Study on the adsorption selection of CH₄ on CuO (110) versus (111) surfaces: a density functional theory study

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Abstract

Finding the active sites of suitable metal oxides is a key prerequisite for detecting CH₄. The purpose of the paper is to investigate the adsorption of CH₄ on intrinsic and oxygen-vacancies CuO (111) and (110) surfaces using density functional theory calculations. The results show that CH₄ has a strong adsorption energy of -0.370 to 0.391 eV at all site on the CuO (110) surface. The adsorption capacity of CH₄ on CuO (111) surface is weak, ranging from -0.156 to -0.325 eV. In the surface containing oxygen vacancies, the adsorption capacity of CuO surface to CH₄ is significantly stronger than that of intrinsic CuO surface. The results indicate that CuO (110) has strong adsorption and charge transfer capacity for CH₄, which may provide experimental guidance.

Keywords CuO · First principle calculations · Oxygen vacancies · Adsorption · CH₄

1 Introduction

In recent years, the development of new gas sensors has received widespread attention. In particular, people are sensitive to toxic, flammable, explosive, and polluting gases present in homes, industrial sites, and the environment [1, 2]. Methane is highly explosive and flammable, so developing a methane sensor with low cost, high sensitivity, good selectivity, and stable performance has become a hot spot [3–6]. In the study of CH₄ adsorption materials, it is usually microporous carbon [7], metal-organic Frameworks [8], layered InN [9], and Ni surface [10]. In recent years, there have been many studies on methane sensors, mainly including light interference methane sensors, metal oxide semiconductor gas sensors, infrared adsorption fiber optic methane sensors, and electrochemical methane sensors. Compared with other types of methane sensors, metal oxide semiconductor gas sensors are cheaper and people are more interested in their research

[11–15]. Among transition metal oxide (TMO) compounds, copper oxide (CuO) is an important transition metal *p*-type semiconductor material and exhibits unique properties, with a narrow bandgap (1.3–1.6 eV) [16, 17]. It has good thermal stability and high durability [18], so it is widely used in many fields such as gas sensors [19, 20] and catalyst carriers [21, 22].

At present, there have been some studies on CuO semiconductor adsorption of small-molecule gases. Maimaiti et al. [23] studied the two different reduction mechanisms of oxygen vacancies (*V_O*) formation and H₂ adsorption on the surface of CuO (111) through the first-principles. CuO reduction provides a mechanism for Cu. Warren et al. [24] found that multilayers of water can be seen at low temperatures, and the surface monolayer has strong chemisorption with CuO samples. Moreno et al. [25] found through the first-principles that the surface of CuO (110) has a better adsorption effect than intrinsic CuO (intrinsic refers to non-defected), and found the best adsorption

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position of CO₂ on the surface of CuO (110). Hao et al. [26] systematically studied the CuO (111) surface, the effect of surface structure on the adsorption and activation of H₂ was studied, including ideal V_O and pre-coated O atoms surfaces. Sun et al. [27] found that CuO (111) also exhibited good adsorption and dissociation properties for O₂, and the presence of V_O could increase the chemical activity of O₂ dissociation and significantly improve the catalytic activity of CuO (111). But the interaction between CH₄ and CuO is unclear. This motivated us to study the adsorption between CuO surface and CH₄.

This article starts with the working mechanism of the CuO semiconductor adsorption CH₄ gas sensor, the adsorption mechanism of CH₄ on (111) and (110) surfaces under intrinsic and V_O was studied. By comparing the adsorption energy and charge transfer amount, we can conclude that the CuO (110) surface has a strong adsorption capacity for CH₄, and it has the strongest adsorption capacity at the CuO (110) with V_O . The active sites of CuO for CH₄ molecules were found and the adsorption mechanism was elucidated, which provided good guidance for the experiment of CH₄ detection or sensor design.

2 Model and computational method

For the two important crystal face (110) and (111) of CuO, we modeled three-layer slab 2×4 and 4×2 supercells containing 96 atoms, respectively. The periodicity of the boundary is suitable for the whole supercell, which can be replicated periodically throughout space. Figure 1 shows the side and top views of CuO (110) and (111) surfaces. Five different surface adsorption sites are considered for each surface, including central 1, central 2, O atom, Cu 1 atom, Cu 2 atom, named A, B, C, D, E, respectively. Directly above each site, there are three different configurations of CH₄ molecules, named up (U), parallel (P), and down (D). When the molecules are adsorbed to the surface site, we use X-Y to express it (X represents the adsorption site, Y represents the orientations of CH₄). In all geometric optimization calculations, The bottom layer of CuO with three-layer structure is fixed to maintain its volume to better study the surface adsorption of CH₄. A vacuum layer perpendicular to the surface for 15 Å in the Z direction is sufficient to avoid periodic plate-to-plate interactions in the atomic layer.

All calculations in this paper using the density functional theory (DFT-D) [28] including dispersion force correction are performed using the CASTEP package [29] and the generalized gradient approximation (GGA) functional. The Perdew–Burke–Ernzerhof (PBE) [30] was selected for calculation. The cut-off energy is set to 420 eV. The geometry of the structure is considered convergent until the energy is

Fig. 1 Schematic representations of the CuO, **a** (110) 2×4 super-cell, **b** (111) 4×2 super-cell. The pink and red balls represent O and Cu atoms, respectively

reduced to 1.0×10^{-5} Ha/ atomic and each atomic force is less than 0.05 eV/Å. The Monkhorst–Pack k -point is $2 \times 2 \times 1$. The interaction strength between CuO surface and CH₄ molecules are expressed by the adsorption energy (E_{ads}) via [31]

$$E_{\text{ads}} = E_{\text{CuO/CH}_4} - E_{\text{CuO}} - E_{\text{CH}_4}$$

where $E_{\text{CuO/CH}_4}$, E_{CuO} , and E_{CH_4} are the total energies of the CuO/CH₄, CuO, and CH₄ systems, respectively.

3 Results and discussion

To verify the consistency of the calculated and experimental values, we first calculated the lattice parameters of CH₄. The calculated C–H bond length and H–C–H bond angle of CH₄ are 1.095 Å and 109.421°, which are close to the experimental values of 1.096 Å and 109.400°, respectively [32]. Then, the next validation test was to predict the lattice constant of intrinsic CuO. The lattice parameters of CuO are in good agreement with the experimental values, such as $a = 4.65$ Å, $b = 3.41$ Å, $c = 5.108$ Å, $\beta = 99.5^\circ$, Cu–O bond distance 1.95 Å [33].

3.1 Adsorption of CH₄ on CuO (1 1 0) and CuO (1 1 1) surfaces with intrinsic and V_O

Table 1 shows the most stable adsorption data of CH₄ at various sites on different CuO surfaces. On the CuO

(110) surface, whether there are V_O or not has little change in electron transfer. However, the adsorption energy ranges of the five sites are $-0.272 \sim -0.335$ eV and $-0.370 \sim -0.391$ eV, respectively. CuO (110) containing V_O is not conducive to the adsorption of CH_4 molecules. The most stable adsorption configurations on the (110) surface are B–D and C–D, respectively. For CH_4 adsorbed on another surface of CuO (111), the adsorption energy ranges between the intrinsic surface and the V_O surface are $-0.156 \sim -0.325$, $-0.182 \sim -0.387$ eV, respectively. The most stable structures are C–D and C–P, the adsorption energy is -0.391 eV and -0.325 eV, and the adsorption distances are 3.154 and 3.332 Å, respectively. Table 1 shows that the most stable adsorption site is above the O atom on the CuO (111) surface. However, on the CuO (111) surface, surfaces with V_O are easier to adsorb CH_4 molecules than intrinsic surfaces. The best adsorption configuration is C–P, and the adsorption energy is -0.387 eV. The result is comparable to the adsorption energy of CH_4 on $\text{Ni}_4/\alpha\text{-Al}_2\text{O}_3$ (0001) surface [34], but higher than that of CH_4 on Nb/G [35] and MgO (100) surface [36].

3.2 Density of states and charge transfer

For the most stable configurations B–D and C–P, the calculated charge transfer (Q) values are -0.17 and -0.20 e, respectively, as shown in Table 1, indicating that CH_4 adsorbs on the CuO surface as a charge acceptor and adsorbs charge from the surface. Next, to get a deeper understanding of the sensitivity mechanism, we computed the partial density of states (PDOS) for the B–D and C–P configurations (Fig. 2). It can be seen from Fig. 2a that the total density of states (TDOS) of CH_4 adsorbed by CuO (110) is mainly contributed by Cu-3d and O-2p orbitals, and there is little change before and after adsorption. After adsorption, the peak of CH_4 shifted to the left, which was contributed by the H-1s and C-2p orbitals of CH_4 at -3.4 eV. In addition, by observing the PDOS of the Cu atom that we selected next to CH_4 , it can be seen that the 3d orbital of the Cu atom before and after adsorption has a slight change. These results indicate that the adsorption system of CH_4 by CuO (110) are stable. Similar to Fig. 2a, b shows the DOS of the C–P configurations and shows that the Cu-3d orbitals contribute almost to the energy band. There are no new electron peaks of CH_4 were observed on these two surfaces, but the electron peaks of CH_4 in the C–P

Table 1 The adsorbed distance (d_{after}), adsorption energy (E_{ads}), and the charge transfer (Q), and the donor/acceptor characteristics between the CH_4 molecules and different surfaces

CuO	Surface	Site	Configu- ration	d_{after} (Å)	E_{ads} (eV)	Q (e)	Style
(110)	Intrinsic	A	D	2.716	− 0.370	− 0.15	Acceptor
		B	D	3.129	− 0.391	− 0.17	
		C	D	2.945	− 0.373	− 0.17	
		D	D	2.842	− 0.370	− 0.18	
		E	D	2.173	− 0.380	− 0.14	
	V_O	A	P	2.941	− 0.310	− 0.16	Acceptor
		B	P	3.295	− 0.320	− 0.13	
		C	D	2.947	− 0.335	− 0.16	
		D	D	2.984	− 0.272	− 0.18	
		E	D	2.961	− 0.296	− 0.15	
(111)	Intrinsic	A	P	2.730	− 0.156	− 0.20	Acceptor
		B	P	3.128	− 0.164	− 0.16	
		C	D	3.470	− 0.325	− 0.10	
		D	U	3.097	− 0.164	− 0.15	
		E	P	2.707	− 0.168	− 0.17	
	V_O	A	D	2.441	− 0.232	− 0.21	Acceptor
		B	P	3.099	− 0.304	− 0.13	
		C	P	2.240	− 0.387	− 0.20	
		D	D	2.733	− 0.182	− 0.18	
		E	D	2.263	− 0.218	− 0.20	
Zhang et al. [34]	−	−	−	2.91	− 0.31	−	−
Jitendra et al. [35]	−	−	−	2.69	− 0.12	−	−
Michal et al. [36]	−	−	−	−	− 0.03	−	−

Fig. 2 Calculated projected PDOS in **a** B–D configuration, **b** C–P configuration. The Fermi level is set as zero in the vertical dash line. ^a means after adsorption, and ^b means before adsorption

configuration were farther away from the Fermi level than those in the B–D configuration. On the one hand, it shows that no new bonds are generated after the system is adsorbed, on the other hand, the B–D configuration is more favorable. Besides, by comparing PDOS of CH₄ molecules before and after adsorption, it is found that there are two discrete peaks of DOS before adsorbing CH₄ molecules. When the CH₄ molecules are adsorbed, the peak shifts to the left about 4.5 eV, indicating that CH₄ molecules becomes stable after adsorption. However, due to the introduction of V_O , the PDOS changes

before and after the Cu atoms next to CH₄ are more obvious, and the 3d orbitals of the Cu atoms after adsorption move about 1 eV to the right, which may be the reason for the higher adsorption energy.

For a more intuitive understanding of the interaction between CH₄ molecules and CuO surfaces, we calculated the Charge density difference, as shown in Fig. 3. Blue areas indicate the gain of electrons, and green areas indicate the loss of electrons. The apparent charge accumulation between the CH₄ molecules and the surface indicates the interaction between the CH₄ molecules and the surface. The Mulliken charge distribution of the CH₄ molecules before and after adsorption is listed in Table 2. For the B–D and C–P configurations, when the CH₄ molecules are adsorbed, the charge transferred by C atom is 0.12 e (1.11 e – 0.99 e) and 0.17 e (1.11 e – 0.94 e), H atoms are 0.29 e (1.11 e – 0.82 e) and 0.37 e (1.11 e – 0.74 e), for B–D and C–P configuration, respectively. The population changed from 0.77 e to 0.86, 0.88 e, respectively, and there is also a slight change in the length of the C–H bond. Moreover, the electron transfer (Fig. 3) between the surface and the CH₄ molecules is –0.17 and –0.20 e, respectively. These results indicate that there are some changes between the inside of the CH₄ molecules, which are consistent with the changes after the CH₄ molecules are adsorbed in Fig. 2.

3.3 The effect of V_O

By studying the adsorption mechanism of B–D and C–P configurations, we find that surfaces containing V_O affect the adsorption. CuO(111) surfaces with V_O enhance the adsorption capacity of CH₄, while CuO(110) surfaces with V_O have a negative effect on CH₄. This is consistent with the results of Sun et al. [27] in studying the adsorption of CH₄ molecules on CuO(111) surface by V_O . Some studies have also shown that the presence of V_O will increase the surface conductivity and enhance the adsorption of CH₄ [37, 38]. It is precise because of the existence of V_O that unsaturated bonds are generated, which leads to a strong adsorption capacity of CuO(111) on CH₄.

Table 2 Mulliken charge distributions CH₄

Model	Species	s (e)	p (e)	Total (e)	Charge (e)	q (e)	Population (e)	Length (Å)
Free CH ₄	C	1.51	3.59	5.10	– 1.11	–	0.77	1.095
	H	2.88	0	2.88	1.11			
B–D	C	1.41	3.58	4.99	– 0.99	– 0.17	0.86	1.095
	H	3.18	0	3.18	0.82			
C–P	C	1.39	3.55	4.94	– 0.94	– 0.20	0.88	1.096
	H	3.26	0	3.26	0.74

Fig. 3 Charge density difference of two configurations (isovalue = $0.002 e / \text{\AA}^3$), **a** B–D configuration, and **b** C–P configuration. Blue and green isosurfaces represent gains and losses of electrons, respectively

4 Conclusions

In conclusion, the adsorption behavior of CH_4 on CuO (110) and CuO (111) with intrinsic and V_O was studied by DFT calculation. It was found that the adsorption capacity of CuO (110) was greater than that of CuO (111) when CH_4 was adsorbed on the CuO surface. On the intrinsic CuO(110) surface, the center of the six-membered ring is the active adsorption site, and on the CuO(111) with V_O , the vacancy is the active adsorption site. During the adsorption process, DOS showed orbital hybridization between CH_4 molecules and surfaces, and the change of CH_4 molecules after adsorption is also obvious. And charge density difference can clearly show the electron transfer between CuO surface and CH_4 molecules. Therefore, this not only provides a reference for the active site of CH_4 adsorption on CuO surface, but also provides a reference for CuO to be a new sensor for detecting CH_4 .

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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