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Structure Sensitivity for Forward and Reverse Water-Gas Shift Reactions on Copper Surfaces: A DFT Study

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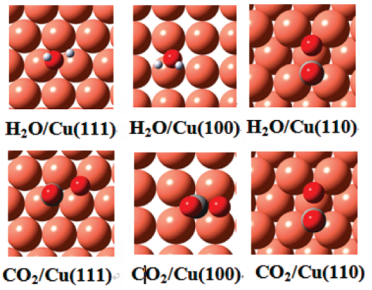
ABSTRACT The DFT-GGA calculations have clearly reproduced the experimentally observed structure-sensitivity of forward and reverse water-gas shift reactions on Cu(111), Cu(100), and Cu(110) assuming the "redox mechanism". The reason for the structure-sensitivity has also been explored by the transition-state structure analysis and the metal d-band center analysis. It is concluded that the difference in virtual adsorption energy of atomic oxygen or other strongly adsorbed species at the transition state is essential to account for the structure-sensitive reactions.

SECTION Surfaces, Interfaces, Catalysis



Catalytic activities of solid surfaces are sometimes significantly different depending on the surface structure. The structure sensitivity of heterogeneous catalysis is one of the most important problems in understanding the active sites. Many catalytic systems have been classified into the structure sensitive reaction by surface science experiments using single crystal surfaces, which have been carried out since the 1970s. However, it has been still under speculation on the atomic level why and how the structure sensitivity appears because of shortage on the quantitative kinetic information such as the detailed catalytic mechanism, the rate determining step, and the kinetics of elementary steps. Theoretical analyses for the transition state (TS) of the surface reaction and the electronic structure are required to clarify the structure sensitive features appeared on different surface orientations. Density functional theory (DFT) study combined with kinetic data obtained by surface science experiments is suitable to solve the problem of the structure sensitivity.

The catalytic water-gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) as well as the reverse water-gas shift (RWGS) reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) on Cu surfaces are well known to be a typical structure-sensitive reaction, in which the reaction rate of WGS on Cu(110) is higher than that on Cu(111).[1,2] However, the reason why both forward and reverse WGS reactions are structure-sensitive is not clear, although some empirical theoretical methods have been used to explore such phenomena.[3,4] The reaction mechanism and the rate-determining step of WGS and RWGS reactions on Cu have been well-studied by using traditional catalytic research techniques and surface science approaches. Two different mechanisms, that is, "redox mechanism"[1,2,5−7] and "carboxyl intermediate mechanism",[8−10] are possible for the forward WGS reaction on copper surfaces, where the latter mechanism has been newly proposed by DFT. The mechanism of the reverse WGS reaction has not been discussed by DFT. In experiments, the following "redox mechanism" has been proposed for both forward and reverse WGS reactions on the Cu(110) surface.[1,2,5−7]

$$H_2O \rightarrow H_2O_a \quad \text{(i)}$$

$$H_2O_a \rightarrow OH_a + H_a \quad \text{(ii)}$$

$$2OH_a \rightarrow O_a + H_2O_a \quad \text{(iii)}$$

$$CO \rightarrow CO_a \quad \text{(iv)}$$

$$CO_a + O_a \rightarrow CO_2 \quad \text{(v)}$$

$$2H_a \rightarrow H_2 \quad \text{(vi)}$$

It should be noted that adsorbed oxygen in the redox mechanism is assumed to be formed by reaction iii, that is, recombination of OH_a, instead of direct dissociation of OH_a into O_a and H_a because reaction iii is a well known reaction taking place on Cu easily at ca. 270 K. In the literature, the mechanism has been called a "water-catalyzed mechanism",[1] in which water molecules are classified into reactant and catalyst, that is, $H_2O(1)$ and $H_2O(2)$ in the following equation.

$$H_2O(1) + H_2O(2) \rightarrow OH_a(1) + OH_a(2) + 2H_a \rightarrow O_a(1) + H_2O(2) + H_2 \quad \text{(vii)}$$

A water molecule, $H_2O(1)$, dissociates into $OH_a(1)$ and then $O_a(1)$, subsequently. The other water molecule, $H_2O(2)$, once dissociates into $OH_a(2)$, which does not further dissociate into surface oxygen but comes back to $H_2O(2)$ after abstraction of proton from $OH_a(1)$. That is, $H_2O(2)$ or $OH_a(2)$ play a role as a

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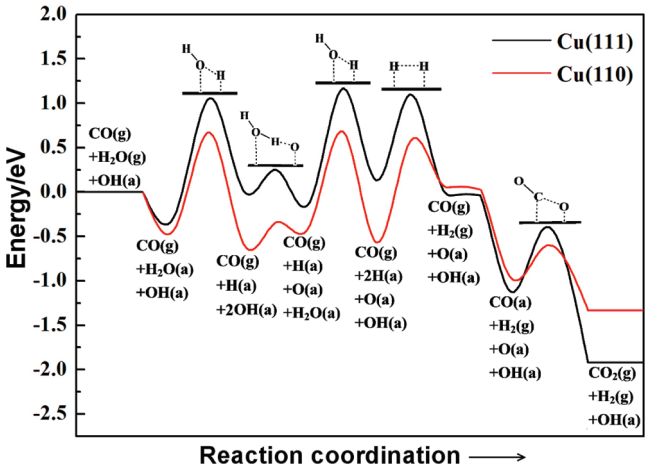

Figure 1. Calculated potential diagram by DFT for the redox mechanism of water-gas shift reaction on Cu(111) and Cu(110).

catalyst for the conversion of OH_a (1) to O_a(1). It is thus possible to call it a "OH_a catalyzed mechanism".

Although the mechanism of the WGS reaction has been studied by DFT,[8−10] the structure sensitivity has not been studied for both forward and reverse WGS reactions so far. In this work, we use the DFT-GGA method with the periodic slab model to study the reaction mechanism of WGS reaction as well as reverse WGS reaction and attempt to explore the nature of the structure sensitivity by analyzing the TS of H_2O or CO_2 dissociation.

In this study, the assumed redox mechanism composed of reactions i−vi was first elucidated by the DFT calculation to see whether the DFT study can be applicable to reproduce the experimental results of the WGS reaction on Cu surfaces. Figure 1 shows the potential diagram for the redox mechanism of the WGS reaction on Cu(111) and Cu(110), obtained by DFT-GGA calculation. The "OH_a-catalyzed mechanism" is involved in this diagram, as shown by OH_a added to reactants and products in Figure 1. The calculated potential diagram for Cu(110) is very similar to that obtained by experiments.[1] That is, the dissociation of adsorbed H_2O reveals the highest barrier for the WGS reaction, whereas the dissociation of CO_2 reveals the highest barrier for the RWGS reaction. It has been accepted that the rate-limiting steps of the WGS and the RWGS reactions are H_2O dissociation and CO_2 dissociation, respectively, based on the measurements of dissociation probabilities of H_2O or CO_2 on Cu as well as pressure dependence of H_2O or CO_2 on the reaction rates of the WGS or the RWGS reactions. The other steps, that is, eqs i, iii, iv, and vi, have not so high barriers, which is also consistent with the experimental results on Cu(111) and Cu(110), as discussed in the literature.[1,2,5,6,11−14]

Now, let us look at the detailed energetics for the elementary steps of the WGS reaction on Cu. In Table 1, the DFT-GGA results of activation barriers for the elementary steps of the forward ($E_{a,f}$) and the reverse ($E_{a,r}$) WGS reactions on Cu(111), Cu(100), and Cu(110) are summarized to compare with experimental data. First, the "water-catalyzed mechanism" was examined by the DFT-GGA calculation. It is confirmed that

Table 1. Activation Energies of Forward ($E_{a,f}$) and Reverse ($E_{a,r}$) Elementary Steps Involved in the WGS Reaction on Cu(*hkl*) Surfaces[a]

	Cu(111)		Cu(100)		Cu(110)	
	$E_{a,f}$	$E_{a,r}$	$E_{a,f}$	$E_{a,r}$	$E_{a,f}$	$E_{a,r}$
H_2O_a=OH_a+H_a	1.28	1.04	1.23	1.10	1.05	1.25
OH_a=O_a+H_a	1.51	0.85	1.60	0.88	1.43	0.57
$2OH_a$=H_2O_a+O_a	0.23	0.36	0.10	0.40	0.24	0.03
$2H_a$=$H_{2,a}$	0.97	1.08	0.62	0.30	1.10	0.56
CO_a+O_a=$CO_{2,a}$	0.71	1.51	0.63	1.26	0.34	0.71

[a] Energy unit in electronvolts.

the activation energy for the step of $OH_a \rightarrow O_a + H_a$ (1.43 to 1.60 eV) is much higher than that of $2OH_a \rightarrow H_2O + O_a$ (0.10 to 0.24 eV), as shown in Table 1, supporting that the adsorbed oxygen atom is easily formed by the associative reaction of $2OH_a \rightarrow H_2O + O_a$ rather than the direct dissociation of OH_a, as suggested in the experiments.[1] This means that the DFT results support the "OH_a-catalyzed mechanism". Mavrikakis et al.[9] have also reported that the OH disproportionation in the "water-catalyzed mechanism" is a facile step for producing atomic oxygen on Cu(111). Their calculated barriers for $OH_a \rightarrow O_a + H_a$ and $2OH_a \rightarrow H_2O_a + O_a$ on Cu(111) are 1.76 and 0.23 eV, respectively, which are comparable to our data, 1.51 and 0.23 eV, respectively. However, they have considered that the OH_a disproportionation is not involved in the WGS reaction mechanism because they have proposed the carboxyl mechanism of $CO_a + OH_a \rightarrow COOH_a \rightarrow CO_2 + H_a$.[9]

The next important point is the structure sensitivity of the WGS and the RWGS reactions on Cu, which should be originated from the structure sensitivity of the rate-limiting step of the H_2O dissociation and the CO_2 dissociation, respectively. Here one can easily find that the calculated activation energies of the H_2O_a dissociation decrease in the order of (111), (100), and (110), with barriers of 1.28, 1.23, and 1.05 eV, respectively. The large difference in the dissociation barrier among these three surfaces implies that the WGS reaction is a structure-sensitive reaction. The calculated activation energies of the H_2O_a dissociation are close to the experimental results of 1.23 eV on Cu(111)[11] and 0.87 eV on Cu(110).[12,13] The calculated barrier for H_2O_a dissociation on Cu(111) here, 1.28 eV, is close to that calculated by Mavrikakis et al., 1.36 eV.[9] Mavrikakis et al.[9] have reported that the activation energy of H_2O on Cu(211) is identical to that on Cu(111), suggesting that the specific bond-breaking event may be quasi-structure-insensitive.

As for the RWGS reaction, the calculated activation energy of the CO_2 dissociation on Cu(111) (1.51 eV) is much higher, as compared with those of Cu(100) (1.26 eV) and Cu(110) (0.71 eV). These agree with the experimentally measured apparent activation energy of the CO_2 dissociation, 0.95 eV on Cu(100)[15] and 0.63 eV on Cu(110),[9] if one assumes a small adsorption energy of CO_2 at 0.1 to 0.3 eV.[16] Both calculated and measured barriers for the CO_2 dissociation are further comparable to the apparent activation energy of the RWGS reaction, 1.40 eV on poly-Cu (mainly Cu(111) at 5 atm),[14] 1.34 eV on Cu(100) at 18 atm,[17] and 0.78 eV at 0.01 to 2.6 atm,[13]

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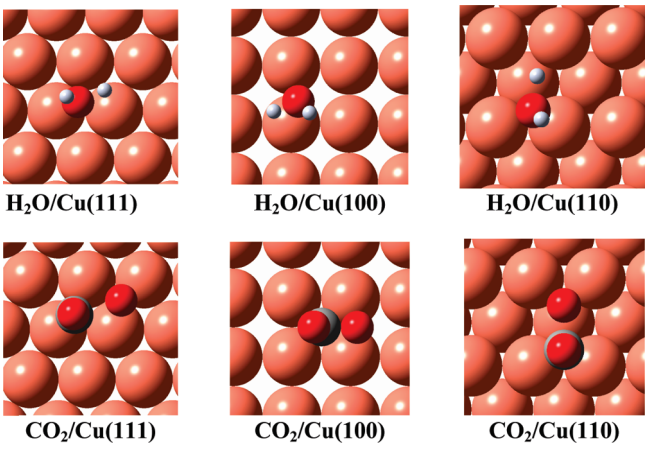

Figure 2. Transition state of H_2O and CO_2 dissociations on Cu(111), Cu(100), and Cu(110).

0.81 eVat 5 atm,[2] and 1.17 eVat 18 atm[17] on Cu(110). Additionally, the larger barrier for Cu(111) has been reported in the previous DFT results, 1.69[9] and 1.93 eV.[18] The significant difference in the barrier of the CO_2 dissociation among these Cu surfaces well explains the structure sensitivity of the RWGS reaction. Note that the dissociation barrier calculated here is for the formation process of adsorbed O and adsorbed CO from adsorbed CO_2, not from gas-phase CO_2. In the experiment, however, apparent activation energy of CO_2 dissociation corresponds to the change in potential energy for the process from gas-phase CO_2 to adsorbed O and adsorbed CO because CO_2 adsorption energy is too small to allow measurement of the dissociation rate of adsorbed of CO_2.

The good agreements in the activation barriers between the experiments and the DFT calculation allow us to apply the DFT calculation for examining more detailed mechanism of H_2O and CO_2 dissociations. The TSs of the H_2O dissociation and the CO_2 dissociations on Cu(111), Cu(100), and Cu(110) have thus been examined, as shown in Figure 2. The local orientation of H_2O and CO_2 to the substrate registry seems to be apparently different depending on the Cu surface plane. However, a common point is there. The adsorbed H_2O or CO_2 molecule seems to have been already dissociated at TS. The structure parameters, that is, bond length, of TS are summarized in Table 2. It turns out that the bond length of H and O (1.23 to 1.59 Å) in H_2O and that of C and O (1.58 to 2.23 Å) in CO_2 are much larger than the O−H bond length (0.96 Å) of a gas-phase H_2O molecule and C═O bond length (1.16 Å) in a gas-phase CO_2 molecule, respectively. This means the bond breaking at TS for both the H_2O dissociation and the CO_2 dissociation. The other bond lengths of O−H (0.99 Å) of OH_a and C−O (1.18 to 1.21 Å) of CO_a are close to those of gas-phase H_2O and CO_2 molecules, respectively. The TS structures for the dissociations of $H_2O_a \rightarrow H_a + OH_a$ and $CO_{2,a} \rightarrow CO_a + O_a$ on copper are thus more like products (CO_a and O_a) rather than reactant ($CO_{2,a}$), which is so-called "late barrier".

In the case of "late barrier" for H_2O dissociation, the O−H bond in H_2O is broken at TS. On the basis of the relative positions of atoms (hydrogen and oxygen) over Cu atoms at TS, virtual adsorption energies of OH_a and H_a at TS as well as

Table 2. Structure Parameter of Transition States for H_2O and CO_2 Dissociations on Copper (Bond Length in angstroms)

	$d_{C\text{-}M}$	$d_{O\text{-}M}$	d_{C-O1}	d_{C-O2}	d_{O-H1}	d_{O-H2}
H_2O on Cu(100)		2.04			0.99	1.23
H_2O on Cu(110)		1.96			0.99	1.59
H_2O on Cu(111)		2.05			0.99	1.34
CO_2 on Cu(100)	2.38	1.88	1.21	1.58		
CO_2 on Cu(110)	2.11	1.93	1.19	1.97		
CO_2 on Cu(111)	2.01	1.90	1.18	2.23		

Table 3. Virtual Adsorption Energies and Interaction Energies of Adsorbed Species at TS for CO_2 Dissociation (Left Half) and H_2O Dissociation (Right Half)[a]

	E_{Oa}	E_{COa}	$E_{Oa/COa}$	E_{Ha}	E_{OHa}	$E_{Ha/OHa}$
Cu(111)	−4.02	−0.63	0.18	−2.06	−2.44	0.39
Cu(100)	−4.02	−0.67	−0.01	−2.01	−2.56	0.23
Cu(110)	−4.32	−0.80	−0.09	−1.86	−2.90	0.15

[a] Energy is estimated based on the atomic position at TS (electronvolts).

interaction energy between OH_a and H_a can be estimated by the DFT calculation. The total energy of TS, E_{TS}, and the energy of Cu substrate, E_{Cu}, are divided into the virtual adsorption energies of OH_a and H_a and the interaction energy between H_a and OH_a, $E_{Ha/OHa}$, as follows

$$E_{TS} + E_{Cu} = E_{Ha} + E_{OHa} + E_{Ha/OHa} \quad \text{(viii)}$$

Table 3 summarizes the virtual adsorption energy of H_a and OH_a at TS of H_2O dissociation as well as the virtual adsorption energy of O_a and CO_a at TS of CO_2 dissociation. The virtual adsorption energy of OH_a decreases in the order of Cu(110), Cu(100), and Cu(111). On the contrary, the virtual adsorption energy of H_a decreases slightly in the order of Cu(111), Cu(100), and Cu(110). The larger adsorption energy leads to lower barrier at TS. That is, the stronger bonding between OH_a and Cu results in reduction of activation barrier of H_2O dissociation. The order of surface planes in the activation energy of H_2O dissociation, Cu(111) > Cu(100) > Cu(110), can thus be explained by the adsorption energy of OH_a, Cu(111) < Cu(100) < Cu(110). The major origin of structure sensitivity for dissociation of H_2O on Cu is thus ascribed to the interaction between OH and Cu atoms at TS. The same argument can be applied to the dissociation of CO_2 on Cu. As shown in Table 3, the virtual adsorption energy of O_a at TS is much larger than that of CO_a. The larger adsorption energy of O_a leads to lower activation energy of CO_2 dissociation. Again, the reason for the lower activation barrier of CO_2 dissociation on Cu(110) is due to the higher adsorption energy of O_a on Cu(110) at TS. It may be a general trend that the structure sensitivity of dissociation reactions with late barrier is due to difference in the adsorption energy of species interacting with surface most strongly at TS. In both cases of H_2O and CO_2 dissociations, the interaction of oxygen atom and copper atom determines the structure sensitivity instead of hydrogen or carbon atoms. Moreover, it can be seen from Table 3 that the interaction energies between two separated

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Table 4. Adsorption Energy of Species Related to WGS Reaction (electronvolts)[a]

	Cu(111)	Cu(100)	Cu(110)
H_2O	0.22	0.25	0.38
H	2.73	2.38	2.61
OH	3.26	3.51	3.62
CO	1.14	0.83	1.03
O	5.30	5.77	5.45

[a] Data are shown for the most stable adsorption sites.

species at TS, H−OH and O−CO, are also correlated with the activation barrier order, that is, the larger attraction energy, the lower activation barrier.

Because it is widely known that the d-band center can be used to predict surface reactivity,[19] the structure sensitivity of H_2O dissociation and the CO_2 dissociation were tried to be elucidated by the d-band center of Cu(111), Cu(100), and Cu(110). In the present study, the d-band center based on the local density of state (LDOS) diagrams were estimated to be −3.00, −2.80, and −2.45 eV for (111), (100), and (110), respectively. The order is consistent with the trend of the activity for dissociation of H_2O and CO_2; that is to say, the closer to the Fermi level for the d-band center, the easier for the dissociation of H_2O as well as CO_2. Note that one cannot always use the d-band center as criteria to predict the structure sensitivity of metal surfaces. Table 4 shows the adsorption energies of species related to the WGS reaction on Cu(111), Cu(100), and Cu(110), in which the adsorption energies at the most stable sites are shown. It is clear that the d-band center criteria cannot apply to predict the order of the Cu surfaces in terms of the largest adsorption energy. For example, the order in the adsorption energy of oxygen on Cu(111), Cu(100), and Cu(110) cannot be explained by the d-band center, where the four-fold hollow site of Cu(100) is the most stable for the adsorption of atomic oxygen. In general, the adsorption energy of atom is dependent on the adsorption site significantly in the case of an identical kind of metal. The d-band center thus may be used to predict a trend in the adsorption energy or the structure sensitivity if the adsorption site is identical on the same kind of metal. As shown in Figure 2, the positions of OH_a of H_2O as well as O_a of CO_2 in the TS structure seem to be all bridge sites. This may be the reason why the d-band center of Cu can be used for the prediction of trend in the activation barriers.

Finally, the proposed picture of the CO_2 dissociation mechanism by the DFT study is compared with the successful DFT results explaining the nature of activation barrier for CO oxidation ($CO_a + O_a \rightarrow CO_2$) on Pt(111) by Hu et al.[20,21] The CO oxidation is the reverse process of the CO_2 dissociation. They have reported that the predominant energy to overcome the activation barrier of the CO oxidation is ascribed to the breaking energy of strong oxygen−metal bond. At the TS, oxygen moves from the most stable three-fold hollow site to bridge site, at which CO_a reacts with O_a. The bridge site of oxygen at TS was also observed for CO_2 dissociation on Cu in this study, as shown in Figure 2. The results of both Hu et al. and us suggest that the atomic oxygen on the bridge site may be very active like the oxygen at the TS of CO_2 dissociation or CO oxidation.

In summary, the structure-sensitivity of forward and RWGS reactions on Cu(111), Cu(100), and Cu(110) surfaces was studied by DFT-GGA calculations assuming the "redox mechanism". The calculation reproduced the experimentally measured potential diagram, in which the dissociation of H_2O is the rate-determining step for the forward WGS reaction, whereas the dissociation of CO_2 is that for the reverse WGS reaction. The activation energies for both dissociations of H_2O and CO_2 decrease in the order of Cu(111) > Cu(100) > Cu(110). At the TS of the dissociations, O−H bond in H_2O as well as C−O bond in CO_2 are broken, that is, "late barrier", so that the activation energies for the dissociation of H_2O and CO_2 are influenced significantly by the virtual adsorption energy of OH_a and O_a at TS, respectively. The difference in the virtual adsorption energy at TS is thus essential to account for the structure-sensitive characters.

CALCULATION MODEL AND METHODS

All calculations are performed using the plane-wave DFT (VASP code).[22,23] The exchange-correlation energy and potential are described by generalized gradient approximation (PW91).[24] The electron-ion interaction is described by the projector-augmented wave (PAW) scheme,[25,26] and the electronic wave functions are expanded by plane waves up to a kinetic energy of 400 eV. A periodical four-layer slab is used with ∼10 Å of vacuum region between slabs. The calculated models are chosen as the unit cells of 2×2 with the corresponding coverage of 1/4 ML. During the calculation, the first two layers and the adsorbed species were allowed to be relaxed. The surface Brillouin zone is sampled using a $4 \times 4 \times 1$ Monkhorst−Pack mesh.[27] The minimization of the reaction pathways and the search of the TSs have been performed with the climbing-image nudged elastic band method (CI-NEB).[28,29]

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