

Chemisorption of atomic oxygen on Pt(1 1 1) and Pt/Ni(1 1 1) surfaces

Timo Jacob, Boris V. Merinov, William A. Goddard III *

Division of Chemistry and Chemical Engineering, Materials and Process Simulation Center, Beckman Institute (139-74), California Institute of Technology, Pasadena, CA 91125-0001, USA

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Abstract

Using density functional theory (B3LYP functional) we systematically studied Pt/Ni alloy clusters (≤ 44 atoms) and found that the Pt/Ni(1 1 1) alloy surface prefers the bulk structure (Pt₃Ni crystal), without showing surface segregation. This leads to an ordered surface with each Ni surrounded by 6 Pt atoms. We then examined the oxygen chemisorption at all surface sites and found strongest binding at a FCC site (2 Pt and 1 Ni atom, 3.50 eV). On pure Pt(1 1 1) oxygen is most stable (3.28 eV) at the FCC site formed by three Pt atoms. This finally leads to a channel-like mobility of oxygen on the alloy surface.

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1. Introduction

Optimization of the electro-catalytic processes at electrodes provides a significant opportunity for improving fuel cell performance. To make progress in developing improved catalysts, it is important to understand the fundamental processes for these catalysts.

Nowadays in PEM fuel cells Pt and Pt-based materials are commonly used to catalyze the reactions at the electrodes. It has been observed that Pt/Ni alloys lead to enhanced reaction rates for the cathode reactions, particularly the oxygen reduction step (ORR) [1]. In this Letter we use first principles quantum mechanics to compare chemisorption of atomic oxygen on the Pt/Ni(1 1 1) alloy surface with that on the pure Pt(1 1 1) surface. It turns out that the oxygen atom binds more strongly on the Pt/Ni alloy than on pure platinum, and the position is more localized on the alloy surface. Both aspects seem to play a role in enhancing the ORR and therefore the reaction rate of the catalytic cathode process. The stronger bond of the oxygen to the surface may

lead to more efficient electron transfer between surface and adsorbate. This aspect and the higher localization on the alloy surface might increase the probability to react with H atoms to form water.

2. Theoretical methods

In our calculations we used the nonlocal B3LYP GGA-functional (generalized gradient approximation) for the exchange–correlation term [2,3]. This combines exact Hartree–Fock (HF) exchange with the local exchange functional of Slater [4], and includes the Becke nonlocal gradient correction [5], the Vosko–Wilk–Nusair exchange functional [6], and the Lee–Yang–Parr local and nonlocal correlation functional [3].

All ab-initio cluster calculations were performed using the Jaguar programs [7]. For both the platinum and the nickel atoms the core electrons were described with the Hay and Wadt core–valence relativistic effective-core potential (ECP) [8]. This potential uses angular momentum projection operators (nonlocal ECP) to enforce the Pauli principle [9,10]. In the Jaguar program the ECP utilizes the LACVP** basis set. For the oxygen atom all electrons were treated explicitly using the 6-31G** basis set.

* Corresponding author. Fax: +1-626-585-0918.
E-mail address: wag@wag.caltech.edu (W.A. Goddard III).

3. Results and discussion

We used a finite cluster to model both Pt(111) and Pt/Ni(111) surfaces. This allows us to more thoroughly investigate the details of the changes in electronic structure than possible with periodic systems. Our cluster might also represent the chemistry of realistic dispersed catalysts, which could have a size as small as

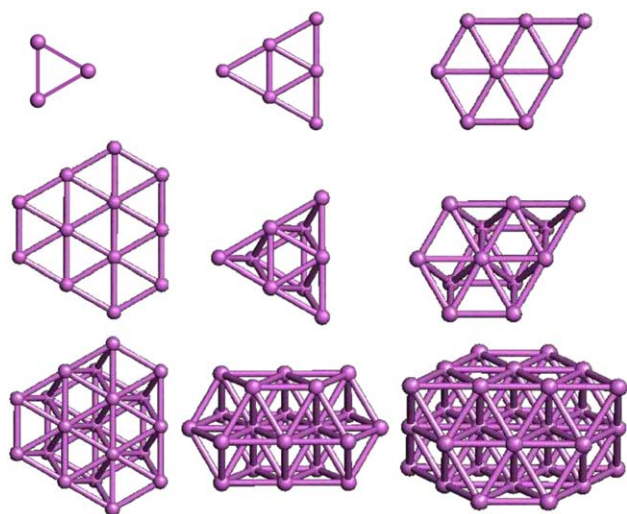


Fig. 1. The figure shows various one-, two-, and three-layer clusters (without adsorbate) studied to find a cluster model for both the Pt(111) and the Pt/Ni(111) alloy surfaces. The view of the one-, and two-layer clusters is to the top of the surface, whereas the three-layer clusters are shown from the side.

2 nm. For this approach it is important to determine the dependence of the chemistry on the cluster size (minimizing border effects). In previous extensive studies [11] we tested the cluster-size and cluster-shape behavior on the chemisorption of atomic oxygen on Pt(111) (see Fig. 1). We found the $Pt_{9,10,9}$ cluster (the indices denote the number of atoms per layer) to be sufficient to model the Pt(111) surface. We also expect this cluster to be appropriate for chemisorption of other species (atoms and small molecules), because oxygen, which is sufficiently electronegative to strongly disturb the electronic structure of the cluster, is well described.

Since oxygen chemisorption on pure Pt(111) is described in [11], here we will only summarize these results. Oxygen was found to bind most strongly at the FCC-site (a three-fold site with no Pt atom in the second layer) with an adsorption energy of 3.28 eV. The experimental value ranges between 3.21 and 3.43 eV [12]. Two Pt–O distances equal to 2.01 Å indicate two short covalent bonds. The distance to the third Pt atom is longer by 0.18 Å, showing evidence for a donor–acceptor bond (charge transfer creating ionic bonding). A similar difference (≈ 0.2 Å) between covalent bonds and donor–acceptor bonds has been observed previously [14]. The experimentally measured bond length is 2.01 ± 0.05 Å [13], which is in very good agreement with our result. These data and those for the other adsorption sites are summarized in Table 1.

Before examining the oxygen chemisorption on the Pt/Ni alloy we determined the optimal composition of Pt and Ni at the alloy surface. Since both Pt and Ni have a

Table 1

Ground spin-states, adsorption energies, bond distances and vibrational frequencies of the oxygen atom on the different adsorption sites of the $Pt_{9,10,9}$ cluster (without adsorbate ground spin-state $S = 9$) and of the $Pt_{10,10,6}Ni_{4,3,2}$ alloy cluster (without adsorbate ground spin-state $S = 11$)

	Spin-state S	E [eV]	R [Å]	ω [cm^{-1}]
<i>Adsorption site on $Pt_{9,10,9}$</i>				
top	9	2.015	1.872	–
bridge	8	2.729	1.990	–
HCP	8	2.946	Pt–O = 2.040 (2x) Pt–O = 2.151 (1x)	531
FCC	8	3.284	Pt–O = 2.005 (2x) Pt–O = 2.185 (1x)	510
<i>Adsorption site on $Pt_{10,10,6}Ni_{4,3,2}$</i>				
top1	11	1.639	Ni–O = 1.722	970
top2	11	1.834	Pt–O = 1.886	746
bridge1	10	2.976	Pt–O = 1.978 Ni–O = 1.885	649
bridge2	10	2.456	Pt–O = 1.971	970
bridge2B	10	3.270	Pt–O = 2.014	902
FCC1	10	3.501	Pt–O = 2.025 Ni–O = 2.016	910
HCP1	10	3.413	Pt–O = 2.033 Ni–O = 1.965	967
FCC2	10	2.327	Pt–O = 2.117 (2x) Pt–O = 1.941 (1x)	866
HCP2	10	3.302	Pt–O = 2.152 (1x) Pt–O = 2.055 (2x)	707

fcc bulk crystal structure, we used a fcc-like bulk unit cell of Pt in which the corner atoms were replaced by Ni, leading to a 3:1 ratio for Pt and Ni (Pt_3Ni). Performing periodic DFT calculations (PBE exchange–correlation functional [15]) the optimal interatomic distances were obtained. These distances were used for the initial geometry of periodic slab calculations to determine surface relaxation. The relaxation effects and the difference between the Pt–Pt and Pt–Ni distances were negligible (<1%), and hence we used the bulk interatomic distance (2.755 Å) to build the Pt/Ni(1 1 1) alloy cluster with fixed atom positions. This behavior is similar to the pure Pt(1 1 1) surface.

From systematic studies of different cluster sizes (also see Fig. 1) with different compositions of Pt and Ni, we finally found $\text{Pt}_{10.10.6}\text{Ni}_{4.3.2}$ to be the best cluster (Fig. 2), indicating no surface segregation. In contrast experiments on Pt_3Ni crystals [16] find strong surface segregation, where the Pt content for the first three surface layers is 100–50–89%. This suggests that dispersed catalysts may not exhibit the segregation found in large

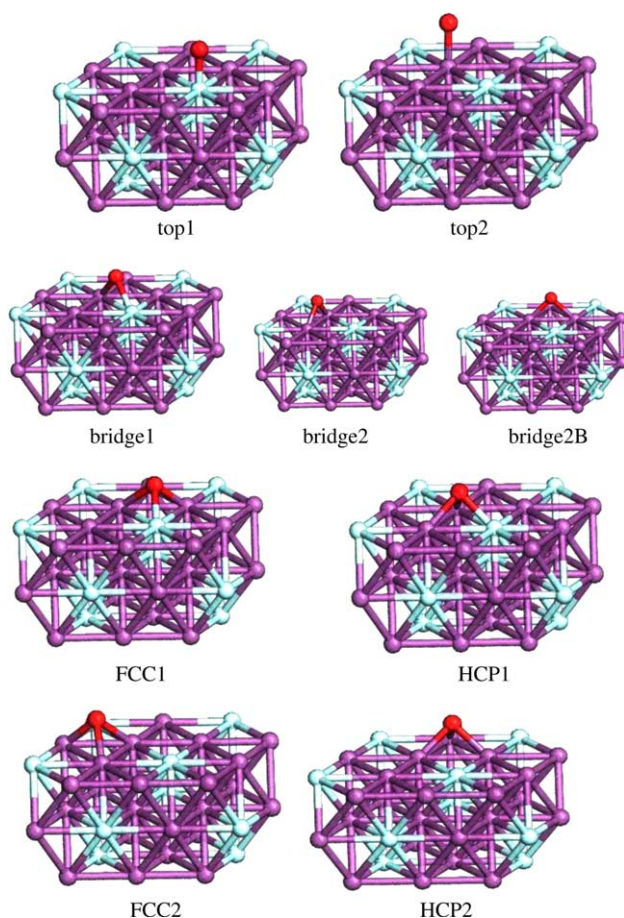


Fig. 2. All distinguishable adsorption sites on the Pt/Ni alloy surface are shown (grey atoms are Pt). For pure Pt there are only four different sites (top, bridge, HCP, and FCC). The difference between bridge2 and bridge2B is due to the different atom type of the second-layer atom located beneath the bridging site: Pt (bridge2) and Ni (bridge2B).

crystals, indicating that our cluster model may be the best representation for those catalysts. Further explanations can be found in [17].

For $\text{Pt}_{10.10.6}\text{Ni}_{4.3.2}$ there are two on top binding sites (Pt or Ni), three two-fold bridge sites, and four three-fold sites (two FCC, and two HCP). All adsorption sites are shown in Fig. 2. The difference between bridge2 and bridge2B comes from the type of the second-layer atom, located beneath the bridge site. All adsorption energies, corresponding distances, ground spin-states, and frequencies of the vibration perpendicular to the surface are summarized in Table 1. It turns out, that oxygen is most strongly bound on the FCC1 site. This is similar to pure Pt, except that FCC1 is formed by two Pt atoms and one Ni atom. The binding distance shows only a difference of ≈ 0.01 Å between both Pt–O bonds and the Pt–Ni bond. The remaining three-fold sites show the same behavior in the bond distance as observed for oxygen on Pt(1 1 1), namely two short and one elongated bonds. Since oxygen has two unpaired electrons, the ground spin-state of the cluster changes by $\Delta S = 1$, as for pure Pt. This equivalence between both systems can be observed for all adsorption sites. Thus, the on top binding does not change the ground spin-state of the system, and the chemisorption on all other sites causes a change of $\Delta S = 1$. For all three-fold sites on the alloy cluster, FCC1, HCP1, and HCP2 the adsorption energies vary by only 0.2 eV. However, there is much weaker binding to the FCC2 three-fold site formed by three Pt atoms. This behavior can be explained by the distribution of the net spin at each site. From an analysis of the Mulliken charges we found a net spin between 1.1 and 1.5 at each Ni, but only 0.5 on the Pt atoms. This should be compared to the pure Pt surface, where the average net spin of the first layer atoms is about 0.7. This reduction in the net spin makes binding to three Pt atoms on the alloy less favorable than on pure Pt(1 1 1). The same behavior was observed for the bridge2 and bridge2B sites. Since at bridge2 there is a Ni atom in the second layer bound to both Pt atoms, which form the bridging site, the net spin on both Pt is reduced, and that finally weakens the bond compared to bridge2B. The binding energies at the on top sites show weaker bonds to the alloy than to the pure Pt surface. Despite Ni having the higher net spin oxygen prefers Pt rather than Ni for the on top binding. Although lots of experimental data have been reported for the oxygen chemisorption on Pt(1 1 1), there are no site-selective values available for the Pt/Ni(1 1 1) alloy surface.

The barrier for O to migrate about fcc sites shared by the same Ni is 0.23 eV, while that for hopping to a site bordering a different Ni is 0.53 eV. For comparison, the barrier on Pt(1 1 1) is 0.56 eV. Thus, oxygen is much more localized on the Pt/Ni alloy surface than on pure Pt and migrates over the alloy surface in channel-like pathways. Analyzing the Mulliken charges shows a

slightly more negative charge (by 0.02e) on the oxygen adsorbed on the alloy than on the pure Pt surface. However, the origin of this charge transfer is different. For the pure Pt surface all nearby Pt atoms contribute to the transfer and reduce their charges, but for the alloy only the Pt atoms oxygen binds to reduce their charges (not the Ni). Thus, the Pt atoms nearby the adsorbate are more positive on the alloy than on the pure Pt surface, leading to higher probability for a proton from the electrolyte to attach to an oxygen on Pt/Ni(1 1 1) than to adsorb on the surface directly.

As a summary, the chemisorption on the alloy cluster and on the pure Pt cluster shows exactly the same behavior of the ground spin-state changes. However, the Ni atoms in the alloy system drastically change the electronic configuration of the cluster and therefore the binding of a single oxygen atom. On the Pt/Ni(1 1 1) alloy surface oxygen is more strongly bound, but the adsorption energies range from 1.64 eV (top1) to 3.50 eV (FCC1) (pure Pt: 2.02–3.28 eV). Thus, oxygen is much more localized than on pure Pt. Both the stronger bond and the higher localization, could explain the enhanced ORR rate and fuel cell performance with Pt/Ni electrodes compared to pure Pt. In addition, since the Pt atoms close to the adsorbate are more positively charged on the alloy, a proton from the electrolyte rather attaches to an adsorbed oxygen than adsorbs to the surface.

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