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Atomistic simulations of the adsorption and migration barriers of Cu adatoms on ZnO surfaces using COMB potentials

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ABSTRACT

Cu/ZnO heterogeneous systems are used to catalyze the CO_2 hydrogenation to methanol, but questions remain about the nature of the active site and the role of Cu–ZnO interactions in the catalyst performance. The way in which ZnO surfaces support Cu clusters and stabilize their active sites is a key factor for maintaining catalyst activity. Processes such as sintering, alloying and encapsulation may play an important role in the activity of the catalyst but are difficult to model directly with density functional theory (DFT). In this work, we report the development of charge-optimized many-body (COMB) potentials to model the Cu/ZnO system. This potential is then used in conjugation with the dimer method, which uses the first derivative of the potential energy and the initial state of the transition to find saddle points, to examine the migration barriers of Cu adatoms on Cu and ZnO surfaces. These findings are validated against the results of density functional theory (DFT) calculations and published experimental data.

1. Introduction

Methanol (CH_3OH) is a potential candidate for the next generation of renewable green fuels because its energy density is sufficiently close to that of gasoline. In addition, methanol exists in liquid form at ambient pressures and temperatures, which makes it easier to store and transport than hydrogen. Methanol synthesis from the hydrogenation of CO_2 is performed commercially using $Cu/ZnO/Al_2O_3$ catalyst [1–6]. Despite numerous experimental [7–10] and theoretical studies [11–15], there are still questions about the nature of the active site of the Cu/ZnO catalysts. Cu metal clusters [2,9,14,16], Cu^+ [17–19], the Cu/ZnO interface [8], and Cu–Zn [7,18,19] alloys have all been proposed as active sites. In addition, different sites might be active for CO_2 hydrogenation but not CO hydrogenation, and vice versa [7]. While Cu/ZnO catalysts have been used in syngas hydrogenation, there is recent interest in using them to examine the electrochemical reduction of CO_2 to produce methanol. This interest is motivated by studies that show that Cu oxide can electrochemically reduce CO_2 to methanol [20–22]. Le and co-workers have correlated methanol formation on the Cu oxide electrodes to the presence of Cu^+ sites [22]. However, Cu oxide electrodes are inherently unstable under reducing conditions and methanol production tapers off with time as the oxide is reduced to metal. Recent results suggest that Cu on ZnO could lead to higher methanol formation rates but the nature of the active site and the stability of the catalysts still need to be explored [23].

Since the morphology of Cu clusters on ZnO surfaces can undergo dynamic changes, it is challenging to experimentally specify the state of the active sites under reaction conditions. Thus, to elucidate the formation of methanol on Cu/ZnO catalysts, the first step is to characterize the behavior of Cu atoms on ZnO surfaces. There have been several surface science studies to characterize Cu growth and stability on polar [10,24–28] and nonpolar [29] ZnO surfaces. Polar surfaces are known to undergo complex reconstructions [30] and are therefore more difficult to examine using density functional theory (DFT). Consequently, the majority of the DFT work [31,32] has been focused on understanding Cu behavior on the nonpolar $ZnO(10\bar{1}0)$ and $ZnO(11\bar{2}0)$ surfaces.

Hu et al. [32] investigated Cu deposition and subsequent growth on the $ZnO(10\bar{1}0)$ and $ZnO(11\bar{2}0)$ surfaces using DFT calculations. Their results indicate that Cu atoms strongly interact with ZnO and become slightly positive with a charge that is between the value suggested by Klier [1] (Cu^+) and by Fleisch [20] (Cu^0). It was further proposed that the charged Cu atoms and the Cu–Zn sites might be the active sites of the system.

While first principle methods, such as DFT, provide high fidelity because of their explicit treatment of electronic structure, they are

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limited in the length and time scales that can be addressed directly. Because of the potential importance of nanometer-scale changes at the Cu/ZnO interface (sintering of the Cu clusters, alloying with the oxide surface, oxidation of the Cu, and adsorbate-induced surface reconstruction) on catalytic activity, a computationally more efficient method is needed. One potential option is the development of potentials (reactive force fields) that are able to capture charge transfer within a system (such as at the Cu and ZnO interface) and are less computationally intensive than first-principles methods. Recently, the reactive force field (ReaxFF) method [33] has been applied to model related complex reactive systems including ZnO/water [34,35] and Cu/Cu_2O/water [36]. However, as yet these potentials have not been directly applied to the Cu/ZnO system.

Here, we report on the development of a second-generation charge optimized many-body (COMB) potential for Cu/ZnO. To date, the second-generation of COMB potentials have been successfully parameterized for the Si/SiO_2 [37], Hf/HfO_2 [38], Cu/Cu_2O [39] and Cu/SiO_2 [40] systems. Their most important features are that they include many-body interactions with directional bonds and dynamic charge transfer, both of which are important to correctly model heterogeneous interfacial systems. The specific focus on this work is the development of the second-generation COMB potential for ZnO and its integration with the existing second-generation COMB potential for Cu [39]. Further, the structure and energy of adsorption of Cu atoms on ZnO surfaces are examined using classical molecular dynamic (MD) simulations. Finally, the dimer method is employed to search for saddle points and determine the migration barriers of Cu adatoms on the ZnO$(10\bar{1}0)$ and Cu(100) surfaces. The COMB potential predictions are validated against the results of DFT calculations and of published experimental data.

2. Method

2.1. COMB potential formalism

The potential is built on the framework of the Cu/Cu_2O second-generation COMB potential developed by Devine et al. [39]. Briefly, the general formalism is

$$E_T = \sum_i \left[E_i^{Self} + \frac{1}{2}\sum_{j \neq i} V_{ij}\left(r_{ij}, q_i, q_j\right) + E_i^{Overcoord} + E_{ij}^{BB} \right], \tag{1}$$

where E_T is the total potential energy of the system, E_i^{Self} is the self-energy term of atom i, $V_{ij}(r_{ij},q_i,q_j)$ is the interatomic potential energy between the ith and jth atoms, r_{ij} is the distance between atoms i and j, and q_i and q_j are the charges of the atoms. $E_i^{Overcoord}$ is the over-coordination correction term, and E_{ij}^{BB} is the bond-bending term. The interatomic potential energy V_{ij} consists of three components, the short-range repulsion energy ($U_{ij}^R(r_{ij})$), the short-range attraction energy ($U_{ij}^A(r_{ij})$), and the long-range Coulombic interaction ($U_{ij}^I(r_{ij},q_i,q_j)$), as shown in Eqs. (2)–(4), respectively:

$$U_{ij}^R\left(r_{ij}, q_i, q_j\right) = f_c\left(r_{ij}\right) A_{ij} \exp\left\{-\lambda_{ij} r_{ij} + \frac{1}{2}\left[\lambda_i D_i(q_i) + \lambda_j D_j\left(q_j\right)\right]\right\}, \tag{2}$$

$$U_{ij}^A\left(r_{ij}, q_i, q_j\right) = -f_c\left(r_{ij}\right) b_{ij} B_{ij} B_{ij}^*\left(q_i, q_j\right) \exp\left(-\alpha_{ij} r_{ij} + \frac{1}{2}\left[\alpha_i D_i(q_i) + \alpha_j D_j\left(q_j\right)\right]\right), \tag{3}$$

$$U_{ij}^I\left(r_{ij}, q_i, q_j\right) = J_{ij}\left(r_{ij}\right) q_i q_j. \tag{4}$$

Based on the empirical Tersoff [41] and the Yasukawa potentials [42], both U_{ij}^R and U_{ij}^A not only exponentially decay with interatomic distance (r) but also vary with charge (q). Therefore, the charge-dependent correction functions, $D_i(q_i)$, are added to the exponential term of the short-range energies to reflect the change in atomic radius with charge. In Eqs. (2) and (3), the leading coefficients A_{ij} and B_{ij}, and the inverse decay lengths λ_{ij} and α_{ij} depend only on the bond types and are derived from element-type parameters by using the Lorentz–Berthelot mixing rules, which are defined as:

$$A_{ij} = \sqrt{A_i A_j}\ ; B_{ij} = \sqrt{B_i B_j}\ ; \lambda_{ij} = \left(\lambda_i + \lambda_j\right)/2; \text{and } \alpha_{ij} = \left(\alpha_i + \alpha_j\right)/2. \tag{5}$$

Because the mixing rules may fail in cases where elements i and j have substantially different electronegativity, these coefficients could be parameterized for specific bond types. In this work, only the Cu–Zn bond is obtained from the mixing rules using Cu and Zn element-specific parameters. The other bond-specific interactions, including Zn–O and Cu–O, are obtained through fitting. $D_i(q_i)$, which is specific to each element type, is defined as:

$$D_i(q_i) = D_{U_i} + \left| b_{D_i}\left(Q_{U_i} - q_i\right)\right|^{n_{D_i}}, \tag{6}$$

$$b_{D_i} = \left(D_{L_i} - D_{U_i}\right)^{\frac{1}{n_{D_i}}} / \left(Q_{U_i} - Q_{L_i}\right), \tag{7}$$

$$n_{D_i} = \ln\left[D_{U_i} / \left(D_{U_i} - D_{L_i}\right)\right] / \ln\left[Q_{U_i} / \left(Q_{U_i} - Q_{L_i}\right)\right], \tag{8}$$

and D_U and D_L are parameters that reflect the change in atomic radius with charge. Likewise, Q_U and Q_L are the atomic charges that correspond to the limit of the valence shell. Additionally, in the attraction energy, the change in the bond order with charge is scaled by the function $B_{ij}^*(q_i, q_j)$ which is defined as:

$$B_{ij}^*(q_i, q_j) = \left(B_i^* B_j^*\right)^{\frac{1}{2}}, \tag{9}$$

$$B_i^* = \left[a_{B_i} - \left| b_{B_i}\left(q_i - Q_{O_i}\right)\right|^{n_{B_i}}\right], \tag{10}$$

$$b_{B_i} = \left| a_{B_i} \right|^{\frac{1}{n_{B_i}}} / \Delta Q_i, \tag{11}$$

$$a_{B_i} = 1 / \left(1 - \left| Q_{O_i} / \Delta Q_i \right|^{n_{B_i}}\right), \tag{12}$$

$$\Delta Q_i = \left(Q_{U_i} - Q_{L_i}\right)/2, \tag{13}$$

$$Q_{O_i} = \left(Q_{U_i} + Q_{L_i}\right)/2, \tag{14}$$

where n_{Bi} is equal to 10 for all elements.

The bond-order term, b_{ij}, captures many body interactions by describing the bond angle, local symmetry, and the number of nearest neighbors:

$$b_{ij} = \left[1 + \left(\beta_i \sum_{j \neq i}^{NN} \sum_{k \neq i}^{NN} \xi_{ijk}\left(r_{ij}, r_{ik}\right) g\left(\theta_{jik}\right)\right)^{\eta_i}\right]^{\frac{-1}{2\eta_i}}, \tag{15}$$

where the symmetry function ξ_{ijk} (r_{ij},r_{ik}) and angular function $g(\theta_{jik})$ are defined as

$$\xi_{ijk}\left(r_{ij}, r_{ik}\right) = f_c(r_{ik}) \exp\left[\alpha_{ij}^{m_i}\left(r_{ij} - r_{ik}\right)^{m_i}\right], \tag{16}$$

$$g\left(\theta_{jik}\right) = 1 + \frac{c_{ij}^2}{d_{ij}^2} - \frac{c_{ij}^2}{d_{ij}^2 + \left(h_{ij} - \cos\theta_{jik}\right)^2}, \tag{17}$$

$$f_c\left(r_{ij}\right) = \begin{cases} 1 & r_{ij} \leq R_{S-ij} \\ \frac{1}{2}\left[1 + \cos\left(\pi \frac{r_{ij} - R_{S-ij}}{S_{S-ij} - R_{S-ij}}\right)\right] & R_{S-ij} < r_{ij} \leq S_{S-ij}\ , \\ 0 & r_{ij} \geq S_{S-ij} \end{cases} \tag{18}$$