Plane-wave Pseudopotential Density Functional Theory periodic Slab Calculations of NO Adsorption on Cu(111) Surface

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ABSTRACT

Plane-wave pseudopotential Density Functional Theory (DFT) periodic slab calculations were performed using the generalized gradient approximation (GGA) to investigate the adsorption of nitric oxide(NO) on the (111) surface of Cu. Copper surface was simulated using the Periodic Slab Method consisting of five atomic layers. Four different adsorption sites (Atop, Bridge, HCP Hollow, and FCC Hollow) were considered. Results specified that the suitable site for NO adsorption in molecular form is the Hollow FCC site, and molecular adsorption is more stable than dissociative adsorption energetically.

Keywords: NO adsorption; Cu(111) surface; DFT; Slab method

INTRODUCTION

Adsorption of NO gas on metal surfaces is of extreme importance within two scientific and industrial aspects. The NO gas is an air pollutant produced from automotive exhausts [1]. In addition, this gas is one of the important products of ammonium oxidation [2]. Considering that, the decomposition of NO is accomplished slowly, in order to remedy this situation, suitable catalysts are employed in automotive exhausts with transition metals used as active material. Therefore, the adsorption of NO gas on metal surfaces has long been the subject of many theoretical and scientific researches [3-10]. Copper has been one of the most important catalysts in this case. For instance, copper-based catalysts are used in methanol synthesis [11]. Furthermore, a majority of industrial chemical reactions are catalyzed using coppers [12-16].

In this paper we consider a perfect Cu(111) surface and employ periodic slab calculations using DFT framework to investigate NO adsorption (geometry and energy of adsorption) at different sites on Cu(111) surface, and compare the results to literature and experimental values.

COMPUTATIONAL METHOD

Our calculations were performed in the framework of density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange-correlation functional due to Perdew-Burke-Ernzerhof (PBE) [17]. Nuclei and core electrons were described by ultrasoft pseudopotential [18]. The Kohn–sham orbitals were expanded in a plane wave basis set with a kinetic energy cut-off of 50 Ry (300 Rt for the charge density cut-off). The Fermi energy was calculated using the Gaussian broadening technique [19] with

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a smearing parameter nf 0.03 Ry. Brillouin-zone (BZ) integrations have been performed with the special point technique[20]. All calculations in this work have been done using the PWscf package[21]. All figures of chemical structures were produced by the XcRysDen [22] graphical package. The perfect surface was modeled by periodic slab consisting of five Cu(111) atomic layers, and molecular adsorption was described with (2×2) surface structure, corresponding tn coverage of 0.25 monolayer (ML). The adsorption on both sides nf slab was considered to avoid lnng-range dipole dipole interactions between translational equivalent unit cell. The thickness nf the vacuum rigion (the distance between facing slabs or facing adsnrbed molecules) was set to about 10Å. The slab was fully relaxed until the forces experienced by the system were smaller than 0.002 Ry/a.u.

RESULTS AND DISCUSSION

1. The Bulk Cu and Cu Atom

We first considered bulk Cu and free Cu atnm. The ground state was nbtained by minimizing the total energy with respect to the lattice constant and hulk modules nf Cu were determined by fitting energy versus lattice constant to the Birch-Marnaghan equation nf state. The calculated lattice constant of hulk Cu is 3.65 Å, which is in good agreement with the experimeutal value [23] of 3.61 Å. The computed cohesive energy and bulk modulus are 135 GPa and 3.49 eV, which are iu agreement with the experimental values [24] of 137 GPa and 3.49 eV respectively. The Brillnuin zone integration for hulk Cu was performed using the (10×10×10) Monkhorst-Pack[20] grid. The energy of isolated single Cu atom was calculated using a large unit cell with dimensions 25×25×25 (a.u.³). The Brillouin zoac integration was performed by use of the (1×1×1) Monkhorst-Pack grid. Cohesive, E_{coh}, is ealculated as

$$E_{coh} = E_{bulk} - N \times E_{Cu} \qquad (1)$$

where E_{bulk} and E_{Cu} are total energy of hulk Cu and isolated single Cu atnm respectively. N is the number of Cu atom in the unit cell.

2. The Cu(111) Surface and NO Free Molecule

The properties of Cu(111) surface were calculated using 5-layer periodic slabs with a (2×2) surface geometry (see figure 1).
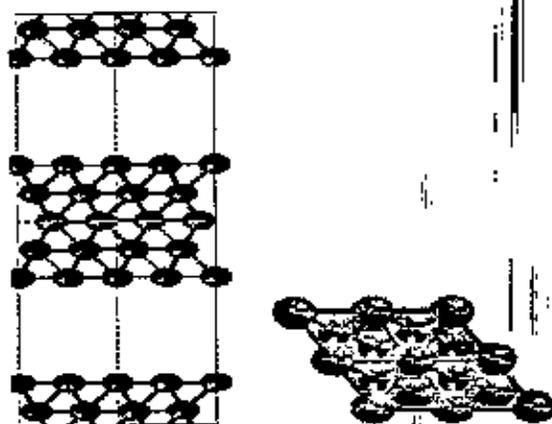
Fig. 1. a) periodic slab model for Cu(111) surface. The slabs are repeated in z-direction and separated by vacuum layers. The NO adsnrbate (not sbown) will be put on top of the free surfaces. b) top view of the top surface layer.

Here Brillouin-zone integrations were performed with a (3× 3 ×1) mesh. The surface energy, σ, was calculated hy use nf the equation

$$\sigma = (E_{slab} - N \times E_{bulk})/2A \qquad (2)$$

where E_{slab} is the total enegy of the slab, E_{bulk} is the total enegy of the bulk per Cu atom. N is the number of Cu atom in the slab and A is unit surface area of the slab. Our GGA calculatinns fnr the clean surface yield a -1.5% inward relaxations nf the first layer, which is io gond agreement with the experimental value [25,26] of -0.7% and other DFT calculatinns[27,28]. The surface energy was calculated to be 0.51eV per surface unit cell, which is in good agreement with other DFT [29,30] and experimcotal [30] values of 0.50 eV and 0.63 eV, respectively.

The properties of free NO molecule were calculated using a large cuhic cell with dimensions 25×25×25 (a.u.³). One ND mnlecule was put in the middle of cell. Spin polarized calculations were performed with a (1×1×1) Monkhorst-Pack gnd [20]. The calculated NO hond length was 1.17 Å with a binding cnergy nf 661.6 kJ/mol whcre the experimental values are 1.15 Å [31] and 639.2 kJ/mol [17,32] and previous theoretical calculations [17,32] have given 1.16 Å and 718 kJ/mol.

3. Cu(111)/NO Adsorption System

The adsorption of NO molecule on the Cu(111) surface was investigated by optimizing the structures from different initial configurations. Molecular adsorption was modeled by o (2×2) surface unit cell corresponding to coverage of 0.25 ML. Four adsorption sites were examined: Atop site, Bridge site, HCP Hollow site, and FCC Hollow site os shown in figure 2.
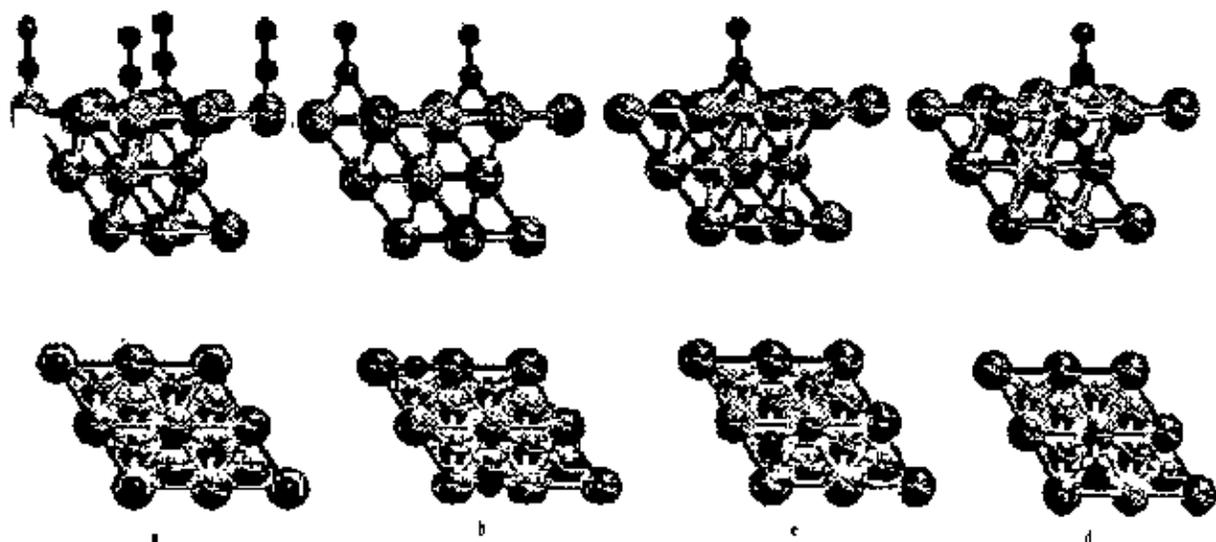
Fig. 2. Adsobed NO molecule on different adsorption sites of Cu(111) surface : (a) Atop (b) Bridge (c)Hollow HCP (d) Hollow FCC. The upper panels show side view, and the lower panels show top view adsorbing systems.

The NO molecule was placed in one of these sites (N-down) and allowed to relax until the total energy was minimized and forces on atoms were smaller than 0.002 Ry/a.u. Spin polarization is not considered in these calculations because it makes o minor contribution to the total energy of the odsorbated systems and the effect on molecular geometries is negligible[33,34]. Four the Brillouin- zone integration a (3×3×1) Monkhorst-Pack [20] mesh was used. The odsorption energy for all the adsorption site of the NO molecule was calculated according to the equotion

$$E_{ads} = (E_{Cu(111)NO} - E_{Cu(111)} - N \times E_{NO})/N \qquad (3)$$

where $E_{Cu(111)NO}$ is the total energy of the Cu slab on which NO is adsorbed, $E_{Cu(111)}$ is the energy of the Cu(111) slab, E_{NO} is the energy of NO molecule in the gas phase, and N is the number of the adsorbed NO molecules oa the surface. Table 1 lists the optimal geometries and the corresponding adsorption energies, where d_{N-O} are the N-O bond lengthes and h_{Cu-N} represents the distances between the N atom and the nearest Cu atom.

Table 1. Calculated adsorption energies and structural parameters of NO adsorbed on various sites of Cu(111) surface[a]

	E_{ads} (eV/molecule)	d_{N-O} (Å)	$h_{surface-NO}$ (Å)
Atop	-0.744	1.184	1.72
Bridge	-1.065	1.203	1.479
Hollow HCP	-1.160	1.217	1.328
Hollow FCC	-1.207	1.219	1.311

[a] The lables d_{N-O} and $h_{surface-NO}$ stands for the N-O distance and the height of NO molecule above the surface, respectively

According to obtained results summarized in table 1, it is observed that the ordinance of NO adsorption stability in terms of energy is FCC site, HCP site, Bridge site, and Atop site, respectively. In order to compare NO adsorption in a dissociated manner, and its molecular adsorption, and the possibility of its dissociation on the surface, the adsorption energy of Oxygen and Nitrogen were separately calculated on the different sites of Cu surface, and the same process was carried out for NO. Results are presented in table 2. Evidently, molecular adsorption is more stable than NO dissociated adsorption.

Table 2. Calculated adsorption energies of NO adsarbed in dissociated manner on different sites on Cu(111) surface

N atom	O atom	E (eV)[a]	
Atop	Atop	+2.867	
Atop	Hollow HCP	+1.206	
Atop	Hollow FCC	+1.090	
Bridge	Atop	+0.699	
Bridge	HollowHCP	-0.692	
Bridge	Hollow FCC	-1.078	
Hollow HCP	Atop	+0.797	
Hollow HCP	Hollow HCP	+0.865	
Hollow HCP	Hollow FCC	-0.980	
Hollow FCC	Atop	+0.697	
Hollow FCC	Hollow HCP	-0.964	
Hollow FCC	Hollow FCC	-1.079	

Values of E were calculated according to equation $E=1/2(E_{N/slab} \pm E_{O/slab} - 2(E_{NO} + E_{slab}))$ where $E_{N/slab}$ and $E_{O/slab}$ indicate total energy of Cu(111)/N and Cu(111)/O adsorbing systems respectively, and E_{no} indicates total energy of free NO molecule.

For studying the electronic structure of adsorbed NO, and surface electron changes due to NO molecule adsorption, density of states(DOS) and projected density of states(PDOS) were calculated. Fig. 3 shows the projected density of states on Cu3d and Cu4s orbitals of a Cu atom located on the surface. As seen, Copper's 3d orbital has not changed because of NO adsorption; however, when adsorption occurs on FCC and HCP sites, the position of Cu3d peak moves to the lower energy level and is more stabilized. The Cu 4s orbital before and after adsorption has completely changed, and appears in a lower energy level. In addition, when adsorption occurs in the FCC site, the Cu4s orbital completely broadens and splits into other peaks.
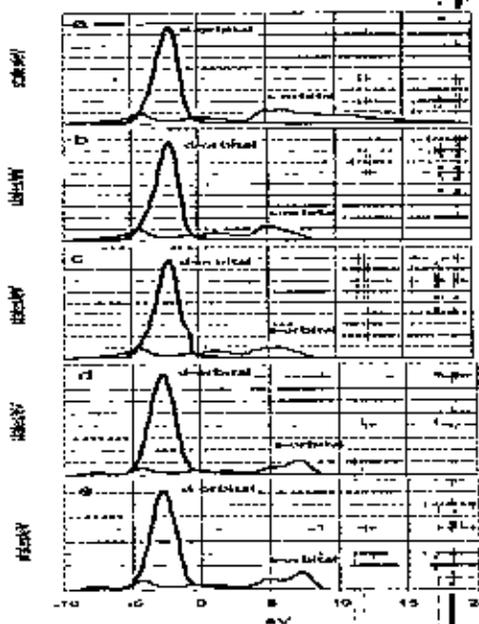
Fig. 3. PDOS projected onto the Cu3d and Cu4s states. a) The PDOS of clean Cu(111) surface. The PDOS of Cu(111)/NO adsorbing system that NO adsorbed in: b) Atop c) Bridge d) HCP Hollow e) FCC Hollow. The Fermi level is set to zero.

Fig. 4 shows the projected density of states for N2p orbital for NO gas-state molecule, and surface-adsorbed NO. When NO is adsorbed in the FCC site, the $2\pi^*$ orbital broadens and transforms to smaller peaks, which shows that the orbital has interacted with surface states.

A lowdin charge population analysis was computed by using the technique described by Sanchez-Portal [35]. The results of this calculations are summarized in table 3. From table 3, an opposite behaviour of the 2s and 2p orbitals of N atom can be seen . The charge population of N 2p increases from 3.1884 to 3.6987 (FCC Hollow site), and that N 2s decreases from 1.7130 to 1.6987. This change is corresponding to the change in charge population of Cu3d orbital.
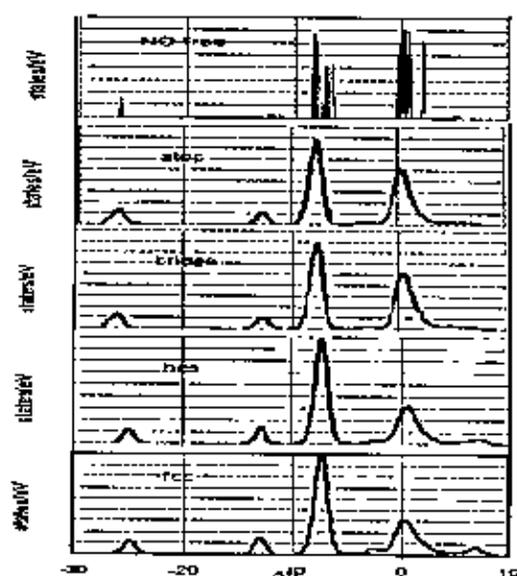
Fig. 4. PDOS\projected onto N2p state of free NO molecule, and adsorbed NO in Atop, Bridge, HCP Hollow, and FCC Hollow Sites. The Fermi level is set to zero.

Table 3. Lowdin charge population results for Cu(111) surface before and after ND adsorption

	O2p	O2s	N2p	N2s	Cu4s	Cu3d
Before adsorption	4.2472	1.6978	3.1884	1.7130	0.4519	9.6617
After adsorption						
Atop	4.3100	1.6703	3.4655	1.4504	0.3815	9.4888
Bridge	4.3211	1.6715	3.5104	1.4107	0.4561	9.5103
Hollow HCP	4.3553	1.6790	3.6707	1.3966	0.4227	9.5793
Hollow FCC	4.3760	1.6798	3.6987	1.3932	0.4248	9.5790

According to Blyholder model [36] upon adsorption of NO on the metallic surface there is an electron donation from the occupied state of NO to the surface (σ donation) and a back donation from the surface to the highest occupied molecular orbital of NO(π back donation). The σ donation removes electrons mainly from N atom, whereas the π back donation increases the density of electrons on N as well as O atoms. The $2\pi^*$ orbital is now experienced an increase in electron density upon adsorption, resulting from interacting with the d-orbitals of the surface. The partial charge transfer leads to the broadening of the $2\pi^*$ orbital with an edge below the Fermi level and the significant elongation of the N-O bond due to the antibonding nature of the $2\pi^*$ orbital.

CONCLUSION

In this research, molecular and dissociative adsorption of NO molecule on Cu(111) surface utilizing DFT with the help GGA approximation, and plane wave basis set were studied. The Copper surface was simulated using the Periodic Slab Method consisting of five atomic layers. Four different sites(Atop, Bridge, Hollow HCP, and Hollow FCC) were examined for the adsorption of NO molecule and Oxygen and Nitrogen atoms on the Cu surface. In addition, calculation related to density of states and Lowdin population analysis were carried out. Results specified that the suitable site for NO adsorption in molecular form is the Hollow FCC site, and molecular adsorption is more stable than dissociative adsorption energetically.

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