


 Cite this: *RSC Adv.*, 2024, 14, 9985

# Dual mechanisms in hydrogen reduction of copper oxide: surface reaction and subsurface oxygen atom transfer

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The study of the reduction of copper oxide (CuO) by hydrogen (H<sub>2</sub>) is helpful in elucidating the reduction mechanism of oxygen carriers. In this study, the reduction mechanism of CuO by H<sub>2</sub> and the process of oxygen atom transfer were investigated through the density functional theory (DFT) method and thermodynamic calculation. DFT calculation results showed that during the reaction between H<sub>2</sub> and the surface of CuO, Cu underwent a Cu<sup>2+</sup> → Cu<sup>1+</sup> → Cu<sup>0</sup> transformation, the Cu–O bond (–IpCOHP = 2.41) of the Cu<sub>2</sub>O phase was more stable than that (–IpCOHP = 1.94) of the CuO phase, and the reduction of Cu<sub>2</sub>O by H<sub>2</sub> was more difficult than the reduction of CuO. As the surface oxygen vacancy concentration increased, it was more likely that the subsurface O atoms transfer to the surface at zero H<sub>2</sub> coverage (no H<sub>2</sub> molecule on the surface), allowing the surface to maintain a stable Cu<sub>2</sub>O phase. However, when the H<sub>2</sub> coverage was 0.25 monolayer (ML) (one H<sub>2</sub> molecule every four surface Cu atoms), the presence of H atoms on the surface made the upward transfer of O atoms from the subsurface more difficult. The rate of consuming surface O atoms in the reduction reaction was greater than the rate of subsurface O atom transfer induced by the reduction reaction and the surface Cu<sub>2</sub>O phase could not be maintained stably. Through thermodynamic analysis, at high H<sub>2</sub> concentration, the reaction between H<sub>2</sub> and CuO was more likely to generate Cu, while at low H<sub>2</sub> concentration, it was more likely to generate Cu<sub>2</sub>O. In summary, the valence state of Cu in the reaction process between CuO and H<sub>2</sub> depended on the concentration of H<sub>2</sub>.

Received 18th February 2024

Accepted 18th March 2024

DOI: 10.1039/d4ra01240b

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## 1 Introduction

Chemical looping combustion (CLC) has been shown to be a promising combustion technology for power production with integrated CO<sub>2</sub> capture.<sup>1–3</sup> In CLC, a metal oxide that acts as an oxygen carrier is alternately reduced by a fuel (syngas or natural gas) in a fuel reactor and oxidized by air in an air reactor. CuO is a good oxygen carrier for chemical looping combustion.<sup>4–6</sup> CuO undergoes a reduction process in the fuel reactor. Numerous studies have been carried out on CuO. However, the reduction mechanism of CuO, especially the influence of reducing gas concentration, is currently unclear. Hydrogen (H<sub>2</sub>) is the most common reducing gas. There were many studies on the reduction of CuO by H<sub>2</sub>. The reaction of H<sub>2</sub> with CuO was experimentally studied using *in situ* X-ray diffraction by Kim *et al.*<sup>7</sup> Samples were loaded in an open sapphire capillary having an inner diameter of 0.5 mm. An inlet gas was a 5% H<sub>2</sub> and 95% He gas mixture. The results showed that under high H<sub>2</sub> flow rate (≈ 15 cm<sup>3</sup> min<sup>–1</sup>), CuO can be directly reduced to metallic Cu

(Cu<sup>2+</sup> → Cu<sup>0</sup>). During the reduction process, no evidence of any intermediate state (Cu<sup>+</sup>) was found. Cu<sub>2</sub>O appeared as an intermediate phase only at very low H<sub>2</sub> flow rates (<1 cm<sup>3</sup> min<sup>–1</sup>); this result has been supported by multiple studies.<sup>8–11</sup>

Maimaiti *et al.*<sup>12</sup> investigated the process of H<sub>2</sub> reduction on the surface of CuO using the density functional theory (DFT) method and concluded that Cu<sup>+</sup> appeared during the reaction. This could not explain the experimentally observed phenomenon that Cu<sup>2+</sup> is directly converted into the Cu<sup>0</sup> phase under high H<sub>2</sub> concentration. This may be due to the fact that, in addition to the reaction between H<sub>2</sub> and the CuO surface, other reaction processes are involved in the reduction reaction. Using the DFT method, Jabraoui *et al.*<sup>13</sup> found that oxygen vacancies play an important role in the decomposition of CuO to release O<sub>2</sub>. Oxygen vacancies on the surface can promote the transfer of internal O to the surface. Yang *et al.*<sup>14</sup> found that rearrangements occurred on the CuO surface as the concentration of surface oxygen vacancies increased. Transition in the surface structure caused by the reaction between H<sub>2</sub> and CuO may in turn affect the reaction between H<sub>2</sub> and CuO.

In this study, the DFT method was adapted to study the reaction between H<sub>2</sub> and the CuO surface initially. Subsequently, subsurface O atom transfer was studied with different

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H<sub>2</sub> coverages (0 ML, 0.25 ML) by DFT. DFT provided a precise approach<sup>15,16</sup> to the theoretical problem of electronic structure. Both the climbing image nudged elastic band (CI-NEB)<sup>17</sup> and dimer<sup>18</sup> methods were applied to find the transition states. The transition state structure of chemical reactions could help us better understand the kinetic properties of chemical reactions. Thermodynamic calculations were applied to the reactions occurring in the H<sub>2</sub> reduction of CuO process.

## 2 Methodology and model

### 2.1 Computational methodology

All DFT calculations were performed using the software Vienna *ab initio* simulation package (VASP).<sup>19,20</sup> The projector augmented wave (PAW) method was chosen for the calculations to handle the effect of the core electrons on the valence electrons.<sup>21</sup> The Perdew–Burke–Ernzerhof (PBE) exchange function under the generalized gradient approximation (GGA) was selected.<sup>22</sup> The Monkhorst–Pack method was used to sample the Brillouin zone,<sup>23</sup> and *k*-point grids with sizes of 8 × 8 × 8 and 4 × 4 × 1 were used for CuO unit cells and CuO slab calculations, respectively. The plane wave cutoff energy was 400 eV. Because the conventional DFT functionals cannot accurately describe the strong correlation effect between the Cu 3d orbital electrons in CuO,<sup>24</sup> the GGA+*U* method<sup>25</sup> was used in order to accurately describe the strongly correlated, highly localized 3d electrons in CuO. To describe the Cu atom, *U* = 7 eV and *J* = 0.98 eV were used.<sup>26</sup> The electron energy was relaxed to an accuracy of 10<sup>−6</sup> eV, and the atomic positions were optimized until the Hellmann–Feynman force was less than 0.02 eV Å<sup>−1</sup>. Projected crystal orbital Hamilton population (pCOHP) calculations were conducted using the LOBSTER code.<sup>27</sup> The structures were visualized by VESTA software.<sup>28</sup> Thermodynamic calculations were conducted using the HSC Chemistry 6.0 software. For H<sub>2</sub> adsorption on the CuO surface, the energy of gas adsorption is

$$E_{\text{ads}} = E(\text{H}_2\text{-surface}) - E(\text{surface}) - E(\text{H}_2) \quad (1)$$

where  $E_{\text{ads}}$  is the gas adsorption energy,  $E(\text{H}_2\text{-surface})$  is the total energy of the system after H<sub>2</sub> is adsorbed to the CuO surface,  $E(\text{surface})$  is the total energy of the CuO surface, and  $E(\text{H}_2)$  is the total energy of H<sub>2</sub>. The activation energy of the reaction is expressed as

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{IS}} \quad (2)$$

where  $E_{\text{TS}}$  is the energy of the transition state and  $E_{\text{IS}}$  is the energy of the initial state. The heat of reaction is

$$\Delta E = E_{\text{FS}} - E_{\text{IS}} \quad (3)$$

where  $E_{\text{FS}}$  is energy of the final state. Microscopically, gas concentration can be reflected by the adsorption surface gas coverage ( $\theta$ ).<sup>29</sup> The formula for adsorption gas coverage is as follows:

$$\theta = N_{\text{g}}/N_{\text{M}} \quad (4)$$

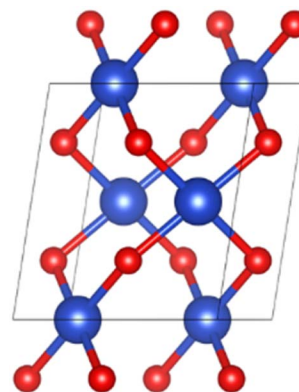


Fig. 1 Unit cell structure of CuO.

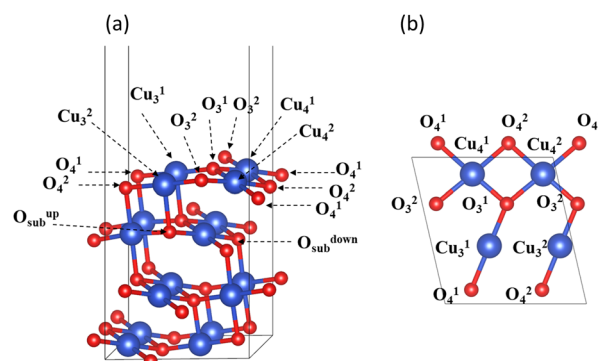


Fig. 2 CuO (111) surface unit cell: (a) front view (b) top view.

where  $N_{\text{g}}$  is the number of adsorbed gas molecules, and  $N_{\text{M}}$  is the number of surface metal atoms. The unit for  $\theta$  is monolayer (ML).

### 2.2 Structural properties

The spatial structure of CuO crystal belonged to the *C2/c* group.<sup>30</sup> Fig. 1 illustrates the unit cell structure of CuO. The CuO unit cell parameters were calculated as  $a = 4.63 \text{ \AA}$ ,  $b = 3.43 \text{ \AA}$ ,  $c = 5.09 \text{ \AA}$ ,  $\beta = 99.43^\circ$ , and the Cu–O bond length was  $1.95 \text{ \AA}$ , which was well aligned with experimental data,<sup>30</sup> proving that the chosen parameter settings were appropriate.

Experiments and calculations have both demonstrated that CuO (111) is the most stable surface of copper oxide and the surface most easily observed in experiments.<sup>31,32</sup> Therefore, the CuO surface model used in this study was CuO (111), as shown in Fig. 2. The CuO (111) surface used for hydrogen reduction and surface structure calculation was a (2 × 1) supercell that retains four layers of atoms. The thickness of the vacuum layer was  $15 \text{ \AA}$ . The lower two of these layers were fixed, and the upper two were relaxed. Inside the unit cell, there were a total of four oxygen atoms on the surface of CuO (111), which were divided into two categories according to the coordination number. The oxygen atoms with a coordination number of three were labeled O<sub>3</sub><sup>1</sup> and O<sub>3</sub><sup>2</sup>, and those with a coordination number of four were labeled O<sub>4</sub><sup>1</sup> and O<sub>4</sub><sup>2</sup>. There were four Cu atoms on the surface in total, namely, the three-coordinated Cu<sub>3</sub><sup>1</sup> and Cu<sub>3</sub><sup>2</sup> and the four-coordinated Cu<sub>4</sub><sup>1</sup> and Cu<sub>4</sub><sup>2</sup>.



### 3 Results and discussion

#### 3.1 Study of the complete reaction paths of hydrogen on copper oxide surface

On the surface of intact copper oxide, two H<sub>2</sub> adsorption sites were considered: the top sites of the three-coordinated Cu and four-coordinated Cu atoms. On the intact CuO surface, the adsorption energy  $E_{\text{ads}}$  of H<sub>2</sub> on Cu<sub>3</sub> was  $-2.30 \text{ kJ mol}^{-1}$ , and  $E_{\text{ads}}$  of H<sub>2</sub> on Cu<sub>4</sub> was  $-2.01 \text{ kJ mol}^{-1}$ . H<sub>2</sub> adsorption on the intact surface of CuO released very little heat, indicating that no chemisorption occurred. However, H<sub>2</sub> adsorption on the three-coordinated Cu<sub>3</sub> still released more energy, and it could be assumed that H<sub>2</sub> was initially adsorbed on the three-coordinated Cu<sub>3</sub>.

Next, the type of O that H<sub>2</sub> reacts with first on the surface was considered. The reaction heat  $\Delta E$  between H<sub>2</sub> and O<sub>3</sub> was  $-182.50 \text{ kJ mol}^{-1}$  and that between H<sub>2</sub> and O<sub>4</sub> was  $-93.31 \text{ kJ mol}^{-1}$ .

H<sub>2</sub> was more likely to combine with the three-coordinated O atoms on the surface of CuO to form H<sub>2</sub>O, so H<sub>2</sub> would react with the three-coordinated O on the surface of CuO first, and then with the four-coordinated O afterward. This has also been confirmed by calculations by Maimaiti *et al.*<sup>12</sup>

The reaction of H<sub>2</sub> with the CuO surface is divided into two parts. First, the dissociation of H<sub>2</sub>, and then the formation of H<sub>2</sub>O from the two dissociated H atoms and a surface O atom. H<sub>2</sub> dissociates in two ways on the surface of metal oxides:<sup>33–36</sup> the first is the dissociation of H<sub>2</sub> to form H<sup>-</sup> and H<sup>+</sup>, which are adsorbed on the metal and oxygen sites, respectively, producing M–H and O–H groups (path 1); the other is the dissociation of H<sub>2</sub> to produce two H atoms, which combine with two O atoms to form two O–H groups (path 2). Both H<sub>2</sub> dissociation pathways are possible during the H<sub>2</sub> reduction of CuO. The two reaction paths of H<sub>2</sub> with CuO are shown in Fig. 3. The energy changes in the process for the two different reactions paths are shown in Fig. 4. In path 1, from 1A to FS was the rate-determining step. In path 2, from 1A' to FS was the rate-determining step. In path 2, the rate-determining step was an endothermic reaction, which increased the difficulty of the reaction.  $X_a$  was used to measure the similarity between the initial and final states, *i.e.*, the root sum squared of the distance between the initial and final states of the corresponding atoms. The smaller  $X_a$  was, the smaller the distance of the atom movement before and after the reaction was. In path 1, the  $X_a$  between 1A and IS was 2.45, and the  $X_a$  between FS and 1A was 3.68. In path 2, the  $X_a$  between 1A' and IS was 3.89, and the  $X_a$  between FS and 1A' was 4.09. From the perspective of H atom diffusion, in path 2, H atoms required more diffusion movement, which increased the difficulty of the reaction in path 2. Hence, the H<sub>2</sub> dissociation approach chosen in this study is path 1.

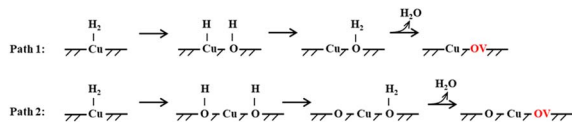


Fig. 3 Two H<sub>2</sub> dissociation modes and CuO reaction paths.

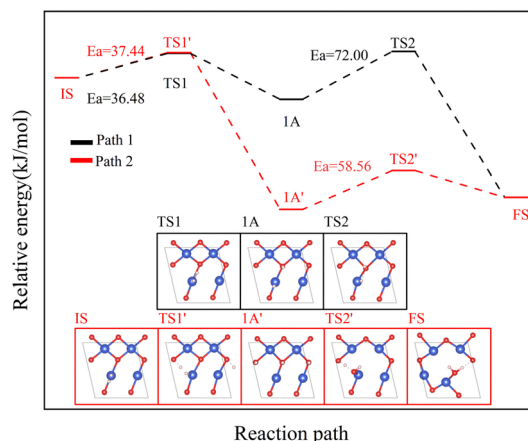


Fig. 4 The two reaction paths of H<sub>2</sub> with CuO (the white atom is the H atom).

Next, the full-path process of H<sub>2</sub> reduction in the surface reaction of CuO was studied by DFT method.

In the process of complete reduction of CuO by H<sub>2</sub>, as the reaction of H<sub>2</sub> with surface O atoms proceeds, H<sub>2</sub>O is formed on the surface of CuO (111) with different oxygen vacancy concentrations until no O atoms remain on the surface. As shown in Fig. 5, for convenience, this article refers to the surfaces of CuO (111) with 25%, 50%, 75%, and 100% oxygen vacancy concentration as surface I, surface II, surface III, and surface IV, respectively. This designation was used to study the effect of different oxygen vacancy concentrations on the reaction between CuO and H<sub>2</sub>. The complete reaction process of H<sub>2</sub> with the CuO (111) surface is shown in Fig. 6.

On the intact surface, the initial state was a state when H<sub>2</sub> adsorbed on the top site of Cu<sub>3</sub>, and the H–H bond length of the adsorbed H<sub>2</sub> molecule was 0.75 Å, which was essentially unchanged compared to the H–H bond length of the gaseous H<sub>2</sub> molecules (0.74 Å). Then, the H–H bond in the H<sub>2</sub> molecule was broken to form an H–O group, and another H atom stayed in the top site of the Cu atom. During this process, the Cu–O bonds were activated, and the Cu–O bonds around O<sub>3</sub> lengthened. Subsequently, another H atom was combined with O<sub>3</sub> to form two H–O bonds on the surface. The two H–O bonds' lengths were 0.97 Å and 1.03 Å, respectively, and the H–O–H bond angle was 106.40°. In the H<sub>2</sub>O molecule, the H–O bond length is 0.99 Å, and the H–O–H bond angle is 104.5°. It can be considered that water molecules were generated on the surface.

On surface I, when H<sub>2</sub> was adsorbed on the top site of Cu<sub>3</sub>, the H–H bond length was 0.80 Å, and the H–H bond was activated. The Cu–O bond around O<sub>3</sub> was longer than that of the intact CuO surface, and when an H–O bond was formed, the Cu–O bonds were also more active than the ones on intact surfaces. Compared to the intact surface, on surface I, the energy barrier for the reaction between H<sub>2</sub> and O<sub>3</sub> atoms to form H<sub>2</sub>O molecules was smaller, the reaction was more likely to occur, and more heat was given off by the entire reaction process. During the reaction, the O atoms on the surface were rearranged, with O<sub>4</sub> on the surface migrating to the original



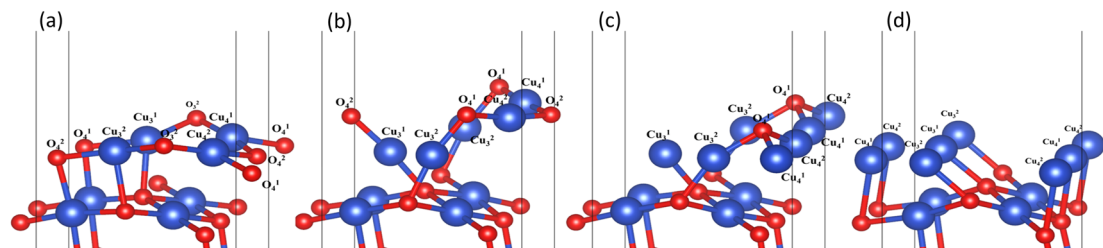


Fig. 5 Surfaces with different oxygen vacancy concentrations as the reaction of  $\text{H}_2$  reduction of CuO occurs: (a) surface I (25% oxygen vacancy concentration), (b) surface II (50% oxygen vacancy concentration), (c) surface III (75% oxygen vacancy concentration), and (d) surface IV (100% oxygen vacancy concentration).

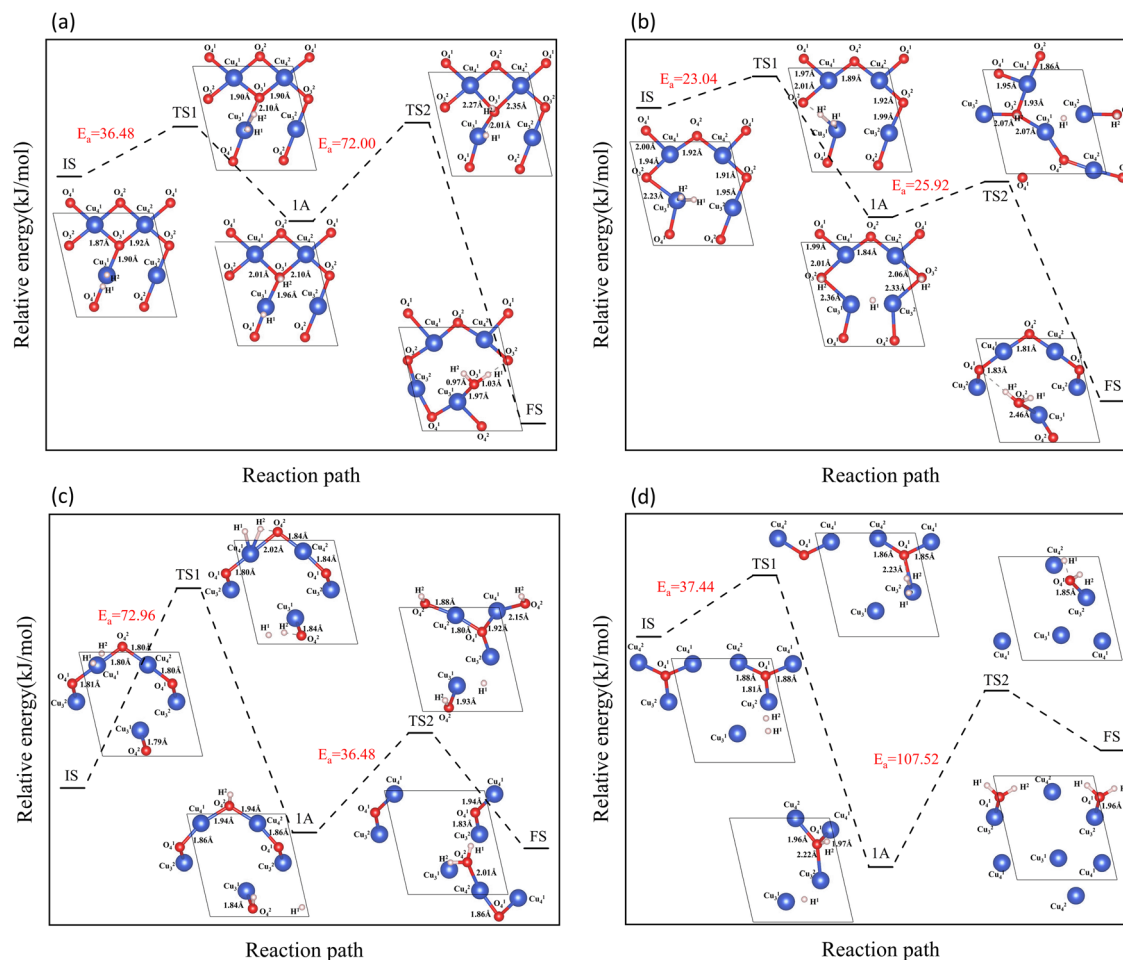


Fig. 6 Entire process of the reaction path of  $\text{H}_2$  reduction on the CuO surface: (a)  $\text{H}_2$  reacts with an intact surface, (b)  $\text{H}_2$  reacts with surface I, (c)  $\text{H}_2$  reacts with surface II, (d)  $\text{H}_2$  reacts with surface III.

position of  $\text{O}_3^2$ . With the dissociation of  $\text{H}_2\text{O}$ , a CuO surface with a 50% oxygen vacancy concentration, which has been denoted as surface II, was formed.

On surface II, the arrangement of Cu and O was similar to the (111) surface of  $\text{Cu}_2\text{O}$ .<sup>37</sup> The length of the Cu–O bond on this surface was shorter than that on both previous surfaces. At the initial state,  $\text{H}_2$  adsorbed on the top site of Cu, and the H–H bond length of the  $\text{H}_2$  molecule was 0.75 Å. They were not activated. The process of cleavage of  $\text{H}_2$  molecules and

formation of an H–O bond had a higher energy barrier. The required energy to break the barrier for the subsequent formation of two H–O bonds was reduced but still high compared to the same reaction process on surface I.

On surface III,  $\text{H}_2$  cannot adsorb on the top sites of Cu, but instead adsorbed on the hollow sites on Cu atoms. The H–H bond length of the adsorbed  $\text{H}_2$  molecule was 0.75 Å. During the cleavage of the  $\text{H}_2$  molecule and the formation of an H–O bond, the required energy barrier was similar to the energy required



**Table 1** Bader charge values of surface atoms under different oxygen vacancy concentration conditions and Cu atoms in CuO, Cu<sub>2</sub>O, and Cu bulks

Surface	Atom								Bulk	Cu
	Cu <sub>3</sub> <sup>1</sup>	Cu <sub>3</sub> <sup>2</sup>	Cu <sub>4</sub> <sup>1</sup>	Cu <sub>4</sub> <sup>2</sup>	O <sub>3</sub> <sup>1</sup>	O <sub>3</sub> <sup>2</sup>	O <sub>4</sub> <sup>1</sup>	O <sub>4</sub> <sup>2</sup>		
Intact surface	10.24	10.24	10.02	10.02	6.90	6.90	6.91	6.91	CuO	10.00
Surface I	10.37	10.36	10.27	10.28		6.99	6.90	6.95		
Surface II	10.44	10.46	10.41	10.41			6.93	6.95	Cu <sub>2</sub> O	10.46
Surface III	10.73	10.50	10.71	10.67			6.92			
Surface IV	10.77	10.77	10.86	10.86					Cu	10.99

for the first step of the reaction on the intact surface. The higher energy required in the formation of two H–O bonds may be due to the fact that more energy was required to rearrange the surface Cu atoms as more surface oxygen vacancies appeared.

In summary, the complete reduction of the CuO surface by H<sub>2</sub> was calculated. The first chemical process in the two-step reaction was mainly the cleavage of the H<sub>2</sub> molecule, the activation of the Cu–O bond, and the formation of the H–O bond. The second step was mainly the breaking of the Cu–O bond and the formation of the H–O–H bond. As the concentration of oxygen vacancies on the surface increased, the reaction between H<sub>2</sub> and CuO was more intense on the surface with a 25% oxygen vacancy concentration. The reaction between H<sub>2</sub> and CuO became more difficult and slowed down as the concentration of oxygen vacancies continued to increase.

### 3.2 Electronic structure analysis

Table 1 lists the Bader charge on the intact surface and on surfaces with four different oxygen vacancy concentrations (0%, 25%, 75%, and 100%), as well as the Bader charge of Cu atoms in CuO, Cu<sub>2</sub>O, and Cu bulks. According to the Bader charge results, it is concluded that on the intact surface, the three-coordinated Cu atoms carry more charge than the four-coordinated Cu atoms, which confirms the choice of three-coordinated Cu as the initial adsorption site for H<sub>2</sub>. The Bader charge of the O atom remained stable throughout the reaction. This was because the O atom is more electronegative with respect to the Cu atom and therefore always attracts charge to fill its empty orbitals. The Bader charge of the Cu atom increased as the reaction proceeded. Compared with the Bader charge of Cu atom in CuO bulk, on the intact surface, the four-coordinated Cu atoms were at +2 valence, and the three-coordinated Cu atoms were at +2 valence approximately because of the presence of surface dangling bonds. On surface II, the Bader charge of the Cu atoms were near the Bader charge of Cu atom in Cu<sub>2</sub>O bulk. Each Cu atom had two coordination bonds, which was consistent with the Cu atom in Cu<sub>2</sub>O bulk. It could be considered that the valence state of Cu atoms on surface II was +1. On surface IV, Cu atoms had no coordination bonds on the surface and only had one coordination bond with the O atoms on the subsurface. Comparing the Bader charge of Cu atoms on surface IV with the Bader charge of Cu atom in Cu bulk, it could be approximated that the Cu atoms on surface IV

were at 0 valence. Therefore, during the reduction of a CuO surface by H<sub>2</sub>, the Cu atoms on the entire surface exhibited a change process of Cu<sup>2+</sup> → Cu<sup>1+</sup> → Cu<sup>0</sup>. Based on the calculation of the transition state, it was found that it is more difficult to reduce Cu<sup>1+</sup> than Cu<sup>2+</sup>, a result that has also been confirmed by experiments.<sup>9</sup>

The molecular orbitals before H<sub>2</sub> adsorption consisted of the σ<sub>1s</sub> bonding orbital formed by the 1s orbitals of the two H atoms, and the σ<sub>1s</sub><sup>\*</sup> antibonding orbital.<sup>38</sup> The σ<sub>1s</sub><sup>\*</sup> antibonding orbitals were mainly located above the Fermi energy level, and with a small projected density of states (PDOS), so the electrons of H<sub>2</sub> were mainly concentrated in the σ<sub>1s</sub> bonding orbitals. The valence charge of the Cu atom was concentrated in the 3d orbital, which was the active orbital of the Cu atom.<sup>39</sup> Fig. 7 shows the PDOS plots of H 1s and Cu 3d before and after H<sub>2</sub> adsorption on different surfaces. On the intact CuO surface, after H<sub>2</sub> adsorption, the 1s orbitals of H were transferred to a lower energy level, whereas the 3d orbitals of Cu remain almost unchanged. The small overlap region between the two suggests that the hybridization between the 1s orbital of H and 3d orbital of Cu is weak, which corresponds to the relatively low adsorption energy. On surface I, the 1s orbitals of H and 3d orbitals of Cu after H adsorption generated new PDOS peaks at lower energy levels and overlapped. This indicated that, when H<sub>2</sub> was adsorbed on surface I, hybrid bonding occurred between the 1s orbital of the H atom and the 3d orbital of Cu, forming a bonding orbital with lower energy, which increased the adsorption energy. At the same time, the original σ<sub>1s</sub> and σ<sub>1s</sub><sup>\*</sup> molecular orbitals of H<sub>2</sub> were destroyed, which led to the activation of the covalent bond of H<sub>2</sub>, which was conducive to the subsequent dissociation and diffusion of the H<sub>2</sub>. On surfaces II and III, after H adsorption, the H 1s orbital of moved to a lower energy level, the 3d orbital of Cu remained essentially unchanged, and the region of overlap between the two was relatively small. This indicated that on both surfaces the reaction with Cu remains weak when H<sub>2</sub> molecular adsorption occurs. The analysis of the PDOS plots led to the conclusion that only surface I activated the covalent bond of H<sub>2</sub> well upon adsorption of H<sub>2</sub>, which facilitated the subsequent dissociation of H<sub>2</sub>.

To understand the bonding of Cu–O on different surfaces, Fig. 8 illustrates the minus projected crystal orbital Hamilton population (–pCOHP) diagrams of Cu–O bonds on CuO



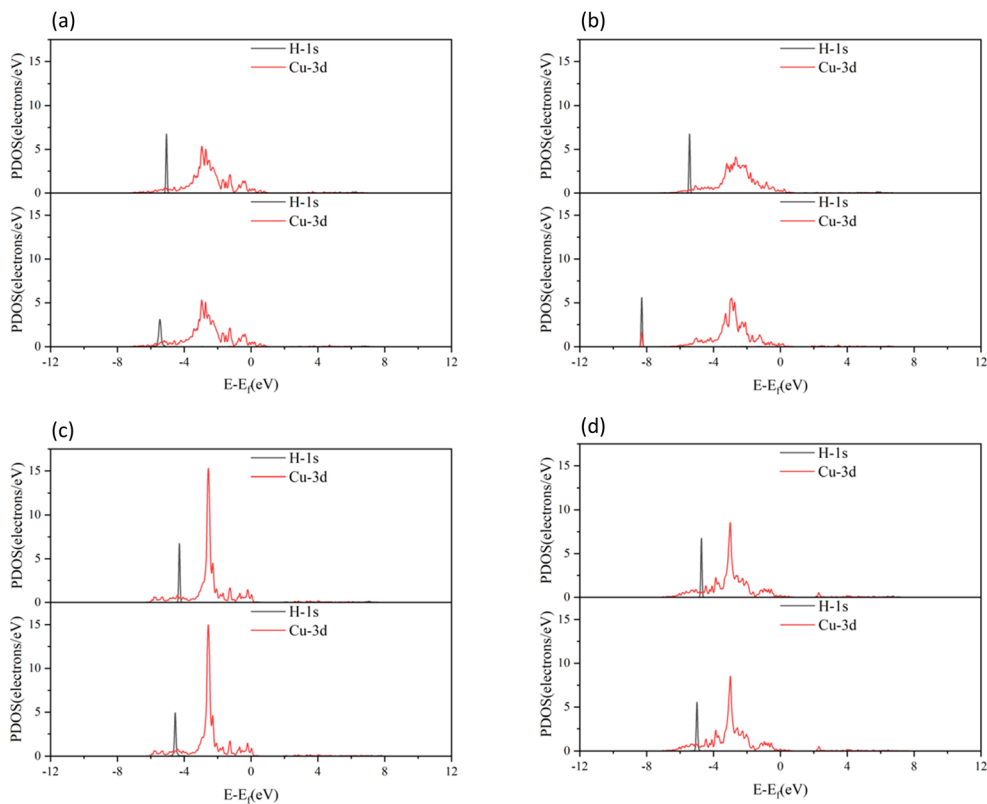


Fig. 7 PDOS plots of  $H_2$  before and after adsorption on different CuO surfaces: (a)  $H_2$  adsorbed on the intact surface, (b)  $H_2$  adsorbed on surface I, (c)  $H_2$  adsorbed on surface II, and (d)  $H_2$  adsorbed on surface III. In all parts, the top figure shows before adsorption, and bottom figure shows after adsorption.

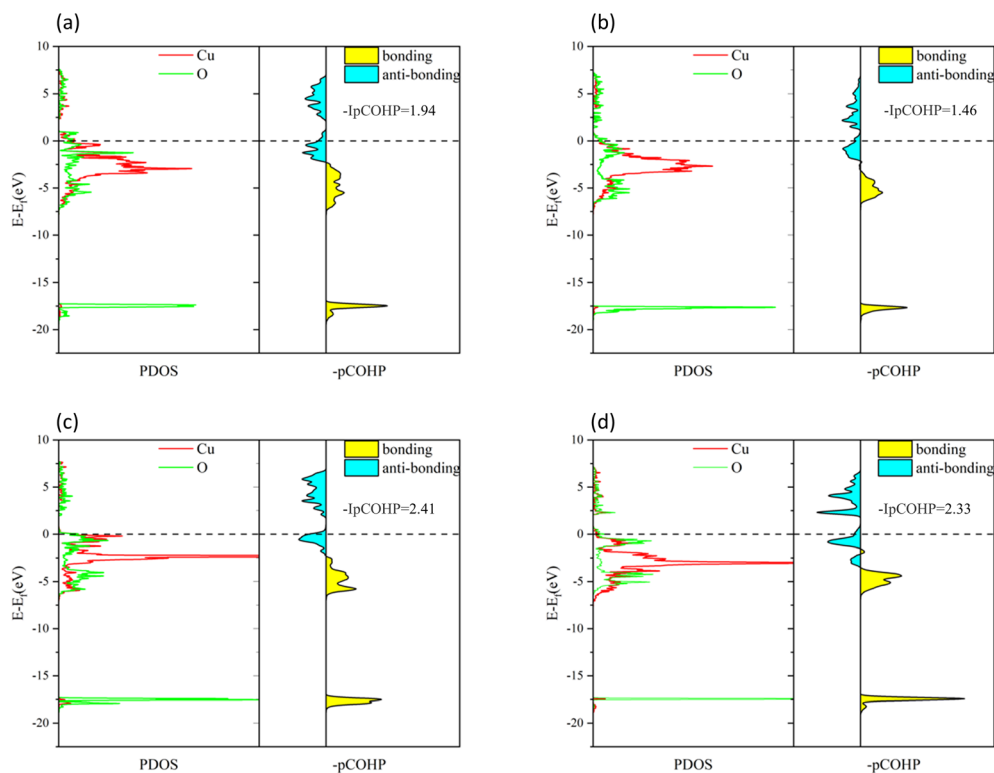


Fig. 8  $-pCOHP$  diagrams of Cu–O bonds on different CuO surfaces: (a) intact surface, (b) surface I, (c) surface II, and (d) surface III.



surfaces with different oxygen vacancy concentrations. The minus integrated projected crystal orbital Hamilton population ( $-IpCOHP$ ) of the Cu–O bond is showed in Fig. 9. It can be found that the strength of the Cu–O bond decreased as the concentration of oxygen vacancies on the surface increased. However, as the oxygen vacancy concentration continued to increase, the surface structure underwent rearrangement to form the  $Cu_2O$  phase. At this point, the strength of Cu–O bond increased again, and then decreased again with further increase in oxygen vacancy concentration. The strength of the Cu–O bond on surface I was reduced, which makes the reaction between  $H_2$  and the CuO surface more likely to occur. Less energy was needed to activate the Cu–O bond, and the entire reaction process occurred more easily. However, with the rearrangement of the surface structure, the strength of the Cu–O bond increased, making the reaction of  $H_2$  with surfaces II and III more difficult again, because the energy requirement for activating the Cu–O bond became higher.

Based on the analysis of the electronic structure, it can be concluded that an appropriate concentration of surface oxygen vacancies enhances the activation capacity of the CuO surface for  $H_2$  molecules and also reduces the strength of the Cu–O bond, which promotes the reaction of  $H_2$  with the surface O atoms. However, an excessive concentration of oxygen vacancies would cause rearrangements on the CuO surface, and the  $Cu_2O$  phase formed would reduce the activation capacity for  $H_2$  molecules and enhance the strength of the Cu–O bond. At the same time, during the reduction of CuO by  $H_2$ , excess oxygen vacancies caused a drastic rearrangement of Cu atoms on the surface of CuO, which increased the reaction energy barrier.

### 3.3 Subsurface oxygen transfer

The process of CuO reduction by  $H_2$  is not a single process in which  $H_2$  reacts with surface O atoms, but also involves the movement of subsurface O atoms to the surface. When oxygen vacancies appear on the surface, subsurface O atoms move upward.  $H_2$  reduction of the CuO surface consumes surface O atoms, and the upward movement of O from the subsurface replenishes the surface O atoms. The two processes compete with each other.

The CuO (111) model utilized in this study with zero  $H_2$  coverage is capable of simulating the transfer of subsurface O

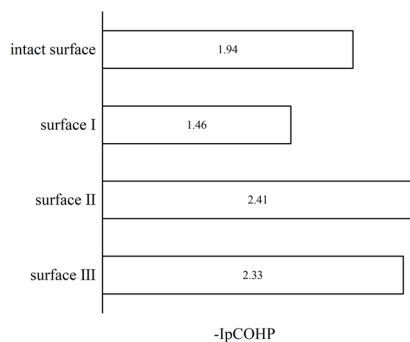


Fig. 9  $-IpCOHP$  diagrams of Cu–O bonds on different CuO surfaces.

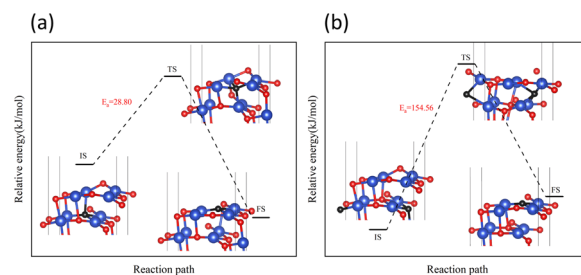


Fig. 10 Transfer paths of two O atoms from the subsurface to the surface: (a)  $O_{sub}^{up}$  transfers (b)  $O_{sub}^{down}$  transfers.

atoms under very low  $H_2$  concentration. As shown in Fig. 2, in the CuO (111) model, there are a total of two types of subsurface O atoms: one is the upward-connected, four-coordinated  $O_{sub}^{up}$  and the other is the downward-connected, four-coordinated  $O_{sub}^{down}$ .

On surface I, both subsurface O atoms could be transferred to the surface to replenish the O, returning the surface to an intact surface. The energy barriers for the upward transfer of these two O atoms were calculated separately. As shown in Fig. 10, on surface I, for the subsurface O atoms to move to the surface, they must first break the Cu–O bonds formed with the subsurface Cu atoms, reaching the transition state in the process. Subsequently, the O atom was bonded with the Cu atoms of the surface. The energy barrier for upward transfer of  $O_{sub}^{up}$  was lower than that of  $O_{sub}^{down}$ , and the transfer of  $O_{sub}^{up}$  to the surface was easier. However, the energy barrier for upward transfer of O atoms in both cases was higher than that for the reaction of  $H_2$  with O atoms on surface I (Fig. 6(b)). Therefore, for surface I, the rate of upward O replenishment at the subsurface was lower than the rate of surface O consumption by  $H_2$ , and the CuO surface became surface II.

Next, the focus was the upward transfer of the subsurface  $O_{sub}^{up}$ , as shown in Fig. 11. For surface II,  $O_{sub}^{up}$  transferred upward, returning the surface to surface I. The energy barrier is as shown in Fig. 11(a). It can be seen that the energy barrier is very high, and it is difficult for subsurface O to transfer upward. Therefore, the CuO surface changed from surface II to surface III.

However, for surface III, the upward transfer of subsurface O became quite easy, and had the upper hand in the competition with  $H_2$  consumption of O on the surface. The CuO surface returned to surface II; that is, the  $Cu_2O$  phase on the surface

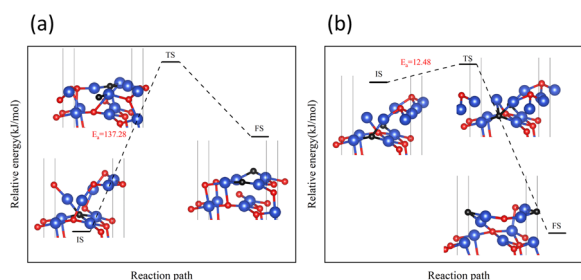


Fig. 11 Transfer path of subsurface  $O_{sub}^{up}$  to the surface on (a) surface II, and (b) surface III.



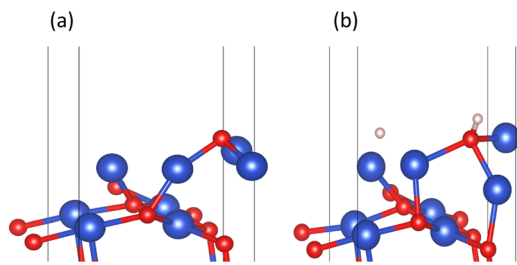


Fig. 12 (a) Surface III and (b) surface III with 0.25 ML  $H_2$  coverage.

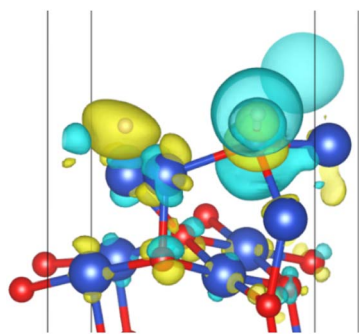


Fig. 13 Surface charge transfer at 0.25 ML  $H_2$  coverage (yellow represents charge increase and blue represents charge decrease).

would remain for a period of time.  $H_2$  continuously consumed O atoms on the surface, and subsurface O atoms were continuously transferred to the surface to replenish it, reaching a dynamic equilibrium. This coincides with the experimental observation of the reaction process  $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$  under low  $H_2$  concentration.

However, in experiments, the  $Cu_2O$  phase<sup>7</sup> was not observed when the  $H_2$  concentration was high. The surface III with  $H_2$  coverage of 0.25 ML could simulate subsurface O atoms transfer under high  $H_2$  concentration, as shown in Fig. 12. This could be considered as having one  $H_2$  molecule on the surface III. However, this  $H_2$  molecule, after dissociation, occupied a surface oxygen vacancy and the top position of an O atom, respectively. Fig. 13 shows the charge transfer on the surface when there are H atoms on the surface. It can be seen that

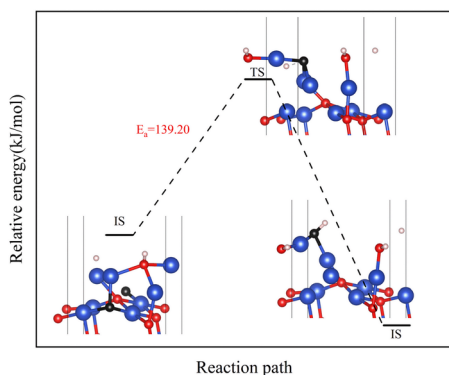
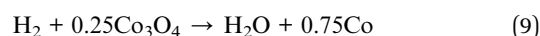
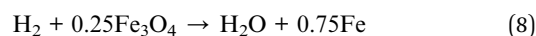
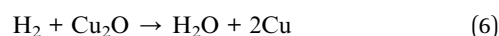
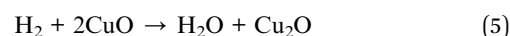


Fig. 14 Transfer path of subsurface  $O_{sub}^{up}$  to the surface at 0.25 ML  $H_2$  coverage.

a large amount of charge was distributed around the H atoms on the oxygen vacancies. Fig. 14 illustrates the energy barrier for the O atom transfer process. For surface III, when oxygen vacancies were occupied by H atoms, the upward transfer of oxygen atoms required a large amount of energy to overcome the barrier. The transition state structure no longer occurred in the process of O atoms breaking the Cu–O bond with subsurface Cu atoms. Instead, it occurred in the process of forming H–O bonds between surface O and H. The transfer of subsurface O atoms was particularly difficult when the oxygen vacancies were occupied by H atoms. This may be due to the fact that H–O bonding replaces the original Cu–O bond breaking as a key step in the upward transfer of subsurface O. In the case of a high  $H_2$  concentration, surface III cannot return to surface II, which requires the replenishment of subsurface O. Instead, the surface changes to surface IV due to the reaction of the surface with  $H_2$ . Therefore, when the  $H_2$  concentration is high, the  $Cu_2O$  phase cannot be stabilized, and only the  $Cu^{2+} \rightarrow Cu^0$  process can be observed in the experiment.

### 3.4 Thermodynamic analysis

The thermodynamic analysis of the  $H_2$  reduction process of CuO was investigated. According to relevant papers on thermodynamics, the change of Gibbs free energy ( $\Delta G$ ) can predict the direction and spontaneity of chemical reactions.<sup>40</sup>  $Fe_3O_4$ ,  $Co_3O_4$  and NiO are other common oxygen carriers for chemical looping combustion.<sup>41–43</sup> The thermodynamic analysis of the reaction between these other common oxygen carriers and  $H_2$  was used for comparison with the reaction between CuO and  $H_2$ . The reactions occurring during the  $H_2$  reduction of CuO and the reactions of other common oxygen carriers with  $H_2$  are listed below.



$\Delta H$  and  $\Delta G$  of each reaction are shown in Fig. 15. All reactions (reaction (5)–(10)) show the same trend. As the temperature increased, both  $\Delta H$  and  $\Delta G$  decreased, indicating that the reactions were more favorable at higher temperatures. The reduction of CuO to  $Cu_2O$  by  $H_2$  (reaction (5)) released more heat compared to the reduction of  $Cu_2O$  to Cu by  $H_2$  (reaction (6)). According to the  $\Delta G$ , it could be concluded that reducing CuO to  $Cu_2O$  by  $H_2$  is easier than reducing  $Cu_2O$  to Cu by  $H_2$ . The DFT calculation in this study obtained the same result that the reduction of CuO to  $Cu_2O$  by  $H_2$  was more likely to occur and released more heat as thermodynamic analysis. The reaction between  $Fe_2O_3$  and  $H_2$  was an endothermic reaction (reaction



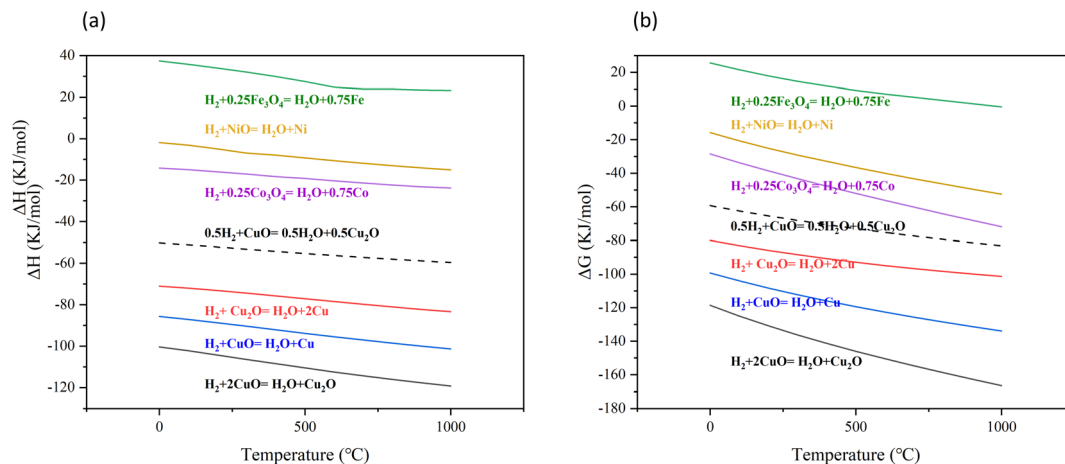


Fig. 15 The trend of  $\Delta H$  and  $\Delta G$  for each reaction with temperature changes.

(8)). The reaction between NiO and  $H_2$  was exothermic, but the heat released was small (reaction (10)). Compared to the reaction between NiO and  $H_2$ , the reaction between  $Co_3O_4$  and  $H_2$  released more heat (reaction (9)). However, in contrast to these common oxygen carriers, the reaction between CuO and  $H_2$  released much more heat. The molar ratio of  $H_2$  to CuO in reaction (5) was 1 : 2 and 1 : 1 in reaction (6). Compared to reaction (6), reaction (5) required more CuO at the same molar amount of  $H_2$ . It can be observed that when the  $H_2$  concentration was low, the amount of CuO was sufficient, and reaction (5) was thermodynamically favorable. However, as the  $H_2$  concentration increased, the amount of CuO limited the reaction. Under the same amount of CuO, reaction (6) was more likely to occur.

## 4 Conclusions

In this study, DFT and thermodynamic calculation were used to study the whole process of the reaction between the CuO (111) surface and  $H_2$  as well as the transfer of subsurface O atoms at different  $H_2$  coverage (0 ML, 0.25 ML). Throughout the entire process of  $H_2$  reduction of the CuO (111) surface, the surface Cu atoms underwent the transformation process of  $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$ . As the reaction proceeded, the concentration of surface oxygen vacancies increased, and the CuO surface underwent rearrangement of O atoms to form the  $Cu_2O$  phase. The Cu–O bond of the  $Cu_2O$  phase was more stable than the Cu–O bond of the CuO phase, and it was therefore more difficult to reduce  $Cu_2O$  with  $H_2$  than to reduce CuO. The surface  $H_2$  coverage could reflect the concentration of  $H_2$ . As the surface oxygen vacancy concentration increased, it was more likely that the subsurface O atoms transfer to the surface at zero  $H_2$  coverage, allowing the surface to maintain a stable  $Cu_2O$  phase. However, when the  $H_2$  coverage was 0.25 ML, the H atoms on the surface hindered the upward transfer of O atoms from the subsurface; therefore, O atoms on the surface was not replenished timely, and the  $Cu_2O$  phase could not be maintained stably. Through thermodynamic analysis, compared to other oxygen carriers ( $Co_3O_4$ , NiO), the reaction between CuO and  $H_2$  released more

heat. The concentration of  $H_2$  affects the reaction products of  $H_2$  with CuO. In summary, the concentration of  $H_2$  affected the valence state of surface Cu by affecting the transfer of subsurface O atoms. It could be considered that as long as the surface oxygen vacancies were occupied by H atoms, subsurface O atoms could not transfer upward in a timely manner, preventing the stable existence of the  $Cu_2O$  phase. However, there are various arrangements of H atoms on the surface of CuO, and this study only investigated one particular configuration to examine its impact on subsurface O atom transfer. The study of the effects of different arrangements of H atoms on the surface of CuO will be a primary focus for future research. Meanwhile, AIMD and KMC are two other excellent methods for studying chemical reactions. The application of AIMD and KMC methods will also become the focus of our future work.

## Author contributions

Y. Wu performed the calculations and the data analysis and R. Fang prepared the draft of the manuscript. L. Shen initialized the project and proposed the supervision. H. Bai provided the VASP software copyright. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (grants no. 52376099).

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