Machine Learning Molecular Dynamics Simulation of CO-driven Formation of Cu Clusters on Cu(111) Surface

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The adsorbate-induced surface reconstruction might critically determine catalytic activity by altering the morphology of the active sites. In this study, we focus on the influence of CO adsorption upon the formation of Cu clusters on the Cu(111) surface as has been observed by high-pressure scanning tunneling microscopy (HPSTM) [1]. A set of molecular dynamics (MD) simulations driven by machine-learning force-field has been performed to elucidate the mechanism of the cluster formation at the atomic level. The reliability of the force-field is ensured not only in terms of the error in the prediction of atomic forces and energy barriers, but also in terms of experimentally measurable quantities such as mean-squared displacement, desorption-rate, and adsorption geometries of Cu-CO systems.

The simulations at 450 K to 550 K show clusters are formed within a hundred of ns when the Cu surface is exposed with CO while no cluster is observed on the clean Cu surface even at 550 K. The statistics of the number and the lifetimes of the clusters at 550 K is shown in (Fig. 1). The clusters can be formed directly through instantaneous detachment of a group of step-atoms or indirectly by agglomeration of wandering Cu monomers on the surface terrace. Set of NEB calculation has been performed to confirm the adsorption of CO promotes the detachment of Cu step-atoms by lowering the detachment barrier. The influence 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 due to the scarce detachment of adatom while raising the temperature results in the formation of bigger clusters but with lower lifetime.

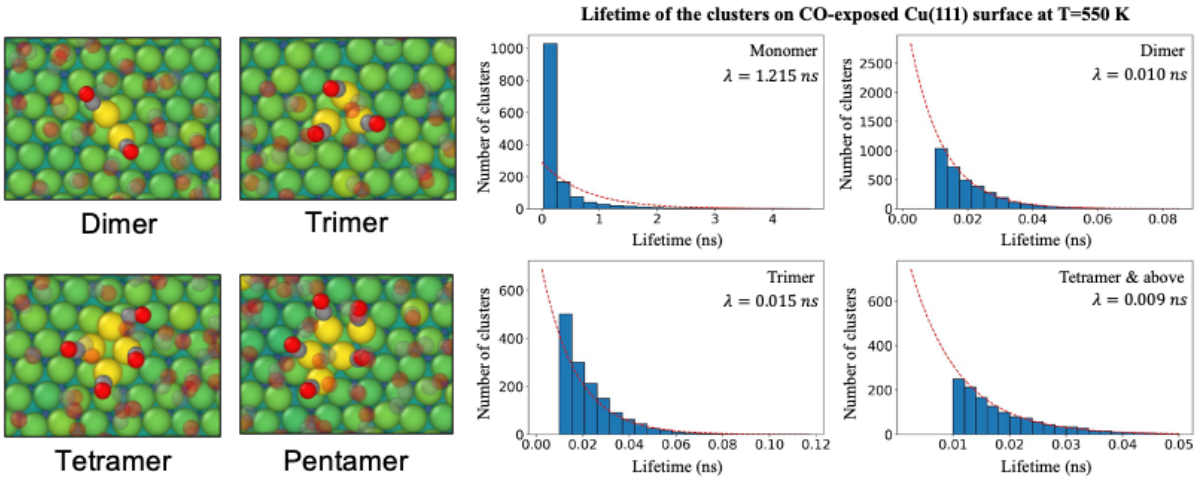

Fig. 1. (a) Plot of number of clusters detected within 100 ns of simulation at 550 K. (b) The histogram of the clusters' lifetime in the simulation at 550 K.

[1] Eren, B. et al., Science, **6273**, 475-478 (2016)