Differentiating Intrinsic Reactivity of Copper, Copper–Zinc Alloy, and Copper/Zinc Oxide Interface for Methanol Steam Reforming by First-Principles Theory

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Supporting Information

ABSTRACT: Identifying the intrinsic activity of the distinct sites which coexist in oxide-supported metal particles is vital but challenging for rational design of catalysts. We treat the challenge here by density functional theory calculations to differentiate unbiasedly the intrinsic reactivity of a variety of sites observed under reaction conditions for methanol steam reforming on Cu/ZnO catalyst. Metallic Cu and CuZn alloy are found to be less active but highly selective toward formaldehyde because water dissociation is demanding, which limits the formation of hydroxyl and subsequent coupling necessary to yield CO2. Cu/ZnO interface is highly active and selective for H2/CO2 because of its superior activity for water and methanol activation. Distinct hydrogen affinity at Cu/ZnO interface also leads to more favorable CO2 production via H2COO* in contrast to via HCOOH at (bi)metallic sites. The distinct reactivity of various structural motifs exposed and the importance of the metal/oxide for selectivity revealed is valuable for optimal design of catalysts.

1. INTRODUCTION

Methanol steam reforming (MSR) provides a promising scheme for generation of hydrogen in various important processes, such as fuel cells and hydrogenolysis of biomass-based compounds.3–5 In this reaction, the high H2 and CO2 selectivities are critical to avoid the poisoning of the fuel-cell Pt anode by CO byproduct and to maximize the hydrogen yield.4–6 The Cu/ZnO catalyst originally designed for methanol synthesis exhibits high activity and selectivity toward H2 and CO2 for MSR. However, the coexistence of a variety of structural motifs/sites, such as Cu, ZnO, CuZn alloy, and Cu/ZnO interface, results in the identification of active sites to be elusive.7–12 For methanol synthesis on Cu/ZnO, there are similar structural motifs coexisting under reaction conditions, and it remains a hot topic of debate, along with which sites are the active sites.13–16 This severely prevents the mechanistic understanding and rational design of catalysts. So far, preparing the supported metal particles with identical sites still represents a significant challenge in catalyst synthesis. The site homogeneity might be worsened further by considering strong-metal-support interaction, which leads to the formation of various uncontrolled boundaries and dynamic response of the supported catalysts under reaction conditions, such as (de)alloying, reactant-induced segregation, oxidation, and reduction just to name a few. We treat the challenge here by density functional theory (DFT) calculations to differentiate unbiasedly the intrinsic reactivity of the various structural motifs/sites observed under reaction conditions.

In MSR, the main detected products include CO, CH2O, CO2, and H2.19 Among these, CH2O and CO come from the partial and complete dehydrogenation of CH3OH.20–23 In the case of CO2/H2 formation, it is generally suggested to be through the reaction of H2O with CO from methanol decomposition, and the CO2 selectivity is determined by the reaction balance of water gas shift reaction.24 Alternatively, a more favorable pathway has been reported recently,25–28 where CH3O* produced by methanol partial dehydrogenation can recombine with OH* or O* from water dissociation, leading to the formation of hydroxyl methoxy (H2COOH*) or dioxo-methylene (H2COO*) intermediate. The intermediates then dehydrogenate sequentially to CO2, and for H2COOH* dehydrogenation discrepancy exists between an initial O–H bond scission (via H2COO*) and C–H bond scission (via HCOOH*).

To differentiate the intrinsic MSR reactivity on the various sites of Cu/ZnO catalyst observed under reaction conditions, we present an unbiased DFT study of MSR pathway on Cu(111), CuZn alloy, and Cu/ZnO interface (see Computational Methods section for a more detailed description of the
models). Since CuZn alloy has been shown to be formed preferentially on stepped Cu(111),
we use the Cu(211) surface with Zn substitution of 33% Cu at the step edge to simulate
Cu/ZnO interface (Figure 1a). For Cu/ZnO interface, the planar,

graphite-like ZnO layer supported on Cu(111) (Figure 1b) is adopted, where the similar structures have been identified on Au(111) and Cu nanoparticles in an industrially relevant Cu/
ZnO/Al2O3 catalyst.30 Despite the high CO2 selectivity, the pristine ZnO is not considered here owing to its low activity for MSR.34

2. COMPUTATIONAL METHODS

DFT calculations were performed by the Vienna ab-initio simulation package (VASP)35 with optPBE-vdW.36 The interaction between the ionic cores and electrons was described by the projector-augmented wave (PAW) method,37,38 and the Kohn–Sham valence electronic wave function was expanded in a plane-wave basis set with a kinetic energy cutoff at 400 eV. The energies were converged to within 10−4 eV/atom, and the forces were converged to within 0.02 eV/Å. The Cu(111) surface was modeled using a four-layer slab with 1/3 Cu substituted by Zn on the step edge, denoted as CuZn(211), was used to simulate Cu/ZnO alloy.15,39 One-layer

(one-layer elementary reactions (E_e in eV), Reaction Energies (E_r in eV), and Geometric Information (d in Å) at the Transition States of the Elementary Reactions Involved in MSR on Cu(111), CuZn(211), and Cu(111)/ZnO Interface

Table 1. Calculated Activation Energies (E_a in eV), Reaction Energies (E_r in eV), and Geometric Information (d in Å) at the Transition States of the Elementary Reactions Involved in MSR on Cu(111), CuZn(211), and Cu(111)/ZnO Interface

<table>
<thead>
<tr>
<th>elementary reactions</th>
<th>Cu(111)</th>
<th>CuZn(211)</th>
<th>Cu(111)/ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_a</td>
<td>E_r</td>
<td>d</td>
<td>E_a</td>
</tr>
<tr>
<td>(1) HCHO + * → H2O + * + H*</td>
<td>1.18</td>
<td>−0.14</td>
<td>1.42</td>
</tr>
<tr>
<td>(2) OH* + * → O* + H*</td>
<td>1.70</td>
<td>0.60</td>
<td>1.57</td>
</tr>
<tr>
<td>(3) CH3OH + * → CH3O* + H*</td>
<td>1.07</td>
<td>−0.18</td>
<td>1.43</td>
</tr>
<tr>
<td>(4) CH2O* + * → CH3O* + H*</td>
<td>1.33</td>
<td>0.99</td>
<td>1.83</td>
</tr>
<tr>
<td>(5) OH* + CH2O* → H2COOH* + *</td>
<td>0.38</td>
<td>−0.39</td>
<td>2.11</td>
</tr>
<tr>
<td>(6) H2COOH* + * → HCOOH + H*</td>
<td>0.92</td>
<td>0.07</td>
<td>1.60</td>
</tr>
<tr>
<td>(7) HCOOH* + * → HCOO* + H*</td>
<td>0.53</td>
<td>−0.51</td>
<td>1.54</td>
</tr>
<tr>
<td>(8) HCOO* + * → CO2* + H*</td>
<td>1.26</td>
<td>0.51</td>
<td>1.53</td>
</tr>
<tr>
<td>(9) H2COOH* + * → HCOO* + H*</td>
<td>1.20</td>
<td>0.21</td>
<td>1.60</td>
</tr>
<tr>
<td>(10) H2COO* + * → HCOO* + H*</td>
<td>0.81</td>
<td>−0.64</td>
<td>1.52</td>
</tr>
<tr>
<td>(11) CH2O* + * → CO2* + H*</td>
<td>0.83</td>
<td>0.31</td>
<td>1.63</td>
</tr>
<tr>
<td>(12) HCO* + * → CO* + H*</td>
<td>0.29</td>
<td>−0.76</td>
<td>1.42</td>
</tr>
<tr>
<td>(13) H* + H* → H2 (g) + 2*</td>
<td>0.90</td>
<td>0.36</td>
<td>0.95</td>
</tr>
<tr>
<td>(14) OZnOH + * → OZnO + H*</td>
<td>1.07</td>
<td>−0.70</td>
<td>1.12</td>
</tr>
<tr>
<td>(15) H2O + * → H2O* + H*</td>
<td>1.18</td>
<td>0.60</td>
<td>1.57</td>
</tr>
<tr>
<td>(16) OH* + * → O* + H*</td>
<td>1.70</td>
<td>0.60</td>
<td>1.57</td>
</tr>
<tr>
<td>(17) CH3OH + * → CH3O* + H*</td>
<td>1.07</td>
<td>−0.18</td>
<td>1.43</td>
</tr>
<tr>
<td>(18) CH2O* + * → CH3O* + H*</td>
<td>1.33</td>
<td>0.99</td>
<td>1.83</td>
</tr>
<tr>
<td>(19) OH* + CH2O* → H2COOH* + *</td>
<td>0.38</td>
<td>−0.39</td>
<td>2.11</td>
</tr>
<tr>
<td>(20) H2COOH* + * → HCOOH + H*</td>
<td>0.92</td>
<td>0.07</td>
<td>1.60</td>
</tr>
<tr>
<td>(21) HCOOH* + * → HCOO* + H*</td>
<td>0.53</td>
<td>−0.51</td>
<td>1.54</td>
</tr>
<tr>
<td>(22) HCOO* + * → CO2* + H*</td>
<td>1.26</td>
<td>0.51</td>
<td>1.53</td>
</tr>
<tr>
<td>(23) H2COOH* + * → HCOO* + H*</td>
<td>1.20</td>
<td>0.21</td>
<td>1.60</td>
</tr>
<tr>
<td>(24) H2COO* + * → HCOO* + H*</td>
<td>0.81</td>
<td>−0.64</td>
<td>1.52</td>
</tr>
<tr>
<td>(25) CH2O* + * → CO2* + H*</td>
<td>0.83</td>
<td>0.31</td>
<td>1.63</td>
</tr>
<tr>
<td>(26) HCO* + * → CO* + H*</td>
<td>0.29</td>
<td>−0.76</td>
<td>1.42</td>
</tr>
<tr>
<td>(27) H* + H* → H2 (g) + 2*</td>
<td>0.90</td>
<td>0.36</td>
<td>0.95</td>
</tr>
<tr>
<td>(28) OZnOH + * → OZnO + H*</td>
<td>1.07</td>
<td>−0.70</td>
<td>1.12</td>
</tr>
</tbody>
</table>

in which E_ads, E_sub are the energy of the optimized adsorption system of adsorbate and substrate, adsorbate in the gas phase, and the clean substrate, respectively.

All transition states (TSs) were located by the force reversed method44 and climbing-image nudged elastic band method (CI-NEB).45 We also performed DFT+U calculations for the correction of the on-site Coulomb repulsion of 3d electrons of Zn atoms. We have tested the two commonly used U − J values of 4.7 eV66 and 8.5 eV77 for Zn in Au(111)/ZnO and found that both values gave rather similar structures and energetics.32 Therefore, a value of U − J = 4.7 eV was used in the present work. The relaxation will stop until the residual forces in each atom are smaller than 0.05 eV/Å. The transition states were verified by vibrational analysis showing a single imaginary mode. Zero-point energies and entropy corrections were neglected. The activation energies (E_a) and reaction energies of elementary reactions (E_r) were taken with respect to isolated reactants/products. The negative values of E_a represent exothermic processes, and positive values of E_r represent endothermic processes.

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3. RESULTS AND DISCUSSION

We first investigate water dissociation on Cu(111), CuZn(211), and Cu/ZnO interface. It can be seen from Table 1 that not only is the $\text{H}_2\text{O}^* + \bullet \rightarrow \text{OH}^* + \text{H}^*$ step more exothermic on Cu/ZnO interface compared with that on Cu(111) and CuZn(211), but the activation energy barrier $E_a$ is also decreased by 1.01 and 0.64 eV on Cu/ZnO interface. Figure 2a shows further that Cu/ZnO interface stabilizes the transition state (TS) and final state (FS) more than the initial state (IS) as compared to Cu(111) and CuZn(211). By examining the structures in Figures 3a and S1, we find that the H atom attaches to the O atom at the Cu/ZnO interface instead of Cu atoms on Cu(111) and CuZn(211) at the TSs and FSs. The clearly distinct structures significantly stabilize H at Cu/ZnO interface, as confirmed by the increased adsorption energy $E_{ads}$ (by about 0.58 eV, Table 2) of H atom at the interfacial oxygen relative to Cu atoms on Cu(111) and CuZn(211). The differential charge density maps show considerable charge withdrawal (Bader charge) from H by interfacial O at Cu/ZnO interface (Figure 4a). However, charge builds up on H when binding with Cu atoms on Cu(111) and CuZn(211) (Figures 4b and 4c), which reflects the different bond nature between H−O and H−Cu bond. In addition, unlike Cu and CuZn, which undergo the considerable rotation of the H−O axes for H−OH bond scission, there is little structural change at Cu/ZnO interface, contributing additionally to the substantial decrease in $E_a$ (see Figure 3a). Likewise, the OH* + * − O* + H* step is also largely enhanced on Cu/ZnO interface owing to the electrophilicity of hydrogen, as shown in Figures 2a and 3b and Table 1. These findings are consistent with the favorable water dissociation observed on Cu/ZnO interface and other interfaces between metal and metal oxides.

Figure 2. Energy profiles of (a) water dissociation and (b) formaldehyde formation on Cu(111) (black line), CuZn(211) (blue line), and Cu(111)/ZnO (red line). The reference zero of the energy scale corresponds to the energy of H$_2$O and CH$_3$OH in gas phase.

Figure 4. Differential charge density map for adsorption of H atom on (a) Cu(111) (with the isosurfaces of 0.003 au), (b) CuZn(211) (with the isosurfaces of 0.003 au), and (c) Cu(111)/ZnO (with the isosurfaces of 0.01 au). Vermilion, blue, red, and white spheres represent Cu, Zn, O, and H, respectively. Blue and yellow insosurfaces indicate charge depletion and accumulation.

Figure 3. Structures at the transition states of (a) H$_2$O$^* + \bullet \rightarrow$ OH$^* +$ H$^*$, (b) OH$^* + \bullet \rightarrow$ O$^* +$ H$^* +$ H$^*$, (c) CH$_3$OH$^* + \bullet \rightarrow$ CH$_3$O$^* +$ H$^*$, (d) CH$_2$O$^* + \bullet \rightarrow$ CH$_2$O$^* +$ H$^*$, (e) H$_2$COOH$^* + \bullet \rightarrow$ H$_2$COO$^* +$ H$^*$, and (f) H$_2$COOH$^* + \bullet \rightarrow$ HCOOH$^* +$ H$^*$ on Cu(111) (I), CuZn(211) (II), and Cu(111)/ZnO (III).

<table>
<thead>
<tr>
<th>intermediates</th>
<th>Cu(111)</th>
<th>CuZn(211)</th>
<th>Cu(111)/ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>−0.50</td>
<td>−0.73</td>
<td>−0.97</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>−2.78</td>
<td>−2.81</td>
<td>−3.02</td>
</tr>
<tr>
<td>CH$_3$O</td>
<td>−0.42</td>
<td>−0.60</td>
<td>−0.50</td>
</tr>
<tr>
<td>HCO</td>
<td>−1.59</td>
<td>−1.79</td>
<td>−1.69</td>
</tr>
<tr>
<td>H$_2$COOH</td>
<td>−2.67</td>
<td>−2.99</td>
<td>−3.13</td>
</tr>
<tr>
<td>H$_2$COO</td>
<td>−4.60</td>
<td>−5.08</td>
<td>−4.85</td>
</tr>
<tr>
<td>HCOOH</td>
<td>−0.50</td>
<td>−0.70</td>
<td>−5.00</td>
</tr>
<tr>
<td>HCOO</td>
<td>−3.23</td>
<td>−3.54</td>
<td>−3.17</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>−0.34</td>
<td>−0.52</td>
<td>−0.59</td>
</tr>
<tr>
<td>OH</td>
<td>−3.51</td>
<td>−3.68</td>
<td>−3.75</td>
</tr>
<tr>
<td>CO</td>
<td>−0.92</td>
<td>−0.90</td>
<td>−1.03</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>−0.19</td>
<td>−0.21</td>
<td>−0.03</td>
</tr>
<tr>
<td>H</td>
<td>−0.18</td>
<td>−0.17</td>
<td>−0.75</td>
</tr>
</tbody>
</table>
dependence on surface structure, with $E_o$ differing by 0.06 eV at most on the three surfaces. Comparing the TS structures in Figures 3c and 3d, we find that the TS for the O—H bond scission of CH$_3$OH$^*$ is reactant-like, while that for the CH$_2$O$^* + $ → CH$_2$O$^* + $ + H$^*$ step is more product-like. The reason is that for O—H bond scission H prefers to bind with both O at the Cu/ZnO interface and in CH$_3$O intermediate at the TSs, which facilitates O—H bond scission. However, a favorable TS structure where H binds simultaneously with interfacial O (planar, graphite-like structure) and C (tetrahedral structure) in CH$_3$O$^*$ is not available for C—H bond scission.

Once H$_2$O is activated and CH$_2$O is formed, the OH$^* +$ CH$_2$O$^*$ → H$_2$COOH$^* +$ step is quite facile on all the systems considered, with the barriers of no more than 0.38 eV. The facile recombinations of CH$_2$O$^*$ and OH were also reported previously on Cu and ZnO supported single atoms for MSR.$^{27,52}$ Then, the resulting H$_2$COOH intermediate can proceed through either O—H bond scission forming H$_2$COO$^*$ intermediate or C—H bond scission forming HCOOH$^*$ intermediate. As shown in Figure 5a and Table 1, Cu/ZnO interface prefers the former pathway, and the $E_o$ of O—H bond scission is substantially lower than that of C—H bond scission by 1.19 eV. However, the latter pathway is more favorable on Cu and CuZn. The C—H bond scission of H$_2$COOH$^*$ intermediate on the two surfaces has similar $E_o$ of 0.90 eV, lower than the corresponding values of 1.20 and 1.34 eV for O—H bond scission.

The different dehydrogenation pathways between Cu/ZnO interface and Cu and CuZn alloy can be assigned to the high activity of interfacial O in the O—H bond scission (Figures 3e and 3f), as discussed above. Subsequently, the HCOO$^*$ intermediate on Cu/ZnO interface undergoes C—H bond scission ($E_o = 0.91$ eV), and HCOOH$^*$ intermediates on Cu and CuZn undergo O—H bond scission ($E_o = 0.53$ vs 0.62 eV), leading to HCOO$^*$ formation. The adsorbed HCOO$^*$ intermediate can decompose into H and CO$_2$, with the barriers of 1.26, 1.45, and 1.19 eV on Cu, CuZn, and Cu/ZnO interface, respectively. Finally, the H$_2$ desorption can be expected to be facile on these systems based on the calculated H$_2$ dissociative binding energies of −0.18 eV (Cu), −0.17 eV (CuZn), and −0.75 eV (Cu/ZnO interface) relative to 1/2 H$_2$ in gas phase. As the coverage of atomic H increases at the interface O (1/3—1 ML), H$_2$ dissociative binding energy decreases by 0.11 eV. Moreover, the entropic contribution of 0.73 eV per H$_2$ molecule at 500 K and standard pressure,$^5$ can also provide additional driving force for H$_2$ desorption. In addition, the previous experimental and theoretical study on FeO(111) monolayer films on Pt(111) showed that the presence of O vacancy can enhance the H$_2$ formation and desorption.$^{54}$ Therefore, it can be expected that H$_2$ desorption could be further promoted by the presence of O vacancy on ZnO.

Besides OH$^*$ species, CH$_3$O$^*$ can recombine with atomic O$^*$, obtained either by the dissociation or by the disproportionation of OH$^*$. The previous DFT study suggests that despite the relatively low barrier (0.25 eV) for OH disproportionation leads to H$_2$O formation,$^{27,51}$ which will be unfavorable as consideration of the reaction balance.$^{55}$ Thus, the O$^*$ species is not considered in this work.

The energy profiles for the most favorable CO$_2$ formation pathways on Cu(111), CuZn(211), and Cu/ZnO interface are illustrated in Figure 6. It is found that the stability of adsorbed intermediate generally follows the order of Cu(111) < CuZn(211) < Cu/ZnO. Compared to Cu(111), CuZn(211) binds the intermediates modestly stronger (Table 2), which agrees well with previous DFT calculations by Studt et al.$^{15,39,56–58}$ Apart from Cu(111) and CuZn(211), they also consider Cu(211) and show that the bond strength of intermediates on Cu(211) is in between Cu(111) and CuZn(211). These results imply that both low coordination number of step and alloying with Zn contribute to the stronger intermediates binding on Cu(211) than on Cu(111). On the Cu/ZnO interface, a significant enhancement of stability of intermediates, such as H$^*$, CH$_3$OH$^*$, H$_2$COOH$^*$, and H$_2$O$^*$, is found. Compared to H$^*$, which shows the largest increase in $E_a$ by 0.58 eV owing to strong H—interface O interaction,

Figure 6. Energy profiles of methanol steam reforming on Cu(111) (black line), CuZn(211) (blue line), and Cu/ZnO (red line). The energy reference zero corresponds to the energy of H$_2$O and CH$_3$OH in gas phase.
CH$_3$OH, H$_2$COOH, and H$_2$O binding at the interface via H-bonding is less strengthened by 0.25−0.47 eV (Figure S1 and Table 2). These increased stabilities would ensure that the intermediates on Cu/ZnO interface would be found at higher surface coverages at equilibrium conditions. In addition, the barrier for O−H bond scission in H$_2$O*, CH$_2$OH*, and H$_2$COOH* is also greatly decreased on the interface, as discussed above, thereby accelerating the CO$_2$ formation. However, the barriers of the elementary steps on Cu and CuZn are comparable in magnitude, suggesting that the activity would not be affected significantly by alloying.

Having discussed the CO$_2$ formation, we now turn to its competitive pathways, namely formaldehyde and CO formation on Cu, CuZn, and Cu/ZnO interface. Note that formaldehyde (CH$_2$O*) is a key intermediate that is related to MSR selectivity. As shown above, it can recombine with OH*, followed by sequential H abstraction, leading to the formation of CO$_2$. In addition, the CH$_2$O* can also desorb or dehydrogenate, with the undesirable formation of CH$_2$O or CO. In the case of CO$_2$ formation, it is controlled by HCOOH* formation, HCOO* dehydrogenation, and CH$_2$O* recombination with OH* on Cu, CuZn, and Cu/ZnO interface, respectively (Figure 6). The calculated corresponding total barriers $E_{\text{total}}$ on these systems are 0.53, 0.95, and 0.38 eV (Figure 5b), which are defined as the highest energies for CO$_2$ formation (HCOOH* formation, HCOO* dehydrogenation, and CH$_2$O* + OH*) relative to CH$_2$O* + OH*. The barrier of CH$_2$O* desorption is characterized by its adsorption energy, and the corresponding values are 0.42, 0.60, and 0.50 eV (Table 2). For CO formation, it is controlled by the CH$_2$O* + * → HCO* + H* step regardless of surface structures, and the total barriers with respect to CH$_2$O* are 0.83, 0.81, and 0.53 eV on Cu, CuZn, and Cu/ZnO interface, respectively. Two main features can be seen from Figure 5b: (1) CO formation is the least favorable on the three surfaces; (2) Cu and CuZn have higher selectivity toward CH$_2$O, whereas Cu/ZnO interface is more selective for CO$_2$ formation. The different selectivity of the three surfaces mainly originates from the significant enhancement of CO$_2$ formation by the electrophilicity of hydrogen at the interface.

Recently, Klotzer and co-workers$^{19}$ compared the MSR activity/selectivity of CuZn (≈10:1) surface alloy and pure Cu foil using temperature-programmed reaction in an UHV-compatible high-pressure cell operated as a recirculating batch reactor. They found that the initial CuZn (≈10:1) surface alloy provides an appropriate near-surface Zn loading for MSR-induced segregation to yield submonolayer ZnO(X) coverage and therefore a high abundance of bimetallic-Cu(Zn)$_{\beta}$/ZnO(X) interface at about $500$ K. They proposed that the redox-active Cu(Zn)$_{\beta}$/ZnO(X) sites assist in water activation and the transfer of hydroxide or oxygen to the latter, thus providing optimum conditions for higher CO$_2$ activity and selectivity. On clean Cu, dehydrogenation ceases with formaldehyde. These experimental findings are in excellent agreement with the present DFT calculations. Different from the experimental speculation of methanol dehydrogenation to formaldehyde on Cu(Zn)$_{\beta}$ regions, the present calculations show that it will take Cu(Zn)$_{\beta}$/ZnO(X) sites as water activation. To provide a quantitative comparison with measurable kinetics, a kinetic Monte Carlo simulation would be crucial and be addressed in the future.

4. CONCLUSIONS

In summary, the distinct reactivities of the metallic copper, bimetallic copper−zinc alloy, and copper/zinc oxide interface coexisting under methanol steam reforming conditions are identified. Two different H species, namely those binding with O at Cu/ZnO interface and binding with metal on Cu and CuZn alloy, are differentiated and play an important role for overall activity and selectivity of MSR on zinc oxide supported copper catalysts. The strong interaction of H−interfacial O facilitates H adsorption and O−H bond scission in H$_2$O, CH$_3$OH, and H$_2$COOH, leading to the highest activity and selectivity toward CO$_2$ and H$_2$. In contrast, the weak H−metal interaction on Cu and CuZn alloy inhibits H adsorption and O−H bond scission, which results in the low activity and high selectivity toward CH$_3$O. Besides the reactivity, the different active sites for H binding also lead to variation in reaction pathway for CO$_2$ formation via H$_2$COO (Cu/ZnO interface) or HCOOH (Cu and CuZn alloy) intermediate. This work highlights the role of metal/oxide interface in improving reactivity of methanol steam reforming at the atomic level, and the insights achieved can be used for catalyst development in MSR and other energy conversion reactions of technological interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07703. Configurations of the intermediates adsorption (Figure S1) and other transition states (Figure S2) involved in MSR on Cu(111), CuZn(211), and Cu/ZnO (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Author Contributions

These authors contributed equally.

Notes

The authors declare no competing financial interest.

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