

## Research Article

# Effect of Coverage on Adsorptions of CO on Ni(110) Surface

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The adsorptions of CO on Ni(110) surface at different coverages have been investigated by first-principle calculations. The results show that CO will be bonded at short bridge site preferentially. And CO preferentially absorbs upright at short bridge sites and top sites at 1/6 monolayer coverage. With increasing coverage to 0.5 ML, the enhanced steric repulsion leads to the slope of CO. For 1/6 and 1/2 monolayer coverage, CO is mainly bonded at short bridge site and atop site simultaneously at a certain ratio. When CO coverage is 1 monolayer, CO absorbs at short bridge site and forms p2mg configuration. As the coverage of CO is increased to finally form the p2mg structure, there is a continuous frequency shift up to the value  $1962.27\text{ cm}^{-1}$ . The vibration frequencies we calculated are consistent with relative experimental results. DOS of CO molecules and Ni atoms are discussed too.

## 1. Introduction

The adsorption of gas on catalyst surface is an important step in catalytic process. Understanding the adsorption structure and postadsorption dynamic behavior can provide theoretical basis for effectively controlling the reaction process CO molecular adsorption on surface of nickel has received considerable attention from experimental and theoretical workers [1–7]. The structural model proposed by Hannaman et al. [8] for the full coverage CO on Ni(110) system is one in which the CO is bonded as a molecule to the short bridge. CO adsorption on Ni(110) was studied by infrared ellipsometric spectroscopy [9]; the interpretation of the spectra obtained at 197 K indicated several structures probably occurs with increasing CO coverage. Ref. [10] believed that CO molecule was adsorbed at the short bridge site. Studies [3] showed that CO was adsorbed at the bridged site and atop site for low CO coverage. The absorption of CO on Ni(110) has been investigated in the temperature range 110–320 K using high resolution infrared spectroscopy together with LEED and TDS [11]; the results showed that atop and bridged sites are occupied for coverages below 0.8 monolayers; atop absorption is dominant, while bridged absorption is dominant, at full monolayer coverage, p2mg configuration formed. Obviously, CO coverage is a key factor affecting CO absorption on Ni(110) surface. These investigations are mainly carried out experimentally. It is nec-

essary to study the effect of CO coverage on adsorption of CO on Ni surface theoretically. In this paper, density functional theory (DFT) was used to study the adsorption of CO on Ni(110) surface at different coverages.

## 2. Calculation Methods

First-principle calculations were performed using the Vienna ab initio simulation package (VASP) [12] in the study. The projector-augmented wave method (PAW) [13] with the Perdew-Burke-Ernzerh (PBE) [14] type exchange-correlation potentials was adopted. The van der Waals force was adopted considering the molecule interaction. The structure optimization and the ground state calculations were performed with a cut-off energy of 400 eV for the basis set. The effect of electron spin polarization is considered during self-consistent calculation. And the 3P electron is treated as valence electron orbital in calculation. Since the interaction between CO and Ni is weak, a van der Waals dispersion correction [15] is applied. Experimentally determined lattice parameter of bulk Ni of  $a = 3.52\text{ Å}$  was used to build slabs including five Ni layers and a vacuum layer with a thickness of 12 Å. The vacuum layer with a thickness of 12 Å can ensure that the interaction force between lamellae is less than  $10^{-3}\text{ eV/nm}$ , and the interaction between different layers can be ignored. Supercells with  $p(3 \times 2)$  and

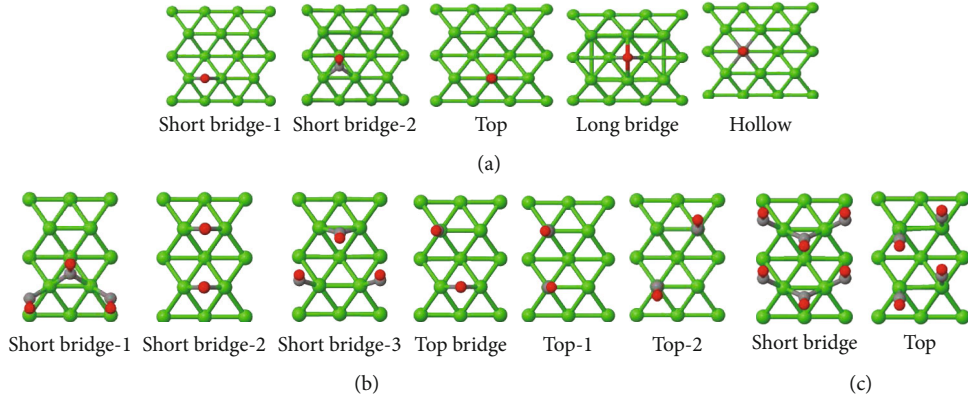


FIGURE 1: Top views of adsorption sites for different coverages: (a) 1/6 monolayer CO coverage; (b) 1/2 monolayer CO coverage; (c) full monolayer CO coverage.

TABLE 1: Total energy, absorption energy, and vibration frequency of five absorption configures at different CO coverages.

CO coverage	Absorption position	Total energy (eV)	Absorption energy (eV)	Vibration frequency (cm <sup>-1</sup> )
1/3	Short bridge-1 site	-329.822	-2.097	1850.52
	Atop site	-329.653	-1.912	1998.08
	Long bridge site	-329.507	-1.907	1574.88
	Hollowed site	-329.323	-1.357	1673.65
	Short bridge-2 site	-329.730	-1.000	1637.71
1/2	Short bridge-1 site	-257.9953	-2.1067	1869.57
	Short bridge-2 site	-257.9878	-2.1029	1902.46
	Short bridge-3 site	-257.9466	-2.0823	1899.64
	Top-bridged site	-257.8305	-2.0242	2024.14
	Atop-1 site	-257.6782	-1.9481	2037.50
	Atop-2 site	-257.6690	-1.9435	2008.17
1	Short bridge site	-291.7358	-2.0761	1962.27
	Top site	-290.3816	-1.7385	2081.37

$p(2 \times 2)$  geometry were employed. For simpleness, the reconstruction was not considered. Positions of the bottom two layers are fixed to provide substrate environment, while the top three layers are movable to simulate the relaxation of surface atoms. The advantage of this process is to reduce the amount of computation under the premise of ensuring the calculation accuracy. The vibrational frequencies were derived from the Hessian matrix calculated by the finite-displacement method. The electronic convergence criteria for the structure optimization and vibrational frequencies are  $10^{-5}$  eV. The atomic force convergence criterion for structural optimization is  $0.03$  eV/Å. Based on the supercell geometries, the  $3 \times 3 \times 1$  and  $4 \times 3 \times 1$   $k$ -point meshes were used for Brillouin zone sampling.

The adsorption binding energy is defined as

$$E_{\text{abs}} = \frac{1}{n} (E_{\text{Ni}(110)+\text{CO}} - E_{\text{Ni}(110)} - nE_{\text{CO}}), \quad (1)$$

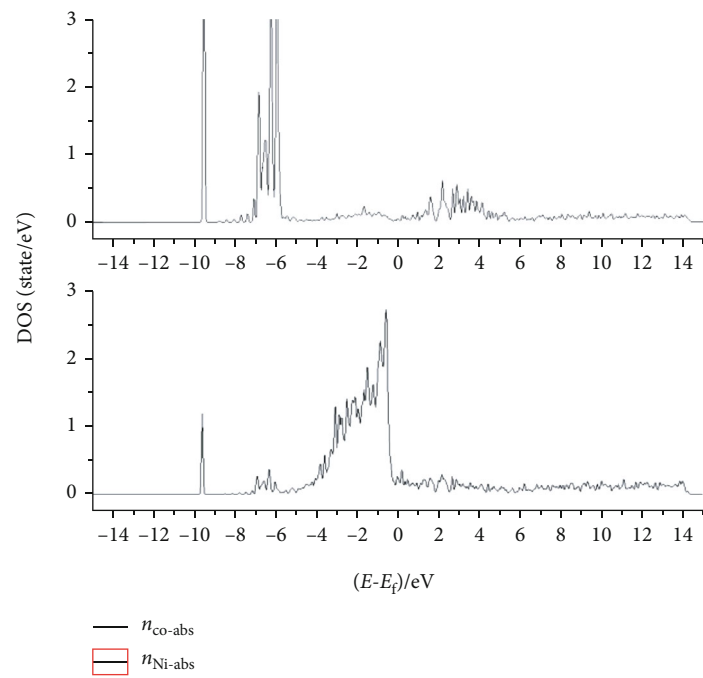
where  $E_{\text{Ni}(110)+\text{CO}}$  is the total energy of CO-adsorbed Ni(110) supercell,  $E_{\text{Ni}(110)}$  is the total energy of the Ni(110) surface

prior to CO adsorption, and  $E_{\text{CO}}$  is the energy of an isolated CO molecule. Based on the definition, the higher absolute value means the higher stability and vice versa.

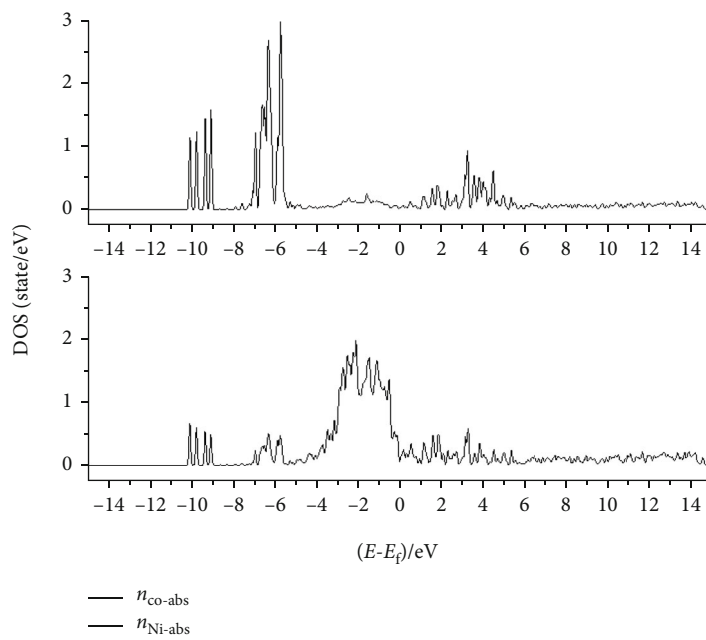
### 3. Results and Discussion

Absorptions of CO on Ni(110) surface are investigated at different CO coverages. Stable absorption configurations are obtained by optimizing possible adsorption at high symmetry points. Figure 1 gives the absorption configurations at different coverages. It can be seen that short bridge absorption and atop absorption are obtained irrespective of coverage. For 1/6 monolayer coverage, four absorption sites (short bridge site, top site, long bridge site, and hollow site) are obtained. While only two absorption sites (short bridge site and top site) are obtained for 1/2 and 1 monolayer coverage, respectively. There are more possible adsorption sites for 1/6 monolayer coverage. It shows the disorder of adsorption at low coverage.

Figure 1 only gives the possible absorption configuration calculated by first principle. In order to further discuss the



(a)



(b)

FIGURE 2: Continued.

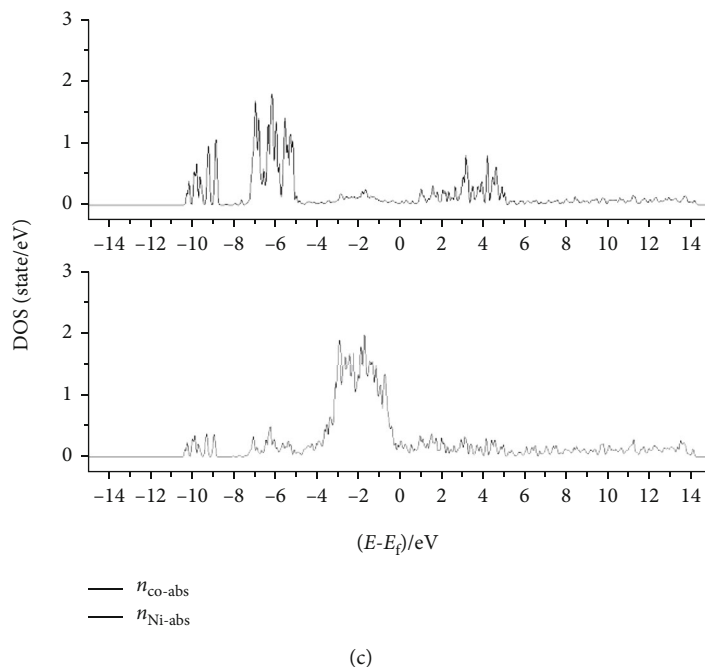


FIGURE 2: DOS of Ni atom and CO molecule with different coverages: (a) 33%; (b) 50%; (c) 100%.

adsorption behavior at different CO coverages, total energies and absorption energies and vibration frequencies are calculated. It can be seen from Table 1 that the total energy and absorption energy of short bridged adsorption are the lowest for different CO coverages, then followed by atop adsorption. The absorption energy difference between short bridged adsorption and atop adsorption is tiny for 1/6 monolayer and 1/2 monolayer coverage. However, it becomes larger (0.3376 eV), when coverage is 1 monolayer. The same is true for the total energies. It shows CO will be bonded at short bridge site preferentially. For 1/6 monolayer and 1/2 monolayer coverages, CO will be bonded at short bridge site and atop site simultaneously, at a certain ratio, due to tiny absorption energy difference. And CO preferentially absorbs upright at short bridge sites and top sites at 1/6 monolayer coverage. With increasing coverage to 0.5 ML, the enhanced steric repulsion leads to the slope of CO. When coverage is 1 monolayer, CO will mainly adsorb at short bridged site and form p2mg configurations. Experimentally two vibrational frequencies were observed at  $1840\text{ cm}^{-1}$  and  $1960\text{ cm}^{-1}$  for CO coverage approaching zero, which were assigned to bridge and top bonded CO, respectively, and they collapsed into one peak at  $1960\text{ cm}^{-1}$  which is due to CO adsorbed in p2mg adlayer at 0.85 monolayer coverage [3]. Table 1 shows the vibration frequencies of different adsorption configurations at different coverages too. As the coverage of CO is increased to finally form the p2mg structure, there is a continuous frequency shift. The vibrational frequencies of short bridged adsorption and atop adsorption for 1/6 monolayer coverage we calculated are  $1850.52\text{ cm}^{-1}$  and  $1998.08\text{ cm}^{-1}$ . And the vibrational frequency of CO adsorbed in p2mg adlayer we calculated is  $1962.27\text{ cm}^{-1}$ . The mentioned frequency values agree with obtained by vibrational spectroscopy [3] and vibrational electron loss spectroscopy [16]. Based on experi-

mental results, it is considered that the disordered adsorbed structure dominates for low CO coverages; CO is adsorbed mainly in two inequivalent sites (short bridge site and atop site) at random. With increasing CO coverage, the disordered adsorption gradually turned to ordered adsorption, until CO coverage reaches a certain value, at which p2mg configurations will be formed. The critical value of CO coverage should be between 1/2 monolayer coverage and 1 monolayer coverage. The difference critical values mentioned references may be caused by different adsorption environment such as temperature and pressure.

In order to analyze adsorption mechanism, density of states of CO molecules and Ni atoms is calculated. Figure 2 shows the DOS and of Ni atoms and CO molecule after adsorption at different coverages. It can be seen that there are orbital hybridizations between Ni atom and CO molecule in the around of -10 eV, -6 eV, -2 eV, and 4 eV. The energy range corresponding to hybridization increases with enhancement of CO coverage. This denotes that the interaction between Ni atoms and CO molecules will become obvious with enhancement of coverage and further influence the adsorption configuration gradually. Orbital hybridization mainly lies below the Fermi energy level. Adsorption of CO on Ni surface is chemical adsorption. To determine orbital components of surface adsorption, the atomic orbitals of CO molecules and Ni atoms are investigated. Figure 3 shows the orbitals of C, O, and Ni atoms. It can be seen that the interaction between the adsorbed CO and Ni substrate is mainly due to hybridization between the  $s$  and  $p$  orbitals of Ni atom and  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$  orbitals of C and O atoms. When CO coverage is low, the orbital hybridization between Ni atom and CO has great influence on adsorption configuration. With enhancement of CO coverage, the interactions among CO molecules will affect the adsorption configuration

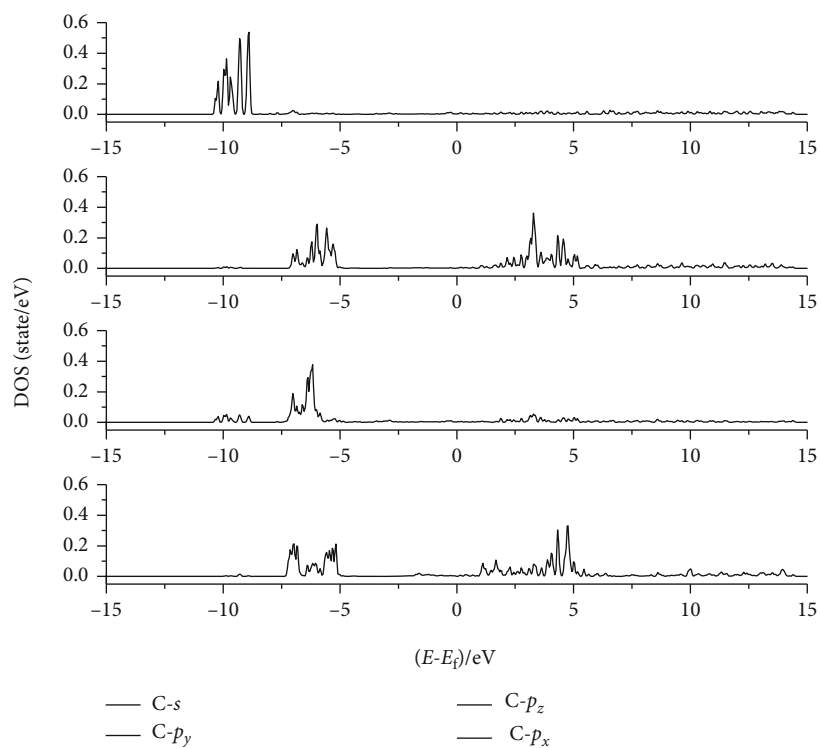
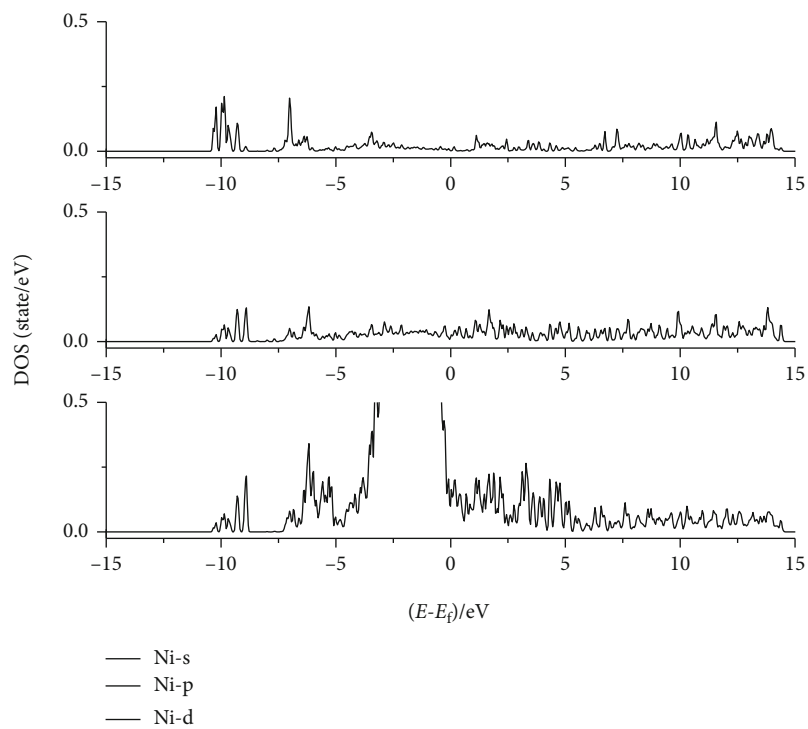


FIGURE 3: Continued.

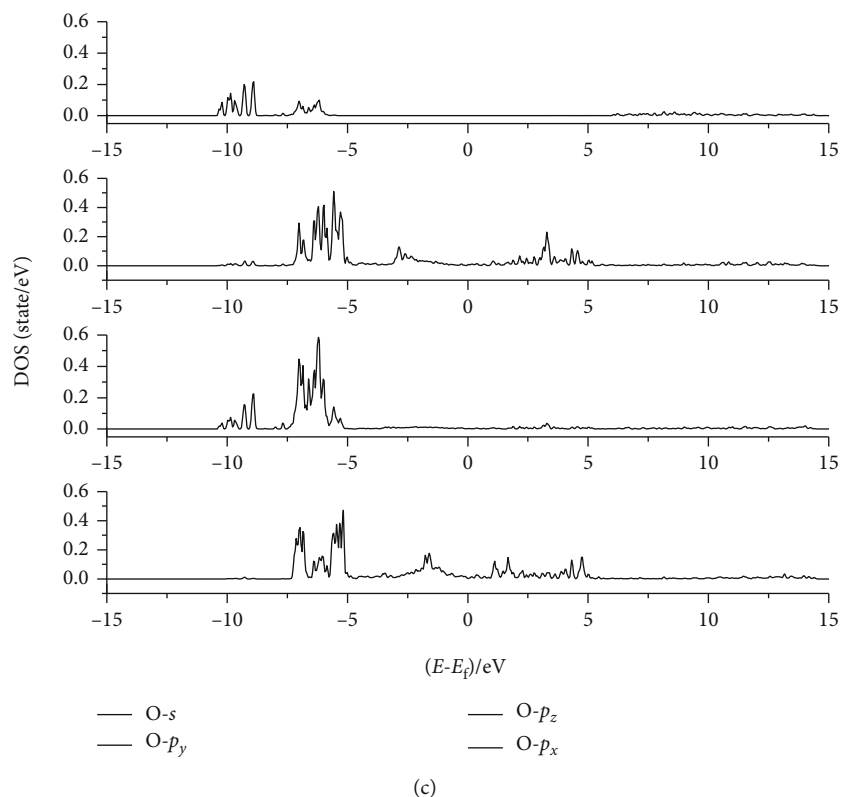


FIGURE 3: PDOS of Ni, C, and O atoms after CO absorption: (a) Ni atom; (b) C atom; (c) O atom.

greatly. It is shown as the enhanced steric repulsion, which leads to the slope of CO. The formation of p2mg symmetry structure depends on CO coverage, which will influence interaction between CO molecules and that of between Ni atom and molecules.

#### 4. Conclusion

The adsorptions of CO on Ni(110) surface at different coverage have been investigated by first-principle calculations. For low CO coverage, the disordered adsorbed structure dominates. CO is mainly adsorbed in two inequivalent sites (short bridge site and top site) at a certain ratio. Under 1/2 monolayer CO coverage, CO is bonded in short bridged sites and atop sites simultaneously at a certain ratio. With increasing CO coverage, the disordered absorption gradually turned to ordered absorption, until CO coverage reaches a certain value, at which p2mg configurations will be formed. The critical value of CO coverage should be between 1/2 monolayer coverage and 1 monolayer coverage. There is a continuous frequency shift with CO coverage enhancement. CO coverage has great influence on absorption configurations. Calculations of DOS show that the interaction between the adsorbed CO and Ni substrate is mainly due to hybridization between the *s* and *p* orbitals of Ni atom and *s*, *p<sub>x</sub>*, *p<sub>y</sub>*, and *p<sub>z</sub>* orbitals of C and O atoms. The reconstruction of the Ni(110) surface under high coverage of CO will be investigated later.

#### Data Availability

All data generated or analyzed during this study are included in this article.

#### Conflicts of Interest

The author declares that he has no conflicts of interest.

#### Acknowledgments

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