Theoretical study of the influence of Na on CO adsorption and dissociation on Pd(1 1 1): Long-range or short-range interactions between co-adsorbates?

Li-Yong Gan [a,b], Ren-Yu Tian [a], Xiao-Bao Yang [a], Yu-Jun Zhao [a,b],*

[a] Department of Physics, South China University of Technology, Guangzhou 510640, PR China
[b] State Key Laboratory of Physics and Chemistry of Luminescence, South China University of Technology, Guangzhou 510640, PR China

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ABSTRACT

The co-adsorption of CO and C, O on Na pre-covered Pd(1 1 1) surface are studied by density functional theory (DFT). CO adsorption is affected by the short-range Na–CO electrostatic interactions, especially the Na–O attraction, and the Na-induced long-range surface polarizability as well as the indirect interactions through substrates. Na stabilizes C and O adsorptions, particularly O adsorption, though both C–Pd and O–Pd bonds are elongated. Na reduces CO dissociation barrier by ~25%. The promotional effects are primarily ascribed to the short-range Na–O electrostatic interaction which stabilizes the transitional state. The Na-induced long-range effects are not significant and hardly promote CO dissociation.

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1. Introduction

Alkali metal (AM) additives, usually used as promoters in many catalytic reactions [1,2] have been always a hot topic both experimentally [3–6] and theoretically [7–10] in heterogeneous catalysis and surface science. Four types of interactions between AMs and co-adsorbates have been suggested to explain its promotional effects in literature so far: direct orbital overlap [7] between the AM and the adsorbate (~3 Å), short-range (~4 Å) electrostatic interaction [7,11,12] of the alkali-induced electric field with the adsorbate-surface bond, long-range indirect interaction through surface electrons [13], and non-local or long-range surface polarizability enhancement [10]. However, the interactions between AM and reactants are still not well defined on the microscopic level, especially the controversy of the local/non-local (or short-range/long-range) features in the electronic interactions between AM and co-adsorbates: whether there is a non-local feature in the electronic interactions between AM and co-adsorbates [6,10].

CO co-adsorption with AM has been always a prototype primarily due to its technological applications (i.e. AM enhanced CO dissociation in Fischer–Tropsch process) [1,2] as well as its scientific simplicity. For a long time, the short-range interactions between AM and CO were believed to be dominant, while the long-range interactions were thought to be overestimated [6,7]. Nonetheless, there are still many studies which have manifested that a remarkable long-range character of alkali-induced effects could also be predominate. He et al. found an evident red-shift of the C–O stretching mode despite CO adsorption is far from the co-adsorbed

Cs on Ru(0 0 0 1) surface [14]. In addition, an upward shift of the C–O mode is observed in K + CO/Ru(0 0 0 1) system with the increased CO exposure, and it is understood through a long-range substrate-mediated interaction between co-adsorbates [15]. In Na + CO/Ni(1 1 1), the desorption activation energies and the stretching frequency of CO would experience noticeable changes at low sodium coverage [16], indicating the existence of non-local effects in the system. Similar results are also obtained in K + CO/Pd(1 1 0) system with K at a low coverage (0.11 ML) [17]. Several theoretical works [8,18] have been carried out on CO co-adsorption with AMs, and most of them only considered CO co-adsorption at the adjacent site of AM, i.e. CO + K/Co(10$\bar{1}$0) case [8], or argued that the AM-induced effect is short ranged, CO + K/Ni(1 1 1) [18]. Very recently, a systematical investigation was conducted on CO adsorption on K/Fe(1 0 0) [9], and the adsorption and activation of CO with respect to the CO–K distance and K coverage are discussed in detail. However, the long-range interactions between CO and AM are still not well documented in general.

As for CO dissociation, the promotional effects were believed predominantly due to the local AM–CO interactions rather than the non-local ones [7]. However, a recent study [10] suggested that alkali adsorption on Pd(1 1 1) could dramatically enhance the surface electronic polarizability, and it is extended into the vacuum by several angstroms (non-local). This significantly enhanced and extended polarizability could soften the C–O stretching mode, and ultimately promote CO related reactions, which challenges previous views seriously.

Therefore, it is of significant importance to provide more direct evidence to ascertain whether there is a predominant long-range character in the AM–CO interactions, and how the long-range interaction affects subsequent CO dissociation if it exists. We carry out a comprehensive density functional theory (DFT) study to

* Corresponding author at: Department of Physics, South China University of Technology, Guangzhou 510640, PR China. Fax: +86 20 87112837.
E-mail address: zhaoyj@scut.edu.cn (Y.-J. Zhao).

systematically investigate the adsorption and dissociation of CO on Na modified Pd(1 1 1) surface at various CO–Na distances in order to get a deeper insight of the fundamental issues involved in heterogeneous catalysis and surface science. We show that the pre-adsorbed Na atom does induce a long-range effect on CO adsorption, while the effect is insufficient to destabilize the C–O bond to an extent for CO dissociation. The promoted CO dissociation is mainly ascribed to the short-range O–Na attraction.

2. Computational details

This work is conducted by the Vienna Ab Initio Simulation Package (VASP) [19–21] with the frozen-core projector-augmented-wave (PAW) method [22,23]. The Perdew Wang (PW91) generalized gradient approximation (GGA) [24,25] functional was employed for the exchange-correlation energy. The surface is modeled with a 5-layer slab with a vacuum thickness of 15 Å. Each layer contains nine Pd atoms. Namely, a (3×3) super cell is used throughout the study. The adsorbed species are put on one side of the slab. The three uppermost layers including the adsorbates are fully relaxed with the residual forces on each relaxed ion less than 0.02 eV/Å, while the two bottommost layers are fixed at their bulk structure with the previous optimized bulk lattice constant, 3.96 Å [26]. A cutoff energy of 500 eV was employed for the plane-wave expansion, and the Monkhorst–Pack k-point grids of $5 \times 5 \times 1$ was used to sample the Brillouin zone for the (3×3) super cell. The frequencies are calculated with the substrates and Na fixed while only CO allowed vibrating in any direction at a displacement of 0.02 Å. The Wigner–Seitz radii for the related elements are $r^{Pd} = 1.434$ Å, $r^{Na} = 1.757$ Å, $r^{C} = 0.863$ Å, $r^{O} = 0.82$ Å, respectively, for the projected density of states (PDOS) calculations.

The co-adsorption energy of X (X = CO, C, and O) on Na pre-adsorbed Pd(1 1 1) is defined as

$$E_{ad} = E_{tot}^{X+Na/Pd(111)} - E_{tot}^{Na/Pd(111)} - E_{tot}^{X}, \qquad (1)$$

$E_{tot}^{X+Na/Pd(111)}$, $E_{tot}^{Na/Pd(111)}$, and E_{tot}^{X} are the total energies of X (X = CO, C and O) and Na co-adsorbed Pd surfaces, Na pre-adsorbed Pd(1 1 1), and X in gas phase, respectively.

In order to straighten out the interactions between Na and CO on Pd(1 1 1) surface at difference Na–CO distances, the charge density difference in selected co-adsorption systems are depicted. Here, the charge density difference is calculated as

$$\Delta \rho = \rho^{CO+Na/Pd(111)} - \rho^{CO/Pd(111)} - \rho^{Na/Pd(111)} + \rho^{Pd(111)}, \qquad (2)$$

where $\rho^{CO+Na/Pd(1 1 1)}$, $\rho^{CO/Pd(1 1 1)}$, $\rho^{Na/Pd(1 1 1)}$, and $\rho^{Pd(1 1 1)}$ are the total charge densities of CO + Na/Pd(1 1 1), CO/Pd(1 1 1), Na/Pd(1 1 1) and the clean Pd(1 1 1) surface, respectively. The atom positions in each isolated system are identical to those in the co-adsorption configuration.

Energy barriers and minimum energy paths (MEPs) have been computed using the climbing-image nudged elastic band (CI-NEB) [27]. The transition state (TS) is further optimized by the quasi-Newton method until the residual forces are less than 0.02 eV/Å. Then, the TS is verified by vibrational frequency analysis, in which the substrates of TS are fixed while the adsorbates are allowed vibrating in any direction. A true TS should have and only have one imaginary frequency.

3. Results and discussions

3.1. CO adsorption on Na pre-covered Pd(1 1 1) surfaces

We first calculated CO adsorption on Na pre-covered Pd(1 1 1) surface, Na/Pd(1 1 1), at various CO–Na distances in order to directly ascertain whether there is a long-range effect on CO adsorption by

Na. Our previous studies [26,28] showed that CO adsorptions at the threefold hollow sites (i.e. fcc, and hcp) on Pd(1 1 1) were energetically preferred. Meanwhile, Na adsorption at the threefold hollow sites on Pd(1 1 1) was also energetically favorable and almost degenerated. As a result, the co-adsorption was modeled with Na at the middle fcc hollow site and CO at various trial fcc and hcp sites on Pd(1 1 1), as shown in Figure 1. The adsorption energies, work function changes, and structural parameters are listed in Table 1. We have also calculated CO adsorption with C or O directly approaching Na and C–O axis either vertical or tilting to the surface to check whether CO molecule can directly interact with the pre-adsorbed Na, then dissociate with low energy barrier. However, the molecular adsorption is extremely unstable, and the corresponding dissociative adsorption is not obtained, either. As a matter of fact, Na adatom is prone to bond with the substrate rather than with CO molecule directly as CO introduced to the Na pre-adsorbed systems. The binding energies of Na with the substrate and with a single CO molecule are −2.51 and ∼0 eV, respectively. Since alkali metal atoms adsorption would induce a pronounced charge transfer between the AMs and the substrate [28,29], we calculated CO adsorption on a negatively charged Pd(1 1 1) surface to simulate the scenario qualitatively that the adsorbed CO molecule is infinitely far away from the pre-adsorbed Na atom. The artificial 'negative surface' is modeled by adding two additional electrons to the neutral Pd(1 1 1) surface, labeled as $Pd^{2-}(1 1 1)$. Similar net charge approaches, by adding electrons to flat surfaces, has been used to study the charge effects on oxygen molecular adsorption on Au(1 1 1) surface [30].

From Table 1, it is clear that CO adsorption at all studied hollow sites on Na/Pd(1 1 1) is more or less enhanced, in agreement with the experimental results that the presence of alkali metal atoms stabilize CO adsorption on transition metal surfaces [31]. The most increment for CO adsorption is found at the first-nearest fcc site (f1), with the adsorption energy 0.27 eV lower than that on the clean Pd(1 1 1). Additionally, CO adsorptions at f2 and h3 are also enhanced by 0.13 eV. The negative polarization of Pd(1 1 1) surface can stabilize CO adsorption by 0.06 eV, suggesting that a non-local interaction between Na and CO exists in the system. CO adsorption at h1 is less stable than that at f1 even though the distance between Na and CO at h1 is much shorter. This may result from a significant Pauli repulsion which causes Na shifting from its original ideal fcc adsorption site by 0.69 Å, getting away from CO in Pd–Na + CO$_{h1}$ configuration.

It can also be seen in Table 1 that the presence of Na can obviously weaken C–O bond strength, consistent with the experimental observations in CO + AM/Ni(1 1 1) and CO + AM/Cu(1 1 1) systems [5]. The calculated C–O bond lengths are 1.22 Å at h1, h2 and f1,
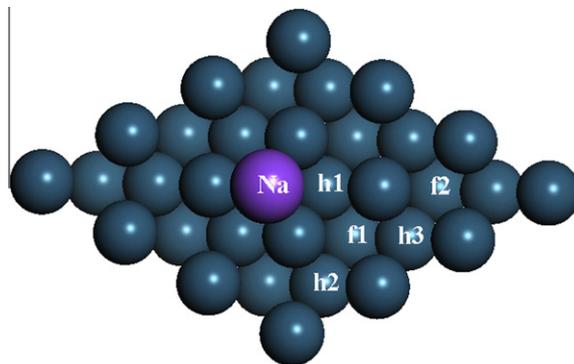
Figure 1. Possible adsorption sites for CO, C and O on Na/Pd(1 1 1). The letters f and h stand for fcc and hcp sites, respectively, while 1, 2, and 3 indicate the first, second and third nearest site relative to the adatom Na, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Adsorption energies of CO, E_{ad}, C–O bond lengths, d_{C-O}, distances between Na and C, d_{Na-C}, distances between Na and O, d_{Na-O}, height changes of Na, ΔZ_{Na}, work function changes, $\Delta\Phi$, and C–O stretching frequencies, f, for CO adsorption on Na pre-adsorbed Pd(1 1 1) and Pd^{2-}(1 1 1)3 × 3 surfaces. CO adsorption at fcc and hcp on clean neutral Pd(1 1 1)3 × 3 is also listed as a reference. The subscript letters and numbers are defined in Figure 1.

Site	E_{ad} (eV)	d_{C-O} (Å)	d_{Na-C} (Å)	d_{Na-O} (Å)	ΔZ_{Na} (Å)	$\Delta\Phi$ (eV)	f (cm^{-1})
Pd–CO$_f$	−2.04	1.19	–	–	–	0.32	1760
Pd–CO$_h$	−2.02	1.19	–	–	–	0.33	1776
Pd–Na+CO$_{h1}$	−2.25	1.22	2.69	2.37	0.21	−1.96	1618
Pd–Na+CO$_{h2}$	−2.22	1.22	2.87	2.49	0.21	−1.92	1612
Pd–Na+CO$_{h3}$	−2.15	1.20	4.40	4.27	0.03	−1.84	1724
Pd–Na+CO$_{f1}$	−2.31	1.22	2.87	2.49	0.13	−1.89	1638
Pd–Na+CO$_{f2}$	−2.17	1.20	4.96	4.85	0.03	−1.84	1730
Pd^{2-}–CO$_f$	−2.10	1.21	∞	∞	–	–	1670

at which the distances between CO and Na are all less than 3 Å. When CO are located at h3 and f2, where the distances between the two co-adsorbates are over 4 Å, the C–O bond lengths shift to 1.20 Å, still longer than those on clean Pd(1 1 1) surface, 1.19 Å. The C–O bond stretching frequencies experience a similar decrease as moving from near to far w. r. t Na, but all the values are smaller than those on clean Pd(1 1 1). On Pd^{2-}–(1 1 1)3 × 3 surface, the C–O bond strength is weakened notably, too. Based on the donation and back-donation model [32], the adsorption of Na donates its valence electrons to the Pd(1 1 1) substrate, facilitates charge transfer from Pd substrate to CO $2\pi^*$ anti-bonding states, and consequently weakens C–O bond strength. The softening of C–O is a non-local effect which can extend over 4 Å.

The calculated work function (Φ) for the clean Pd(1 1 1) is 5.51 eV, in good agreement with the experimental value of 5.6 eV [33] and previous DFT calculation, 5.53 eV [34]. The work function decreases by 2.43 eV upon Na adsorption at fcc, while increases by 0.32 and 0.33 eV for CO at fcc and hcp sites, respectively. When CO adsorbs on Na/Pd(1 1 1), it is reduced by 1.96 eV at the first nearest hollow site (h1) and converged to 1.84 eV at h3 and f2, where the distances of CO–Na are more than 4 Å in the two co-adsorption configurations. The decrement of work function (−1.84 eV) in Pd–Na + CO$_{f2}$ is lower than the sum of −2.43 eV for Na at fcc in p(3 × 3)–Na and 0.32 (fcc) or 0.33 eV (hcp) in p(3 × 3)–CO, clearly indicating long-range mutual depolarization between the two adsorbates.

To further investigate the effects of the pre-adsorbed Na atom on CO electronic structures at difference range, the projected density of states (PDOS) of CO in Pd–Na + CO$_{f1}$, Pd–Na + CO$_{f2}$ are shown in Figure 2. As a reference, PDOS of CO adsorption on clean Pd(1 1 1) is also presented. From the PDOS plots, one can see that the adsorption Na can induce a shift of all CO molecular orbitals

deeper away form the Fermi-level due to the AM-induced modification of the electrostatic potential in the surface region [35]. This effect can leads to a further occupation of CO $2\pi^*$ anti-bonding states, and weakens the C–O bond consequently, with C–O stretching frequencies 1638 cm^{-1} for CO at f1, which is 122 cm^{-1} lower than that on the clean Pd(1 1 1) surface. This phenomenon can be also seen in Pd^{2-}–CO$_f$, suggesting that the modification of surface electrostatic potential results from the charge transfer from AM to the substrates, a non-local effect. Figure 3 depicts the charge density difference plots of Pd–Na + CO$_{f1}$ and Pd–Na + CO$_{f2}$. It clearly indicates a pronounced polarization in CO $2\pi^*$ states in O atom, especially for CO at f1 site. In Pd–Na + CO$_{f1}$, the calculated O–Na distance is 2.49 Å. Such short distance combined with the induced polarization in CO molecule suggest that an ionic bonding *trend* between Na$^{\delta+}$ and O$^{\delta-}$ (short-range) may be more dominant than the simple attractive interaction between Na$^{\delta+}$ and CO$^{\delta-}$ molecule as a whole, which was deduced from the K-induced charge polarization at O component in CO + K/Co(1 0 $\bar{1}$ 0) [8]. A long-range Pd-mediated interaction feature between co-adsorbates can be also observed in Pd–Na + CO$_{f2}$, which unambiguously demonstrate that Na induced long-range effects through surface electrons can also influence CO adsorption. Both the PDOS plots and the charge difference contours confirm that the short-range and long-range effects together influence CO adsorption properties.

In turn, Na adsorption is also influenced upon the co-existence of CO on Pd(1 1 1). Firstly, Na atom will be further ionized through the Bader charge analysis [36]. Then, in all CO + Na co-adsorption geometries (c.f. Figure 1), the subsequent CO adsorption can lift Na position by 0.03 Å at h3 and f2, and 0.21 Å at h1 and h2, confirming the high-resolution electron energy loss spectroscopy (HREELS) results [4,37] that CO adsorption can shift the Na-substrate vibration energy down. We argue that the red-shift of the
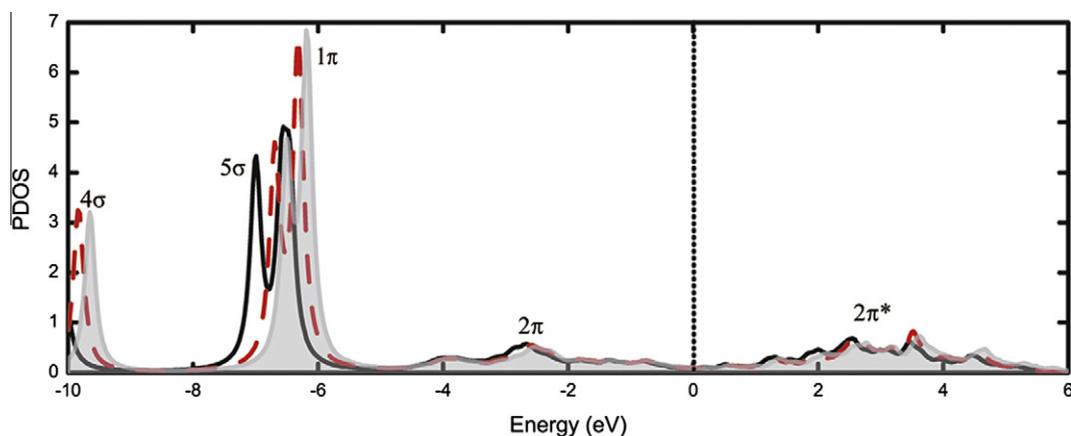
Figure 2. PDOS of CO in Pd–Na + CO$_{f1}$ (black solid line), Pd–Na + CO$_{f2}$ (red dashed line) and Pd–CO$_f$ (shaded). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
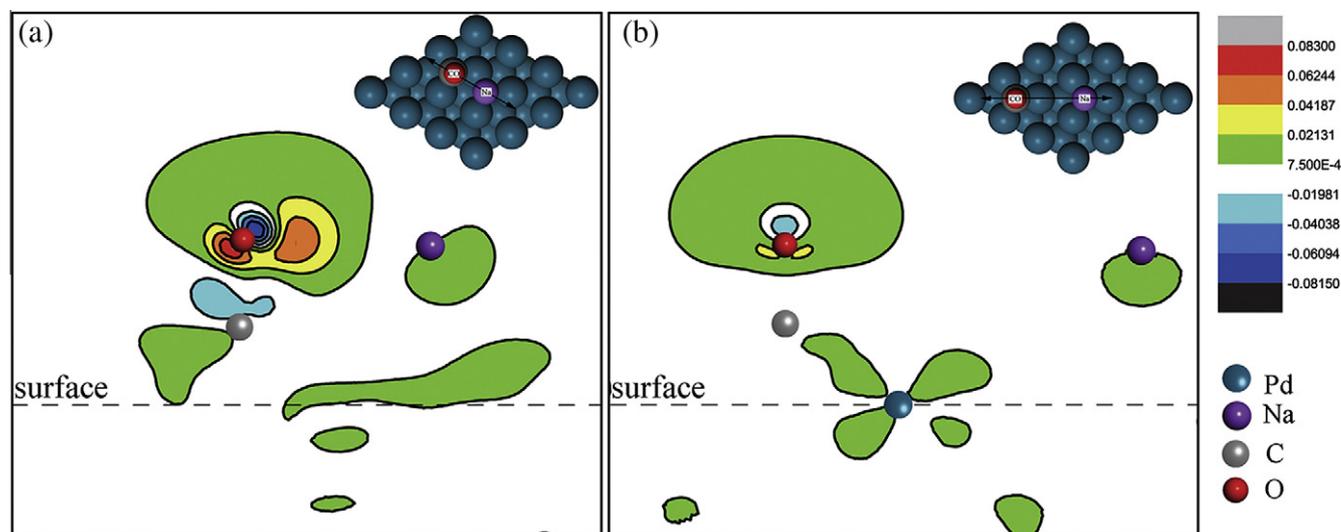
Figure 3. Charge density difference plots of (a) Pd–Na + CO$_{f1}$, and (b) Pd–Na + CO$_{f2}$. The cutting plane is shown in the upper right corner of each panel. Warm and cool contours correspond to charge accumulation and depletion, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Na-surface vibration should be assigned to the coordinated electrostatic interaction between Na and CO interactions: Na–O attraction and Na–C repulsion. From Table 1, one can see that all the O–Na distances are shorter than those corresponding C–Na distances, suggesting that CO adsorption makes Na get away from the surface but close to the O atom. This process helps stabilizing the co-adsorption structures at the cost of Na-substrate bond softening.

The alkali atoms (e.g. Na) induced effects on CO adsorption can be divided into predominant local and non-local effects in principle. The former corresponds to the AM–CO electrostatic attraction, especially the AM–O electrostatic attraction, demonstrated by the remarkable polarization at O atom in Pd–Na + CO$_{f1}$. The latter is correlated with the AM–CO mutual depolarization, AM-induced surface polarizability and indirect interactions through surface electrons. These long-range features should account for the CO stabilization and C–O bond strength softening at the non-adjacent sites (over 4 Å) of Na.

3.2. C and O adsorption on Na pre-covered Pd(1 1 1) surfaces

We have calculated C and O (the products from CO dissociation) adsorption at various hollow sites on Na pre-covered Pd(1 1 1) surfaces (c.f. Figure 1) since their atop and bridge adsorption is much less stable. Our calculation shows that C/O adsorptions at bridge sites are unstable and would relax spontaneously to the nearby hcp/fcc, and at atop are over 2 eV less stable than those at hcp/fcc, respectively. The results are listed in Table 2. C and O prefer to hcp and fcc sites with the adsorption energies of −7.07 and −4.75 eV, respectively. Both C and O adsorption is enhanced by the pre-covered Na, and the impact on O is relatively more remarkable. The most increment of O (C) is found 0.21 eV (0.06 eV) at f1 (f2), respectively. However, on the negatively polarized surface Pd^{2-}(1 1 1)3 × 3, C adsorption is destabilized, while O is stabilized. Firstly, the surface net charges would accumulate in C/O $2p_z$ anti-bonding states [7] on Pd^{2-}(1 1 1)3 × 3 w. r. t. that on neutral Pd(1 1 1)3 × 3. Then, the bonding energy of C and O on Pd(1 1 1) can be divided into two parts [38]: the ionic contribution of charge transfer from surface to C/O atom, and the covalent contribution of hybridization between Pd d and C/O p states (the s orbitals of C and O are rather delocalized). The electronic structures of isolated C and O are $2s^2 2p^2$ and $2s^2 2p^4$, and their Pauling's electronegativities are

Table 2
Adsorption energies of X (X = C and O), adsorption energy changes of X upon Na, ΔE_{ad}, bond lengths of X–Pd, d_{X-Pd}, for X adsorption on Na/Pd(1 1 1) and Pd^{2-}(1 1 1)3 × 3 surfaces. C or O adsorption at fcc and hcp on clean neutral Pd(1 1 1)3 × 3 is also listed as a reference. The subscript letters and numbers are defined in Figure 1.

	X = C			X = O		
	E_{ad} (eV)	ΔE_{ad} (eV)	d_{C-Pd} (Å)	E_{ad} (eV)	ΔE_{ad} (eV)	d_{O-Pd} (Å)
Pd–X$_f$	−7.05	–	1.88	−4.75	–	2.00
Pd–X$_h$	−7.07	–	1.89	−4.57	–	2.00
Pd–Na+X$_{h1}$	−7.10	+0.03	1.90	−4.76	+0.19	2.07
Pd–Na+X$_{h2}$	−7.07	+0.00	1.90	−4.61	+0.04	2.04
Pd–Na+X$_{h3}$	−7.08	+0.01	1.89	−4.59	+0.02	2.02
Pd–Na+X$_{f1}$	−7.07	+0.02	1.89	−4.96	+0.21	2.06
Pd–Na+X$_{f2}$	−7.11	+0.06	1.88	−4.81	+0.06	2.02
Pd^{2-}–X$_f$	−6.99	−0.06	1.89	−4.78	+0.03	2.03
Pd^{2-}–X$_h$	−7.01	−0.06	1.90	−4.58	+0.01	2.03

2.55 and 3.44, respectively. On the basis of the extended Huckel approximations [12,39], C–Pd bonding should be more covalent, while O–Pd should be more ionic. An energy cost due to the additional $2p_z$ anti-bonding occupation in C–Pd prevails, while an energy gain via ionic bonding in O–Pd dominates, and destabilizing/stabilizing C and O adsorption on Pd^{2-}(1 1 1)3 × 3 consequently. This may also be responsible for the results of C on Na/Pd, where there is a competition between the direct C–Na attraction and the Na induced destabilization. Due to the occupation in C and O $2p_z$ anti-bonding on Na/Pd(1 1 1) and Pd^{2-}(1 1 1)3 × 3, the calculated bond lengths of all C–Pd and O–Pd are obviously elongated on the two surfaces, consistent with the HREELS observations in O + K/Ni(1 1 1) system [40]. The elongation of C–Pd and O–Pd bonds is primarily an indirect interaction through surface electrons.

3.3. CO dissociation on Na pre-covered Pd(1 1 1) surfaces

The above co-adsorption studies have covered most of the alkali atoms induced effects on the adsorption properties of CO, C and O. However, whether the long-range contributions can promote CO dissociation is still controversial [7,10]. In this section, CO dissociations on Pd(1 1 1) surface with and without Na pre-adsorbed are studied. In addition, CO dissociation on the negatively polarized

$Pd^{2-}(1\,1\,1)3 \times 3$ surface is also presented to simulate the case with CO infinitely far away from Na. This is expected to mimic the Na induced surface polarizability and offer a direct answer to the long-range effect. All the initial states are chosen to be the most favorable CO adsorption configurations on each surface (c.f. Table 1), while the final states are all modeled with the two products located at two adjacent hcp sites, as shown in Figure 4. The reaction potential energy surfaces (PES) on the three surfaces are summarized in Figure 4.
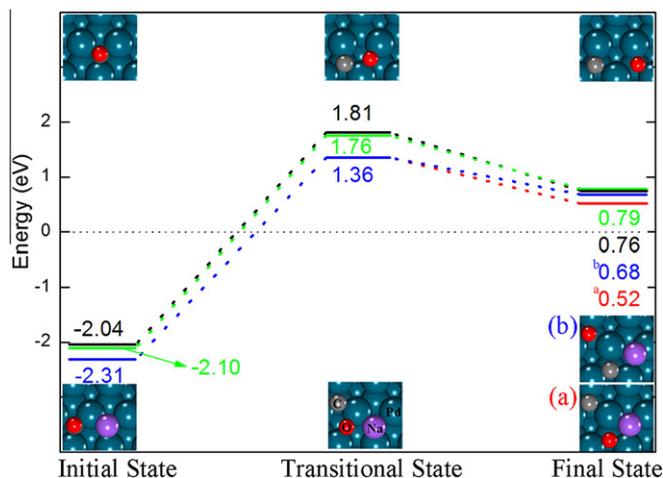
Figure 4. Potential energy surfaces for CO dissociation on clean Pd(1 1 1) (black lines and fonts), Na/Pd(1 1 1) (blue and red lines and fonts), and $Pd^{2-}(1\,1\,1)3 \times 3$ (green lines and fonts). The energies (in eV) of the various configurations are referred to CO in its gas phase. The structures at IS, TS and FS of CO dissociation on Pd(1 1 1) and $Pd^{2-}(1\,1\,1)3 \times 3$ are shown in the upper panels, while on Na/Pd(1 1 1), two possible final states are considered: one with O approaching Na (labeled as 'a', shown in red fonts) and the other one with C closer to Na (labeled as 'b', shown in blue fonts). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

On clean Pd(1 1 1) surface, the reaction barrier for CO dissociation is determined to be 1.81 eV w. r. t. the configuration with CO in its gas phase. In the TS configuration (c.f. Figure 5a), the C–O bond length is stretched to 2.05 Å, almost twice as long as C–O bond length at adsorption, 1.19 Å, suggesting that the TS is more product-like state with C atom near an hcp site and O almost at a bridge site. The TS energy, therefore, is more dependent on the energy of the final state (FS), similar to CO dissociation on Rh(1 1 1) surface [7,41].

On Na/Pd(1 1 1) surface, two possible final states were taken into account: one with O approaching Na (inset (a) of Figure 4), while the other one with C closer to the Na atom (inset (b) of Figure 4). The former is a little more energetically favorable than the latter, 0.52 eV versus to 0.68 eV, but both of them are stabilized by Na, suggesting a thermodynamic promotional effect. The remarkable electrostatic interactions between Na and the two products (C and O) offset the bonding competition between C and O. Interestingly, the CI-NEB calculated TS are identical corresponding to both the final states. The TS configuration is shown in Figure 5b, with O atom closer to Na. The calculated CO dissociation barrier is reduced by ∼25% with respect to that on clean Pd(1 1 1) surface. The C–O distance keeps unchanged in the TS, while both the O–Pd and C–Pd bond lengths are elongated slightly by the presence of Na. This is consistent with our above co-adsorption results that Na can elongate the C–Pd and O–Pd bond lengths. On the negatively polarized surface $Pd^{2-}(1\,1\,1)3 \times 3$, no remarkable changes are found in either PES or TS structure of CO dissociation w. r. t. those on neutral $Pd(1\,1\,1)3 \times 3$. The reaction barrier on the polarized surface is calculated to be 1.76 eV. The C–O bond length is also 2.05 Å in the TS, similar to the cases on clean Pd(1 1 1) and Na/Pd(1 1 1) surfaces, and the C–Pd and O–Pd bond lengths are elongated slightly.

The three calculated TS's are very similar to each other and all FS-like, so all the TS energies should be strongly dependent on the energies of final states, implying that stabilizing the final states
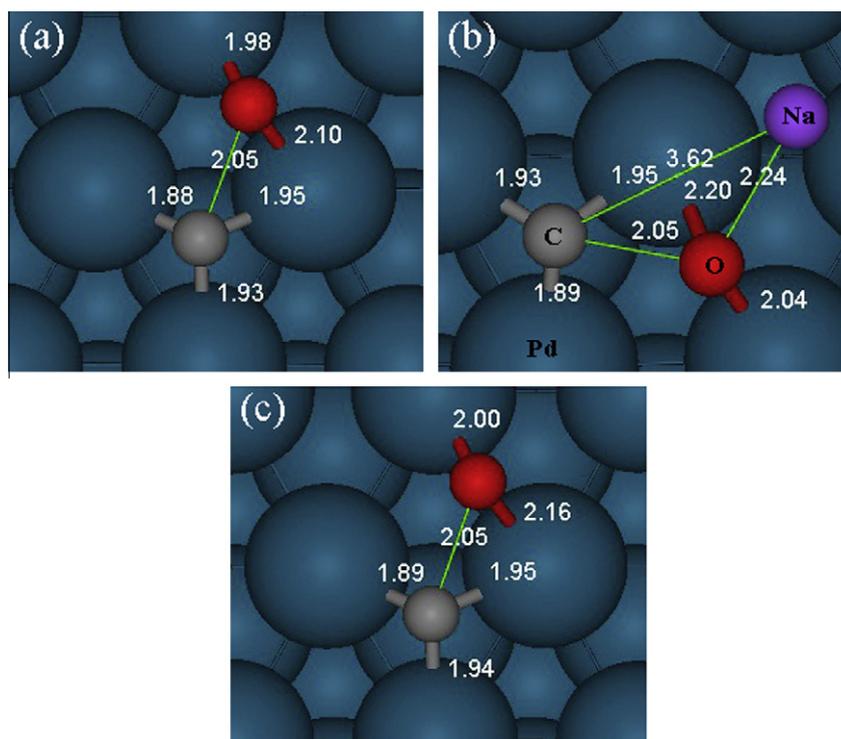
Figure 5. Structural parameters (Å) of the transitional states for CO dissociation on (a) Pd(1 1 1), (b) Na/Pd(1 1 1), and (c) $Pd^{2-}(1\,1\,1)3 \times 3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

can reduce the dissociation barrier efficiently. A recent study about K effects on CO adsorption and activation on Fe(1 0 0) [9] suggested that there are two important effects of K contributing the promotion of CO activation: one is the stabilization of C and O in TS by K; the other is the reduction of bonding competition between C and O in TS due to the increased separation of C and O atom from the surface. Our results agree well with those findings. Both stabilization of C and O by Na (c.f. Section 3.2) and C–Pd (O–Pd) (c.f. Figure 5a and b) elongation are found when C and O adsorbed on Na pre-covered Pd(1 1 1) surface. Nonetheless, an increased separation of C and O from the surface can be also observed on $Pd^{2-}(1\ 1\ 1)3 \times 3$ (c.f. Figure 5c), where CO barrier is only reduced trivially (0.05 eV). This suggests that the reduction of the bond competition in TS due to Na-induced charge donation may only play a *minor* role in CO dissociation on Na/Pd(1 1v1). Furthermore, it has been shown that O adsorption energy enhancement by Na is more obvious than that of C on Pd(1 1 1). Combined with the obtained TS of CO dissociation on Na/Pd(1 1 1), it suggests that the Na-reduced dissociation barrier is *primarily* ascribed to the Na–O electrostatic interaction (short-range).

The presence of Na can really cause a drastic long-range enhancement of the metal surface electronic polarizibility, which does soften C–O bond strength [10]. This softening effect is demonstrated by the model of negatively polarized substrate in our calculations. However, the calculation of CO dissociation on $Pd^{2-}(1\ 1\ 1)3 \times 3$ indicates that the weakening of C–O bond strength (long-range effect) can hardly promote subsequent molecular dissociation. This is consistent with the fact that the TS structure is more FS-like and that C and O adsorption is relatively insensitive to the surface polarization (see Table 2). This indicates that the Na induced long-range effects, including the C–O softening and the separation of C and O from the surface have little influence on CO dissociation. The efficient way to lower the dissociation barrier for CO should be stabilizing O atomic adsorption on the catalysts.

4. Summary

The Na-induced effects on the CO adsorption on Pd(1 1 1) surface are investigated by first-principles calculations. It is demonstrated that CO molecular adsorption is influenced by both the short-range and the long-range indirect interactions by the pre-adsorbed Na. The former corresponds to the Na–CO electrostatic attraction, particularly the Na–O electrostatic attraction, while the latter includes the Na-induced surface polarizability and indirect interactions through substrates, which are responsible for the red shift of C–O bond stretching mode at the non-adjacent sites relative to Na. As for the two atomic species (C and O), both are stabilized by the presence of Na, especially the O atom, even though the C–Pd and O–Pd bonds are elongated. Furthermore, the presence of Na can substantially lower CO dissociation barrier when CO is close to Na (i.e. CO at f1), and the promotional effects are *mainly* ascribed to the short-range Na–O interaction, which stabilizes the final-state-like transition state. The long-range effects of Na on CO dissociation, i.e. C–O softening as well as the reduction of C and O atom bonding competition, are not remarkable and

hardly promote the CO dissociation. It is suggested that the efficient way to lower the CO dissociation barrier on Pd(1 1 1) is stabilizing the atomic adsorption of oxygen.

References

[1] H.K.R. Schlögl, in: G. Ertl, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, 2008, p. 2501.
[2] H.K.B.E. Koel, J. Kim, in: G. Ertl, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis (Second Ed.), Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, 2008, p. 1593.
[3] M.S. Luo, B.H. Davis, Applied Catalysis a-General 246 (2003) 171.
[4] A. Politano, V. Formoso, R.G. Agostino, E. Colavita, G. Chiarello, Phys. Rev. B 76 (2007) 233403.
[5] A. Politano, V. Formoso, G. Chiarello, J. Chem. Phys. 129 (2008) 5.
[6] A. Politano, R.G. Agostino, V. Formoso, G. Chiarello, Chem. Phys. Chem. 9 (2008) 1189.
[7] Z.P. Liu, P. Hu, J. Am. Chem. Soc. 123 (2001) 12596.
[8] S.J. Jenkins, D.A. King, J. Am. Chem. Soc. 122 (2000) 10610.
[9] D.C. Sorescu, Surf. Sci. 605 (2011) 401.
[10] S. Stolbov, T.S. Rahman, Phys. Rev. Lett. 96 (2006) 186801.
[11] J.J. Mortensen, B. Hammer, J.K. Nøskov, Phys. Rev. Lett. 80 (1998) 4333.
[12] B. Hammer, J.K. Nøskov, Adv. Catal. 45 (2000) 71.
[13] P.J. Feibelman, D.R. Hamann, Phys. Rev. Lett. 52 (1984) 61.
[14] P. He, K. Jacobi, J. Chem. Phys. 106 (1997) 3417.
[15] R.A. De-Paola, J. Hrbek, F.M. Hoffmann, J. Chem. Phys. 82 (1985) 2484.
[16] F. Zaera, Catal. Lett. 1 (1988) 317.
[17] S.J. Pratt, D.A. King, Surf. Sci. 540 (2003) 185.
[18] A.H. Zhang, J. Zhu, W.H. Duan, Phys. Rev. B 74 (2006) 045425.
[19] G. Kresse, J. Furthmuller, Comput. Mater. Sci. 6 (1996) 15.
[20] G. Kresse, J. Furthmuller, Phys. Rev. B 54 (1996) 11169.
[21] G. Kresse, J. Hafner, Phys. Rev. B 48 (1993) 13115.
[22] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[23] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[24] J.P. Perdew, W. Yue, Phys. Rev. B 33 (1986) 8800.
[25] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[26] L.Y. Gan, Y.X. Zhang, Y.J. Zhao, J. Phys. Chem. C 114 (2010) 996.
[27] G. Henkelman, B.P. Uberuaga, H. Jonsson, J. Chem. Phys. 113 (2000) 9901.
[28] L.Y. Gan, Y.J. Zhao, J. Chem. Phys. 133 (2010) 094703.
[29] W.Z. Lai, D.Q. Xie, J. Phys. Chem. B 110 (2006) 23904.
[30] G. Mills, M.S. Gordon, H. Metiu, J. Chem. Phys. 118 (2003) 4198.
[31] A.P. Farkas, F. Solymosi, J. Phys. Chem. C 113 (2009) 19930.
[32] G. Blyholder, J. Phys. Chem. 68 (1964) 2772.
[33] H.B. Michaelson, J. Appl. Phys. 48 (1977) 4729.
[34] M. Methfessel, D. Hennig, M. Scheffler, Phys. Rev. B 46 (1992) 4816.
[35] E. Wimmer, C.L. Fu, A.J. Freeman, Phys. Rev. Lett 55 (1985) 2618.
[36] R. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, New York, 1990.
[37] A. Politano, R.G. Agostino, E. Colavita, V. Formoso, L. Tenuta, G. Chiarello, J. Phys. Chem. C 112 (2008) 6977.
[38] Z.P. Liu, P. Hu, A. Alavi, J. Am. Chem. Soc. 124 (2002) 14770.
[39] R. Hoffmann, Rev. Mod. Phys. 60 (1988) 601.
[40] A. Politano, V. Formoso, R.G. Agostino, E. Colavita, G. Chiarello, J. Chem. Phys. 128 (2008).
[41] X.F. Ma, H.Y. Su, H.Q. Deng, W.X. Li, Catal. Today 160 (2011) 228.