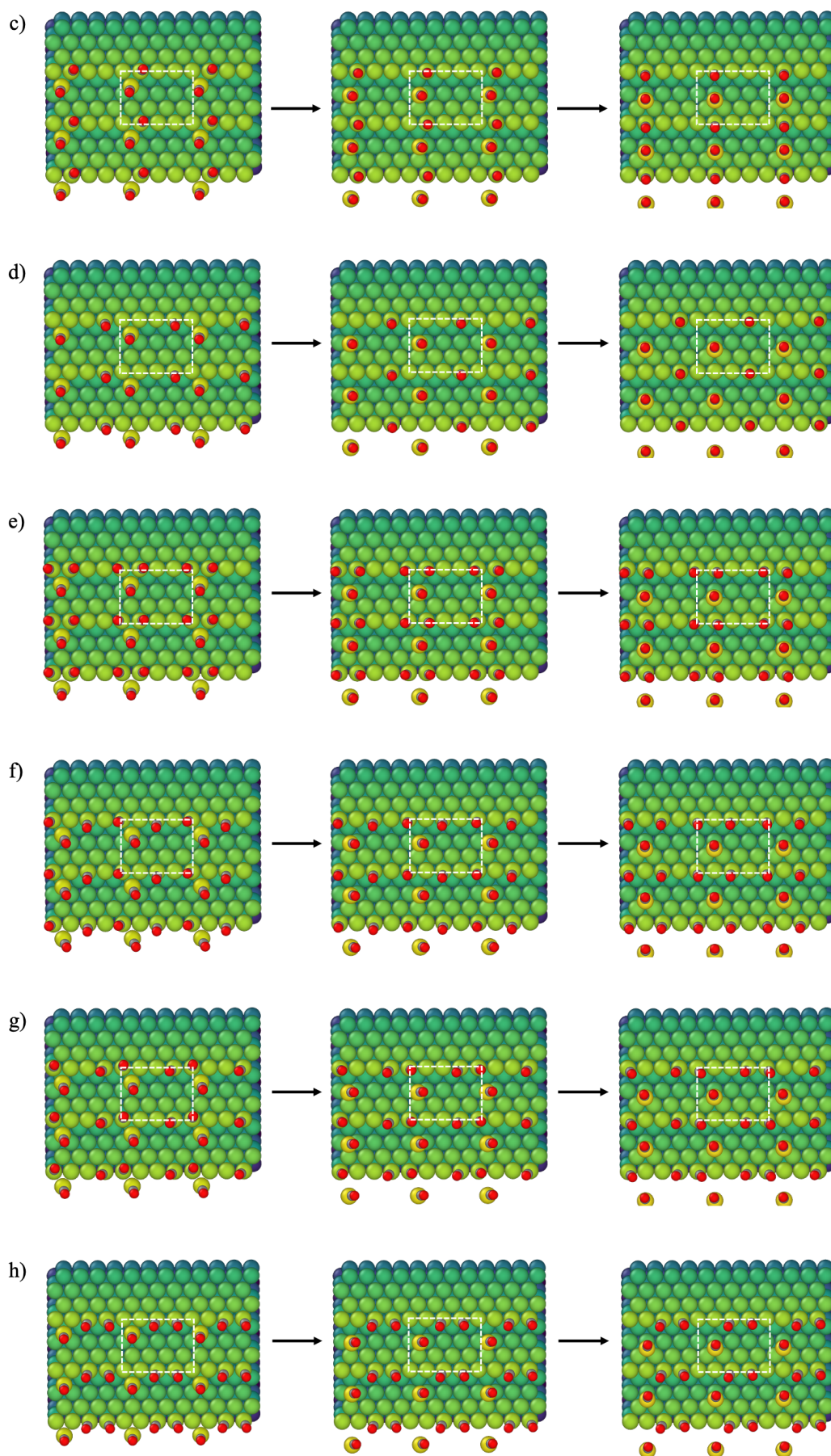


Figure C.15: Detachment of Cu step-adatom from A-step: (a) without CO adsorption, (b) with 1 adsorbed CO / unit cell, (c-d) with 2 adsorbed CO / unit cell, (e-h) with 3 adsorbed CO / unit cell, (i) with 4 adsorbed CO / unit cell, and (j) with 5 adsorbed CO / unit cell.





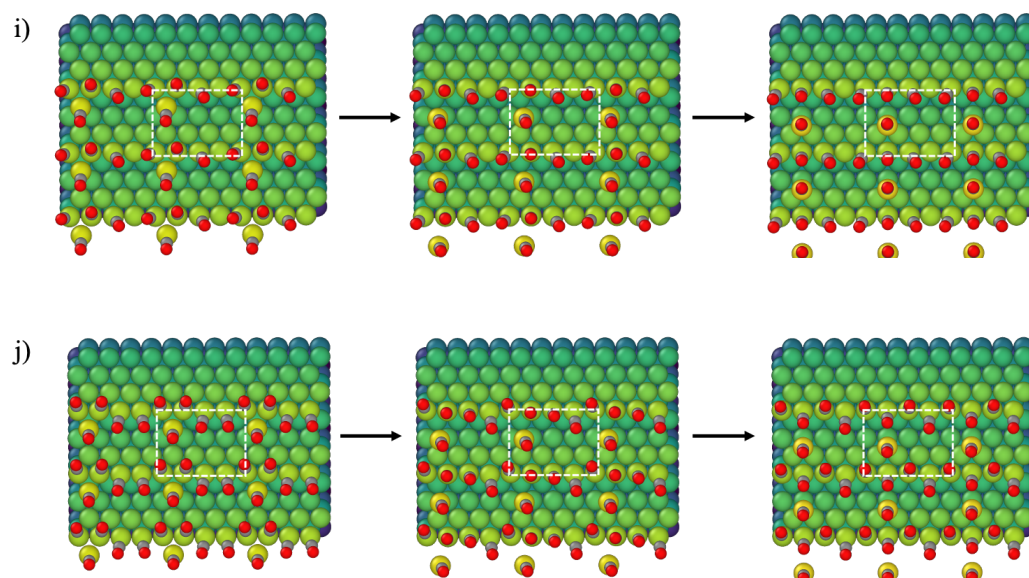
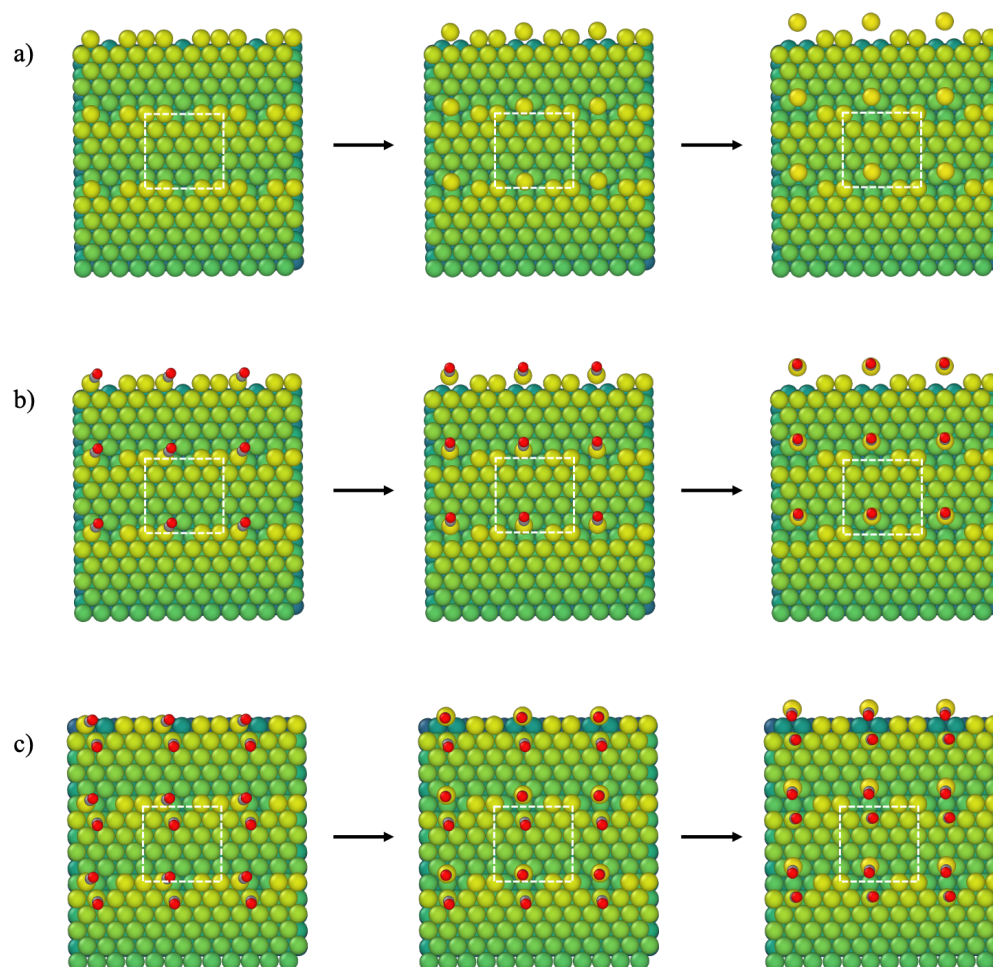
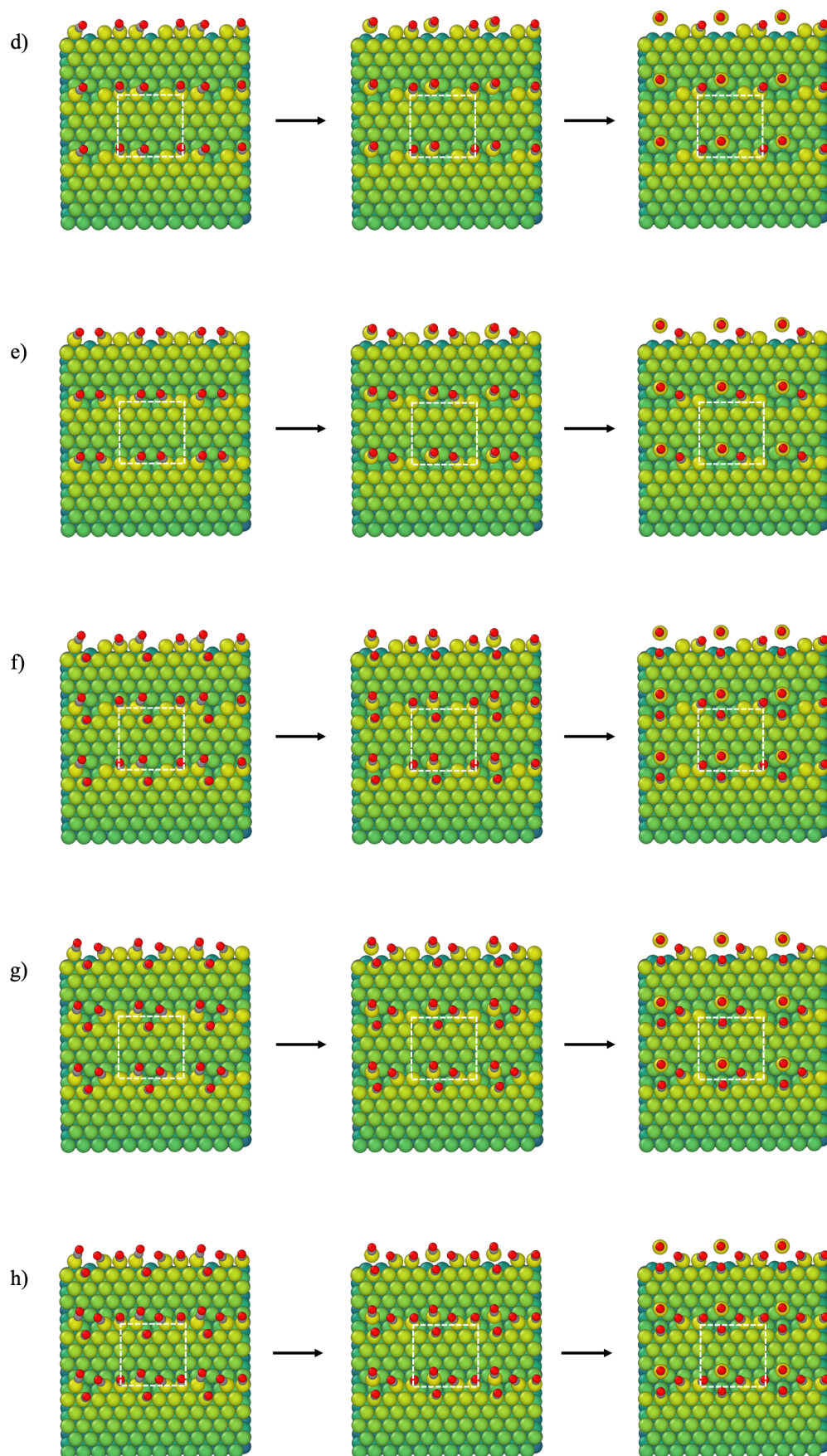


Figure C.16: Detachment of Cu step-adatom from B-step: (a) without CO adsorption, (b) with 1 adsorbed CO / unit cell, (c-d) with 2 adsorbed CO / unit cell, (e-h) with 3 adsorbed CO / unit cell, (i) with 4 adsorbed CO / unit cell, and (j) with 5 adsorbed CO / unit cell.





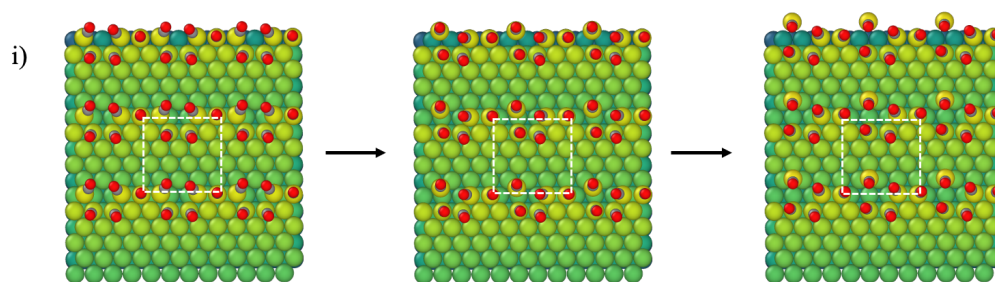
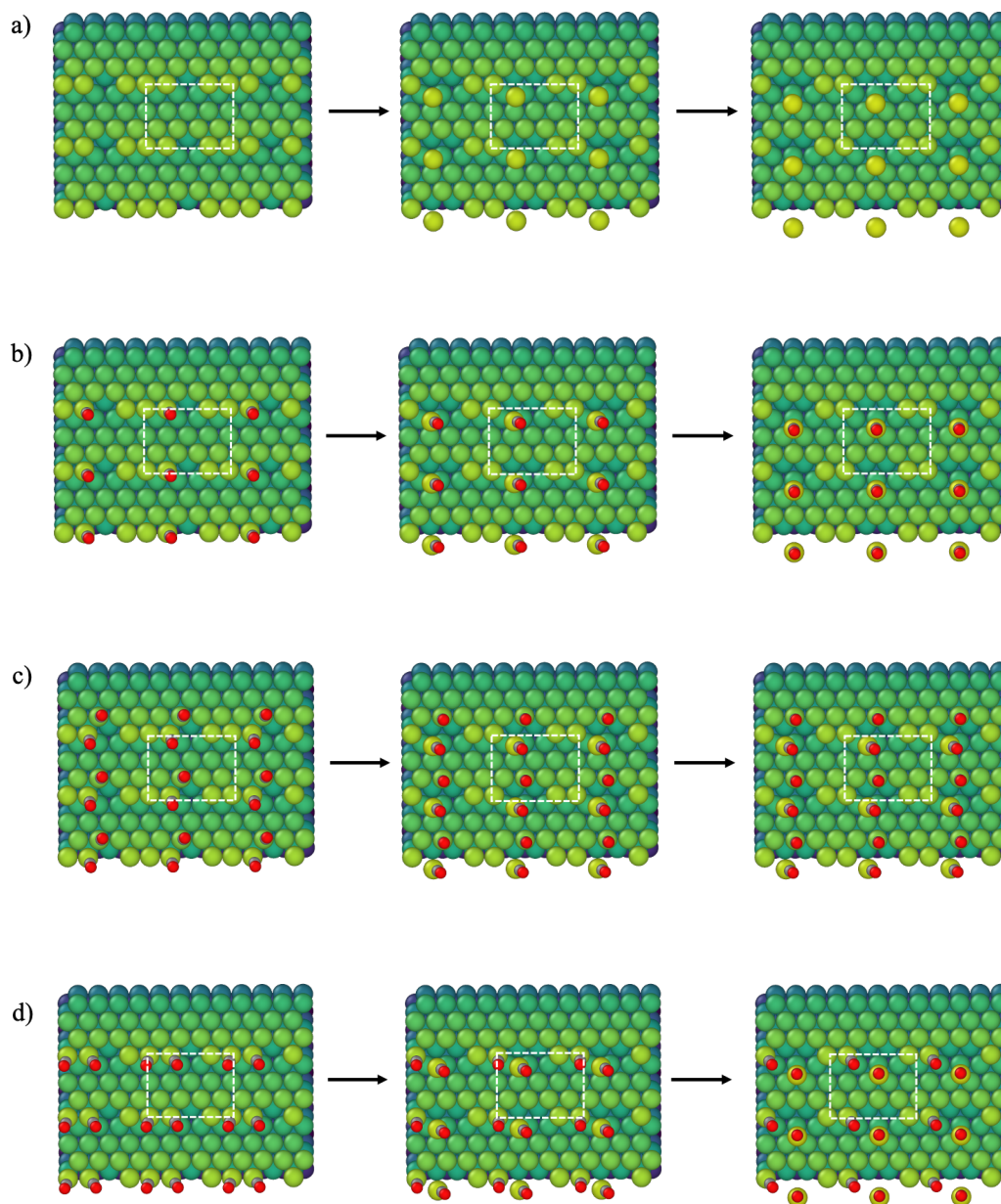


Figure C.17: Detachment of Cu kink-atom from A-step: (a) without CO adsorption, (b) with 1 adsorbed CO / unit cell, (c-e) with 2 adsorbed CO / unit cell, (f-g) with 3 adsorbed CO / unit cell, (h) with 4 adsorbed CO / unit cell, and (i) with 5 adsorbed CO / unit cell.



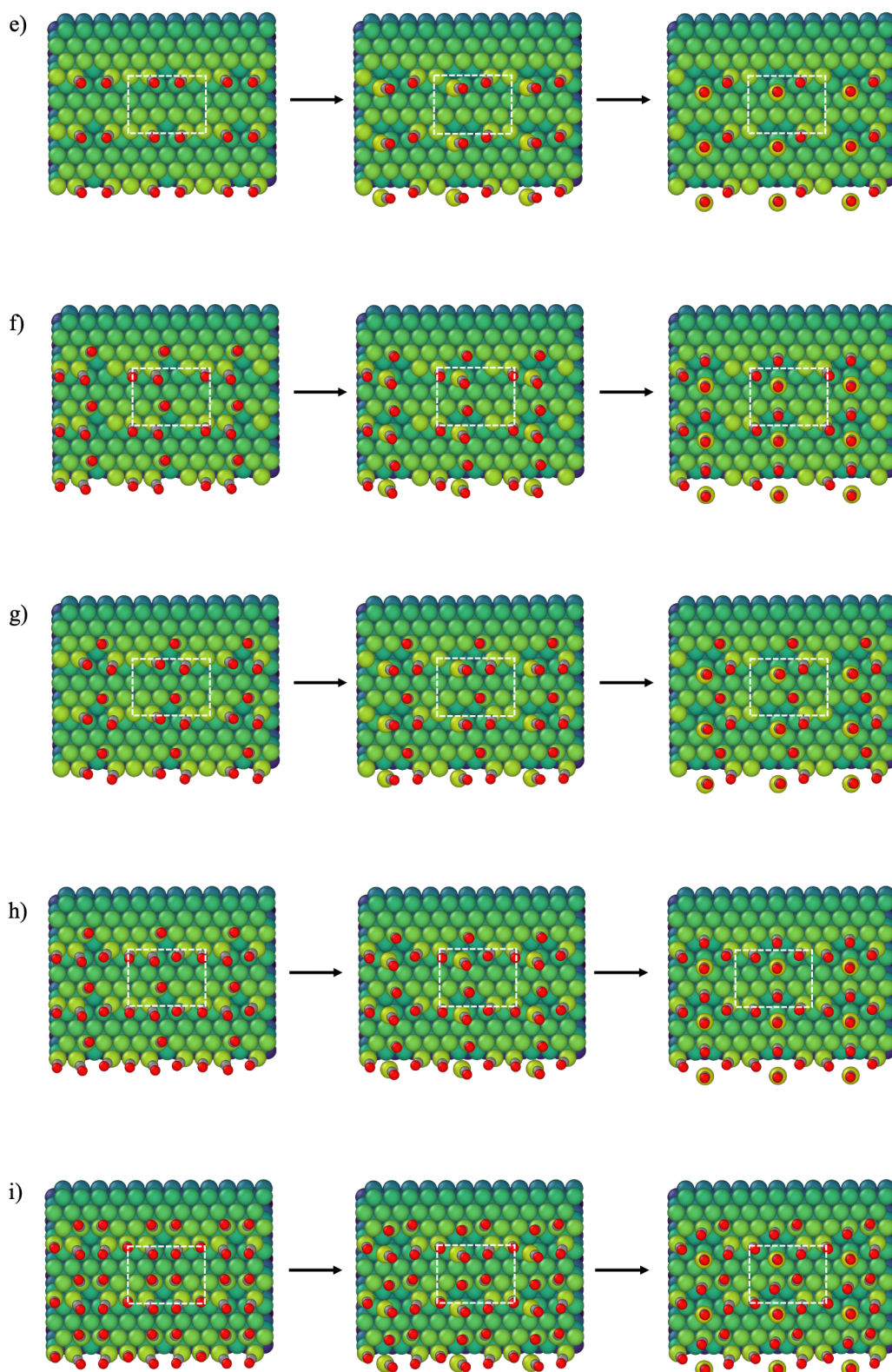


Figure C.18: Detachment of Cu kink-atom from B-step: (a) without CO adsorption, (b) with 1 adsorbed CO / unit cell, (c-e) with 2 adsorbed CO / unit cell, (f-g) with 3 adsorbed CO / unit cell, (h) with 4 adsorbed CO / unit cell, and (i) with 5 adsorbed CO / unit cell.

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Biography

List of Publications

- Halim., H. H., Putra, S. E. M., Muttaqien, F., Hamada, I., Inagaki, K., Hamamoto, Y., and Morikawa, Y. "Multi-scale Simulation of Equilibrium Step Fluctuations on Cu(111) Surfaces". *ACS Omega* **6**, 5183-5196. <https://doi.org/10.1021/acsomega.0c05064> (2021).
- Halim., H. H. & Morikawa, Y. "Elucidation of Cu-Zn Surface Alloying on Cu(997) by Machine-Learning Molecular Dynamics". *ACS Physical Chemistry Au* **2**, 430-447. <https://doi.org/10.1021/acspphyschemau.2c00017> (2022).
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- Halim., H. H., Putra, S. E. M., Muttaqien, F., Hamada, I., Inagaki, K., Hamamoto, Y., and Morikawa, Y. "Density Functional Kinetic Monte Carlo Simulation of Surface Step Fluctuation on the Cu(111) Surface". Presented in online session on the Physical Society of Japan (JPS) Autumn Meeting 2020. September 2020.
- Halim., H. H., Putra, S. E. M., Muttaqien, F., Hamada, I., Inagaki, K., Hamamoto, Y., and Morikawa, Y. "Multi-scale Simulation of Equilibrium Step Fluctuations on Cu(111) Surfaces". Presented on online poster session in the conference of Hyper-ordered Structural Science, May 2021.
- Halim., H. H. & Morikawa, Y. "Multi-scale Simulations on Cu-Zn Surface Alloying". *ACS Physical Chemistry Au* **2**. Presented online on hybrid oral session in the 9th Tokyo Conference on Advanced Catalytic Science and Technology. Fukuoka, Japan, July 2023.
- Halim., H. H. & Morikawa. "Elucidation of Cu-Zn Surface Alloying on Cu(997) by Machine-Learning Molecular Dynamics". Presented on hybrid oral session in International Workshop on Exploration of Atomistic Disorder in Conference of Long-Range Ordered Systems and of Order in Disordered Materials. Grenoble, France, September 2022.
- Halim., H. H. & Morikawa. "Elucidation of Cu-Zn Surface Alloying on Cu(997) by Machine-Learning Molecular Dynamics". Presented on online oral session on Kansai Thin Films and Surface Physics Seminar. November 2022.
- Halim., H. H. & Morikawa. "Elucidation of Cu-Zn Surface Alloying on Cu(997) by Machine-Learning Molecular Dynamics". Presented in oral session on the 22nd International Vacuum Congress (IVC-22). Sapporo, Japan, September 2022.

- Halim., H. H. & Morikawa. "Elucidation of Cu–Zn Surface Alloying on Cu(997) by Machine-Learning Molecular Dynamics". Presented in hybrid poster session on the 12th International Conference on Environmental Catalysis (ICEC2022). Osaka, Japan, July 2022.
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- Halim., H. H. & Morikawa. "Machine Learning Molecular Dynamics Simulation on CO₂ Hyrdrogenation on Cu(111) Surface. Presented in online poster session on the Physical Society of Japan (JPS) Spring Meeting 2023. March 2023.

List of Awards

- The Forest Award in the Conference of Hyper-ordered Structural Science, May 2021.
- The EBARA Student Prize at the 22nd International Vacuum Congress (IVC-22), Sapporo, Japan, September 2022.