Adaptive Kinetic Monte Carlo Simulation of Methanol Decomposition on Cu(110)

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Introduction

Identification of complex reaction mechanism for catalytic reaction is one of the biggest challenges in heterogeneous catalysis. The mechanism of a heterogeneous catalytic reaction generally consists of a series of elementary steps such as the adsorption of reactants, surface reactions, diffusion of surface intermediates, and desorption of products. Density functional theory (DFT) calculations are widely used to obtain the thermochemistry and the kinetics of the assumed elementary step. Firstly, the initial and final state firstly should be locally optimized and a transition state along the minimum energy pathway then is identified. However, different reaction pathways might exist for each elementary step. Only one pathway with assumed initial and final states for each elementary step is not enough to illustrate the complex reaction potential energy surface on the catalyst surface. On the other hand, the initial state and the final state in the possible reaction path that we determined in the separate calculations might not be in the configurations when the bond-breaking or bond-making process occurs. In this work, we present a new computational methodology, i.e. adaptive kinetic Monte Carlo simulation that combines DFT calculations and dimer method saddle point searches [1-3] to identify catalytic reaction mechanisms in an unbiased way. We use this method to map out the entire potential energy landscape of methanol decomposition on the clean Cu(110) surface.

Computational Method

Periodic plane-wave DFT calculations combined with minimum mode following saddle point searches were carried out to explore possible reaction and diffusion pathways in methanol decomposition on the Cu(110) surface. Ion-electron interactions were modeled with the use of ultrasoft pseudopotentials within the framework of the projector augmented wave method. The generalized gradient approximation with the Perdew-Wang 91 functional was used in the calculations. The geometry of all stationary points were found with the conjugate-gradient algorithm, and considered converged when the force on each ion dropped below 0.001 eV/ Å. The Cu(110)-2×2 surface was modeled with a super cell containing a slab of six atomic layers. Periodic images of the slab were separated by a 10 Å vacuum gap. The bottom four layers were held frozen at equilibrium bulk positions; all other atoms were fully relaxed in our optimizations. A $2\times2\times1$ Monkhorst-Pack k-point mesh and a (2×3) surface size were found to result in relative energies converged to within 0.1 eV.

Results and Discussion

Starting from the initial state that stable adsorbed methanol at the short-bridge site on Cu(110), we have identified multiple reaction pathways for each possible bond (O–H, C–H and C–O) scission process in methanol decomposition. Figure 1 shows the reaction network of

methanol decomposition on Cu(110). We found that adsorbed methanol most favorably proceeds as follows: $CH_3OH \rightarrow CH_3O \rightarrow CH_2O \rightarrow CHO \rightarrow CO$. After the initial O–H bond scission of methanol, three consecutive C–H bond scissions most likely occur in methanol decomposition route on the clean Cu(110) surface. The rate-limiting step in this methanol decomposition route is the abstraction of an methylic hydrogen from methoxy due to the fact that the barrier for C–H bond scission of methoxy to formaldehyde is at least 0.5 eV higher than other steps in the route. Furthermore, the barrier of the reverse process that methoxy recombines with atomic hydrogen forming methanol is 0.92 eV, which is lower than the methoxy decomposition barrier of 1.11 eV. This suggests that methoxy even prefers to form back to methanol rather than dissociate into formaldehyde. This is consistent with experimental observations that methoxy was found as the most abundant surface intermediate on the Cu(110) surface.
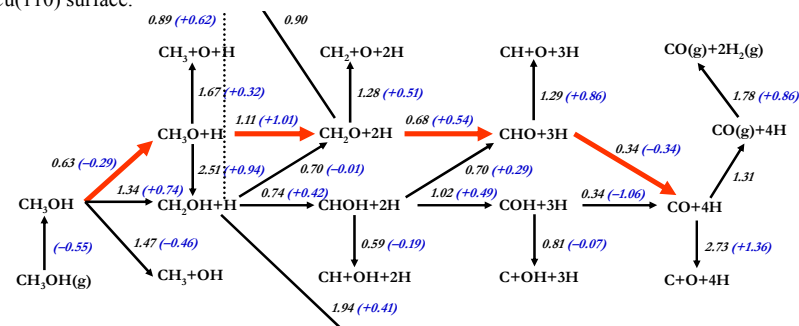

Figure 1. Reaction network of methanol decomposition on Cu(110). The solid and dashed lines denote all the pathways identified in the present work. The lowest activation barrier and the reaction energy (in the parenthesis) of each step are listed.

Significance

By combining standard DFT calculations with the dimer saddle point searching method, we demonstrated that adaptive kinetic Monte Carlo simulation used in this work provides a powerful tool to investigate complex heterogeneous catalytic reaction mechanisms. The potential energy surface for the catalytic reaction is determined through identifying multiple reaction pathways for each elementary step without *a priori* chemical intuition.

References
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