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The Investigation of Self Optimization of Active Sites by Reaction Intermediates during Non-Equilibrium States of CO₂ Hydrogenation to Methanol

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1. Introduction

Heterogenous catalysts plays critical roles in the human civilization by facilitating the synthesis of essential compounds. Given in-depth understanding of interactions between catalysts and chemicals, enhancing the performance can be achieved by tuning the morphology of the catalyst, especially the structure of the active sites. However, elucidating the active sites is non-trivial due to the dynamic of the catalyst during operating condition (i.e., non-equilibrium states) which might reconstruct the active sites far from the as-prepared condition.

In this study, we aim to elucidate the active sites at non-equilibrium states by taking CO_2 hydrogenation to methanol as a case study. The utilization of greenhouse gas CO_2 to methanol and the application of methanol in a fuel-cell are appealing solutions to tackle the global warming, but development beyond the conventional catalyst (i.e., $Cu/ZnO/Al_2O_3$ or CZA) is hindered by the controversy in the active sites. Industrially, methanol is synthesized from the mixture of $CO_2/CO/H_2$ gas and there is a strong possibility that the adsorbates and intermediates existed during the reaction might induced surface transformation, thereby form the new active sites. We regard this phenomenon as "self-optimization of the catalyst" since the origin of the new active sites come from the system itself without any additional surface engineering.

In the raise of computing power, simulation of catalysis is highly promising to unbiasedly elucidate the catalyst reconstruction by providing explicit atomistic picture of catalytic events. In general, the simulation requires the *interatomic potential*, from which the energy and forces of atoms that govern the dynamic of the system can be derived. Accurate potential can come from a very computationally-expensive method called Density Functional Theory (DFT). Fortunately, given the rapid progress in machine-learning (ML) technique, DFT results can be accurately predicted by an ML model after learning from adequate database. This framework results in faster and more efficient method called machine-learning molecular dynamics (MLMD) [1].

In this article, we highlight our application of MLMD to uncover atomic-level phenomena in the self-optimization of active sites, first focusing on the formation of small clusters on Cu surfaces induced by CO. This study, which has been published in reference [2], has been conducted utilizing the SQUID super computer of Osaka University.

2. Machine Learning Molecular Dynamics

In practice, we apply the MLMD by integrating four frameworks including DFT, ML, MD, and the analysis tool that we called *elucidator*. The schematic is shown in Fig.1 and each of them is discussed in the following.
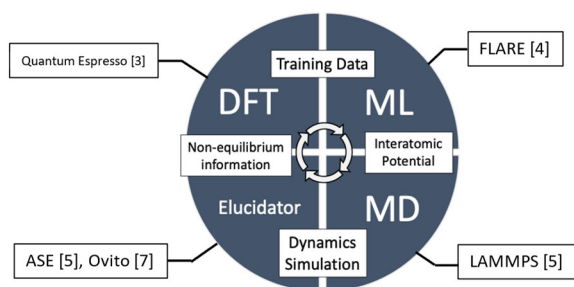

Fig. 1：The framework of MLMD

2.1 Density Functional Theory (DFT)

We employed DFT software Quantum Espresso [3] to provide the energy and atomic forces for each training data that consist of atomic environments of the Cu surface interacting with various configurations of CO molecules (both in gas and adsorbed states). Some snapshots of the training data are shown in Fig 2.
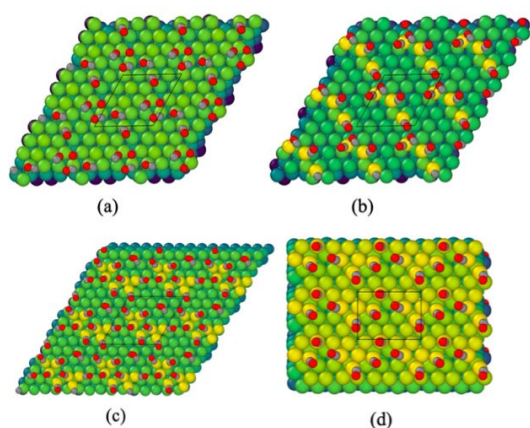

Fig. 2：Some snapshots of training data: (a) CO on the flat Cu(111) surface, (b, c) CO with some Cu clusters, and (d) CO on Cu step surface.

2.2 Machine-Learning (ML)

After generating the database with the corresponding target values (i.e., energy and atomic forces), we proceeded with constructing a machine-learning interatomic potential. In this study, we employed the Gaussian Process Regression (GPR)

machine-learning algorithm, implemented within the FLARE software [4]. GPR was selected due to its capability to provide prediction uncertainty based on the database, facilitating the active learning approach. This method utilizes high uncertainty values as criteria for including atomic environments in the database, ensuring each data point is sufficiently distinct, resulting in a compact and minimally correlated database. To ensure the reliability of the potential, the atomic force of each atom is evaluated. All the Mean Absolute Error (MAE) is below 0.1 eV/Å. The result of the validation is shown in Fig. 3.
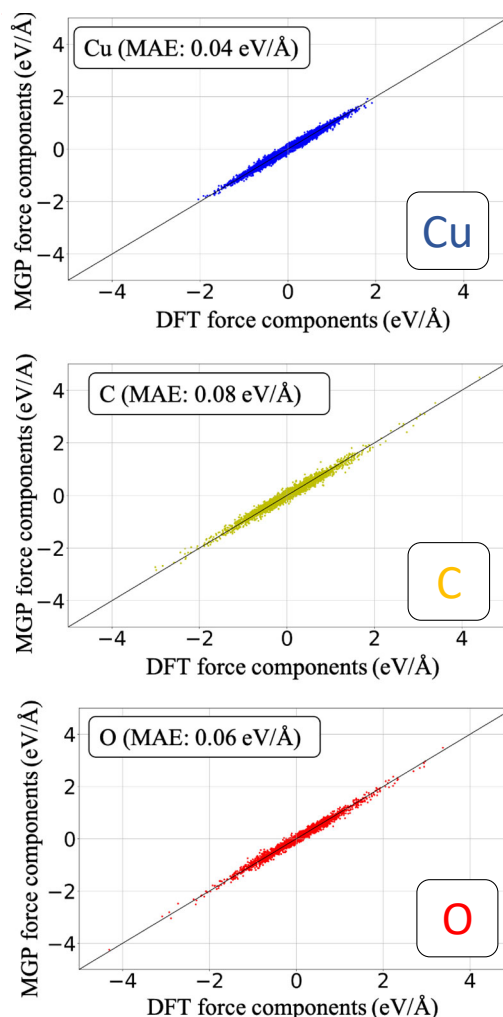

Fig. 3：The parity plots showing the validation of the atomic forces of each element: (a) Cu with MAE of 0.04 eV/Å, (b) C with MAE of 0.08 eV/Å, and O with MAE of 0.06 eV/Å.

2.3 Molecular Dynamics (MD)

The LAMMPS [5] package is utilized to conduct MD simulations employing both MPI and OMP parallelization techniques. This software reads the ML potential and computes energy and forces of the system at each time step, resulting in dynamics of the atoms.

2.4 Elucidator

Elucidator is a set of analysis tool that we used to post-process the trajectory of the MD simulations. This tool is Python-based program which relies on two libraries, namely ASE [6] and Ovito [7]. Tasks that are performed includes: the visualization of the dynamics, identification of the size and shape of the clusters, as well as analyzing the mechanism of the cluster formations.

3. The formation of Cu nano-clusters on Cu surface induced by CO adsorptions

With the help of MLMD, we succeeded in capturing the atomic level events of the formation of active sites in the form of small nano-clusters. Such formation is induced by the interaction of Cu surface with CO adsorbates as no similar behavior is observed when the Cu surface is not exposed with the CO. The snapshot of the Cu surface at 550 K without and with CO exposure are shown in Fig. 4 and Fig. 5, respectively.
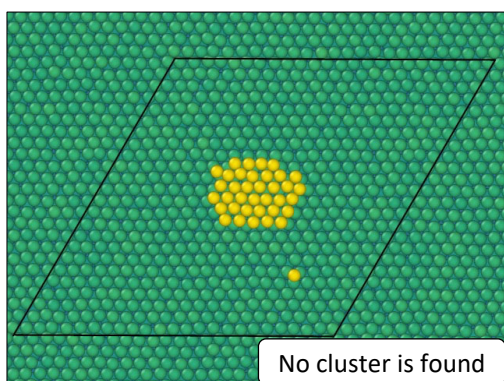

Fig. 4 : Snapshot (top-view) of Cu island (yellow) deposited on Cu(111) surface (green atoms).
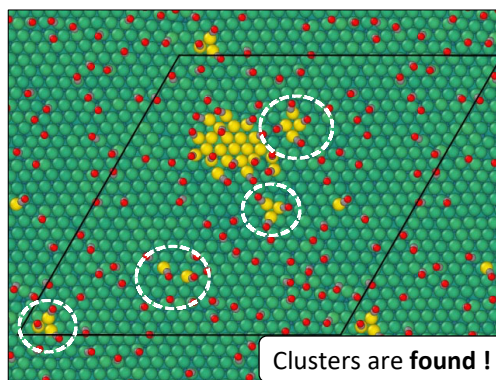

Fig. 5 : Snapshot (top-view) of Cu island (yellow atoms) deposited on Cu(111) surface (green atoms). The island is decomposed to small clusters due to the interaction with the CO adsorbates.

With the help of elucidator, the shapes and sizes of the nano-clusters formed during the simulation can be identified. As shown in Fig.6, the size of the clusters is ranged from dimer (consists of 2 atoms) to heptamer (consists of 7 atoms). In all cases, the CO is adsorbed on the edge of the cluster, which is consistent with the DFT calculations that suggest that CO is favorably adsorbed on low-coordinated atoms.
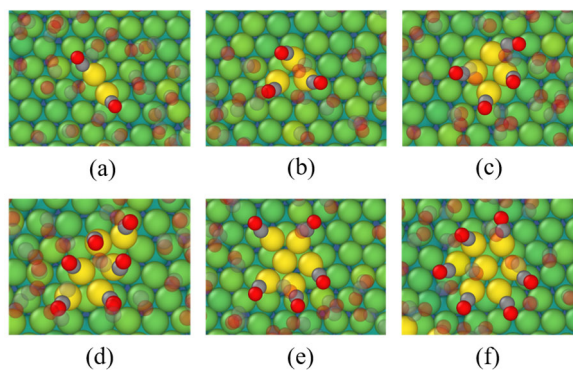

Fig. 6 : Snapshots of the clusters formed during the simulation of CO interacting with Cu surface: (a) dimer, (b) trimer, (c) tetramer, (d), pentamer, (e) hexamer, and (g) heptamer. The CO in the gas phase is drawn in semi-transparent color.

Further, the mechanism of the cluster formation can be clarified from the results of MD simulations. We

found that the clusters are mainly formed by the agglomeration of the Cu-CO complex(s) which then grow bigger over the time. Such process is typically initiated by the detachment of monomers from the island. The time evolution of this mechanism in the scale of ns is shown in Fig. 7.
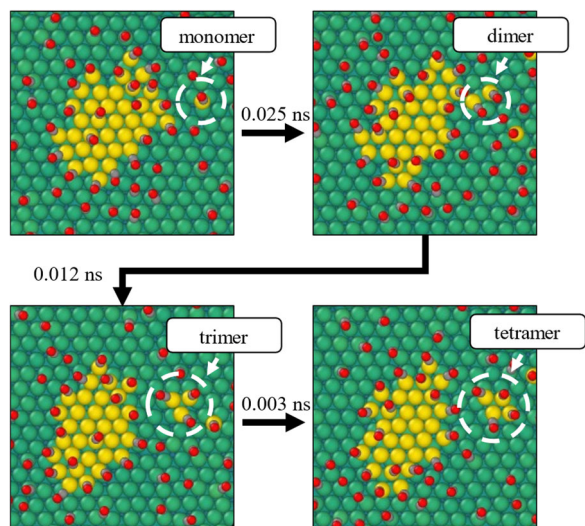

Fig. 7 : The mechanism of the formation of Cu clusters induced by CO adsorptions. The event is initiated by detachment of the monomer from the island, followed by subsequent agglomerations that form bigger cluster over the time.

We attribute the origin of the surface transformation due to the lowering of the detachment barrier of the Cu adatoms from the step edge when the CO adsorbs on the Cu atoms. The DFT calculated barriers shown in Fig. 8. clearly shows that the more CO adsorb on the step edge, the lower the detachment barrier of the Cu atom. For instance, without the CO adsorbate, the adsorption of detachment barrier for a single Cu adatom is as high as 0.72 eV but when the Cu step edge is fully occupied with CO the barrier reduces to 0.12 eV. Interestingly, the high coverage of CO also slightly increases the re-attachment barrier of the adatoms which further favor the stability of the small clusters over the island.
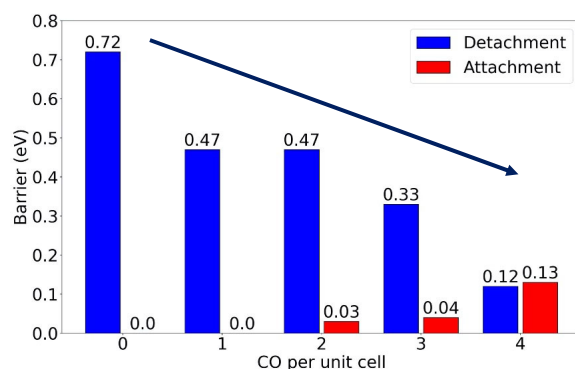

Fig. 8 : The detachment barrier of Cu adatom from the step edge given different number of adsorbed CO.

4. Conclusion

Overall, we apply molecular dynamics accelerated with machine learning to provide the direct observation to the influence of CO adsorption upon the formation of Cu clusters on the Cu(111). This Cu clusters might become the new active sites for further reaction in the methanol synthesis. The clusters, ranging from dimer to heptamer, are formed indirectly by agglomeration of smaller clusters. The main origin of the cluster formation is attributed to the reduction in the detachment barrier of Cu adatom when the CO adsorbs on top of it.

Bibliography

(1) V. L. Deringer, et al., Chem. Rev., **121**, 10073−10141, (2021).
(2) H. H. Halim et.al., Journal of Physics: Condensed Matter, **35**. 495001, (2023)
(3) P. Giannozzi., et.al., J. Phys. Condens. Matter., **21,** 39550, (2009).
(4) J. Vandermause., et.al., npj Comput Mater., **6**, 20, (2020).
(5) A.P. Thompson, et.al., Comp Phys Comm, **271** 10817, (2022).
(6) A. H. Larsen, et al., J. Phys.: Condens. Matter., **29,** 273002, (2017).
(7) A. Stukowski., Modelling Simul. Mater. Sci. Eng., **18**, 015012 (2010).