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Coadsorption of potassium and carbon monoxide on Ni(111): A density functional theory study

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Corresponding to an experimental study with high-resolution electron energy loss spectroscopy [D. Pacilé *et al.*, Chem. Phys. Lett. **413**, 420 (2005)], three possible coadsorption structures of $\frac{1}{8}$ ML potassium with $p(2\times4)$ periodicity and $\frac{1}{2}$ ML carbon monoxide with $c(2\times4)$ periodicity on Ni(111) are calculated using density functional theory. The analysis of bond lengths and electronic structures of CO molecules with different distances to K shows that the K-induced effect is short ranged. The coadsorption structure formed by exposing CO after K is suggested to be the $p(2\times4)$-K/4CO structure with K occupying the *hollow* site of the $c(2\times4)$ CO pattern. In addition, the possible reason for the observed difference in efficiencies of CO_2 formation with respect to different exposing orders of adsorbates is discussed.

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I. INTRODUCTION

Coadsorption of alkali-metal atoms and carbon monoxide on transition-metal surfaces has been widely investigated in the past due to its promotion in surface catalytic activity.[1–4] On the Ni(111) surface, a half coverage of CO forms a $c(2\times4)$ low-energy electron-diffraction (LEED) pattern, with molecules adsorbed at both hcp and fcc threefold hollow sites.[5,6] For a coverage of about 0.25 ML, K atoms form an ordered $p(2\times2)$ structure and occupy the atop sites.[7] A photoelectron diffraction (PED) study of the Ni(111)-K/CO system showed there is no change in the adsorption sites for either CO or K upon coadsorption.[8] Recently, the coadsorption of K and CO on Ni(111) was studied with high-resolution electron energy loss spectroscopy (HREELS) by Pacilé *et al.*[9] It was showed that the mechanism underlying the carbon dioxide formation is the Boudouard process ($CO+CO\rightarrow C+CO_2$). In the experiment, the HREEL spectra were recorded at 160 K by exposing a Ni(111) surface (a) to CO at 160 K, followed by K, or (b) to K at 240 K, followed by CO at 160 K. It was interestingly found that the efficiency of CO_2 formation is higher in (b) procedure than in (a) procedure. In this work, different coadsorption structures of K and CO are calculated and the possible reason for the efficiencies associated with different adsorption orders is discussed.

II. METHOD

In this paper, the total-energy calculations were performed within the framework of the spin-polarized density functional theory (DFT), which is implemented in the plane-wave-based Vienna *ab initio* simulation package (VASP).[10,11] In all of the calculations, the Perdew-Wang (PW91) generalized gradient approximation for the exchange-correlation functional, a plane-wave cutoff energy of 875 eV (when CO is involved) or 500 eV (when only K is involved), and the electron-ion interaction potential described by the projector-augmented-wave method[12] were used. The equilibrium geometry was determined by relaxation until all the forces were below 0.04 eV/Å. The vibration frequencies were calculated from the forces due to finite displacements (±0.02 Å) of the adsorbates. The Ni(111) surface was modeled by a supercell consisting of four or five layers of close-packed nickel atoms ($a_{\mathrm{Ni}}=3.523$ Å) and a separating vacuum layer of 12 Å.

III. RESULTS AND DISCUSSION

A. Establishment of the method

As a test of the method and model, some related systems were calculated and compared with the reported experimental measurements. The calculated and the corresponding experimental quantities such as bond lengths (d), vibration frequencies (ν), height differences (z), surface buckling (b_1), and adsorption energies (E_{ad}) are listed in Table I. Overall, the good agreement between the theoretical and experimental values indicates that it is feasible to retrieve reliable information from such calculations.

There are two cases that need to be mentioned. (i) For Ni(111)-$p(2\times2)$-K, the calculated adsorption energy difference is rather small for different adsorption sites; however, the trend of adsorption energy agrees with the fact that the preferred site for K adsorption is the atop site. (ii) The $z_{\text{C-O}}$ and $z_{\text{C-Ni}}$ are well predicted for Ni(111)-$p(2\times2)$-K/2CO, but there is a large difference in $z_{\text{K-Ni}}$. The possible reason for the difference is that the PED experiment is less sensitive to the "rumpling" of the surface atoms.[8] For Ni(111)-$p(2\times2)$-K, the calculated buckling agrees well with the LEED measured value.[7] Since the adsorption of K lowers the Ni atom below it and the adsorption of CO lifts its neighboring Ni atoms, a larger buckling of the Ni surface should be expected for the coadsorption of K and CO. The calculated difference between the height of K and the average height of the top layer is 3.006 Å, which corresponds reasonably to the measured 3.02(5) Å.

TABLE I. Comparison between the experimental and calculated quantities for the systems listed in the first column. The d, ν, z, and b_1 values represent the bond length, the vibration frequency, the height difference, and the surface buckling, respectively. E_{ad} is the total energy with K occupying different adsorption sites, and the zero energy is taken as the total energy of the hcp adsorption system. The units for length, frequency, and energy are Å, meV, and meV, respectively.

		Experimental	Calculated
Free CO[a]	d_{CO}	1.13	1.134
	$\nu_{\text{C-O}}$	265	266
Ni(111)-$p(2\times2)$-K[b]	E_{ad}		top: −5, hcp: 0, fcc: 0, bridge: −1
	$d_{\text{K-Ni}}$	2.82(4)	2.831
	b_1	0.12(2)	0.13
Ni(111)-$c(2\times4)$-2CO	d_{CO}	1.15(7), 1.18(7)[c]	1.177, 1.177
	$z_{\text{C-Ni}}$	1.34(7), 1.29(8)[c]	1.365, 1.358
	$\nu_{\text{C-O}}$	236[d]	232
	$\nu_{\text{Ni-CO}}$	50[d]	46
Ni(111)-$p(2\times2)$-K/2CO[e]	$z_{\text{K-Ni}}$	3.02(5)	3.228
	$z_{\text{C-O}}$	1.21(7)	1.222, 1.223
	$z_{\text{C-Ni}}$	1.25(5)	1.283, 1.291
	b_1	~0.03	0.30

[a] Reference 13.
[b] Reference 7.
[c] Reference 14.
[d] Reference 9.
[e] Reference 8.

B. Coadsorption structures of $\frac{1}{8}$ ML K and $\frac{1}{2}$ ML CO on Ni(111)

In the experiment carried out by Pacilé *et al.*,[9] Ni(111) was exposed to CO followed by K and then in the inverse order. The $c(2\times4)$ LEED pattern with half coverage was observed after an exposure of 1 langmuir CO on the clean Ni(111). Considering the estimated coverage of K is 0.13 ML, the $p(2\times4)$ surface unit cell is used and three adsorption sites for K with respect to the $c(2\times4)$ structure of CO are considered: *hollow*, bridge of long edge (*leb*), bridge of short edge (*seb*). The plan views of the equilibrium coadsorption structures are shown in Fig. 1. As for the *hollow* site, K is initially placed at the atop site neighboring CO^b [i.e., over the Ni atom shown above the CO molecule labeled b in Fig. 1(a)]. After relaxation, K shifts away from the atop site and locates at the center of the quadrilateral formed by four neighboring CO molecules. Note that the equilibrium position of K in the *hollow* configuration does not coincide with the conventional threefold hollow site of Ni(111). The relative total energies of the coadsorption structures and the bond lengths of CO are calculated and listed in Table II. From the table, it is seen that the most energetically preferred adsorption site for K is the *hollow* site. The variation of CO bond lengths reveals that the bonds of CO molecules in the vicinity of K are more significantly weakened. For example, when K is adsorbed at the *seb* site [cf. Fig. 1(c)], the bond lengths of the two CO molecules that form the short edge of the quadrilateral are about 0.02 Å more lengthened than the other two CO molecules.

To examine the change of electronic structures due to the coadsorption of K, the difference in charge densities between Ni(111)-$p(2\times4)$-K/4CO and Ni(111)-$p(2\times4)$-4CO plus the unsupported K is calculated. Figures 2(a) and 2(b) correspond to the equilibrium structure with K adsorbed at the *hollow* site, and Figs. 2(c) and 2(d) correspond to the *leb* site. The depletion of charge around K nuclei and the accumulation of charge above K can be attributed to the polarization of the 4s electron of K and the counterpolarization of 3p electrons,[15] respectively. For CO, there is an obvious increase of the charge of the molecular $2\pi^*$ antibonding character, together with a depletion of the 5σ bonding charge. Due to the large surface unit cell, it is possible to directly check the influence range of K by comparison of two CO molecules with different distances to K. Figures 2(b) and 2(d) show the changes of charge density for CO^a and CO^b upon the adsorption of K in the *hollow* and *leb* configurations. It can be seen from the figures that the charge density distribution of the farther CO^a is much less altered than the neighboring CO^b.

The local density of states (LDOS) projected onto C in Ni(111)-$c(2\times4)$-2CO and C of CO^a and CO^c in Ni(111)-$p(2\times4)$-K/4CO is calculated and shown in Fig. 3. It is found that the energies of states are shifted to larger binding energies with respect to E_F due to the coadsorption of K. The short-ranged influence of K is observed again as the energies of states corresponding to the neighboring CO^c are shifted further below E_F than the farther CO^a.

These findings in electronic structures agree well with the work of Wimmer *et al.* and can also be explained by the K-induced modification of the electrostatic potential in the surface region.[16] The K-induced energy shift of the molecular levels causes the $2\pi^*$ states to be partially occupied (the

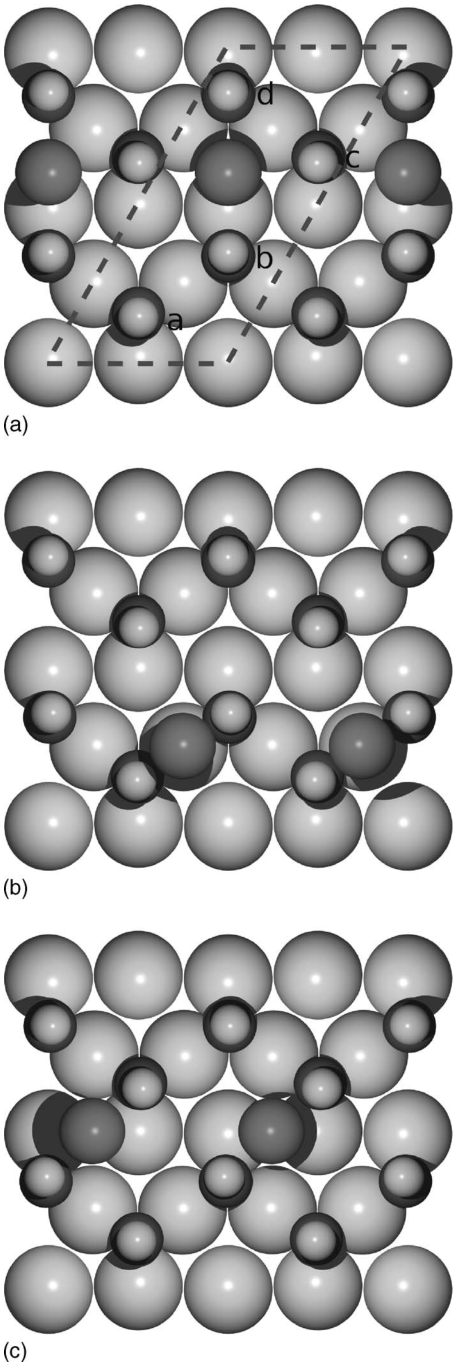

FIG. 1. Plan views of equilibrium coadsorption structures of $\frac{1}{2}$ ML CO and $\frac{1}{8}$ ML K on Ni(111). The initial configurations are the $c(2\times4)$ CO with K placed (a) over the Ni atom within a minimal quadrilateral of CO (*hollow*), (b) over the Ni atom at the midlle of the short edge of the quadrilateral (*seb*), and (c) over the middle point of the long edge of the quadrilateral (*leb*). The $p(2\times4)$ surface unit cell is indicated by the dashed line and the CO molecules are labeled for the convenience of discussion. The large (small) light balls represent Ni (O) atoms, and the large (small) dark balls represent K (C) atoms.

peak about 2 eV below E_F), hence softening the C-O bond. Our analysis of the variation of CO bond lengths, the charge density redistribution, and the energy shift of molecular levels indicates that the K-induced effect is short ranged.

TABLE II. Relative adsorption energies (E_{ad}), bond lengths of CO (d_{CO}) [listed in the order of a, b, c, and d in Fig. 1(a)], and the height difference of K and its nearest-neighbor Ni ($z_{\text{K-Ni}}$) in the equilibrium structures of Ni(111)-$p(2\times4)$-K/4CO with K adsorbed at the hollow, long-edge bridge, and short-edge bridge sites (cf. Fig. 1).

	Hollow	Long-edge bridge	Short-edge bridge
E_{ad} (meV)	−964	−320	0
d_{CO} (Å)	1.186	1.192	1.210
	1.202	1.209	1.210
	1.217	1.209	1.192
	1.202	1.192	1.191
$z_{\text{K-Ni}}$ (Å)	3.806	4.200	4.400

C. Possible reasons for different efficiencies

Calculation of vibration spectra has been an important method to determine adsorption structures by comparison with the experimental spectra. The Γ-point frequencies of K-Ni and C-O vibrations in three coadsorption structures proposed above are calculated with Hessian matrices derived from finite differences. The 27 degrees of freedom of four CO molecules and the K atom are used to construct the Hessian matrix, and the calculated values are listed in Table III, together with the measured values for the adsorption structure obtained by first exposing K followed by CO [i.e., (b) procedure]. From the table, it is seen that the theoretical values agree well with the experimental values, but the difference between the proposed structures cannot manifest which one corresponds to the adsorption structure formed in the experiment. However, in view of the exposing order and the relative stableness of the three candidate structures, we

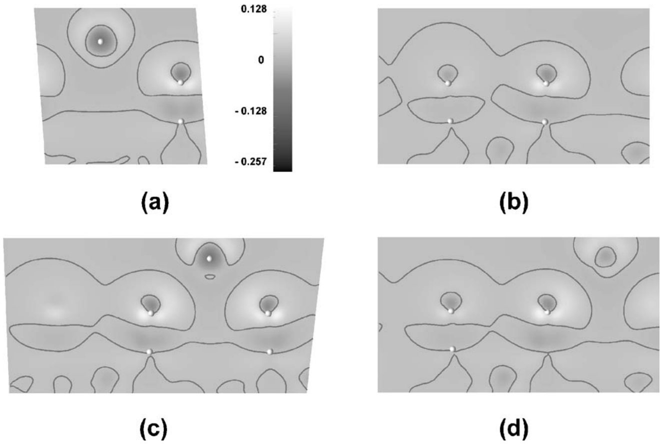

FIG. 2. Two-dimensional cuts of the charge density difference between Ni(111)-$p(2\times4)$-K/4CO and Ni(111)-$p(2\times4)$-4CO plus the unsupported K. The cut planes are selected as those (a) through K and CO^c in Fig. 1(a), (b) through the bond centers of CO^a and CO^b in Fig. 1(a) and perpendicular to the surface, (c) through K and O atoms in CO^b and CO^c in Fig. 1(c), and (d) through the bond centers of CO^a and CO^b in Fig. 1(c) and perpendicular to the surface. The unit for the legend is e/Å^3, and the same color map is used for all cuts.

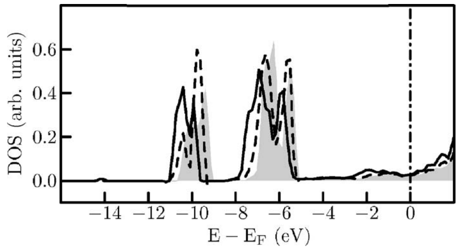

FIG. 3. Local density of states projected onto C in Ni(111)-$c(2\times 4)$-2CO (shaded) and C of CO^a (dashed line) and CO^c (solid line) in Ni(111)-$p(2\times 4)$-K/4CO.

TABLE III. Calculated frequencies of C-O and K-Ni vibrations in the proposed structures in Fig. 1 and the measured frequencies for the adsorption structure formed by first exposing K followed by CO on Ni(111).

	ν(C-O)	(meV)	ν(K-Ni) (meV)
Hollow	223	211	15
Long-edge bridge	222	214	15
Short-edge bridge	222	212	16
Experiment^a	222	212	14

^{a}Reference 9.

would assign the one with K adsorbed at the *hollow* site to the experimental structure formed in (b) procedure. After first exposing K to Ni(111), K will adsorb at the atop site with height of about 2.8 Å. The following CO will adsorb around K to form the most stable *hollow* configuration, in which K is shifted a bit away from the atop site and raised to height of about 3.8 Å (cf. Table II). The less stable *leb* and *seb* configurations with higher sites for K should be unlikely to form by the exposing order in (b) procedure. It is observed that the efficiency of CO$_2$ formation is lower in (b) procedure than in (a) procedure. In (a) procedure, the first exposed CO leads to the Ni(111)-$c(2\times 4)$-2CO structure and the next exposed K causes a quick reaction at surface, resulting in an HREEL spectrum composed of an intense peak associated to the ν_2 vibration mode of physisorbed CO$_2$ and a broad peak corresponding to the stretching vibration of CO in a local disordered state. This phenomenon can be understood by a combination of the short-ranged effect of K on CO and the exposing order. In addition to our analysis in the previous section, calculations by Liu and Hu[17] showed that K promotion in CO dissociation on Rh(111) strongly depends on the distance between K and CO. The dissociation barrier can be significantly reduced due to the stabilization of the transition state by a K-O interaction if the CO-K distance is less than 3 Å, while the effect of K is relatively small if the distance is greater than 4 Å. The dissociation of CO is also necessary for the reaction of formation CO$_2$, so these findings should apply as well to the reaction studied here. When K is exposed to the CO precovered Ni(111) surface, there exists the possibility that K is trapped into local minima of surface potential, such as the *leb* and *seb* sites. At these sites, K is close to CO and promotes the reaction, resulting in a higher efficiency of formation CO$_2$.

IV. SUMMARY

In this work, the possible coadsorption structures of $\frac{1}{8}$ ML K and $\frac{1}{2}$ ML CO on Ni(111) are calculated within the framework of density functional theory. The analysis of the variation of CO bond lengths, the charge density redistribution, and the energy shift of molecular levels indicates that the K-induced effect is short ranged. By considering the stableness and geometries of these structures and the exposing order, the coadsorption structure formed by exposing of CO after K is suggested to be the $p(2\times 4)$-K/4CO structure with K adsorbed at the *hollow* site of the $c(2\times 4)$ CO pattern. In addition, the observed difference in the efficiencies of CO$_2$ formation with respect to different exposing orders of adsorbates is explained and the possible reason may be that the reaction is initiated by the adsorption of K at sites close to CO, which are more easily accessed by K when the surface is precovered by CO.

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