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The Elucidation of Non-equilibrium States of Catalysis by Machine Learning Aided Atomic Simulations

Yoshitada Morikawa（Grad. School of Engineering, The University of Osaka）

Atomic - scale catalytic events under operating conditions drive the synthesis of essential compounds but often occur far from equilibrium and remain experimentally inaccessible. In this project, we employ machine - learning molecular dynamics (MLMD), training interatomic potentials on density functional theory (DFT) data to achieve near–DFT accuracy at a fraction of the cost, and generate explicit “molecular movies” of reactive processes that include CO_2 hydrogenation on Cu surfaces, thermo-catalytic graphitization inhibition on diamond via surface hydrogen termination, and reactive dynamics at diamond-metal interfaces that reveal facet - dependent wear pathways. Our results demonstrate MLMD power to predict complex, non-equilibrium catalysis under realistic conditions and open pathways for data - driven catalyst design.

1. Basic Information

(1) Collaborating JHPCN Centers

Osaka University

(2) Theme Area

Data science/data usage area

(3) Project Members and Their Roles

Prof. Yoshitada Morikawa supervised the research. Harry Handoko Halim performed the research on the CO_2 hydrogenation. John Isaac Enriquez and Nguyen Trinh Bao Anh performed research on the dynamic of the diamond surface and the metal interface.

2. Purpose and Significance of the Research

Catalysis is critical in our sustainable development by aiding synthesis of various essential compounds. However, the advancement of this field is hindered by the unelucidated atomic events under operating condition. Despite modernization of the characterization techniques, observations are usually limited to the equilibrium state (i.e., the condition before and after the catalysis occurs) due to the intractable behavior of the system at the atomic level. Such limitations hinder the identification of the promoting (or demoting) factors of the catalysis that eventually play their roles during the non-equilibrium states.

In the raise of computing power, atomic simulation is highly capable to elucidate the non-equilibrium states of catalysis by providing explicit ‘molecular movie’ of catalytic events. This approach works by constructing the *interatomic potential*, from which the energy and forces of atoms that govern the dynamic of the system can be derived. Accurate potential can be constructed by method called Density Functional Theory (DFT), resulting in simulation called ab-initio molecular dynamics (AIMD). However, DFT calculations are very expensive for large number of atoms, thus it is inefficient to simulate catalysis at realistic operating condition.

Given the rapid progress in machine-learning (ML) technique, DFT results can be accurately predicted by ML model after learning from adequate DFT database. This framework thus eliminates the necessity in AIMD to perform DFT at every timestep, resulting in faster and more

efficient method called machine-learning molecular dynamics (MLMD). However, the MLMD relies on high-throughput and automated calculations to build reliable database used to train ML model, therefore, the large-scale computer system is inevitably necessary. In this project, we aim to elucidate the non-equilibrium states including the catalytic system involving CO_2 hydrogenation as well as chemical reactions on the diamond and diamond-metal interface.

3. Significance as JHPCN Joint Research Project

This research is an interdisciplinary project since it involves the field of physics, chemistry, material science, chemical engineering, and data science. The resources from JHPCN are necessary to build the database, train ML model, run dynamics simulation, and analyze large observation data.

4. Outline of Research Achievements until FY2023

This project starts from FY2024 and thus it is not a continuous project.

5. Details of FY2024 Research Achievements

This section is divided into three parts: the project related to the CO_2 hydrogenation, the elucidation of the thermo-catalytic etching on the diamond surfaces, and the catalytic reactions on diamond and metal interface.

(a) The CO_2 hydrogenation.

In this subproject, we aim to elucidate the importance of vibrational mode in CO_2 hydrogenation, by using MLMD simulations. Unlike the molecular beam used in experiment, MD allows precise control of the initial vibrational mode of CO_2 (i.e., bending and stretching modes) combined with translational energy and incident angles. Ultimately, the dependence between reaction probability and a specific mode of CO_2 can be obtained. The results of MD shows that the successful hydrogenation of CO_2 as well as the desorption of CO_2 due to the Pauli repulsion can be simulated with satisfying accuracy under experimental surface temperature. Moreover, by coupling MD with Transition Interface Sampling (TIS), a more accurate hydrogenation reaction rate (in terms of crossing probability) was obtained compared to conventional approaches (**Figure 1**). TIS allows for a comprehensive sampling of reaction pathways under actual reaction conditions.

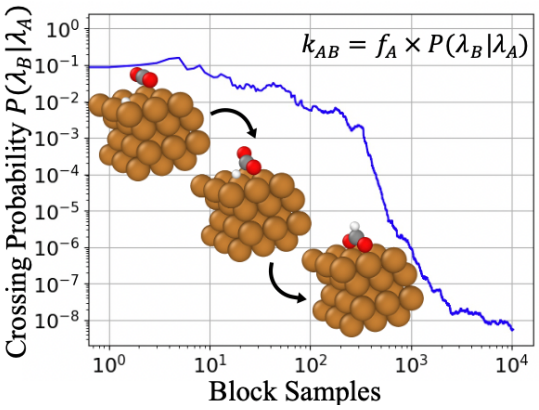

Figure 1. Crossing probability of CO_2 hydrogenation obtained from TIS.

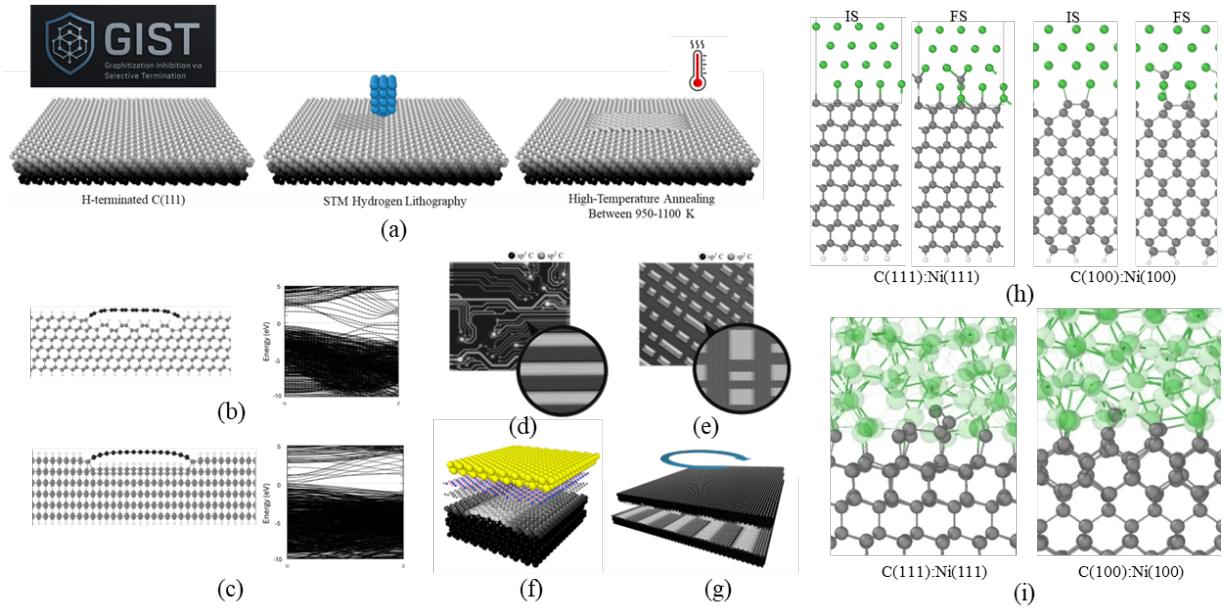

Figure 2. (a) The proposed Graphitization Inhibition by Selective Termination (GIST) method. (b) Zigzag and (c) armchair Graphene Nanoribbons on Diamond (GRiD) structure. Proposed applications in (d) all-carbon circuit, (e) memory storage, (f) van der Waals heterostructures, and (g) twistronics for topological devices. (h) NEB simulations of single-atom etching of C atoms at diamond-nickel interface. (i) MLMD simulations of thermos-catalytic wear at diamond-nickel interface.

(b) Thermo-catalytic etching on the diamond surface.

We proposed the Graphitization Inhibition by Selective Termination (GIST) method (**Figure. 2**), which uses surface terminations to control graphitization sites. MLMD and DFT simulations showed that hydrogen effectively suppresses graphitization, enabling the design of Graphene Nanoribbons on Diamond (GRiD)—structures where conductive sp^2 carbon regions are embedded in insulating diamond. Electronic structure calculations revealed semiconducting and spin-polarized states, with potential applications in electronics, spintronics, and quantum technologies. To investigate thermo-catalytic etching in diamond device manufacturing and accelerated wear during diamond cutting of metals, we studied the diamond–nickel interface using DFT and MLMD. DFT simulations showed anisotropic behavior: carbon atoms detach more easily from the (100) surface than from the (111) surface, consistent with experimental anisotropic etch rates. Ongoing MLMD simulations further incorporate adatoms, surface vacancies, and nano-islands to assess how local structure affects wear rates.

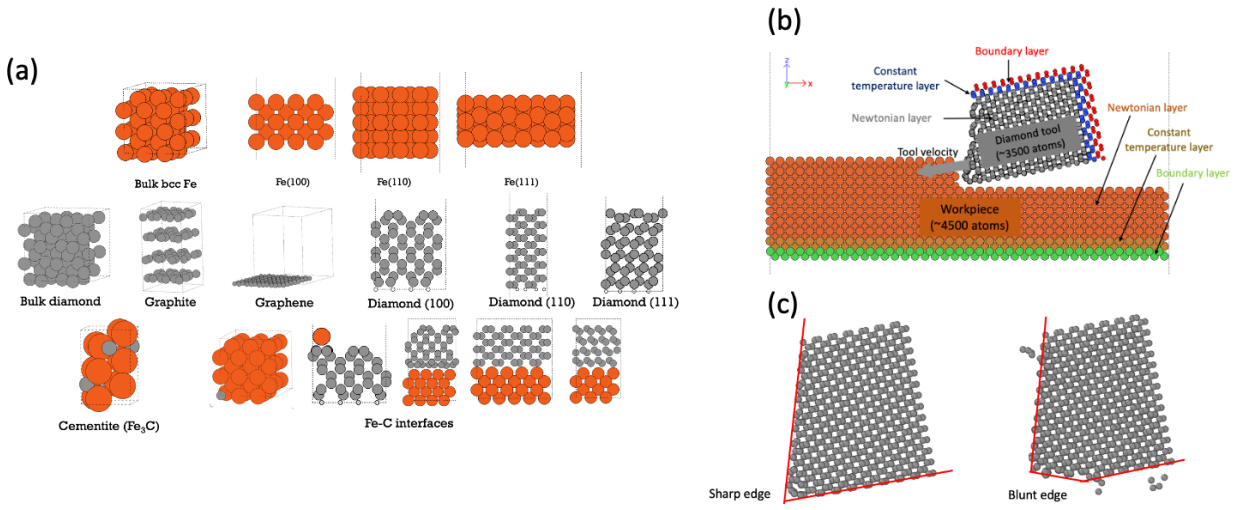

Figure 3. Some typical structures in iron-carbon database (b) The cutting simulation model (c) Unworn (left) and Worn (right) (110)[001] tool, taken at t = 0 ns and t = 3.1 ns.

(c) The catalytic reactions on the diamond-metal interface.

To clarify the interface reactions during diamond turning of ferrous metals, we have developed a graph neural network-based interatomic potential and conducted long time-scale cutting simulations (**Figure 3**). Our MLMD results indicate that diamond tool wear primarily occurs on the clearance face, which directly impacts cutting accuracy and increases the surface roughness of the machined material. Maintaining a low-temperature cutting environment helps reduce the wear rate. Among the commonly used diamond crystal facets, the (100) facet demonstrates greater wear resistance compared to the (110) facet; although the (111) facet is rarely used due to fabrication challenges, it remains a potential candidate for tool design. The wear behavior observed in our MLMD simulations closely resembles experimental findings: Wear initiates at the tool tip, progressively dulling the cutting edge and degrading performance over time. Initially, wear progresses rapidly; however, as simulation time increases, the wear rate stabilizes and aligns with experimental measurements. Ongoing analysis is now focused on the atomistic mechanisms of carbon atom removal from the tool. This includes investigating how factors such as crystal facet, cutting temperature, tool velocity, and the presence of iron influence the wear process at the atomic level.

6. Self-review of Current Progress and Future Prospects

In the first year of this JHPCN joint research project, we have demonstrated the feasibility and accuracy of machine-learning molecular dynamics (MLMD) for three distinct systems:

(i) CO_2 hydrogenation on Cu surfaces: By combining MLMD with Transition

Interface Sampling (TIS), we accurately reproduced mode-specific reaction probabilities and obtained hydrogenation rates that closely match experimental trends under surface temperatures of interest.

(ii) Thermo-catalytic etching of diamond: Our Graphitization Inhibition by Selective Termination (GIST) method enabled controlled formation of graphene nanoribbons within diamond, and revealed anisotropic etch-rate behavior at the diamond-nickel interface.

(iii) Diamond-metal interface reactions: A graph-neural-network interatomic potential allowed long-timescale cutting simulations, uncovering facet-dependent tool wear mechanisms that agree with experimental observations.

Overall, we have used all the provided resources and now preparing for the publications.