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Nitrogen doping can greatly increase $O_w$ activity, which affect the mercury oxidation/chemical adsorption abilities on CuCo$_2$O$_4$(110) surface.
Effect of nitrogen doping on the mercury oxidation/chemical adsorption on CuCo$_2$O$_4$ (110) surface: a molecular-level description

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Based on density functional theory (DFT) calculations, the detailed mercury oxidation/chemical adsorption mechanisms on the N-doped CuCo$_2$O$_4$ (110) surface are studied. The DFT calculations show that O$_a$ (bonded with one Cu$^{2+}$ ion and one Co$^{3+}$ ion) is far more active than O$_b$ (bonded with three Co$^{3+}$ ions) and the mercury oxidation/chemical adsorption activation energy ($E_a$) on virgin CuCo$_2$O$_4$(110) surface involving O$_a$ is 0.85 eV. The physical adsorbed mercury overcomes the $E_a$ and enters energy well that plays an important role in the mercury oxidation/chemical adsorption. Nitrogen doping can greatly increase the activity of O$_a$ and decrease the activity of O$_b$ at the same time, which greatly affect the mercury oxidation/chemical adsorption abilities on CuCo$_2$O$_4$(110) surface and the $E_a$ variation of the mercury oxidation/chemical adsorption are as follows: 0.85 eV (virgin CuCo$_2$O$_4$(110)) → 0.76 eV (one N-doped CuCo$_2$O$_4$(110)) → 0.69 eV (two N-doped CuCo$_2$O$_4$(110)) → 0.48 eV (three N-doped CuCo$_2$O$_4$(110)). In addition, N-doping can decrease the adsorption energy of mercury and mercuric oxide. The effect of N-doping on the bonding mechanism of mercury adsorption on CuCo$_2$O$_4$(110) surface is analyzed by local density of state (LDOS) and natural bonding orbit (NBO). The calculation results are corresponding well to the experimental data.

1. Introduction

Complex oxides (containing two or more types of cations) with spinel structure are of intense interests in material research because of their remarkable optical, electrical, magnetic, catalytic properties and widespread applications in science and engineering.$^1$ Among these, spinel cobaltites (MC$_2$O$_4$: M = Co, Cu, Mn, Ni, Zn, Mg, etc.) have recently drawn considerable attention by virtue of their superior physicochemical properties and tremendous potential for many technological applications, ranging from catalysts and sensors to electrode materials and electrochromic devices.$^2$

Copper cobaltite with the general formula Cu$_x$Co$_{3-x}$O$_4$ is well known for the catalytic activity towards the oxidation of CO to CO$_2$, carbon monoxide hydrogenation, mercury oxidation, anode for lithium-ion batteries, automobile pollution control and oxygen evolution.$^3$-$^{10}$ Copper cobaltite spinel crystals with various structural/morphological characteristics (i.e., particle size, shape, stoichiometry and cation distribution) can be prepared by diverse synthetic routes including nitrate decomposition,$^4$ urea combustion,$^11$ co-precipitation,$^{12}$ sol-gel$^{13}$, hydrothermal$^{14}$, aerosol pyrolysis$^{15}$, anodic electrodeposition$^{16}$ and so forth.

The nonmetal doping technique has been investigated as an alternative approach to the photocatalytic degradation of various environmental pollutants and the interstitial nonmetal atoms are responsible for visible-light response.$^{17}$ Halide ions, such as Cl$^{-}$ and F$^{-}$, are used to decrease lattice oxygen activity and enhance the redox strength of perovskite-type oxides (ABO$_3$). The halogen-doped process can convert these materials to selective catalysts for the oxidation of ethane to ethene.$^{18,19}$ Usually, the cation Cu$^{2+}$ in spinel CuCo$_2$O$_4$ is used to replace the Co$^{3+}$ in CoCo$_2$O$_4$ to modify its catalytic activity. Except for the cation, the anion O in CoCo$_2$O$_4$ or CuCo$_2$O$_4$ can be replaced by other nonmetal elements to modify their catalytic activity. In previous work, nitrogen-doping is used to improve the Hg$^{2+}$ oxidation/chemical adsorption ability of CuCo$_2$O$_4$. However, the associated reaction mechanisms are not clear and need to be further explored.$^{21}$ This is because the reaction mechanisms can help us understand how the doped nonmetals affect the activity of CuCo$_2$O$_4$. Specifically, it is of great interest to know the location of the doped nonmetals, to predict the properties of the materials doped with other nonmetals, and to understand the mechanisms involved, which can help building a new atlas for the design of cost-effective materials.

To study the mercury oxidation/chemical adsorption mechanism on different nitrogen doped CuCo$_2$O$_4$, the density functional theory (DFT) that has been widely used to research the mechanisms of reactions on the surface of transition metals and metal oxides is needed.$^{22-25}$ In the present work, a periodic self-consistent DFT investigation in mercury oxidation/chemical adsorption on the surfaces of virgin CuCo$_2$O$_4$(110) and other different N-doped CuCo$_2$O$_4$(110) is performed, and the thermochemistry and detailed energetic aspects of the elementary steps are discussed.

2. Methods

The calculations of the total energy associated with the Hg adsorption on the surface of CuCo$_2$O$_4$(110) are carried out using the CASTEP in Materials Studio software package. Ultrasoft pseudopotential (USP) is chosen as the parameter in all calculations. The generalized gradient approximation (GGA) proposed by Perdew et al. (Perdew–Burke–Ernzerh, PBE) is employed to estimate the exchange-correlation potential.$^{26}$ Because the N-doped system that bring problems for the U and J determination and our concerns, DFT+U is not used. In this
study, the clean surfaces of four-layer p(2x2)-CuCo$_2$O$_4$(110) slab separated by a vacuum of 20 Å are modeled. The cut-off energy of plane-wave is 380 eV. A 4x4x1 k-point grid for the p(2x2) cell with Monkhorst-Pack scheme is used because preliminary calculations indicated that energy is sufficiently convergent. During our calculations, the positions of two top layers of CuCo$_2$O$_4$(110) slab and Hg molecules are assumed to be mobile with the forces on the ions being less than 0.02 eV/Å while the positions of two bottom layers are fixed. Furthermore, a 0.1 eV Fermi broadening band is chosen to smear the occupation of the bands around $E_F$ using a finite-T Fermi function under condition of 0 K. The lattice parameters calculated with the method described are close to the experimental results (see S1).

The binding energy (54 Kcal/mol) of HgO is corresponding well with the values $53 \pm 8$ Kcal/mol obtained from experiments. Transition states are located with synchronous transit method that works best when reasonable structures of the reactants and products exist. Complete LST/QST calculations are conducted to confirm the predicted structures of the transition states.

3. Results and Discussion

In this section, the characteristics of minimum energy path identified for each elementary steps considered in this work (Figures 2 to 6) are discussed. Finally, Figure 7 compares the various pathways for mercury oxidation/chemical adsorption on CuCo$_2$O$_4$(110), based on the energetic of these steps.

3.1. The mercury oxidation/chemical adsorption on CuCo$_2$O$_4$(110)

Shima thought that Cu exists as Cu$^{2+}$ in Co$_2$O$_4$ spinel crystal and the structure can be written as: (Cu$^{2+}$)$_x$(Co$^{3+}$)$_{4-x}$O$_4$. Yogesh Sharma synthesized nano CuCo$_2$O$_4$ with the structure of Cu$_x$Co$_{1-x}$O$_4$ ($x \geq 0.95$). Its cell length (i.e., a, 8.129 Å) is close to that of Cu$_{95}$Co$_{25}$O$_{4}$, 8.133 Å. Although virgin CuCo$_2$O$_4$ crystal is difficult to be acquired, it can be used as a model on behalf of Cu$_{95}$Co$_{25}$O$_{4}$ for study of the mercury oxidation/chemical adsorption micro-mechanism. As we can see, CuCo$_2$O$_4$ derived from spinel Co$_2$O$_4$ whose (110) crystal face was reported to be one of naturally exposed surfaces. For comparison with CuCo$_2$O$_4$(110), in this paper, a periodic self-consistent DFT investigation of mercury oxidation/chemical adsorption on the surfaces of CuCo$_2$O$_4$(110) and different N-doped CuCo$_2$O$_4$(110) is performed.

The notation of atoms in the CuCo$_2$O$_4$(110) slab are shown in Fig. 1. Based on their locations and functions, oxygen atoms in CuCo$_2$O$_4$(110) slab are classified into three types: $O_a$, $O_s$, and $O_w$. $O_a$ represents the oxygen atoms in the bulk of CuCo$_2$O$_4$(110) slab while $O_s$ and $O_w$ stand for those on the CuCo$_2$O$_4$(110) surface. $O_a$ is bonded with one Cu$^{2+}$ ion and one Co$^{3+}$ ion while $O_s$ is bonded to three Co$^{3+}$ ions. $O_w$ and $O_t$ are in different crystal fields, thus possessing different reactivity.

The Hg atom around the $O_a$, $O_s$, and Co$^{3+}$ (the subscript “t” in Co$^{3+}$ means the Co$^{3+}$ on the top layer) on the CuCo$_2$O$_4$(110) surface can take different locations, but only one adsorption state (Hg$_t$), located at the top of Co$^{3+}$ is energetically favorable for physical adsorption.

The elementary steps associated with physical and chemical adsorption on the CuCo$_2$O$_4$(110) surface, and the relevant energy profiles for possible reaction routes involving $O_a$, $O_t$, and $O_s$ have been studied. The results are presented in Fig. 2 (See S1 for the structure data).

The energy change in the first step or physical adsorption of gas-phase elementary mercury on CuCo$_2$O$_4$(110) is -0.25 eV and thus is exothermic. The calculated inter-atomic distances of Hg-Co$^{2+}$, Hg-O$_{as}$, and Hg-O$_s$ are 2.75, 3.17 and 3.33 Å, respectively, which indicates no chemical bonds are formed among Hg-Co, Hg-O$_s$, and Hg-O$_{as}$. In other words, Hg atoms are only physically adsorbed on the surface of CuCo$_2$O$_4$(110). The physical adsorption of Hg$^0$ on the CuCo$_2$O$_4$(110) surface leads to the proximity of the Hg$^0$ atom to either O$_a$ or O$_s$ and the formation of intermediates containing Hg-O-Co$^{2+}$ bond after passing the transition states of (Hg-O-Co$_t$) or (Hg-O-Co$_s$) with energy barriers of 0.85 or 1.83 eV, respectively. For the reverse reaction, the activation energy involving O$_a$ is 0.28 eV and higher than that involving O$_s$ (0.05 eV). Therefore, the intermediate M1 involving O$_s$ is more stable than the intermediate involving O$_a$. Based on the activation energy values of forward and reverse reactions, the formation of M1 is a favorable mercury oxidation/chemical adsorption route. The bond length of Hg-O$_{as}$ in (Hg-O-Co$_t$)$_{TS}$ is 2.56 Å, which decreases to 2.47 Å when (Hg-O$_{as}$)$_{TS}$ change into M1.

For M1, there are three possible reaction pathways as shown in Fig. 3. The first pathway is the escape of HgO molecule from M1 to flue gas and leaves an oxygen vacancy (O$_{as}$) site, which is endothermic and needs 4 eV energy. The re-oxidation of O$_{as}$ by O$_s$ in the flue gas leads to the healing of the surface and leaves an O radical. The second reaction pathway is the reaction between M1 and oxygen radical to produce HgO-slab and heal the O$_{as}$, which needs 1.71 eV activation energy and releases 1.75 eV energy as presented in Figure 3b. The third reaction pathway is that M1 overcomes 0.085 eV energy to form another intermediate M1’ (Fig. 2). M1’ can react with O$_2$ to form HgO-O-slab and release 1.05 eV energy. HgO-O-slab can further form HgO-slab and O-slab and the activation energy is 0.63 eV. Among them, HgO-slab is on behalf of the mercury oxide adsorption on CuCo$_2$O$_4$(110) surface and the adsorption energy is 3.13 eV.

3.2. The mercury oxidation/chemical adsorption on 1N doped CuCo$_2$O$_4$(110)
Fig. 2 Reaction pathways of Hg adsorption and oxidation on the virgin CuCo$_2$O$_4$ (110) surface. (Solid line: the reaction way through O$_w$; dot line: the reaction way through O$_s$).

Fig. 3 Energy profile of the different reaction pathways between (a) M1 and O$_2$ and (b) M1 and O radical.

As presented in Fig. 1, there are three types of O atom (O$_b$, O$_w$, O$_s$) on CuCo$_2$O$_4$(110) slab, and all of them may be substituted by nitrogen atoms. When O$_b$ is substituted by one N atom, there are two different reaction pathways involving O$_b$ and O$_w$, respectively. Similarly, O$_w$ or O$_s$ can be substituted by N atom and there is one reaction pathway pertaining to O$_w$ or O$_s$, respectively. The energy profiles of the four possible reaction pathways are shown in Fig. 4 (See S1 for the structure data). Among the structures resulting from different N substitutions, the one containing N$_b$ has the lowest energy. This suggests that N atom prefers to replace the O atom in the bulk rather than on the surface, due to the fact that N is trivalent while O is divalent, and the bulk is better than the surface to satisfy the bonding requirement of N and reduce the formation of the dangling bonds on the surface. When O$_b$ is substituted by Nitrogen atom, the transition state of the reaction pathway (solid line in Fig. 4) involving O$_w$ has the lowest activation energy. Therefore, the mercury oxidation/chemical adsorption pathway involving O$_w$ on the O$_b$ substituted CuCo$_2$O$_4$(110) surface is favorable.

The first step of mercury oxidation/chemical adsorption on the surface of N-doped CuCo$_2$O$_4$(110) is the physical adsorption of mercury on slab (Hg$_a$), which releases 0.2 eV energy. The adsorption site is Co$^{3+}$ and the length between Hg and Co$^{3+}$ is 2.83 Å. The second step is similar to the oxidation/chemical adsorption of Hg on the surface of virgin CuCo$_2$O$_4$ (110) and the physically adsorbed Hg atom interacts with O$_w$ to form M2.
intermediate that contains Hg-O\textsubscript{a}-Co\textsuperscript{3+} structure through overcoming an energy barrier of 0.76 eV.

As shown in the Fig. 4 (solid line), the transitional state and stable intermediate species of the most favorable reaction pathway are TS(Hg-O\textsubscript{a})\textsubscript{N} and M2, respectively. The distance between Hg and O\textsubscript{a} changes from 3.21 to 2.59 Å, when Hg existence form changes from Hg\textsubscript{a} to the transitional state, TS(Hg-O\textsubscript{a})\textsubscript{N}. The distance continue decrease from 2.59 to 2.51 Å, when the Hg existence form changes from TS(Hg-O\textsubscript{a})\textsubscript{N} to M2. The structural parameter variation suggests a process of mercury adsorption going through physical adsorption to chemical adsorption on the N doped CuCoO\textsubscript{4} (110) surface. Compared with that (0.85 eV) on virgin CuCoO\textsubscript{4}(110) surface, the activation energy (E\textsubscript{a}) of mercury oxidation/chemical adsorption on 1N doped CuCoO\textsubscript{4}(110) decreases to 0.76 eV.

3.3. The mercury oxidation/chemical adsorption on 2N doped CuCoO\textsubscript{4}(110)

In this section, the mercury oxidation/chemical adsorption on two nitrogen doped CuCoO\textsubscript{4}(110) surface is studied. When two O\textsubscript{b} atoms on the virgin CuCoO\textsubscript{4}(110) surface are substituted by the corresponding Nitrogen atoms, theoretically, two reaction pathways involving the O\textsubscript{a} or O\textsubscript{b} respectively should exist. However, the reaction pathway involving O\textsubscript{b} cannot be found due to its low activity. For the same reason, when two N atoms substitute one O\textsubscript{b} atom and one O\textsubscript{a} atom, the reaction pathway involving the O\textsubscript{a} does not exist. When two N atoms substitute one O\textsubscript{b} and one O\textsubscript{a}, the reaction pathway involving the O\textsubscript{b} exists. The energy profiles of the two mercury oxidation/chemical adsorption pathways on 2N doped CuCoO\textsubscript{4}(110) surface are shown in Fig. 5 (See S1 for the structure data).

Among different 2N doped CuCoO\textsubscript{4}(110) slab, the CuCoO\textsubscript{4}-N\textsubscript{bb}(110), which represent the structure where two O\textsubscript{b} in CuCoO\textsubscript{4}(110) are substituted by Nitrogen, has the lowest energy, and is the most stable species. On the contrary, the structure of CuCoO\textsubscript{4}-N\textsubscript{bs}(110) possesses the highest energy. Although the reaction on the CuCoO\textsubscript{4}-N\textsubscript{bs}(110) surface requires the lowest activation energy (0.68 eV), it is not the most favorable reaction pathway due to its highest substitution energy. The doped structure must be thermally stable since it may decompose in a high temperature environment. Therefore, the pathway of mercury oxidation/chemical adsorption on CuCoO\textsubscript{4}-N\textsubscript{bb}(110) surface involving O\textsubscript{b} is favorable under the situation of 2N doped CuCoO\textsubscript{4}(110). The activation energy E\textsubscript{a} of mercury oxidation/chemical adsorption on CuCoO\textsubscript{4}-N\textsubscript{bb}(110) surface (0.69 eV) is lower than that on 1N doped CuCoO\textsubscript{4}-N\textsubscript{bs}(110) surface as obtained in the previous section (0.76 eV).

3.4. The mercury oxidation/chemical adsorption on 3N doped CuCoO\textsubscript{4}(110)

For 3N doped CuCoO\textsubscript{4}(110), theoretically, there are two mercury oxidation/chemical adsorption pathways. When three N atoms substitute two O\textsubscript{b} atoms and one O\textsubscript{a} atom, the reaction pathway involves O\textsubscript{b}. When three N atoms substitute two O\textsubscript{b} and one O\textsubscript{a}, the reaction pathway involves O\textsubscript{a}. However, no reaction pathway exists when the mercury is adsorbed on 3N doped CuCoO\textsubscript{4}-N\textsubscript{bb}(110) surface due to the low mercury oxidation/chemical adsorption ability of O\textsubscript{b}. The energy profiles of mercury oxidation/chemical adsorption on 3N doped CuCoO\textsubscript{4}-N\textsubscript{bb}(110) surface is given in Fig. 6. Although the mercury oxidation/chemical adsorption on 3N doped CuCoO\textsubscript{4}-N\textsubscript{bb}(110) surface involving O\textsubscript{a} atom possesses lower E\textsubscript{a} (0.48 eV) and higher reverse reaction activation energy than that of the pathway on 2N doped CuCoO\textsubscript{4}(110), it may not exist due to its thermodynamic instability. This is because structure CuCoO\textsubscript{4}-N\textsubscript{bb}(110) has higher energy than CuCoO\textsubscript{4}-N\textsubscript{bs}(110). Therefore, 3N doped CuCoO\textsubscript{4}(110) is difficult to oxidize/chemical adsorb the mercury.

Based on the discussion of sections 3.1 - 3.4, the mercury oxidation/chemical adsorption network on CuCoO\textsubscript{4}(110) and...
different N-doped CuCo$_2$O$_4$(110) surface is shown in Fig. 7. The factors affecting the mercury oxidation/chemical adsorption ability of different N doped CuCo$_2$O$_4$(110) include the activation energy of forward reaction ($E_a$) and reverse reaction ($E_a^{-1}$), the energy levels of N doped CuCo$_2$O$_4$(110) slab, and the number and location of N atoms doped on CuCo$_2$O$_4$(110). It should be emphasized that doped N atoms will replace O atoms located on the CuCo$_2$O$_4$(110) surface and thus reduce the number of the oxygen atoms that can oxidize the mercury. Therefore, there should be an optimal N-doping dosage to balance the effect of the O atoms decrease on the N-doped CuCo$_2$O$_4$(110) surface and that of activation energy decrease due to N-doping. The experiment showed that, for N doped CuCo$_2$O$_4$, the optimal doping ration of N to Co is 30 mol\%[20].

3.5 General comments on the mechanism of Hg$^+$ adsorption
Fig. 7 Reaction network for mercury oxidation/chemical adsorption on CuCo$_2$O$_4$(110) and N-doped CuCo$_2$O$_4$(110) surface. The unit of thermochemistry and kinetic barrier data for the elementary steps is given in electron volts.

Fig. 8 The LDOS analysis of Co$^{3+}$ and Hg before and after mercury physical adsorption on CuCo$_2$O$_4$(110) surface [a: Hg; b: Hg adsorbed on CuCo$_2$O$_4$(110); c: Co$^{3+}$; d: Co$^{3+}$ with Hg adsorption].

on the different N-doped CuCo$_2$O$_4$(110) surfaces

The parameters $\Delta E_{ad}$, $\Delta E_{HgO}$, $E_a$ and $E_{a-1}$ of the favorable reaction pathways for virgin and N-doped CuCo$_2$O$_4$ (110) surfaces show some kinds of variation trends. Here, $\Delta E_{ad}$ is the mercury physical adsorption energy, $\Delta E_{HgO}$ is HgO adsorption energy; $E_a$ is activation energy; and $E_{a-1}$ is the activation energy of reverse mercury oxidation/chemical adsorption. In addition to reducing the $E_a$, N-doping can also decrease the adsorption energies of mercury and mercuric oxide (S1 table2).

Experiments on mercury oxidation/chemical adsorption show that with a continuous increase of adsorption temperature from 373 to 623 K, the Hg$^0$ removal ability of CuCo$_2$O$_4$ increases from 10 to 71.3%. Compared with virgin CuCo$_2$O$_4$, the Hg$^0$ oxidation ability of N doped CuCo$_2$O$_4$ reaches 91% at 623 K and is significantly higher, especially at low temperatures. The temperature independence of N doped CuCo$_2$O$_4$ indicates that N-doping greatly lowers the active energy of oxidation reaction. This is consistent with our DFT calculation results. When the temperature is above 623 K, the Hg$^0$ removal abilities of CuCo$_2$O$_4$ and N doped CuCo$_2$O$_4$ decreases and those of N-doped CuCo$_2$O$_4$ decrease even faster than CuCo$_2$O$_4$[20]. The lower the $E_{a-1}$ is, the easier the reverse reaction of mercury oxidation will be.
As we can see, N-doping process decreases the $E_a$ and $E_{t1}$ at the same time. Furthermore, higher temperature would help the release of HgO from the sorbents' surface (i.e. the reactions of HgO-(slab-O$_t$) → HgO$^-$ + (slab-O$_t$) and HgO-slab → HgO + slab). Due to these factors in forward and backward directions, there should be an optimal adsorption temperature to maximize the Hg$^0$ removal ability and capacity for CuCo$_2$O$_4$(110) and N-doped CuCo$_2$O$_4$(110). When the temperature increases over the optimal temperature in an environment of lower mercury partial pressure, the chemically adsorbed mercury can be released into gas phase and spent CuCo$_2$O$_4$ can be regenerated.

Natural Bond Orbital (NBO) analysis using Gaussian 03 shows that when mercury adsorbs on CuCo$_2$O$_4$(110) surface, its 6s(o) orbital hybridizes with Co$^{3+}$ orbital forming BD(1)$^*$Co$^{3+}$Hg and BD*(1)$^*$Co$^{3+}$Hg (BD represents bonding orbital and BD* represents anti-bonding orbital) which distribute the electron over the system (S1 table3 and table 4). When O$_t$ is substituted by N, the interaction between LP(6s)Hg (LP represents lone pair) and BD(1)$^*$Co$^{3+}$O$_t$ will be replaced by the interaction between LP(6s)Hg and BD(1)$^*$Co$^{3+}$N$_t$. The latter has less second order perturbation stabilization energies. Therefore, N-doped sorbents will have lower physical Hg$^0$ adsorption energies.

Local Density of State (LDOS) analyses show the contribution of an atom’s electronic states to the electronic hybridization in the system and thus the qualitative reflection in the energy spectrum. Fig. 8 shows that when mercury is not adsorbed by CuCo$_2$O$_4$(110) slab, the energy band of its 6s orbital is located at -1.3 eV and that of 5d is located at -4.5 eV. When mercury is physically adsorbed by CuCo$_2$O$_4$(110), its 6s and 5d energy bands shift to -2.7 and -5.6 eV, respectively. The energy bands of Co$^{3+}$ are located between -7.5 and 2 eV. Since the size of Co$^{3+}$ is much smaller than that of Hg$^0$ atom and Co$^{3+}$ located on the surface of slab, its electronic orbitals are hard to be polarized. Thus, the energy bands of Co$^{3+}$ do not have apparent changes before and after Hg$^0$ adsorption.

In order to understand the effect of N-doping on CuCo$_2$O$_4$(110) slab, the LDOS analyses of Hg adsorption on virgin CuCo$_2$O$_4$(110) and 3N doped CuCo$_2$O$_4$(110) surfaces are shown in Fig. 9. N doping will affect the orbit hybrid status of Co$^{3+}$ in the slab. From Figure 9, we can see that the replacement of O$_t$ and O$_b$ by N will introduce a new energy band for Co$^{3+}$ between -13 and -16 eV, but reduces the peak height of the energy band between -18 and -20 eV. The electronic status change of Cu$^{2+}$ can affect the electronic status of O$_b$ bonded to Co$^{3+}$. We can see that the small energy band of O$_b$ at -19.5 eV disappears, and a new small energy band appears at -15 eV. However, the energy band of Cu$^{2+}$ connecting to O$_t$ does not shift (keeps between -17 and -20 eV). Therefore, the bond strength between O$_t$ and Cu$^{2+}$
is decreased and O$_a$ of 3N doped CuCo$_2$O$_4$(110) becomes more active than that of CuCo$_2$O$_4$(110).

4. Conclusions

The mercury oxidation/chemical adsorption on virgin CuCo$_2$O$_4$(110) and different N doped CuCo$_2$O$_4$(110) surfaces are studied. The detailed energy profiles of the possible reaction pathways are discussed. Based on their activation energy, the energy levels of N doped CuCo$_2$O$_4$(110) slab, the stability of physical or chemical adsorption intermediates, the favorite reaction pathways are selected and thus the detailed mechanisms are provided. By analyzing the calculation results, we found that the O$_a$ is the most active site on the surface of CuCo$_2$O$_4$(110) and the N-doping can increase the activity of O$_a$ through increasing the LDOS at higher energy and deactivate that of O$_b$ at the same time. Due to O$_a$’s high activity, the activation energy of mercury oxidation/chemical adsorption decreases from 0.85 eV (virgin CuCo$_2$O$_4$(110)) to 0.69 eV (2N doped CuCo$_2$O$_4$(110)). The LDOS analyses demonstrate that the doped N atom decrease the bond strength between O$_a$ and Cu which activate O$_a$ further.

Notes and references

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