

# 2

## Oxide-Supported Metal Thin-Film Catalysts: The How and Why

Valentino R. Cooper, Alexie M. Kolpak, Yashar Yourdshahyan and Andrew M. Rappe\*

### 2.1. INTRODUCTION

Oxide-supported metals play an important role in a wide variety of industrial chemical processes such as the catalytic treatment of automotive exhaust. The ability to exercise greater control over the interactions of molecules on metal surfaces will create new possibilities for pollution control and the provision of novel power sources. Furthermore, a deeper understanding of molecule surface interactions will present numerous opportunities for the design of nanocatalysts.

In recent years, metal nanoparticles and thin films supported on oxides have become fundamental components of many devices as their small dimensions present structures with new chemical and physical properties, often enhancing the reactivity of these surfaces relative to their bulk counterparts. Numerous theoretical and experimental studies show that the metal particle size and shape as well as direct adsorbate interactions with the oxide support can each play a key role in enhancing the reactivity of these surfaces.<sup>1-7</sup> Further investigations imply that the support material may

---

The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

\* To whom correspondence should be addressed. E-mail: rappe@sas.upenn.edu

also influence the metal's intrinsic reactivity at these surfaces.<sup>2,5,8-13</sup> However, these studies were not able to isolate this effect from those of particle size, shape, and direct adsorbate-support interactions.

It was not until recently that Chen and Goodman probed the influence of the oxide support material on the intrinsic properties at the metal surface.<sup>14</sup> By covering a titania support with one or two flat atomic layers of gold they eliminated, direct adsorbate-support interactions as well as particle size and shape effects. Their results definitively showed that the electronic properties at the metal surface changed due to charge transfer between the support and the metal. Furthermore, their comparison of one- and two-layer films highlighted the dependence of these effects on the thickness of the metal slab.

These studies indicate that the charge transfer at the metal-oxide interface alters the electronic structure of the metal thin film, which in turn affects the adsorption of molecules to these surfaces. Understanding the effect that an oxide support has on molecular adsorption can give insight into how local environmental factors control the reactivity at the metal surface, presenting new avenues for tuning the properties of metal thin films and nanoparticles. Coupled with the knowledge of how particle size and shape modify the metal's electronic properties, these results can be used to predict how local structure and environment influence the reactivity at the metal surface.

### *2.1.1. The Theory of Molecular Adsorption on Metal Surfaces*

While there is no complete theory of surface reactivity, an understanding of how reactant, intermediate, and product adsorbates interact with a surface often gives insight into the catalytic properties of a metal. Quantum mechanical theories show that as long as the perturbation due to the interacting systems is small, the interaction of two isolated systems can be estimated using second order perturbation theory:

$$\Delta E = \frac{|V_{ij}|^2}{\varepsilon_i - \varepsilon_j},$$

where  $\varepsilon_i$  and  $\varepsilon_j$  are the eigenvalues of the unperturbed isolated systems, and  $V_{ij}$  represents the coupling matrix for these interactions. When a molecule interacts with a metal surface, the interaction involves both a transfer of electrons from the molecule's highest occupied molecular orbital (HOMO) to the metal surface (direct bonding) and a shift of electrons from the metal surface to the molecule's lowest unoccupied molecular orbital (LUMO)(back bonding). For transition metal surfaces, the exchange of electrons is achieved through interactions with the metal  $d$  orbitals.

Using perturbation theory, Hammer and Nørskov developed a model for predicting molecular adsorption trends on the surfaces of transition metals (HN model). They used density functional theory (DFT) to show that molecular chemisorption energies could be predicted solely by considering interactions of a molecule's HOMO and LUMO with the center of the total  $d$ -band density of states (DOS) of the metal.<sup>15,16</sup> In particular,

their work showed that the chemisorption energy of a molecule to a metal surface is closely related to the center of the total  $d$ -band DOS of the metal:

$$E_{chem} = -4 \left[ f \frac{V_{LUMO}^2}{\varepsilon_{LUMO} - \varepsilon_d} + f S_{LUMO} V_{LUMO} \right] - 2 \left[ (1 - f) \frac{V_{HOMO}^2}{\varepsilon_d - \varepsilon_{HOMO}} + (1 + f) S_{HOMO} V_{HOMO} \right],$$

where  $f$  is the filling of the metal  $d$  orbital and  $S$  is the overlap integral between the molecular orbital and the metal  $d$  orbitals. In this model, upward shifts in the  $d$ -band center will result in larger chemisorption energies, while downward shifts give weaker binding. This model has been successfully applied to the adsorption of CO and H<sub>2</sub> on a number of unsupported metal surfaces. However, nanoparticles may result in complicated rearrangements in the population and energy levels of the surface  $d$  orbitals due to the size and shape of the nanoparticle. Furthermore, supported particles and thin films can have changes in their electronic structure due to covalent or ionic bonding present at the metal–support interface. Such modifications of the metal surface  $d$  orbitals can have considerable consequences for molecular adsorption, by altering the interactions of the molecules’ HOMO and LUMO orbitals with modified metal states.

In this chapter, we shall use DFT to investigate the extent to which the oxide support alters the electronic structure of the deposited metal as a result of charge transfer at the metal–oxide interface. We will use CO chemisorption as a function of Pt film thickness to demonstrate how changes in the metal electronic structure can lead to chemisorption trends that deviate from expectations based on the current theory of molecular adsorption.

## 2.2. METHODOLOGY

We examined the deposition of Pt thin films onto the strongly polar O-terminated (O<sub>T</sub>)  $\alpha$ -alumina surface. Studies have shown that this surface is stabilized by the adsorption of hydrogen or a supported metal.<sup>17</sup> We used a slab geometry with an in-plane  $\sqrt{3} \times \sqrt{3} \mathbf{R}30^\circ$  unit cell and periodic boundary conditions to model the alumina surface.<sup>18</sup> The layer stacking can be represented by the formula (Al-O<sub>3</sub>-Al)<sub>4</sub>-Al-O<sub>3</sub>-(Pt<sub>3</sub>)<sub>*n*</sub>, where  $n$  is the number of Pt layers. The interfacial Pt atoms are in the energetically preferred registry, directly above the surface O atoms, forming a Pt (111) film. All calculations were performed using density functional theory (DFT)<sup>19,20</sup> with the generalized gradient approximation<sup>21</sup> for the exchange-correlation functional, as implemented in the dacapo code,<sup>22</sup> with a plane-wave cutoff of 30 Ry, ultrasoft pseudopotentials<sup>23</sup> and a  $2 \times 2 \times 1$  Monkhorst–Pack<sup>24</sup>  $k$ -point mesh. All slab calculations were performed with at least 12 Å of vacuum between periodic images in the [0001] direction. Total energies were tested to ensure that there were no surface interactions through the slab or the vacuum. The theoretical  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in-plane lattice constant of 4.798 Å was used (experimental = 4.759 Å<sup>25</sup>). In order to eliminate strain effects, all adsorption energies were compared to unsupported Pt (111) calculations at the same in-plane geometry as the supported metal. (This corresponds to the experimental Pt (111)

TABLE 2.1. CO top site binding energies relative to Pt (111), center of the total  $d$ -band DOS and the center of the partial DOS composed of unoccupied  $d_{z^2}$  states and occupied  $d_{xz}$  and  $d_{yz}$  states for the  $n$ Pt/Al<sub>2</sub>O<sub>3</sub> system. All energies are in eV.<sup>29,30</sup>

Pt Film Layers	Top Site $\Delta E_{\text{chem}}$	Total $d$ -Band Center	$d_{z^2} + d_{xz} + d_{yz}$ Band Center
1	0.68	-2.28	-1.20
2	-0.19	-1.72	-1.68
3	0.07	-1.68	-1.49
4	0.03	-1.69	-1.54
5	0.06	-1.70	-1.54
Pt (111)	0.00	-1.69	-1.53

in-plane lattice constant of 2.77 Å). For our simulations, we fixed the ions in the bottom two alumina layers to their theoretical positions, relaxed the third layer perpendicular to the surface, and fully relaxed the remaining alumina layers, Pt layers and adsorbates until the force on each atom was less than 0.01 eV/Å. We corrected for known DFT CO chemisorption errors<sup>26,27</sup> using the extrapolation method of Mason and coworkers<sup>28</sup> and estimated the error bar for computed chemisorption energies to be 0.01 eV.

### 2.3. CO CHEMISORPTION TO ALUMINA-SUPPORTED PT THIN FILMS

Table 2.1 shows the top site chemisorption energy for the adsorption of CO onto the Pt/O<sub>T</sub>  $\alpha$ -alumina system as a function of metal layers, relative to Pt (111). For the monolayer of metal on the surface there is an enhancement of the CO top site binding energy relative to Pt (111). On the other hand, the second layer of Pt/O<sub>T</sub> shows a dramatic decrease in the top site chemisorption energy. For three layers of Pt on this surface, the chemisorption energy oscillates above the Pt (111) energy, eventually returning to the Pt (111) value for  $n > 4$ .

According to the HN model, an increase in chemisorption energy should correlate to an upward shift in the total  $d$ -band center of the metal. Contrary to this theory, the monolayer of Pt/O<sub>T</sub> system shows stronger chemisorption but a large decrease (0.59 eV) in the  $d$ -band center (-2.28 eV) relative to bulk Pt (111) (-1.69 eV). Furthermore, the downward shift in the  $d$ -band center of the bilayer Pt/O<sub>T</sub> system (0.03 eV) is too small to account for the reduction in chemisorption energy. To explain these deviations, it is necessary to understand how CO binds to a metal surface and how the oxide support alters the electronic properties of the metal surface to allow for changes in molecular adsorption.

#### 2.3.1. CO Binding to Transition Metal Surfaces

Due to its importance in many industrial processes, the prototypical reaction of CO binding to metal surfaces has received much attention. Using Hückel molecular orbital theory, Blyholder showed that CO bonding at top sites consists of the donation of electrons from the filled CO  $5\sigma$  HOMO to the metal  $d_{z^2}$  orbitals with a back-donation of electrons from the metal  $d_{xz}$  and  $d_{yz}$  orbitals to the CO  $2\pi^*$  LUMO.<sup>31</sup> Consequently,

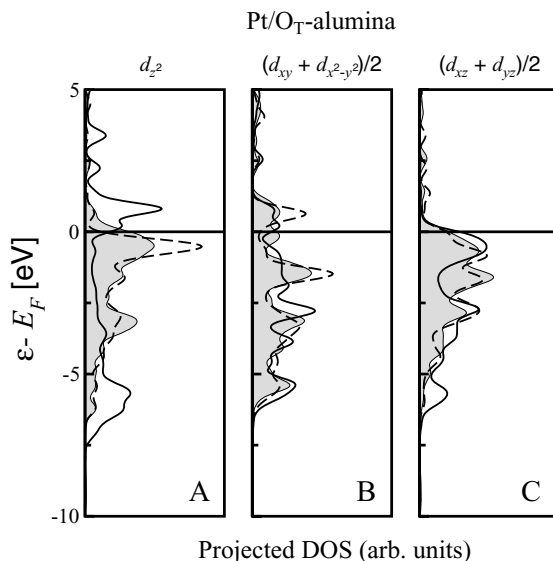


FIGURE 2.1. Orbital-projected DOS plots for the surface Pt atoms of the Pt/O<sub>T</sub>-alumina system. The shaded regions represent the DOS of the Pt (111) surface, the solid (—) lines are for the Pt monolayer, and the dashed (---) lines are for the bilayer.

it follows that to understand bonding at the top site it is necessary to consider changes in the free  $d_{z^2}$  DOS (for direct bonding) and the filled  $d_{xz}$  and  $d_{yz}$  DOS (for back-bonding). As such, the remainder of this chapter will focus on how charge transfer from the Al<sub>2</sub>O<sub>3</sub> support material to the Pt thin film will alter the electronic structure of the individual Pt  $d$  orbitals, and the implications of these changes on the direct and back bonding of molecules to these surfaces.

### 2.3.2. Metallic Deposition on an Electronegative Support: Pt/O<sub>T</sub>

The absence of Al atoms on the O<sub>T</sub>  $\alpha$ -alumina surface leaves the surface oxygen ions electron deficient. As a result, the deposition of a metal onto this support will result in the formation of hybrid orbitals between the metal  $d$  orbitals and the oxygen  $p$  orbitals. Figure 2.1 shows the projected DOS of the surface Pt atoms for one and two layers of Pt deposited onto an O<sub>T</sub>-alumina surface. Since the Pt atoms are deposited directly on top of oxygen ions, hybrid orbitals are formed with metal  $d$  orbitals with components perpendicular to the oxide surface ( $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$ ). Each of these  $d$  states participates in a higher energy anti-bonding state and a lower energy bonding state. For the  $d_{z^2}$  orbital, the higher energy state is unoccupied ( $\sim 1$  eV above the Fermi level). Forming this hybrid orbital increases the number of free  $d$  states available for direct bonding with incoming adsorbate molecules. However, the newly formed  $d_{z^2}$  bonding orbital is quite low in energy ( $\sim 6$  eV below the Fermi level). This hybrid orbital reduces the number of occupied states near the Fermi level and results in a downward shift in the center of the metal  $d$ -band. The newly formed  $d_{xz}$  and  $d_{yz}$  bonding hybrid orbitals also decrease the number of filled states with energies just below the Fermi level and

increase the number of states with energies below  $-5.0$  eV, with little or no change in the number of free states in these orbitals. Therefore, the formation of bonding hybrid orbitals will weaken the back bonding of molecules to these states and shift the center of the metal  $d$ -band downward. For a monolayer of Pt on  $\text{Al}_2\text{O}_3$ , the large enhancement in CO chemisorption energy is due to the formation of strong direct bonds between the filled  $\text{CO } 5\sigma$  and the unoccupied  $d_{z^2}$  antibonding hybrid states.

The second layer of Pt on  $\text{O}_T \text{Al}_2\text{O}_3$  shows a smaller deviation from the HN model than the monolayer. In this system, Pt atoms on the surface occupy hollow sites of the interfacial Pt atoms, as in a fcc (111) surface. This allows the  $d$  orbitals of the interfacial Pt atoms to directly interact with the  $d_{xz}$  and  $d_{yz}$  orbitals of the second-layer atoms, forming metallic bands. Due to the influence of bonding at the metal–oxide interface, the  $d_{xz}$  and  $d_{yz}$  orbitals exhibit a slight downward shift in the center of the metal bands relative to Pt (111), implying that these orbitals will have only a slight change in their back bonding relative to Pt (111). On the other hand, the  $d_{z^2}$  states gain a fraction of an electron in response to the decreased electron–electron repulsions in the Pt atom due to the loss of electrons from the other  $d$ -orbitals. This gain in charge results in a dramatic reduction in free  $d_{z^2}$  states and shifts the  $d_{z^2}$  DOS upward due to strong electron–electron repulsions within this orbital. These changes suggest that the  $d_{z^2}$  orbitals will form much weaker direct bonds with adsorbed molecules as they will have fewer states to accept electrons. Therefore, the large decrease in bonding at the metal surface is due to the reduction in the number of unoccupied  $d_{z^2}$ . For three or more layers of Pt, metal charge screening effects prevail and the DOS of the surface atoms shift's back to Pt (111) values, thereby defining the length scale of the metal-support interactions.

### 2.3.3. Correlating Chemisorption Trends with Shifts in DOS

Models of CO adsorption show that top site binding is governed by the CO HOMO ( $5\sigma$  orbital) donating electrons into the metal unoccupied  $d_{z^2}$  states, with simultaneous back-donation of electrons from the metal's occupied  $d_{xz}$  and  $d_{yz}$  states into the CO LUMO ( $2\pi^*$  orbital). Therefore, it follows that the standard chemisorption model, which considers shifts in the total  $d$ -band center, can be inaccurate for systems in which individual molecular orbitals, involved in bonding with the adsorbate, shift differently due to external interactions. In particular, we have shown that the formation of hybrid orbitals with the support material can lead both to downward shifts in the metal  $d$ -band center, which do not affect the adsorption of molecules to the metal surface, and to upward shifts that are vitally important.

An understanding of molecule–metal interactions suggests that in these systems it is necessary to only consider changes in states that are involved in bonding (i.e.  $d_{z^2}$  free states and  $d_{xz}$  and  $d_{yz}$  occupied states). Figure 2.2 shows a comparison of a partial  $d$ -band DOS center (constructed from only the  $d_{z^2}$  states and the  $d_{xz}$  and  $d_{yz}$  states) to the top site chemisorption energies for CO binding to the Pt/ $\text{O}_T$  system. Here we see that the chemisorption energy is directly related to the shifts in this partial DOS, confirming that the CO binding energy is dependent only on these states. Furthermore, these results suggest that chemisorption energies to transition metal surfaces can be predicted solely by using modified DOS  $d$ -band centers.

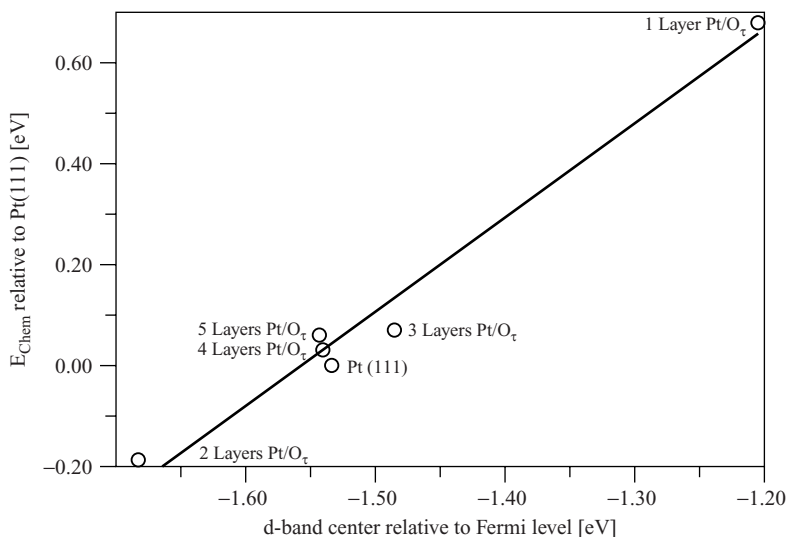


FIGURE 2.2. Comparison of DFT chemisorption energies (relative to Pt (111)) and the partial  $d$ -band center of the  $d_{z^2}$  free states and  $d_{xz}$  and  $d_{yz}$  occupied states as a function of Pt layer thickness for Pt/O<sub>T</sub>  $\alpha$ -alumina system.

## 2.4. SUMMARY/CONCLUSION

In this chapter, we have illustrated how chemisorption trends for oxide-supported metal systems can be correlated to shifts in the  $d$ -band center of a modified DOS constructed from the occupied and unoccupied states that are involved in bonding with the adsorbate molecule. While we presented specific results for Pt supported on an O<sub>T</sub> alumina surface, similar investigations on Pd and Rh supported on the Al<sub>T</sub> and O<sub>T</sub> surfaces indicate that these results may be generalized for transition metals deposited on electronegative and electropositive supports. Furthermore, we use DFT and the adsorption of CO to the Pt surface to demonstrate how the orbital-specific electronic structure of a metal surface can be used to predict the strength of the metal's interaction with molecular adsorbates. We show that orbital-specific considerations are necessary to predict bonding, as metal–oxide interfacial charge transfer can have significant effects on the electronic structure of molecular orbitals which may result in shifts in the total  $d$ -band center which are not related to the binding of a molecule to the metal surface. The fact that these effects are greatly diminished at four or five layers indicates that the metal–support interactions have a small characteristic length scale on the order of the metal interlayer spacing. While it is known that low-coordinated sites greatly enhance the reactivity of metal particles, these results demonstrate the importance of metal–support charge transfer in defining the properties at the metal surface, offering further support for the recent work of Chen and Goodman. In addition, our findings suggest that increased reactivity at the perimeter of metal particles with diameters <5 nm may be partially attributed to the strong metal–oxide coupling accessible at

these boundaries. These concepts may be useful for applications as diverse as chemical sensors, fuel cells, and photochemical reactions.

## ACKNOWLEDGMENTS

We thank Sara E. Mason and Ilya Grinberg for discussions on CO adsorption energy corrections. This work was supported by the Air Force Office of Scientific Research, Air Force Materiel Command, USAF, under Grant No. FA9550-04-1-0077 and by the NSF MRSEC Program, Grant DMR05-20020. Computational support was provided by the Defense University Research Instrumentation Program, and by the NSF CRIF Program, Grant CHE-0131132. V.R.C. thanks IBM and ACS for support through the IBM Graduate Student Award in Computational Chemistry. A.M.K. was supported by a GAANN fellowship.

## REFERENCES

1. G. Mills, M. S. Gordon, and H. Metiu, The adsorption of molecular oxygen on neutral and negative  $\text{Au}_n$  clusters ( $n=2-5$ ), *Chem. Phys. Lett.* **359**, 493–499 (2002).
2. Z. L. Wang, T. S. Ahmad, and M. A. El-Sayed, Steps, ledges and kinks on the surfaces of platinum nanoparticles of different shapes, *Surf. Sci.* **380**, 302–310 (1997).
3. J. W. Yoo, D. J. Hatcock, and M. A. El-Sayed, Propene hydrogenation over truncated octahedral Pt nanoparticles supported on alumina, *J. Catal.* **214**, 1–7 (2003).
4. B. Yoon, H. Hakkinen, and U. Landman, Interaction of  $\text{O}_2$  with gold clusters: molecular and dissociative adsorption, *J. Phys. Chem. A* **107**, 4066–4071 (2003).
5. M. Haruta, Size- and support-dependency in the catalysis of gold, *Catal. Today* **36**, 153–166 (1997).
6. M. Valden, X. Lai, and D. W. Goodman, Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, *Science* **281**, 1647–1650 (1998).
7. A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Hakkinen, R. N. Barnett, and U. Landman, When gold is not noble: nanoscale gold catalysts, *J. Phys. Chem. A* **103**, 9573–9578 (1999).
8. C. Bozo, N. Guilhaume, and J.-M. Herrmann, The role of the ceria-zirconia support in the reactivity of platinum and palladium catalysts for methane total oxidation under lean conditions, *J. Catal.* **393**, 393–406 (2001).
9. E. J. Walter, S. P. Lewis, and A. M. Rappe, First-principles study of carbon monoxide adsorption on zirconia-supported copper, *Surf. Sci.* **495**, 44–50 (2001).
10. L. M. Molina, and B. Hammer, Active role of oxide support during CO oxidation at Au/MgO, *Phys. Rev. Lett.* **90**, 206102–206101 (2003).
11. R. Lindsay, E. Michelangeli, B. G. Daniels, M. Polick, A. Verdini, L. Floreano, A. Morgante, J. Muscat, N. M. Harrison, and G. Thornton, Surface to bulk charge transfer at an alkali metal/metal oxide interface, *Surf. Sci.* **547**, 859 (2003).
12. S. Roberts, and R. J. Gorte, A comparison of Pt overlayers on  $\alpha\text{-Al}_2\text{O}_3(0001)$ ,  $\text{ZnO}(0001)\text{Zn}$ , and  $\text{ZnO}(000\bar{1})\text{O}$ , *J. Chem. Phys.* **93**, 5337–5344 (1990).
13. W. T. Petrie, and J. M. Vohs, Interaction of platinum films with the  $(000\bar{1})$  and  $(0001)$  surfaces of ZnO, *J. Chem. Phys.* **101**, 8098–8107 (1994).
14. M. S. Chen, and D. W. Goodman, The structure of catalytically active gold on titania, *Science* **306**, 252–255 (2004).
15. B. Hammer, and J. K. Nørskov, Electronic factors determining the reactivity of metal surfaces, *Surf. Sci.* **343**, 211–220 (1995).
16. B. Hammer, Y. Morikawa, and J. K. Nørskov, CO chemisorption at metal surfaces and overlayers, *Phys. Rev. Lett.* **76**, 2141–2144 (1996).



17. P. J. Eng, T. P. Trainor, G. E. Brown Jr., G. A. Waychunas, M. Newville, S. R. Sutton, and M. L. Rivers, Structure of the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surface, *Science* **288**, 1029–1033 (2000).
18. L. Pauling, and S. B. Hendricks, The crystal structure of hematite and corundum, *J. Am. Chem. Soc.* **47**, 781 (1925).
19. P. Hohenberg, and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, 864 (1964).
20. W. Kohn, and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, 1133 (1965).
21. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Atoms, molecules, solids and surfaces: Applications of the generalized gradient approximation for exchange and correlations, *Phys. Rev. B* **46**, 6671–6687 (1992).
22. B. Hammer, L. B. Hansen, and J. K. Nørskov, Improved adsorption energetics within density-functional theory using Perdew-Burke-Ernzerhof functionals, *Phys. Rev. B* **59**, 7413–7421 (1999).
23. D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Phys. Rev. B Rapid Commun.* **41**, 7892–7895 (1990).
24. H. J. Monkhorst, and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188–5192 (1976).
25. W. E. Lee and K. P. D. Lagerlof, Structural and electron diffraction data for sapphire( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), *J. Electron Microsc. Techn.* **2**, 247 (1985).
26. P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic, The CO/Pt(111) puzzle, *J. Phys. Chem. B* **105**, 4018–4025 (2001).
27. I. Grinberg, Y. Yourdshahyan, and A. M. Rappe, CO on Pt(111) puzzle: A possible solution, *J. Chem. Phys.* **117**, 2264–2270 (2002).
28. S. E. Mason, I. Grinberg, and A. M. Rappe, First-principles extrapolation method for accurate CO adsorption energies on metal surfaces, *Phys. Rev. B Rapid Commun.* **69**, 161401–161404 (2004).
29. Y. Yourdshahyan, V. R. Cooper, A. M. Kolpak, and A. M. Rappe, Catalytic behaviour at the nanoscale: CO adsorption on Al<sub>2</sub>O<sub>3</sub>-supported Pt cluster, in *Proc. SPIE Int. Soc. Opt. Eng.*, edited by T. Lian and H.-L. Dai (2003), pp. 223–232.
30. V. R. Cooper, A. M. Kolpak, Y. Yourdshahyan, and A. M. Rappe, Support-mediated activation and deactivation of Pt thin-films. *Phys. Rev. B Rapid. Comm.* **72**, 081409(R) (1-4) (2005)
31. G. Blyholder, Molecular orbital view of chemisorbed carbon monoxide, *J. Phys. Chem.* **68**, 2772–2778 (1964).