PHYSICAL REVIEW B **74**, 205418 (2006)

Effect of coadsorption and Ru alloying on the adsorption of CO on Pt

B. C. Han and G. Ceder*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA

(Received 5 June 2006; published 16 November 2006)

We present a study of the factors that influence the adsorption of CO on a Pt(111) surface. Coadsorption of O and OH, as well as alloying of Ru is investigated. We find that coadsorption of CO either with O or OH on Pt weakens the strength of the Pt-CO bond, through a largely strain mediated interaction. Alloying Pt with Ru on the surface only slightly enhances the adsorption energy of CO relative to that of pure Pt. However, once Ru is oxidized by O or OH the adsorption energy of CO on a neighboring Pt is dramatically reduced. These findings as well as some information on the competitive adsorption behavior are discussed in the context of designing CO-tolerant Pt catalysts.

DOI: 10.1103/PhysRevB.74.205418 PACS number(s): 82.45.Jn, 82.65.+r, 68.43.Bc

INTRODUCTION

The oxidation of CO is a key aspect of low temperature fuel cell operation. CO can exist as an impurity in the fuel itself (e.g., in a Proton Exchange Membrane Fuel Cell) or be produced in the process of fuel oxidation (e.g., in a Direct Methanol Fuel Cell).[1–3] Unoxidized CO binds strongly to Pt and poisons the catalyst by removing sites that can participate in the catalysis. In general, alloying Pt with other metals tends to improve the CO tolerance of the catalyst, and one of the most effective alloys is Pt-Ru.[4] The effect of alloying on the CO tolerance of Pt is likely to be complex though some facets of it are understood: CO is removed from the surface by oxidation to CO_2 and the activation barrier for a reaction between CO and an adsorbed oxidant on the surface has been found to depend directly on the adsorption energy of both species.[5–8] Hence, it is critical to understand the adsorption energies of the species under complex conditions, such as segregation of alloying elements and coadsorption of other species. Several groups have focused on the direct changes in the Pt-CO bond strength when Ru is nearby in the surface layer. While it is known experimentally that alloying Ru reduces the CO poisoning of Pt electrodes,[4,9–12] first principles calculations point to a complex picture: A computational study performed by Ge *et al.*[13] indicates that the CO adsorption energy decreases (i.e., binds less strongly) on the surface of a bulk Pt-Ru alloy, but increases when Ru is only present in the surface layer of an otherwise pure Pt bulk material. Furthermore, they argued that the surface strain induced by the size mismatch of Pt and Ru increases the adsorption energy for CO on Pt, when Ru is present nearby in the surface layer. While instructive, it is not clear that such pure surface calculations are relevant to fuel cell operation conditions where various chemical species, such as CO, O_2, O, OH and water are available to adsorb on the surface. We recently found that under most practical conditions Ru on the surface of Ru-Pt alloys is oxidized and that this oxidation can even drive the segregation of Ru to the surface.[14] A limited amount of work has been done on the effect of coadsorption of other species on the Pt-CO bond strength.[6,15–18] Bleakely *et al.*[18] concluded from *ab initio* density functional theory (DFT) studies that the interaction between CO and O on a Pt(111) surface is localized and that there is no bonding competition between CO and O on the Pt(111) surface. Our work shows somewhat different results and indicates stronger and more long range coadsorption effects through the relaxations that adsorption induces in the surface layer (not considered in Ref. 18). There is considerable evidence that coadsorption and oxidation of the surface modifies the CO oxidation rate significantly.[5,19–21] In a key paper, Hendriksen *et al.*[21] observed experimentally that CO oxidation on pure Pt becomes faster as the O_2 pressure is increased. In addition, oxides have considerably better CO oxidation properties than metals.[5,22] In this paper, we investigate the effect of Ru alloying, and coadsorption of O and OH on the CO adsorption energy on Pt. We find that adsorption of O or OH weakens the Pt-CO bond strength. On the other hand, alloying Ru in the bare surface layer of Pt(111) slightly enhances or leaves the CO adsorption energy on Pt unchanged. However, the adsorption of OH or O on the surface Ru atoms (common in most environments) reduces the CO adsorption energy on Pt. Hence, the adsorption energy of CO on Pt is a complex function of the environment.

MODEL AND METHODOLOGY

Adsorption energies are calculated on a six layer fcc slab of Pt or (Pt, Ru) atoms with a (111) surface. Periodic boundaries are imposed with varying periodicities in the surface layer. The slab is augmented with 14 Å of vacuum (equivalent to the thickness of six layers of slab) perpendicular to the surface, and periodic boundary conditions are imposed on the slab+vacuum unit. The atoms of the top four layers and adsorbates are fully relaxed, while the atoms of the bottom two layers are fixed to their bulk positions. All DFT energies were calculated with the projector augmented wave (PAW) method[23,24] using the generalized gradient approximation (GGA) with Perdew-Wang exchange correlation functional[25,26] as implemented in VASP.[27,28] These pseudopotentials and exchange correlation functional give a calculated lattice parameter of 3.98 Å for bulk fcc Pt which agrees reasonably well with the experimental value of 3.92 Å.[29] A plane wave basis set with cut-off energy of 275 eV was used. Reciprocal space integrations were done on a 21×21×1

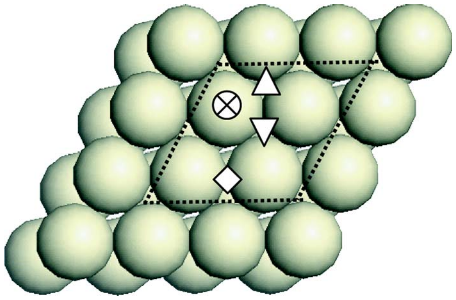

FIG. 1. (Color online) Relevant adsorption sites on a Pt(111) surface: ⊗-ATOP, △-FCC, ∇-HCP, and ◇-BRIDGE site. The dotted line is a $p(2\times2)$ supercell.

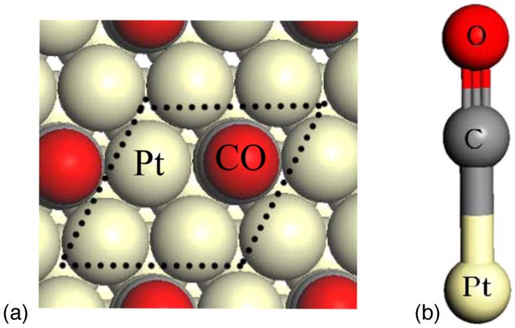

FIG. 2. (Color online) Surface geometry of a Pt(111)-$p(2\times2)$ surface unit cell with CO at the top site. (a) a top view, (b) a lateral view.

grid for a (1×1) surface unit cell and proportionally smaller meshes for larger supercells. All adsorption energies are calculated with respect to the atom/molecule in vacuum, unless otherwise stated. Figure 1 shows the different adsorption sites on a Pt(111) surface.

RESULTS

Coadsorption of CO and O

Experimentally, CO has been observed to form $p(4\times4)$ or $p(8\times8)$ structures on Pt(111) at low CO coverage,[30] but a $p(2\times2)$ cell has been found to provide enough dilution to approximate the adsorption energy of an isolated CO molecule.[31,32] Hence, the adsorption of CO on a Pt(111) surface was studied in a Pt(111)-$p(2\times2)$ surface unit cell. The surface geometry of Pt(111)-$p(2\times2)$-CO is shown in Fig. 2.

The adsorption energy for CO is calculated on the atop site, where CO is observed experimentally to adsorb,[30,33] even though it is not the most stable site in the GGA approximation.[34,35] The adsorption energy for an adsorbate (ad) is defined as

$$E_{ad}^{ads} = -[E_{ad/\mathrm{Pt}} - E_{\mathrm{Pt}(surface)} - E_{ad}],$$

where E_{ad} is the energy of the isolated molecule in a supercell of dimension $8\times8\times1$. Hence, a more positive E_{ad}^{ads} value in our calculation indicates stronger adsorption on the surface. Our results in Table I for CO on pure Pt(111) ($E_{CO}^{ads} \approx 1.75$ eV) agree well with previous calculations[35] and with experimental data.[36]

Atomic oxygen was placed in various sites but only found to be stable in the fcc, hcp, and atop sites. The oxygen atom is unstable at the bridge site and slides off to the fcc site. We find that the fcc site is preferred for oxygen with an adsorption energy of about 4.7 eV referenced to atomic oxygen in vacuum which is in good agreement with other experimental[37,38] and theoretical investigations[39–41] [Table I(a)].

To study O and CO coadsorption in a $p(2\times2)$ cell, two geometries are possible [Figs. 3(a) and 3(b)]. We chose the configuration displayed in Fig. 3(a) as it is energetically more favorable by approximately 0.63 eV than that in Fig 3(b).

The CO adsorption energy in the presence of adsorbed oxygen [bottom line in Table I(b)] is reduced from its value for a pure Pt surface. The reduction we find (~200 meV) is considerably larger than what has been found by Bleakely *et al.* (~40 meV).[18] We believe this discrepancy is due to the different computational approximations. In Ref. 18 Pt atoms were not relaxed as CO and O adsorb, while all Pt atoms in

TABLE I. Adsorption energy of O (a), and (b) CO with and without adsorbed oxygen. For CO-Pt experimental data (in parenthesis) are also given for comparison.

(a) O on Pt(111)

Site	Chemisorption energy (eV)	d(O-Pt) (Å)
FCC	4.67	2.05
HCP	4.19	2.06
ATOP	3.08	1.84

(b) CO on Pt(111) with or without presence of O

Surface	Chemisorption energy (eV)	d(O-Pt) (Å)	d(C-Pt) (Å)	d(C-O) (Å)
CO-Pt	1.75 (1.66±0.08) (Ref. 36)	3.04	1.84 (1.85±0.10) (Ref. 42)	1.20 (1.15±0.05) (Ref. 42)
CO-Pt-O	1.57	2.06	1.85	1.19

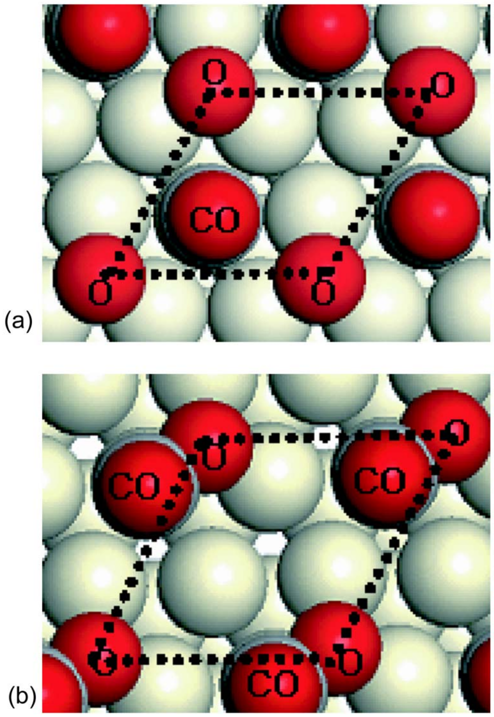

FIG. 3. (Color online) Two possible geometries for the coadsorption of CO and O in a $p(2\times2)$ supercell (dotted line). The structure (a) is more stable than (b) by approximately 0.63 eV.

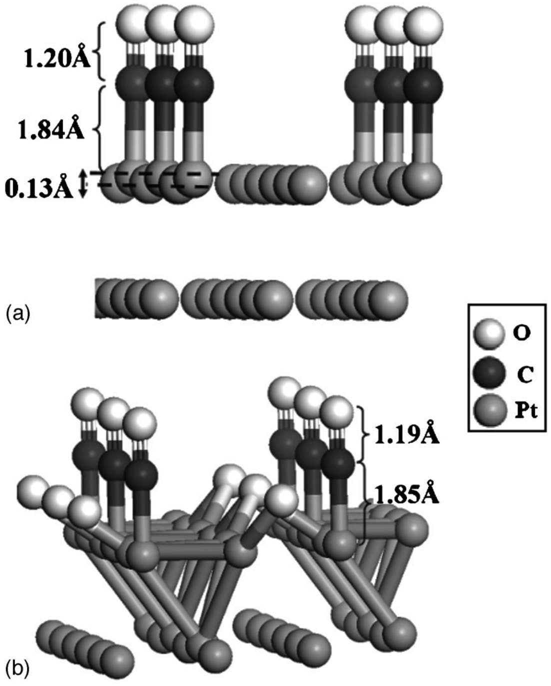

FIG. 4. The surface structures of Pt(111)-$p(2\times2)$ with only adsorption of CO in (a) and coadsorption of CO and O in (b). The coadsorption of CO and O reduces the surface corrugation.

the top four layers of our six layer slabs are relaxed. Indeed, by freezing the Pt atoms in the slab we also find a much smaller coadsorption effect (~70 meV) similar to that of Bleakely *et al.*[18] (Table II). The significance of surface relaxations in the coadsorption energy shift can be seen by comparing Fig. 4(a) (only CO adsorbed) with Fig. 4(b) (CO and O coadsorbed). In Fig. 4(a) the Pt atom on which CO adsorbs is pulled out from the surface by about 0.13 Å with respect to the bare Pt (having no CO). However as O coadsorbs with CO [Fig. 4(b)], less surface corrugation occurs since oxygen adsorbed on the fcc site pulls up Pt around it by 0.08 Å and CO displaces Pt by only 0.03 Å with respect to the bare Pt. Hence, under coadsorption the surface tends to be flatter.

To evaluate more in detail the effect of relaxation on the coadsorption effects Table II illustrates the adsorption energies of CO for relaxed, and unrelaxed *three* layers Pt(111) slabs (the same model system as that of Ref. 18). Without surface relaxations, the CO adsorption energies on the Pt(111)-$p(2\times2)$-O surface differ from the clean Pt(111) only by 70 meV. But once the top surface is allowed to relax, the differences increase to approximately 170 meV. Hence, coadsorption of CO and O decreases the adsorption energy of CO with respect to the clean Pt(111) regardless of the surface relaxation. However, with surface relaxation the bond strength of Pt-CO is much weaker and the coadsorption effect is enhanced. Thus we find that the effect of surface relaxations is important in mediating the interaction between adsorbants.

It is notable that even though oxygen coadsorption reduces the energy for CO adsorption by almost 0.2 eV, the (C-Pt) bond distance is practically unaffected by the O adsorption. This result is consistent with the recent explanation that different orbitals are involved in for controlling the bond length and stiffness of Pt-C-O than for the adsorption energy[43] and similar to what has been observed in the combined cyclic voltammetry, NMR study of Lu *et al.*[44] who observed that the changes in electronic structure of the CO-Pt bond and its bond strength were somewhat independent. The lowering of the CO adsorption energy that we find when oxygen coadsorbs is in agreement with the experimental observation that the CO oxidation rate increases under oxidizing conditions.[21]

TABLE II. Effect of O coadsorption on E_{CO}^{ads} with and without surface relaxation. With surface relaxation the bond strength of CO-Pt is weakened (~170 meV) more than without relaxations (~70 meV).

All Pt atoms are fixed			Pt atoms on the top layer are allowed to relax		
ΔE_{co}^{ads} (meV)	d(C-Pt) (Å)	d(C-O) (Å)	ΔE_{co}^{ads} (meV)	d(C-Pt) (Å)	d(C-O) (Å)
−76	1.86	1.20	−173	1.84	1.20

TABLE III. Adsorption energy on the Pt(111) surface for OH (a) and (b) CO in the presence of OH [all in a $p(2\times2)$ supercell]. Bond lengths and angles are compared with previously calculated values (Ref. [49]) in parenthesis.

(a) OH on Pt(111)

Site	Chemisorption energy (eV)	d(O-Pt) (Å)	d(O-H) (Å)	(Pt-OH)
BRIDGE	2.89	2.16	1.00	66° (67°)
ATOP	2.85 (2.31)	2.00 (2.01)	0.99 (0.98)	73° (73°)
FCC	2.61	2.21	0.99 (0.98)	0° (0°)
HCP	2.36	2.30	0.99 (0.98)	0° (0°)

(b) CO on the Pt(111) surface with the presence of OH on atop site of Pt

Surface	Chemisorption energy (eV)	d(O-Pt) (Å)	d(O-H) (Å)	d(C-Pt) (Å)	d(C-O) (Å)	(Pt-OH)
CO-Pt-OH	1.64	2.01	0.99	1.86	1.19	72.3°

Coadsorption of CO and OH

A hydroxyl group (OH) is another important chemical species in the oxidation of CO. It is observed experimentally as an intermediate of water dissociation on the Pt-electrode.[45,46] Within the context of the bifunctional mechanism it plays an important role as an adsorbate facilitating CO oxidation by providing a source of oxygen on the surface. A $p(2\times2)$ supercell was used to study OH (coverage=0.25) adsorption, which is similar to the cell choice in previous work.[45,47,48] All degrees of freedom were relaxed so that the OH molecule can also change its orientation with respect to the surface plane. Table III shows the OH adsorption energy on various Pt(111) surface sites with their equilibrium bond lengths and bond angles. The most stable configuration of OH is on the bridge site with the OH bond rotated towards the surface by about 70° from the surface normal direction. Its energy is only slightly below that on the atop site, in agreement with previous theoretical work.[48] When increasing the OH coverage to 1/3 (in a $p(\sqrt{3}\times\sqrt{3})$ cell) OH is actually a bit more stable on the atop site than on the bridge site. Hence, we used the atop site to study OH adsorption on Pt(111). In the fcc and hcp hollow sites, the Pt-OH bond is perpendicular to the surface though these sites have considerably weaker adsorption. Compared to the clean Pt(111) surface, OH coadsorption reduces the energy for CO adsorption by 0.12 eV although the C-Pt bond distance remains practically the same as in the case of oxygen coadsorption.

Figure 5 shows the surface structure of Pt(111) with OH in (a), and with coadsorption of CO and OH in (b). The surface Pt atoms are displaced up by OH (0.15 Å) and by CO (0.22 Å) as compared to a clean Pt(111) surface.

Alloying of Ru in Pt

Two mechanisms are generally called upon to explain the increased CO-oxidation rate when Ru is alloyed into Pt electrode particles: In the *bifunctional* mechanism adsorbates play a direct role by providing oxygen on the surface for CO oxidation.[1,10] The *electronic* effect on the other hand focuses on the direct effect alloying may have on the weakening of the Pt-CO bond strength.[50,51] We have tried to separate these effects by performing calculations on PtRu(111) surfaces with and without adsorbates. Calculations are performed in a $p(2\times2)$ supercell with one Ru at the surface and all layers below the surface pure Pt. The adsorption energies for CO on the surface Ru atom, and Pt next to it, are given in Table IV

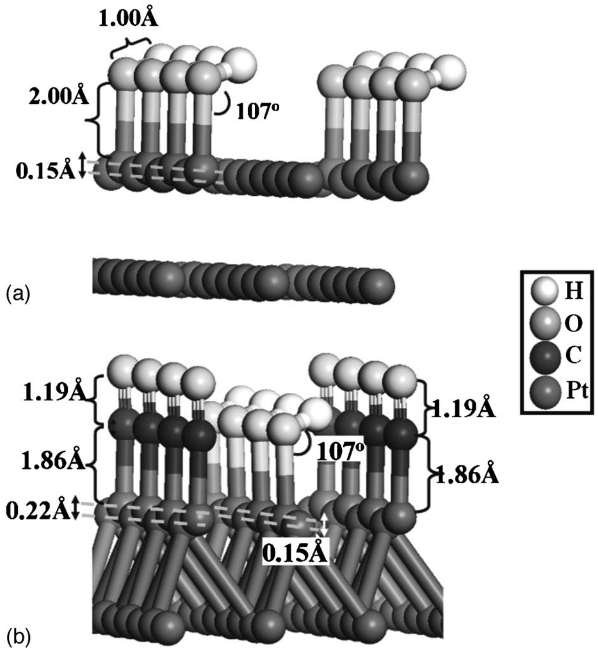

FIG. 5. The surface structures of Pt(111)-$p(2\times2)$ with only OH in (a) and coadsorption of CO and OH in (b).

TABLE IV. Adsorption energies, bond lengths for CO on the Pt-Ru alloy surface. ΔE^{ads} is the difference with the CO adsorption energy on the pure Pt(111) surface.

Surface	E^{ads} (eV)	ΔE^{ads} (meV)	d(C-Pt) (Å)	d (C-O) (Å)	(Pt-CO)
CO-PtRu	1.75	+6	1.84	1.20	0°
CO-RuPt	2.31	+561	1.85 d(C-Ru)	1.20	0° (Ru-CO)

with their relevant bond lengths and angles. Figure 6 shows the surface structures of CO-PtRu and CO-RuPt. In both cases CO binds on the atop site.

Alloying Ru in the surface does not weaken the bond strength of (CO-Pt). In fact it slightly enhances the adsorption of CO on Pt (+6 meV higher than for pure Pt). Ge *et al.*[13] studied the adsorption of a CO on the PtRu(111) alloy and claimed that the surface strain induced by the size mismatch of Pt and Ru (Ru is smaller than Pt by about 5%) increases CO adsorption. To quantitatively estimate the surface strain effect on the CO adsorption on PtRu(111) we recalculated the adsorption energy of CO in a supercells, $p(2\times2)$ having all atoms fixed at the positions that atoms would have for a pure Pt surface except for CO. In this way, we can remove any strain effect from the variation in adsorption energy. Table V shows the CO adsorption energy on the frozen slabs.

As expected, as the surface relaxation is removed, the Pt-CO bond strength is reduced by about 120 meV on pure Pt(111). But more importantly, without relaxation, Ru *lowers* the CO adsorption energy on Pt. Hence, it is the relaxation in the surface that makes bare Ru increases the CO adsorption energy on Pt. Given that the strain plays such an important role in the effect Ru has on the Pt-CO bond strength, our results may be somewhat affected by the choice and size of the supercell and Ru coverage. Hence, the increase of the Pt-CO adsorption energy by 6 meV should be taken to indicate the general effect is small.

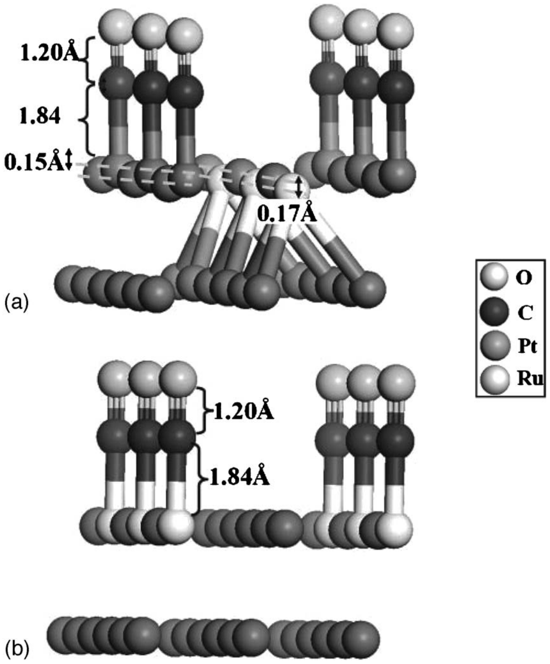

FIG. 6. Surface structure of CO-PtRu(111)-$p(2\times2)$ in (a) and CO-RuPt(111)-$p(2\times2)$ in (b). While adsorption of CO on the atop site of Pt induces surface corrugation, binding with Ru keeps the surface flat.

The bare Ru result may not be that important because under typical fuel cell conditions oxygen containing species, such as O or OH, are present on Ru islands. We show in the next section that such oxidized Ru is much more potent in reducing the Pt-CO bond strength than bare Ru might be.

Simultaneous coadsorption and alloying

While many studies have investigated the effect of Ru on adsorption on Pt in vacuum conditions, it is more likely that in realistic electrode conditions, Ru sites are covered with oxygen or with hydroxyl groups. Indeed, our previous analysis, in which PtRu surfaces were equilibrated in environments with varying oxygen chemical potential, shows that under most conditions Ru islands on the surface are covered with oxygen.[14] Hence, we study the effect of Ru on the CO-Pt bond strength under the condition that either O or OH is adsorbed near the Ru site. Calculations are performed in a $p(2\times2)$ supercell. The atop site is used for OH adsorption whereas the oxygen atom adsorbs on the FCC site. Figure 7 illustrates the calculated surface structures and Table VI shows the variation of the CO-Pt bond strength/angles with varying alloying and adsorption conditions. All ΔE^{ads} are calculated with respect to the reference of CO on a pure Pt(111) surface. While alloying Ru only has a weak (enhancement) effect in the Pt-CO bond strength (see Table VI), its effect becomes more pronounced as Ru is oxidized by O or OH. In all cases the Pt-CO bond strength is reduced without any significant modification to the bond length and angle, corroborating the idea that different orbitals are responsible for the bond length and bonding energy.[43]

Our results would indicate that the largest component of the electronic effect of Ru as an alloying element is indirect.

TABLE V. Adsorption energy of CO on the PtRu(111) surface without surface relaxation. ΔE^{ads} is the difference in the adsorption energy of CO on PtRu(111) and on pure Pt(111) (both unrelaxed).

Supercell	E^{ads} (eV)	ΔE^{ads} (meV)
$P(2\times2)$	1.63	−123

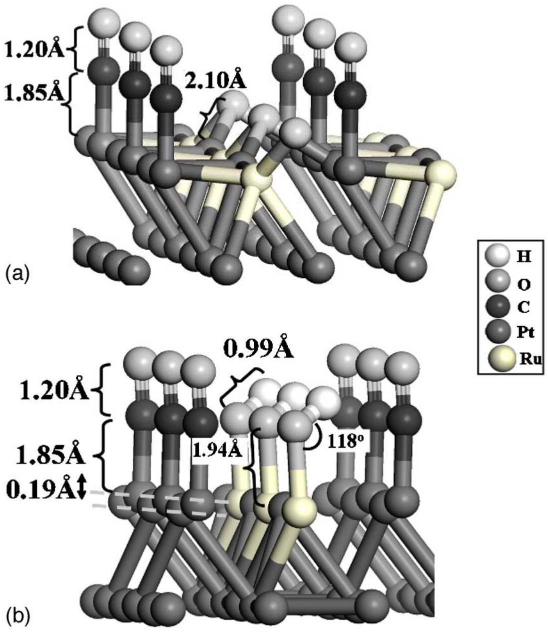

FIG. 7. (Color online) Surface of CO-PtRu(111)-$p(2\times2)$-O in (a) and CO-PtRu(111)-$p(2\times2)$-OH in (b).

It is only when Ru becomes oxidized that a significant bond strength reduction of the neighboring Pt-CO occurs. Hence the bifunctional mechanism [having Ru-O(H) close to the Pt-CO], and the electronic mechanism [having Ru-O(H) reduce the Pt-CO bond strength] both benefit the CO oxidation and may not be separable in experiments where only the overall CO throughput is measured. An elegant combination of cyclic voltammetry (CV) and temperature programmed desorption (TPD) did separate the two effects concluding that the bi-functional mechanism is about four times more effective in reducing the activation barrier for CO oxidation than is the ligand field effect.[44] Since our results point at the interfaces of Ru-Pt on the surface as important places for CO oxidation, the island structure predicted by our recent Monte Carlo simulations under mild oxidizing conditions may be particularly interesting for making electrodes with high activity.[14] Surface Ru with O(H) bonded to it is beneficial for CO oxidation for two reasons: It reduces the Pt-CO adsorption, and provides an oxidation source for CO. The reduction of the CO-Pt adsorption energy that we find is somewhat larger, but in reasonable agreement with the value suggested by Lu *et al.* (~2 kcal/mol).[44]

Competitive adsorption on Ru and Pt

So far we have assumed that CO is bonded to surface Pt, and Ru on the surface is covered by either O or OH. This is

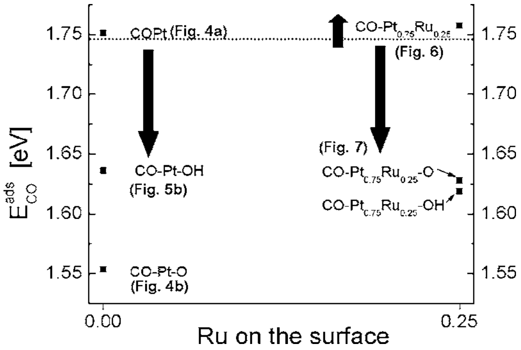

FIG. 8. The variation of adsorption energies of CO on the Pt(111) surface as a function of coadsorption and alloying of Ru into Pt surface. While coadsorption of O or OH always decreases the bond strength of CO-Pt, alloying Ru into Pt(111) surface enhances it. But once Ru is oxidized by O(H) the adsorption energy of CO reduces dramatically.

a reasonable assumption as in methanol oxidation CO is generated on the Pt sites. This does not however represent the thermodynamically favored state. Table VII shows the energy for exchanging CO or OH between Pt and Ru sites. The surface consists of all Pt except a single Ru near to Pt, and all atoms in the sub-surfaces are Pt. Both of the adsorbates favor Ru and hence they will compete in bonding. If both CO and OH are present the thermodynamically favored state has CO on Pt and OH on Ru. If there are no adsorbates on the PtRu surface except for CO, it has a strong driving force to move from Pt to Ru. If the suggestion in the literature that the activation barrier for CO diffusion on PtRu(111) surface is low[52–54] is correct, the displacement of CO from Pt toward Ru is kinetically feasible. Hence the displacement of CO from Pt towards Ru is not only thermodynamically driven but also kinetically feasible. Under coadsorption of CO and OH, Ru relatively binds OH more strongly than CO. Hence, Pt will remain more exposed to CO.

DISCUSSION

Figure 8 summarizes the variation of CO chemisorption energy on a Pt(111) surface as a function of coadsorption and Ru alloying. The coadsorption of O or OH reduces the bond strength of Pt-CO under all circumstances. While some of this effect is electronic, our controlled calculation on frozen surfaces indicates that a substantial part of this coadsorption interaction may be attributed to surface relaxation effects. A crucial factor seems to be whether CO can "isolate" the Pt to which it binds by pulling it out of the surface. The difference between the calculation with and without surface relaxation

TABLE VI. Adsorption energy of CO on Pt (or Ru) when coadsorption on nearby Ru (or Pt) is present. All ΔE^{ads} are referenced to the adsorption energy of CO for pure Pt(111) surface.

Surface	E^{ads} (eV)	ΔE^{ads} (meV)	d (C-Pt) (Å)	d(C-O) (Å)	d (Ru-O) (Å)	d(O-H) (Å)	(Ru-OH)
CO-PtRu-O	1.63	−123.4	1.85	1.20	1.94	—	—
CO-PtRu-OH	1.62	−132.1	1.85	1.20	1.94	1.00	61.9°

(Table II) confirms that CO strengthens its bond to Pt when the latter comes up from the surface. This can be understood by the bonding competition a Pt atom experiences between the CO adsorbed on Pt and its neighbors in the surface. Pulling the Pt out of the surface reduces the competition from the neighboring Pt atoms and makes a stronger Pt-CO bond. All of the adsorbates, (CO, O, and OH) pull surface Pt atoms up, but because oxygen bonds to three neighboring Pt atoms at the fcc site, it makes the surface more flat than OH, which adsorbs at the top site of a single Pt. This difference in surface strain explains why O is slightly better in reducing the adsorption energy of CO on Pt than OH. Hence, our results indicate that surface relaxations caused by coadsorption are very important in understanding the CO adsorption energy. While these relaxation effects are important on flat surfaces as studied here, they are even more likely to be significant in nanoparticle catalysts where the relaxation of surface atoms is less constrained.

Campbell *et al.*[6] reported that the rate of CO_2 production increases and its activation energy decreases as the oxygen coverage increases on the Pt(111) surface. They argue that the reduction of the adsorption energy is due to the repulsive interaction between the adsorbates, reducing the metal $-2\pi^*$ CO electron back donation by oxygen. Gland *et al.*[16] also observed that the activation energy of CO_2 formation changes as a function of the surface concentration of oxygen and CO, from 40 kcal/mol on an almost clean Pt(111) surface to 17 kcal/mol at the saturation coverage. They attributed this decrease to the repulsive interactions between CO and O. They also observed both CO and O to form an island structure on the Pt(111) surface, with the oxidation reaction occurring as CO diffuses into the boundaries of the island structure of oxygen atoms. These results are consistent with our findings. The reduction of the CO-Pt adsorption energy by O is equivalent to a repulsive interaction between the two adsorbed species.

When surface relaxation is prohibited the presence of Ru near Pt decreases the CO adsorption energy, but surface relaxation washes this effect out and actually turns it slightly in the other direction. The effect of pure Ru is in each case rather small and likely not relevant under practical catalyst operating conditions: However, once Ru is oxidized by O or OH adsorption (a likely scenario) the CO adsorption energy on a neighboring Pt is reduced by 0.12–0.13 eV.

All species preferentially adsorb on Ru when both Ru and Pt are present in the surface, though the simultaneous adsorption is more complicated. When both CO and a stronger oxidizing species such as O or OH are present on the surface, CO prefers Pt, and OH and O prefer Ru. Assuming CO is formed on Pt—a reasonable assumption in the catalysis of hydrocarbons—its possible migration to a Ru site depends on the external (electro) chemical potentials of O and OH. If these are high enough to cause adsorption on Ru, CO will remain on Pt and the surface will consist of CO-Pt and Ru with O or OH coverage. In this case CO removal from Pt can only proceed by oxidation to CO_2 (likely to occur at the boundary between Pt and Ru islands). For low O or OH chemical potentials, CO is at least thermodynamically favored to migrate from Pt to Ru. It seems from these approximate arguments that an *ideal* situation would be one where Ru is somewhat covered with O or OH to provide oxidants but not fully covered so that CO can still migrate there from Pt.

TABLE VII. The energy for exchanging CO or OH, either separately or together between the Pt and Ru sites. The structure having a positive ΔE is energetically more stable. For example, CO-PtRu-OH is thermodynamically more favored structure to the CO-RuPt-OH by 200 meV.

System	ΔE (meV)
CO-PtRu	0.00
CO-RuPt	+561.43
OH-PtRu	0.00
OH-RuPt	+702.60
CO-PtRu-OH	0.00
CO-RuPt-OH	−201.89

CONCLUSION

We studied the adsorption energy of CO on Pt(111) surface as a function of varying chemical conditions, such as the coadsorption of O(H) and alloying with Ru. Our results show that coadsorption of either O or OH always decreases the CO adsorption energy for both pure Pt and a Pt-Ru surface alloy. The surface relaxation effect is a key factor that transfers the interaction between adsorbed CO and O or OH. Alloying Ru to a Pt(111) surface in fact enhances CO adsorption slightly, but once Ru next to Pt is oxidized by O(H) the bond strength of Pt-CO decreases dramatically. Considering that the adsorbates can induce surface segregation of Ru and form island structures,[14] the boundaries of these structures can be very important place for the chemical reaction of CO oxidation.

ACKNOWLEDGMENTS

This research was supported by the MURI program of the Army Research Office under Grant No. DAAD19-03-1-0169. Additional support came from NSF (Grant No. CI-9619020) through computing resources by NPACI at the San Diego Supercomputer Center. The authors also thank Kristin Persson, Caetano Miranda, and Chris Fisher for valuable discussions.

*Corresponding author. Email address: gceder@mit.edu

[1] H. A. Gasteiger, N. M. Markovic, and P. N. Ross, J. Phys. Chem. **99**, 8290 (1995).

[2] E. P. M. Leiva, E. Santos, and T. J. Iwasita, J. Electroanal. Chem. Interfacial Electrochem. **215**, 357 (1986).

[3] O. A. Petrii and G. A. Tsirlina, Electrochim. Acta **39**, 1739 (1994).

[4] H. A. Gasteiger, N. Markovic, P. N. Ross, and E. J. Cairns, J. Phys. Chem. **97**, 12020 (1993).

[5] X. Q. Gong, Z. P. Liu, R. Raval, and P. Hu, J. Am. Chem. Soc. **126**, 8 (2004).

[6] C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, J. Chem. Phys. **73**, 5862 (1980).

[7] M. Xu, J. Liu, and F. Zaera, J. Chem. Phys. **104**, 8825 (1996).

[8] J. Narayanasamy and A. B. Anderson, J. Electroanal. Chem. **554**, 35 (2003).

[9] P. Liu, A. Logadottir, and J. K. Nørskov, Electrochim. Acta **48**, 3731 (2003).

[10] M. Watanabe and S. Motoo, J. Electroanal. Chem. Interfacial Electrochem. **60**, 267 (1975).

[11] G. A. Somorjai, *Surface Chemistry and Catalyst* (John Wiley & Sons, New York, 1994).

[12] M. S Liao, C. R. Cabrera, and Y. Ishikawa, Surf. Sci. **445**, 267 (2000).

[13] Q. Ge, S. Desani, M. Neurock, and K. Kourtakis, J. Phys. Chem. B **105**, 9533 (2001).

[14] B. C. Han, A. Van der Ven, G. Ceder, and B.-J. Hwang, Phys. Rev. B **72**, 205409 (2005).

[15] F. Zaera, J. Liu, and M. Xu, J. Chem. Phys. **106**, 4204 (1997).

[16] J. L. Gland and E. B. Kollin, J. Chem. Phys. **78**, 963 (1983).

[17] A. L. Gerrard and J. F. Weaver, J. Chem. Phys. **123**, 224703 (2005).

[18] K. Bleakely and P. Hu, J. Am. Chem. Soc. **121**, 7644 (1999).

[19] A. Eichler and J. Hafner, Phys. Rev. B **59**, 5960 (1999).

[20] J. G. Wang, W. X. Li, M. Borg, J. Gustafson, A. Mikkelsen, T. M. Pedersen, E. Lundgren, J. Weissenrieder, J. Klikovits, M. Schmid, B. Hammer, and J. N. Andersen, Phys. Rev. Lett. **95**, 256102 (2005).

[21] B. L. M. Hendriksen and J. W. M. Frenken, Phys. Rev. Lett. **89**, 046101 (2002).

[22] X. Q. Gong, R. Raval, and P. Hu, Phys. Rev. Lett. **93**, 106104 (2004).

[23] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[24] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[25] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[26] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[27] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[28] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[29] N. W. Ashcroft and N. D. Mermin, in *Solid State Physics* (Saunders College Publishing, Philadelphia, 1976).

[30] M. Tushaus, E. Schweizer, P. Hollins, and A. M. Bradshaw, J. Electron Spectrosc. Relat. Phenom. **44**, 305 (1987).

[31] J. Yoshinobu and Maki Kawai, J. Chem. Phys. **103**, 3220 (1995).

[32] N. Materer, U. Starke, A. Barbieri, K. H. R. Döll, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **325**, 207 (1995).

[33] Y. T. Wong and R. Hoffmann, J. Phys. Chem. **95**, 859 (1991).

[34] P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic, J. Phys. Chem. B **105**, 4018 (2001).

[35] H. Orita, N. Itoh, and Y. Inada, Chem. Phys. Lett. **384**, 271 (2004).

[36] Y. Yeo, L. Vattuone, and D. A. King, J. Chem. Phys. **106**, 392 (1997).

[37] U. Starke, N. Materer, A. Barbieri, R. Döll, K. Heinz, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **287**, 432 (1993).

[38] J. L. Gland, B. A. Sexton, and G. B. Fisher, Surf. Sci. **95**, 587 (1980).

[39] A. Bogicevic, J. Stromquist, and B. I. Lundqvist, Phys. Rev. B **57**, R4289 (1998).

[40] B. Hammer and J. K. Nørskov, Adv. Catal. **45**, 71 (2000).

[41] Y. Xu, A. V. Ruban, and M. Mavrikakis, J. Am. Chem. Soc. **126**, 4717 (2004).

[42] D. F. Ogletree, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **173**, 351 (1986).

[43] I. Dabo and N. Marzari (private communication).

[44] C. Lu, C. Rice, and R. I. Masel, P. K. Babu, P. Waszczuk, H. S. Kim, E. Oldfield, and A. Wieckowski, J. Phys. Chem. B **106**, 9581 (2002).

[45] S. Volkening, K. Bedurftig, K. Jacobi, J. Wintterlin, and G. Ertl, Phys. Rev. Lett. **83**, 2672 (1999).

[46] G. B. Fisher and B. A. Sexton, Phys. Rev. Lett. **44**, 683 (1980).

[47] A. Eichler and J. Hafner, Phys. Rev. Lett. **79**, 4481 (1997).

[48] A. Michaelides and P. Hu, J. Chem. Phys. **114**, 513 (2001).

[49] M. T. M. Koper, T. E. Shubina, and R. A. Van Santen, J. Phys. Chem. B **106**, 686 (2002).

[50] H. Igarashi, T. Fujino, Y. M. Zhu, H. Uchida, and M. Watanabe, Phys. Chem. Chem. Phys. **3**, 306 (2001).

[51] M. Watanabe, Y. M. Zhu, H. Igarashi, and H. Uchida, Electrochemistry (Tokyo, Jpn.) **68**, 244 (2000).

[52] M. T. M. Koper, J. J. Lukkien, A. P. J. Jansen, and R. A. Van Santen, J. Phys. Chem. B **103**, 5522 (1999).

[53] P. K. Babu, J. H. Chung, S. T. Kuk, T. Kobayashi, E. Oldfield, and A. Wieckowski, J. Phys. Chem. B **109**, 2474 (2005).

[54] Y. Tong, H. S. Kim, P. K. Babu, P. Waszczuk, A. Wieckowski, and E. Oldfield, J. Am. Chem. Soc. **124**, 468 (2002).