Atomistic Thermodynamic Approach for Determining Cu Catalyst Morphologies Under Reactive Water-Gas-Shift Conditions

Nilay Inoglu and John R. Kitchin*
Department of Chemical Engineering, Carnegie Mellon University,
5000 Forbes Avenue Pittsburgh, PA 15213-3890 USA
* jkitchin@andrew.cmu.edu

Introduction

The water gas shift reactions (WGS) are widely used in several industrial processes and are catalyzed by Cu catalysts. WGS is used to produce high purity hydrogen for ammonia synthesis and the reverse reaction (RWGS) is essential for upgrading CO_2 to CO for use in syngas as a first step in the utilization of CO_2, such as methanol synthesis. In many fossil fuel derived CO_2 feedstocks, there are sulfur (S) impurities which can adsorb on the Cu surfaces and block the active sites of the catalyst for the desired reaction and can result in catalyst deactivation. If the concentration of S is high enough then inactive copper sulfide phases can form on the catalyst. However, there is significant hydrogen pressure which can destabilize the adsorbed S by forming H_2S which may desorb from the surface of the Cu catalyst. The extent of destabilization depends on the chemical potentials of the sulfur, hydrogen and hydrogen sulfide which are determined by reaction conditions. On the other hand, it is also possible to observe inactive copper oxide phases due to moisture in the reactive environment. However, the presence of H_2 gas could destabilize the adsorbed O by forming H_2O and the extent of destabilization depends this time on the chemical potentials of the O, H_2 and H_2O that are determined by reaction conditions. Finally, CO may adsorb competitively blocking sites for S adsorption. Real catalysts are often composed of supported nanoparticles that expose a variety of crystal facets to the reactive environment, each of which may interact differently with the environment. The low Miller index surfaces, (111), (100) and (110) tend to be the facets with the largest surface areas on particles. This study presents a first principles DFT investigation of CO, O and S adsorption on Cu(111), (100) and (110) facets for different coverages on a range of different adsorption sites. A first principles atomistic thermodynamics approach is utilized to evaluate the stability of the different adsorbate structures on Cu surfaces in contact with a reactive environment through the surface free energy of the structures. Moreover the stability of these different structures are also compared with H and CO_2 adsorbed Cu surfaces. Finally, the impact of the adsorption on Cu particle shape is studied.

Theoretical Calculations

Density Functional Theory (DFT) calculations were used to identify likely adsorption sites and structures in environments that are typical of reaction conditions. An atomistic thermodynamic framework [1] was developed that relates the DFT results to thermodynamic quantities that are relevant to experimental conditions. With this framework we considered the stability of different surface structures based on surface free energies that are a function of an appropriate thermodynamic quantity, the Gibbs free energy, G (T, p). We derived an equivalent formulations composed of a contribution from the clean surface energy, a contribution due to adsorption, and a contribution from the environmental conditions.

Results and Discussion

The adsorption properties of each adsorbate on all the Cu surfaces were determined and all of the adsorption energies are presented through their role in the surface free energies which are calculated for each adsorption site and coverage for each adsorbate. Based on these surface energies, we determined the relative stabilities of these configurations under different environmental conditions which showed that at very low adsorbate chemical potentials the clean surface is the most stable surface structure; as the chemical potential increases, structures with increasing coverage become more stable until the formation of bulk phases.

We also studied the adsorbate-terminated Cu systems under the specific WGS reaction conditions of a total pressure of 50atm at which the Cu surfaces are found to be not clean, but partially covered by CO due to its stronger adsorption energy than oxygen adsorbates from water. At sufficiently high concentrations of H_2S in the reactive environment, S-terminated surfaces begin to become more stable than any other adsorbate covered surface. The H and CO_2 terminated structures were thermodynamically less favorable than the other surface configurations of more strongly adsorbed species at low temperatures. At higher temperatures, however, poisoned Cu systems could be regenerated to clean surfaces in the presence of H_2.

The equilibrium crystal shape can be determined from a Wullf construction under different S chemical potentials that corresponds to different experimental conditions of temperatures and pressures [3]. We constructed 3D crystal structures at different S chemical potentials from the surface energies using the program WINXMORPH. We found out that the crystal shape changes significantly from one dominated by (111) and (100) facets at low chemical potentials to a shape dominated by (110) facets at high chemical potentials (Figure 1). This suggests that the distribution of reactive sites may change under reaction conditions.

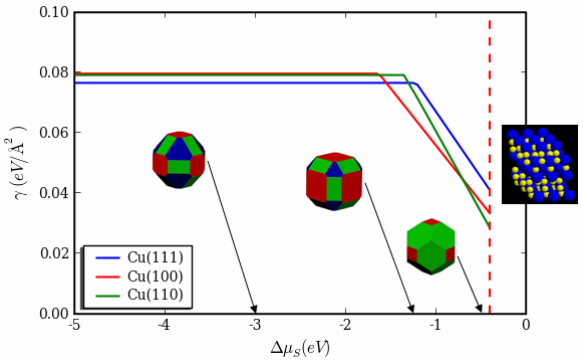

Figure 1. Surface energies of most favorable structures for all different facets with the 3D image of Cu catalyst at different S chemical potentials.

Significance

DFT calculations are utilized to investigate the interactions between adsorbates and low Miller index facets of Cu in the presence of a reactive environment. The shape of the catalyst particle under reactive environment was found to change significantly, indicating that the reactive site distribution may change under reaction conditions.

References

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