

NO Chemisorption on Pt(111), Rh/Pt(111), and Pd/Pt(111)

Hairong Tang and Bernhardt L. Trout*

*Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139**Received: May 21, 2005; In Final Form: July 16, 2005*

The chemisorption of NO on clean Pt(111), Rh/Pt(111) alloy, and Pd/Pt(111) alloy surfaces has been studied by first principles density functional theory (DFT) computations. It was found that the surface compositions of the surface alloys have very different effects on the adsorption of NO on Rh/Pt(111) versus that on Pd/Pt(111). This is due to the different bond strength between the two metals in each alloy system. A complex d-band center weighting model developed by authors in a previous study for SO₂ adsorption is demonstrated to be necessary for quantifying NO adsorption on Pd/Pt(111). A strong linear relationship between the weighted positions of the d states of the surfaces and the molecular NO adsorption energies shows the closer the weighted d-band center is shifted to the Fermi energy level, the stronger the adsorption of NO will be. The consequences of this study for the optimized design of three-way automotive catalysts, (TWC) are also discussed.

1. Introduction

Alloys have attracted considerable interest in the field of heterogeneous catalysis because their catalytic properties are often superior to those of pure metals. Enhanced properties are due to either the electronic effect or the ensemble effect or both.¹ To narrow down the parameter space for choosing an alloy with desirable properties in catalyst design, it is desirable to have composition–property relationships, so that the properties of reactions could be predicted on different surfaces, such as monometallic surfaces, alloy surfaces, and overlayers. An approach to this in the literature is based on the d-band center and weightings of it, which have been found to correlate well with the chemical activity of different metal surfaces.^{2–7} The interactions of simple adsorbates with a single type of metal atom on monometallic or pseudomorphic overlayer surfaces, such as the adsorption of CO at the top site of Pt(111) or Cu/Pt(111), can be correlated directly to the d-band center of that metal atom.⁴ A simple weighting is usually necessary to properly treat the interactions between adsorbates and surfaces on which the adsorbates form bonds equally with more than one type of metal surface atom, such as hydrogen chemisorption on the hollow site of Pd–Re alloyed overlayers and alloyed surfaces.⁶ It is likely that a more complicated d-band center weighting would need to be used for the binding of chemisorbed molecules which bind unequally to multiple types of surface atoms, such as the adsorption of SO₂ on the Pt(111) surface, alloy surfaces, and overlayers.⁷

The adsorption of NO on metal surfaces has been widely studied due to its importance in various heterogeneous catalytic processes.^{8–11} One of the important examples is the reduction of toxic NO_x gas in automobile exhaust. This reaction, along with the oxidation of CO and hydrocarbons (HCs), proceeds simultaneously on the so-called three-way catalyst (TWC), which usually consists of platinum, palladium, and rhodium. The performance of the catalyst can be adjusted by changing its composition. However, hitherto, no detailed and systematic studies have been carried out for the adsorption of NO on Rh or Pd alloyed Pt(111) surfaces.

Similarly, the dissociation of NO on metal surfaces has also been the subject of many experimental^{12–15} and theoretical^{16–18} investigations due to its importance to environmental catalysis. It plays a key role in the catalytic transformation of NO into harmless molecules. By using high-resolution X-ray photoelectron spectroscopy (XPS) and temperature-programmed XPS, Zhu et al. found that no dissociation of NO takes place on Pt(111).¹² NO dissociation is also found to be unfavorable on the Pd surfaces, especially the Pd(111) surface.^{16–18} The calculated dissociation barriers are found to be much smaller at Pd steps and edges compared to the values on Pd(111).^{16,17} The order of the effective dissociation activation energies on Pd surfaces is step (511) [1.54 eV] < (100) [1.63 eV] < terrace (511) [1.77 eV] < (111) [2.44 eV].¹⁶ The dissociation therefore takes place at the step of Pd surfaces. Rh surfaces are far superior over Pd surfaces in terms of NO dissociation.¹⁸ However, the dissociation of NO on Rh is strongly dependent on the structure of surfaces. Both experimental^{13–15} and theoretical^{16–18} studies found that the NO dissociation reaction is much faster on the open Rh(100) surface and the stepped Rh(331)/(511) surface than on the dense Rh(111) surface. Because of the low dissociation activity of NO on Pt(111), Pd(111), and Rh(111), NO dissociation is not considered to be important on Rh/Pd alloyed Pt(111) surfaces and, therefore, not studied here.

In this paper, we study the adsorption of NO on clean Pt(111) surfaces, Rh/Pd alloyed Pt(111) surfaces, and Rh/Pd overlayers with Pt(111) as the substrate. D-band center models are used to analyze the relationship between the adsorption strength of NO on surfaces and the surface compositions. Qualitatively different behaviors are found in the different systems. We explain this difference via the difference in the bonding strength between Pt atoms and the metal atoms added to form the alloy. A fundamental study of the properties of metals surfaces that govern their interactions with NO could lead to a better understanding of the reaction mechanisms and specific reaction pathways.

2. Computational Details

First principles density functional theory (DFT) methods were used to study the adsorption of NO on various surfaces. (The

* To whom correspondence should be addressed. E-mail: trout@mit.edu.

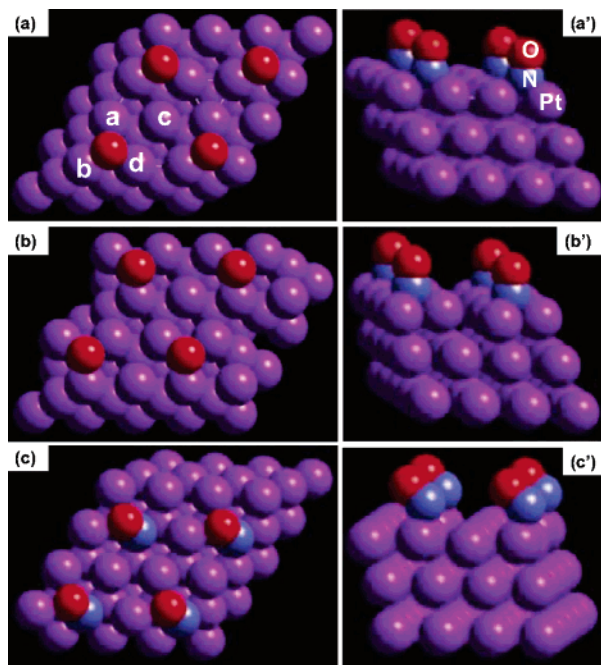


Figure 1. Schematic of NO adsorbed at various sites on clean Pt(111) surfaces: (a) top view of NO at fcc sites; (a') side view of NO at fcc sites; (b) top view of NO at hcp sites; (b') side view of NO at hcp sites; (c) top view of NO at top sites; (c') side view of NO at top sites.

GNU publicly licensed software DACAPO was used.¹⁹ We first studied the adsorption of NO at different sites on clean Pt(111) surfaces including face-centered cubic (fcc), hexagonal close-packed (hcp), top, and bridge. The top view and side view of each adsorption configuration are plotted in Figure 1. The bridge-site adsorption is not plotted, since the geometry optimization ended up as the fcc adsorption. A (2×2) unit cell and a three-layer slab model were used throughout the study. The applicability of this slab model to describe accurately the properties of atomic and molecular adsorbates has been tested thoroughly by publications from our group and from others.^{4,6,7,20–27} The adsorption geometry of NO and the positions of the atoms in all but the bottom Pt layer in the slab model were relaxed during the optimization, with the bottom Pt layer being fixed at the calculated bulk lattice constant, 4.00 Å. A vacuum of ~ 10 Å was used to separate the slabs. Between these slabs, a point dipole was included in the Z direction (the direction perpendicular to the slabs) in order to eliminate the interactions among periodic images. The ionic cores are described by ultrasoft pseudopotentials,^{28,29} allowing the plane wave basis set to have a kinetic energy cutoff of 25 Ry (340 eV). The gradient-corrected exchange-correlation functional PW91-GGA³⁰ was applied self-consistently. All of the surface Brillouin zones were sampled at $4 \times 4 \times 1$ Monkhorst–Pack k-point mesh.³¹ Although a gas phase NO molecule is spin polarized, previous studies of NO on transition metal surfaces indicate that chemisorbed NO is not spin polarized due to a strong interaction between the adsorbate and the substrate.^{32–35} Therefore, all of the calculations were nonmagnetic in this study.

To be consistent with our previous paper,⁷ the surface alloys and overlayers are designated as $nM^x/\text{Pt}(111)$, modeled by replacing n Pt atoms in the top Pt layer with other metal atoms (M) such as Rh and Pd. $n = 1, 2$, or 3 are surface alloys with different local concentrations of M, such that $n = 4$ is an overlayer; x represents the sites replaced, as marked in Figure 1a. The initial geometries of NO on all of the alloy surfaces

TABLE 1: Adsorption Energies (AEs) and Geometric Parameters for NO Chemisorption at Various Sites on Clean Pt(111) Surfaces

| site | AE ^a (eV) | AE ^b (eV) | $d_{\text{N-O}}^a$ (Å) | $d_{\text{N-O}}^c$ (Å) | $d_{\text{N-Pt}}^a$ (Å) | $d_{\text{N-Pt}}^c$ (Å) |
|------|-------------------------|--------------------------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| fcc | 2.10 | 2.09 ^b /2.05 ^c | 1.219 | 1.224 | 2.107 | 2.094 |
| hcp | 1.97 | 1.92 | 1.214 | 1.221 | 2.113 | 2.089 |
| top | 1.69 | 1.61 | 1.193 | 1.199 | 1.967 | 1.956 |

^a This work. ^b Reference 20. ^c Reference 24.

and overlayers were taken from the most stable adsorbed configuration of NO on the clean Pt(111) surfaces, as illustrated in Figure 1a and a'.

3. Results and Discussions

3.1. Adsorption of NO on Clean Pt(111) Surfaces. Table 1 lists the adsorption energies and the main geometric parameters for NO adsorption at various sites on clean Pt(111) surfaces. The bridge site was found to be an unstable site. It does not correspond to an energy local minimum, and NO goes to the fcc site during the geometry optimization. This phenomenon was also observed by Aizawa et al.²⁰ As shown in Table 1, the chemisorption of NO on Pt(111) follows the stability order $\text{fcc} > \text{hcp} > \text{top}$. The most stable adsorption site of NO on Pt(111) is the fcc hollow site, while the top site has a much lower adsorption energy as compared to those of the 3-fold hollow sites. This is in agreement with previous theoretical studies.^{20,24} Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy,³⁶ dynamic low-energy electron diffraction (LEED),^{37,38} and high-resolution X-ray photoelectron spectroscopy (XPS)¹² all found that NO is adsorbed in a 3-fold fcc site with a $p(2 \times 2)$ structure at low coverages ($\theta \leq 0.25$ ML).

Geometry optimizations for NO at the fcc and hcp sites resulted in the molecule being perpendicular to the surface with the N end down (refer to Figure 1a, a', b, and b'). On the other hand, adsorption of NO at the top site resulted in a tilted geometry (refer to Figure 1c and c'), with N–O not perpendicular to the surface but with an angle of 54.7° , predicted to be 54.4° in Burch et al.'s calculations.²⁴ This bent structure has also been reported for NO chemisorption on Pd(111).³⁹ This upright adsorption geometry at a 3-fold hollow site and tilted orientation at an on-top site has also been found in NEXAFS³⁶ and LEED studies.³⁸ The last four columns in Table 1 indicate that the geometry parameters that we obtained are in accordance with previous calculations.²⁴ At a fcc site, the chemisorbed NO bond distance is about 1.22 Å and the N–Pt bond distance is about 2.11 Å in our calculations, in agreement with both NEXAFS ($d_{\text{N-O}} = 1.24 \pm 0.05$ Å)³⁶ and LEED measurements ($d_{\text{N-O}} = 1.18 \pm 0.04$ Å and $d_{\text{N-Pt}} = 2.07$ Å).³⁷

Since the most stable adsorption site of NO on clean Pt(111) is the fcc site, the initial geometries of NO on all of the alloy surfaces and overlayers were chosen to be at the fcc sites formed by a, b, and d surface atoms, as shown in Figure 1a. Our assumption that the fcc site is the most preferred NO adsorption site on alloys has been tested and confirmed.

3.2. NO Chemisorption at the fcc Site on Alloy Surfaces and Overlayers.

3.2.1. NO Chemisorption at the fcc Site on Rh/Pt(111). The adsorption energies of NO on various Rh alloyed Pt(111) surfaces are summarized in part a of Table 2. It can be seen that, among the single substitution series (1Rh^x/Pt(111), $x = a, b, c$, or d), the substitution of site c does not affect the adsorption energy of NO. On the other hand, the substitution of the other sites (a, b, or d) which form the fcc site increases the binding strength of NO by about 38 kJ/mol.

TABLE 2: Adsorption Energies (AEs) of NO Chemisorption on (a) Rh/Pt(111) Surfaces and (b) Pd/Pt(111) Surfaces

| (a) Rh/Pt(111) | | (b) Pd/Pt(111) | |
|------------------------------|-------------|------------------------------|-------------|
| system | AE (kJ/mol) | system | AE (kJ/mol) |
| clean Pt(111) | -202.6 | clean Pt(111) | -202.6 |
| 1Rh ^a /Pt(111) | -240.2 | 1Pd ^a /Pt(111) | -211.5 |
| 1Rh ^b /Pt(111) | -240.7 | 1Pd ^b /Pt(111) | -211.9 |
| 1Rh ^c /Pt(111) | -201.9 | 1Pd ^c /Pt(111) | -215.9 |
| 1Rh ^d /Pt(111) | -240.2 | 1Pd ^d /Pt(111) | -211.3 |
| 2Rh ^{ab} /Pt(111) | -273.8 | 2Pd ^{ab} /Pt(111) | -216.1 |
| 2Rh ^{ac} /Pt(111) | -239.8 | 2Pd ^{ac} /Pt(111) | -224.8 |
| 2Rh ^{bc} /Pt(111) | -240.8 | 2Pd ^{bc} /Pt(111) | -225.5 |
| 2Rh ^{ad} /Pt(111) | -273.2 | 2Pd ^{ad} /Pt(111) | -216.6 |
| 2Rh ^{bd} /Pt(111) | -274.0 | 2Pd ^{bd} /Pt(111) | -216.1 |
| 2Rh ^{cd} /Pt(111) | -239.8 | 2Pd ^{cd} /Pt(111) | -224.8 |
| 3Rh ^{bcd} /Pt(111) | -275.1 | 3Pd ^{bcd} /Pt(111) | -230.3 |
| 3Rh ^{acd} /Pt(111) | -273.8 | 3Pd ^{acd} /Pt(111) | -230.5 |
| 3Rh ^{abd} /Pt(111) | -300.5 | 3Pd ^{abd} /Pt(111) | -218.4 |
| 3Rh ^{abc} /Pt(111) | -275.1 | 3Pd ^{abc} /Pt(111) | -230.2 |
| 4Rh ^{abcd} /Pt(111) | -301.4 | 4Pd ^{abcd} /Pt(111) | -232.9 |

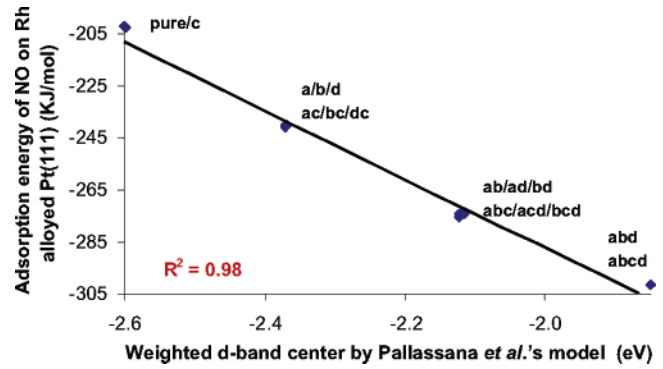
Similarly, double substitution in which site c is one of those substituted has a similar binding strength to that of the single substitution without replacing site c, which is about -240 kJ/mol. Triple substitution with site c replaced has a similar adsorption energy to that of the double substitution without a substitution of the c site, which is about -274 kJ/mol. Also, NO adsorbed to the overlayer of Rh on a Pt(111) substrate has an adsorption strength similar to that on the triple substituted 3Rh^{abd}/Pt(111). Therefore, the effect of substituting site c is negligible in *n*Rh^x/Pt(111) systems. This is easy to understand from intuition. For the Rh/Pt(111) alloy surfaces, the geometry optimizations show that, when adsorbed upright to the fcc site on the surface, molecular NO bonds almost equally close to the three surface metal atoms (a, b, and d) which form the fcc site, and it is further from site c than from sites a, b, and d, as illustrated in Figure 1a and a'.

This is similar to the case of the adsorption of atomic hydrogen at the hollow site on Pd-Re alloy surfaces.⁶ Therefore, the relatively simple weighted d-band center model proposed by Pallassana et al.⁶ is expected to be applicable to this system. Figure 2 shows the adsorption energy of NO on the Rh/Pt(111) surface as a function of the weighted d-band center energy calculated by Pallassana et al.'s weighted d-band center model⁶ as expressed in eq 1:

$$E_{d\text{-weighted}}^{\text{ref6}} = \frac{\sum_M V_M^2 E_d^M N^M}{\sum_M V_M^2 N^M} \quad (1)$$

where V_M^2 is the d-band coupling matrix for the surface metal atom M, which has been tabulated as a database by Ruban et al.⁴⁰ E_d^M is the d-band center of the surface metal atom M calculated by taking the first moment of the normalized d-projected density of states (pDOS) about the Fermi level. N^M is the number of bonds between the surface metal atom M and molecule NO. Figure 2 shows that the adsorption energy of NO on Rh alloyed Pt surfaces has a very strong linear correlation with the weighted d-band center model of Pallassana et al., with R^2 being 0.98. The closer the weighted d-band center shifts to the Fermi energy level, the stronger the adsorption of NO will be.

3.2.2. NO Chemisorption at the fcc Site on Pd/Pt(111). Pt, Rh, and Pd are the major active components of the three-way automotive catalyst (TWC). Having studied the NO chemisorp-

**Figure 2.** Adsorption energies of NO on Rh alloyed Pt(111) surfaces and overlayers vs the weighted d-band center of the surfaces calculated by Pallassana et al.'s model.⁶

tion on Rh/Pt(111) in the last subsection, we look at the NO chemisorption on Pd/Pt(111) in this subsection. Part b of Table 2 lists the adsorption energies of NO on various Pd alloyed Pt(111) surfaces. All of the adsorption energies of NO on Pd alloyed Pt(111) surfaces are between 210 kJ/mol and 230 kJ/mol. Although experimental data do not exist for these alloy systems so far, an experimental value for NO adsorption on a pure Pd(111) surface has been obtained as 221.65 kJ/mol (about 2.3 eV) with the temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), and electron stimulated desorption ion angular distribution (ESDIAD) techniques.⁴¹ Here, a very different phenomenon from NO chemisorption on Rh/Pt(111) is found in the adsorption of NO on Pd/Pt(111). Among the single substitution series (1Pd^x/Pt(111), $x = a, b, c, \text{ or } d$), substitution of site c results in a stronger effect on the adsorption energy of NO than substitutions of each of the other sites (a, b, or d). Also, double substitutions which include site c result in a larger binding strength of NO than those which do not include the substitution of site c. Similarly, among the triple substitution series (3Pd^x/Pt(111)), 3Pd^{abd}/Pt(111) has the lowest adsorption energy of NO, because all of the other triple substitutions include the substitution of site c. In contrast to *n*Rh^x/Pt(111) systems, the effect of the substitution of site c is found to be stronger than that of the other sites (a, b, or d) in *n*Pd^x/Pt(111) systems. This is in contradiction to our intuition. The reason for the difference between Rh/Pt and Pd/Pt will be explained in detail in the next subsection.

Since site c has a strong effect on the adsorption of NO on Pd/Pt(111) surfaces, NO must bind unequally to multiple surface atoms. (Site c is unequal to sites a, b, and d.) Considering this, a more complicated way for weighting the d-band center of various alloyed surfaces or overlayers proposed by the authors in the previous study of SO₂⁷ should be used for NO chemisorption on Pd/Pt(111). This more complex weighting model is expressed in eqs 2 and 3:

$$E_{d\text{-weighted}}^{\text{ref7}} = \frac{\sum_M V_M^2 E_d^M (\sum_i N^{M-i} S^{M-i})}{\sum_M V_M^2 (\sum_i N^{M-i} S^{M-i})} \quad (2)$$

where V_M^2 and E_d^M are the same as those in eq 1. Similar to N^M in eq 1, N^{M-i} is the number of bonds between the surface metal atom M and atom i in the adsorbate molecule. Different from eq 1, S^{M-i} is introduced in eq 2. It represents the bond strength between the surface metal atom M and the atom i in the adsorbate. Inclusion of S^{M-i} is important, as will be seen in the

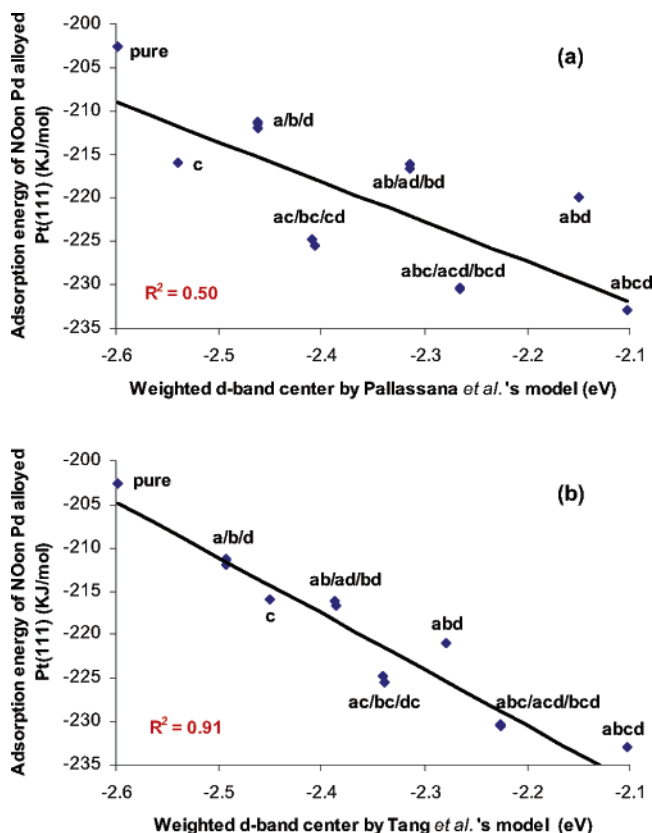


Figure 3. Adsorption energies of NO on Pd alloyed Pt(111) surfaces and overlayers vs the weighted d-band center of the surfaces: (a) by Pallassana et al.'s model;⁶ (b) by Tang et al.'s model.⁷

comparison in Figure 3. It is added to account for the inequality in the interaction of atoms in the adsorbate and the metal surface atoms (x). The form of S^{M-i} is chosen to be electrostatic:⁷

$$S^{M-i} = \frac{C^M C^i}{d_{M-i}} \quad (3)$$

where C^M and C^i are the Pauling electronegativities of the metal atom M and atom i in the adsorbate⁴² and d_{M-i} is the distance between these two atoms. More computational details about using this d-band center weighting model can be found in ref 7. In the case of NO adsorption on Rh/Pt(111) alloy surfaces, because the effect of substituting site c is negligible and NO bonds almost equally to the three surface metal atoms (a , b , and d in Figure 1a) which make up the fcc site, the S^{M-i} terms in the denominator of eq 2 and those in the numerator of eq 2 will cancel out. The complex d-band center weighting model in eq 2 is therefore reduced to the same model as that expressed in eq 1.

In Figure 3, the behavior of applying the weighted d-band center model from Pallassana et al.⁶ to NO adsorption on Pd/Pt(111) (refer to Figure 3a) is plotted and compared to that of applying our more complex weighted d-band center model⁷ to the same system (refer to Figure 3b). As shown in Figure 3a, the linearity of the correlation between the adsorption energy of NO on Pd/Pt(111) and the simple weighted d-band center⁶ is very poor ($R^2 = 0.50$). The general trend of the NO adsorption strength versus simple weighted d-band center⁶ still corresponds to that in Figure 2: the closer the d-band center is shifted to the Fermi energy level, the stronger the adsorption of NO. However, in each series, such as the single substitution series, the adsorption energy of NO versus the simple weighted d-band

TABLE 3: Bond Strength and Bond Length between Alloyed Species and Platinum Atoms (the Adsorption Energy (AE) of NO at an fcc Site on 1M^c/Pt(111) Is Also Listed for Reference)

| bond (Pt–M) | bond strength (kcal/mol) | bond length (Å) | AE ^a on 1M ^c /Pt(111) (kJ/mol) |
|-------------|--------------------------|-----------------|--|
| Pt–Pt | −64.6 | 2.378 | −202.6 |
| Pt–Rh | −68.4 | 2.377 | −201.9 |
| Pt–Pd | −39.0 | 2.380 | −215.9 |
| Pt–Ru | −79.9 | 2.361 | −191.7 |

^a Adsorption energy of NO at an fcc site (formed by sites a , b , and d) on 1M^c/Pt(111).

center has an opposite trend to the general one. The poor linearity in Figure 3a can be dramatically improved by applying our more complex weighted d-band center model, as shown in Figure 3b. R^2 can be enhanced to 0.91. In addition, the trend of NO adsorption strength versus weighted d-band center⁷ in each series now also follows the general trend.

3.2.3. Explanation for the Different Behaviors of Rh/Pt(111) and Pd/Pt(111). The different behavior of NO chemisorption on Rh/Pt(111) versus that on Pd/Pt(111) can be explained by the bond order conservation (BOC) concept: In a many-body system, the total bond order of all interacting two-center bonds is conserved. The “body” means an atom or group of atoms that may be treated as a single entity.⁴³ By applying the BOC concept to the systems of NO adsorption on surfaces, as illustrated in Figure 1a, the summation of bond order for sites a , b , and d with site c ($a,b,d-c$) and that for sites a , b , d and NO ($a,b,d-NO$) is conserved. Here, we treat the group of atoms (a , b , and d in Figure 1a) as a single entity. The gas phase pairwise bond strength and bond length between different alloyed species and platinum atoms, which are calculated by the Gaussian 03 programs with the DFT/B3-LYP method, are summarized in Table 3. As listed in Table 3, for Rh/Pt systems, the bond strength of Pt–Rh (−68.4 kcal/mol) is not very different from that of Pt–Pt (−64.6 kcal/mol), which means that the bond order of $a,b,d-c$ is similar to that of clean Pt(111) surfaces. Therefore, according to the BOC concept, the bond order of $a,b,d-NO$ is expected not to change very much from that on clean Pt(111) surfaces. This is in agreement with our calculations. The adsorption energy of NO at the fcc site on 1Rh^c/Pt(111) is −201.9 kJ/mol, which is only about 0.7 kJ/mol higher than that on the clean Pt(111) surfaces. (Refer to the last column in Table 3.) The NO adsorption energy on the other single-site (site a , b , or d) substituted surface is dramatically different from that on clean Pt(111) surfaces. This is due to the change of the electronic structure of the surface, as measured by the change of the d-band center. As can be seen in Figure 2, this can be captured by the d-band center weighting model. In Pd/Pt systems, the bond strength of Pt–Pd (−39.0 kcal/mol) is much smaller than that of Pt–Pt. In other words, the bond order $a,b,d-c$ is much weaker than that of clean Pt(111) surfaces. The BOC concept predicts the bond order of sites a , b , d , and NO for NO-Pd/Pt to be much stronger than that for NO-clean Pt(111) systems. Our calculated results show that the adsorption energy of NO at the fcc site on the Pt(111) surface with site c substituted by Pd is −215.9 kJ/mol, which is about 13.3 kJ/mol stronger than that on the pure Pt(111) surfaces. Since Koper et al.'s study found that the Pt–Ru bond was stronger than the Pt–Pt bond,⁴⁴ the Ru/Pt system is therefore calculated to test the generality of our explanation. As listed in the last row of Table 3, the bond strength of Pt–Ru is about 15.3 kcal/mol stronger than that of Pt–Pt, which suggests the bond order of a , b , d , and NO to be smaller from the BOC's point of view.

This is also true in our calculations: the adsorption of NO at the fcc site on 1Ru°/Pt(111) is about 10.9 kJ/mol less stable than that on the clean Pt(111) surface. From Table 3, we can also see that the bond strength is consistent with the bond length. The longer the Pt–M bond length is, the weaker the Pt–M bond strength and vice versa. Therefore, a simple measure of the change of the adsorption strength of NO on alloyed surfaces is the change of the bond length between the alloyed species and platinum atoms.

4. Conclusions

We conclude that a recently proposed d-band center weighting model⁶ well describes some simple systems, such as the adsorption of molecular NO at the fcc site on Rh alloyed Pt(111) surfaces, but has limitations for other simple systems, for example, the adsorption of molecular NO at the fcc site on Pd alloyed Pt(111) surfaces. Actually, NO adsorption on Pd/Pt(111) is not as simple as one might intuit: NO does bind equally to the three metal surface atoms (a, b, and d) which make up the fcc site, but NO binding is affected by site c, which is not part of the fcc site (refer to Figure 1a). This is because the bond strength between surface metal atoms can affect adsorption energies, in agreement with the BOC concept, and this additional effect should be considered while considering the binding of adsorbates to the surfaces. The limitation of Pallassana et al.'s model⁶ can be improved by the approach proposed by us for more complicated systems, in which the adsorbates bind unequally to multiple metal surface atoms.⁷ In each surface alloy system, the molecular NO adsorption strength depends linearly on the weighted position of the d states of the surface relative to the Fermi level. The closer the weighted d-band center is to the Fermi level, the stronger the adsorption is. These correlations should be useful in selecting which type and local concentration of surface atoms to choose for optimal alloy catalysts.

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References and Notes

- (1) Sachtler, W. M. H. *Vide* **1973**, 28, 67.
- (2) Hammer, B.; Morikawa, Y.; Nørskov, J. K. *Phys. Rev. Lett.* **1996**, 76, 2141.
- (3) Hammer, B.; Nørskov, J. K. *Surf. Sci.* **1995**, 343, 211.
- (4) Mavrikakis, M.; Hammer, B.; Nørskov, J. K. *Phys. Rev. Lett.* **1998**, 81, 2819.
- (5) Hammer, B.; Nørskov, J. K. *Adv. Catal.* **2000**, 45, 71.
- (6) Pallassana, V.; Neurock, M.; Hansen, L. B.; Nørskov, J. K. *J. Chem. Phys.* **2000**, 112, 5435.
- (7) Tang, H.; Trout, B. L. *J. Phys. Chem. B* **2005**, 109, 6948.
- (8) Brown, W. A.; King, D. A. *J. Phys. Chem. B* **2000**, 104, 2578.
- (9) Shelef, M.; Graham, G. W. *Catal. Rev.—Sci. Eng.* **1994**, 36, 433.
- (10) Taylor, K. C. *Catal. Rev.—Sci. Eng.* **1993**, 35, 457.
- (11) Schmatloch, V.; Kruse, N. *Surf. Sci.* **1992**, 270, 488.
- (12) Zhu, J. F.; Kinne, M.; Fuhrmann, T.; Denecke, R.; Steinrück, H. P. *Surf. Sci.* **2003**, 529, 384.
- (13) Delouise, L. A.; Winograd, N. *Surf. Sci.* **1985**, 159, 199.
- (14) Borg, H. J.; Reijerse, Jfcjm; Vansanten, R. A.; Niemantsverdriet, J. W. *J. Chem. Phys.* **1994**, 101, 10052.
- (15) Villarrubia, J. S.; Ho, W. J. *J. Chem. Phys.* **1987**, 87, 750.
- (16) Loffreda, D.; Simon, D.; Sautet, P. *J. Catal.* **2003**, 213, 211.
- (17) Hammer, B. *J. Catal.* **2001**, 199, 171.
- (18) Loffreda, D.; Simon, D.; Sautet, P. *J. Chem. Phys.* **1998**, 108, 6447.
- (19) <http://www.fysik.dtu.dk/CAMP/dacapo.html>.
- (20) Aizawa, H.; Morikawa, Y.; Tsuneyuki, S.; Fukutani, K.; Ohno, T. *Surf. Sci.* **2002**, 514, 394.
- (21) Lin, X.; Schneider, W. F.; Trout, B. L. *J. Phys. Chem. B* **2004**, 108, 250.
- (22) Lin, X.; Hass, K. C.; Schneider, W. F.; Trout, B. L. *J. Phys. Chem. B* **2002**, 106, 12575.
- (23) Alavi, A.; Hu, P.; Deutsch, T.; Silvestrelli, P. L.; Hutter, J. *Phys. Rev. Lett.* **1998**, 80, 3650.
- (24) Burch, R.; Daniells, S. T.; Hu, P. *J. Chem. Phys.* **2002**, 117, 2902.
- (25) Li, X.; Gewirth, A. A. *J. Am. Chem. Soc.* **2003**, 125, 7086.
- (26) Tang, H.; Van der Ven, A.; Trout, B. L. *Phys. Rev. B* **2004**, 70, 045420.
- (27) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. *Phys. Rev. Lett.* **2004**, 93, 156801.
- (28) Vanderbilt, D. *Phys. Rev. B* **1990**, 41, 7892.
- (29) Laasonen, K.; Pasquarello, A.; Car, R.; Lee, C.; Vanderblit, D. *Phys. Rev. B* **1993**, 47, 10142.
- (30) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, 46, 6671.
- (31) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, 13, 5188.
- (32) Tsai, M.-H.; Hass, K. C. *Phys. Rev. B* **1995**, 51, 14616.
- (33) Hass, K. C.; Tsai, M.-H.; Kasowski, R. V. *Phys. Rev. B* **1996**, 53, 44.
- (34) Hammer, B.; Nørskov, J. K. *Phys. Rev. Lett.* **1997**, 79, 4441.
- (35) Hammer, B. *Phys. Rev. Lett.* **1999**, 83, 3681.
- (36) Esch, F.; Greber, T.; Kennou, S.; Siokou, A.; Ladas, S.; Imbihl, R. *Catal. Lett.* **1996**, 38, 165.
- (37) Materer, N.; Barbieri, A.; Gardin, D.; Starke, U.; Batteas, J. D.; Vanhove, M. A.; Somorjai, G. A. *Surf. Sci.* **1994**, 303, 319.
- (38) Matsumoto, M.; Tatsumi, N.; Fukutani, K.; Okano, T. *Surf. Sci.* **2002**, 513, 485.
- (39) Hansen, K. H.; Sljivancanin, Z.; Hammer, B.; Laegsgaard, E.; Besenbacher, F.; Stensgaard, I. *Surf. Sci.* **2002**, 496, 1.
- (40) Ruban, A.; Hammer, B.; Stoltze, P.; Skriver, H. L.; Nørskov, J. K. *J. Mol. Catal. A: Chem.* **1997**, 115, 421.
- (41) Ramsier, R. D.; Gao, Q.; Waltenburg, H. N.; Lee, K. W.; Nooij, O. W.; Lefferts, L.; Yates, J. T. *Surf. Sci.* **1994**, 320, 209.
- (42) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, 17, 215.
- (43) Shustorovich, E.; Sellers, H. *Surf. Sci. Rep.* **1998**, 31, 1.
- (44) Koper, M. T. M.; Shubina, T. E.; van Santen, R. A. *J. Phys. Chem. B* **2002**, 106, 686.