

Effect of particle size and surface structure on adsorption of O and OH on platinum nanoparticles: A first-principles study

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Using first-principles density functional theory, we study the effect of particle size and surface structure on the chemisorption energy of OH and O on nanoparticles of Pt. We find that the chemisorption energies of O and OH are strongly affected by the size and structure of the Pt particle varying by up to 1.0 eV at different adsorption sites and particle sizes.

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I. INTRODUCTION

To surface scientists, it is of interest to understand the detailed mechanism of electrocatalysis on the atomic scale since it leads to better control of the chemical reactions and may result in the rational design of better catalysts.¹

Modern electrocatalysts in fuel cells are Pt-alloy metallic nanoparticles dispersed on supports² such as carbon, aluminum oxide, or titanium oxide. Both experimental measurements³⁻⁵ and computational calculations^{6,7} seem to indicate that nanosized electrocatalysts show a considerably different catalytic activity from extended flat surfaces. These investigations would indicate that changes observed with particle size reduction go well beyond the increase in surface area and involve fundamental physical and chemical changes in the catalytic steps.

The unique activity of nanosized electrocatalysts is still under debate.^{1,8-10} For example, on the basis of the XPS measurement, Mukerjee and McBreen¹⁰ explained that the amount of *d*-band vacancies of metal catalysts, which control the surface reactivity with adsorbates,¹¹ depends on the geometrical arrangements of the atoms around the adsorption sites as well as on the support materials and alloying.¹² Hammer and Nørskov^{1,13} attempted to explain the general trend of the chemical adsorption energies as a function of the metallic catalysts and its particle size through a *d*-band center model. According to the model, it is the relative shift of the *d*-band center (ϵ_d) of the catalyst atoms with respect to the Fermi energy (ϵ_F) that controls the surface reactivity. This model has been intensively used to describe the experimentally measured chemical activity over a series of transition metals.^{1,14,15} Several computational studies have reported that a simple parameter such as the *d*-band center,¹ density of states around the Fermi energy,¹⁶ a hole concentration of *d*-band around the Fermi level¹¹ may not be enough to fully elucidate the effect of particle size and structure of adsorption site.¹⁷⁻¹⁹

The general mechanism by which particle size influences catalytic activity is difficult to elucidate experimentally, as it is not easy to synthesize catalysts with well defined size and structure. In addition, the activity of catalysts is measured by turnover frequencies, which are quantities *averaged* over different particle sizes and active sites. While *ab initio* computational modeling offers, in principle, full control over the

size and shape of the catalyst, it has typically been limited to bulk materials or systems of small size:²⁰⁻²³ the morphology of the surface (i.e., the distribution of the various types of surface sites) changes with size and cannot be fully *decoupled* from the size effect. This is particularly true for particles with very small size for which the equilibrium shape often changes drastically with size.^{24,25} Considering that the average size of catalyst particles in commercial fuel cells is around a few nanometers, it may be important to understand this simultaneous effect of size and surface structure.

In this paper, we therefore chose to study explicitly Pt nanoparticles of 1 and 2 nm sizes and compare their chemical adsorption properties to those of an extended flat Pt(111) surface. We focus on the chemisorption energies of atomic oxygen (O) and the hydroxyl group (OH) and investigate how their chemisorption energies are modified by the particle size and by the reduction in coordination for Pt at the surface. Chemical adsorption is an important step in the catalytic process which can be related to catalytic activity,²⁶ and O and OH are two species of considerable importance in the electrocatalysis step of low temperature fuel cells.^{27,28}

II. METHODOLOGY

To investigate the effect of Pt particle size and surface morphology on chemisorption, we set up three model systems shown in the Fig. 1: an extended flat Pt(111) surface and Pt nanoclusters of 1 and 2 nm in size. The Pt(111) surface model consists of a six layer slab, as described in our previous work.²⁸ The 2 nm Pt cluster is a 201-atom truncated octahedron of which 122 atoms (60%) are on the surfaces. The surface consists of (100) and (111) facets. For the 1 nm Pt cluster structure, we take the experimentally observed^{29,30} cuboctahedron composed of 55 Pt atoms of which 42 atoms (76%) are on the surface. The relevant adsorption sites on the surface of these model systems are represented in Table I. The coordination number (*Z*) of an adsorption site is defined as the average nearest neighbor coordination of the Pt atom(s) that defines the adsorption site (e.g., one Pt for atop adsorption and three for fcc and hcp site adsorption).

Computation of all chemisorption energies was performed in the spin polarized generalized gradient approximation to density functional theory (DFT) with Perdew-Wang exchange correlation functional.^{31,32} The projector augmented

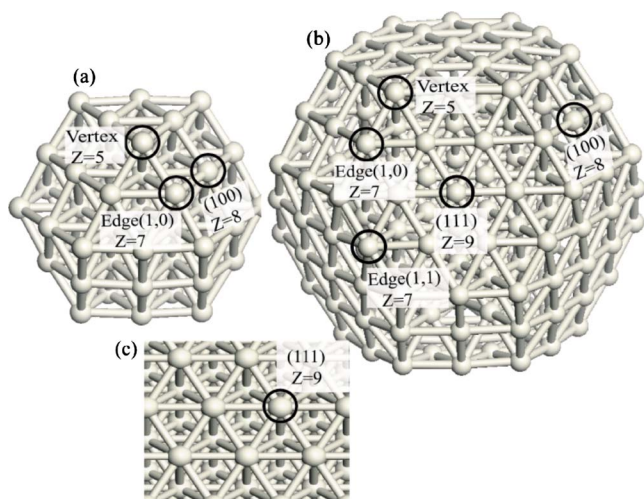


FIG. 1. (Color online) Different model systems used in our study: (a) a 1 nm Pt cluster, (b) a 2 nm Pt cluster, and (c) an extended flat Pt(111) surface. Surface sites of different symmetries are depicted in the model systems. The coordination number Z of the adsorption site is as defined in the text.

wave method^{33,34} was used as implemented in VASP.^{35,36} In the Pt(111) slab, all adsorbates and the topmost four layers of Pt atoms are relaxed, while the bottommost two layers are fixed to the positions of the relaxed pure Pt slab. In the Pt nanoparticles, all atoms, including adsorbates, are *fully* relaxed, and periodic boundary conditions are implemented with a large enough vacuum to preclude interactions between the cluster and its images. The reciprocal space integration

was performed with the gamma point. Increasing the Brillouin zone sampling to 27 irreducible k points for the 1 nm Pt cluster only changed the chemisorption energies by 10–30 meV, indicating that there is little interaction between the periodic images. All degrees of freedom are relaxed.

The chemical adsorption energy (E_{ad}^{ads-Pt}) is calculated from the total energy difference between the system with the adsorbate (E_{Pt}^{ads}), the pure Pt system [$E_{Pt}(s)$], and the adsorbate in the gas phase [$E_{ads}(g)$],

$$E_{ad}^{ads-Pt} = E_{Pt}^{ads} - [E_{Pt}(s) + E_{ads}(g)]. \quad (1)$$

III. RESULTS

A. Chemisorption energy of O

Figure 2 shows the chemical adsorption energies of O at different adsorption sites on the three model systems. For the extended flat Pt(111) surface, oxygen atoms prefer to adsorb on the high symmetry sites, such as the fcc [which is the most stable site on the bulk Pt(111) surface] and hcp sites. Chemisorption on an *atop* site is much weaker. On the *bridge* site, oxygen is not stable and slides off to the fcc site. These bulk results agree well with previous calculations^{1,37,38} and experimental observations.^{39,40}

Oxygen atoms show a significantly different chemical adsorption on the Pt nanoclusters. In general, the surface of the 1 nm Pt cluster attracts O much more strongly than the surface of the 2 nm Pt particle or the bulk surface. (The fcc site is a notable exception and will be discussed in the next section.) Undercoordinated Pt atoms created by edges and ver-

TABLE I. Relevant adsorption sites on the surface of the three model systems with their location and coordination number. An “N/A” means that the adsorption site is not available in the model system.

Adsorption site	Location	Coordination number of Pt (Z)		
		1 nm	2 nm	Pt(111)
AV	Atop site at vertex	5	6	N/A
AE(1,0)	Atop site at the edge of (111) and (100) facets	7	7	N/A
A(100)	Atop site at (100) facet	8	8	N/A
A(111)	Atop site at (111) facet	N/A	9	9
BE(1,0)	Bridge site at the edge of (111) and (100) facets	6	6.5	N/A
BE(1,1)	Bridge site at the edge between (111) facets	N/A	6.5	N/A
B(100)	Bridge site on (100) facet	7.5	7.5	N/A
B(111)	Bridge site on (111) facet	7	9	9
F-1 (H-1)	fcc (hcp) site around the center of (111) facet	7 (6.3)	9 (9)	9 (9)
F-2 (H-2)	fcc (hcp) site set up with 2 Pt at (111) facet and 1 Pt at the edge of (111) and (100) [(111)] facet	N/A	8.3 (8.3)	N/A
F-3 (H-3)	fcc (hcp) site set up with 2 Pt at the edge of (111) and (100) facets and 1 Pt at (111) facet	N/A	7.3 (7.3)	N/A

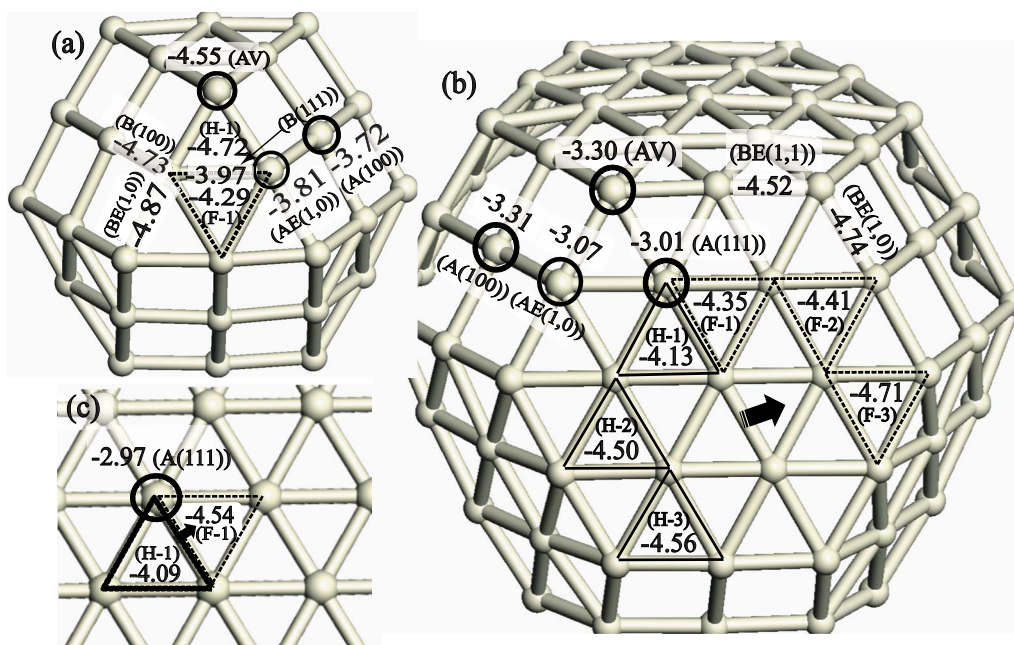


FIG. 2. (Color online) Chemisorption energies of O at various surface sites of the Pt model systems: (a) 1 nm and (b) 2 nm clusters and (c) Pt(111) surface. Solid (dashed) triangles denote an hcp (fcc) site. An oxygen atom at the bridge site on the (111) facet of the 2 nm cluster and on the Pt(111) surface is unstable and moves to an fcc site (indicated by solid arrows).

tices can be seen to have a particularly high chemical reactivity. For example, on the 1 nm cluster, the chemisorption energy of O at the atop position changes from -3.72 eV at the center of the (100) facet [A(100), $Z=8$] to -4.55 eV at the vertex (AV, $Z=5$). For the 2 nm cluster, the atop adsorption energies vary from -3.01 eV at the (111) facet [A(111), $Z=9$] to -3.30 eV at the vertex (AV, $Z=6$). The coordination number effect can be observed for all adsorption sites (fcc, hcp, atop, etc.). In general, as the sites are further away from the center of the (111) facet, the O-Pt bond strength becomes stronger.

Although for the extended flat Pt(111) surface and the 2 nm Pt cluster *fcc* sites are more stable than hcp sites, their stability is reversed in the 1 nm Pt cluster. This can be understood by considering the local environment of these sites. As Fig. 2 shows, one of the three Pt atoms creating the hcp site in the 1 nm cluster is located at a vertex, leaving it significantly under coordinated compared to atoms in the fcc site and enhancing its binding energy with O.

Figure 3 shows the adsorption energy of O as a function of bond length for the various sites and systems. Clearly, the bond length does not correlate with the variation of adsorption energies, as was already pointed out for the adsorption of other molecules on Pt.⁴¹ The bond distance of O-Pt is largely controlled by the nature of the adsorption site regardless of particle size.

B. Chemisorption energy of OH

Figure 4 shows the chemical adsorption energies of OH at different adsorption sites on the three model systems. In contrast to oxygen, OH preferentially adsorbs at the atop or

bridge position of the extended Pt(111) surface, with the Pt-O-H bond angle about 70° from the surface normal. At fcc or hcp sites, such tilting of the Pt-OH bond angle would bring the H too close to Pt surface atoms, and the equilibrium configuration is a linear Pt-O-H bond.^{28,42} The bonding angles do not change considerably on the 1 and 2 nm Pt clusters. Similar to O, OH binds to the 1 nm Pt particles more strongly than to the 2 nm particles for *all* sites. However, the most stable sites vary with particle size: for the 1 nm particle, the atop at a vertex (AV) is most stable, while on a 2 nm particle, the bridge between (111) and (100) facets [BE(1,0)] has the strongest adsorption energy.

The chemisorption energy of OH is also influenced by the coordination number of the adsorption site. For instance, for the 1 nm particle, the bond strength at an atop site varies from -2.61 eV at the center of the (100) facet [A(100), $Z=8$] to -3.35 eV at a vertex of the particle [AV, $Z=5$]. In the 2 nm cluster, the atop adsorption energies change from

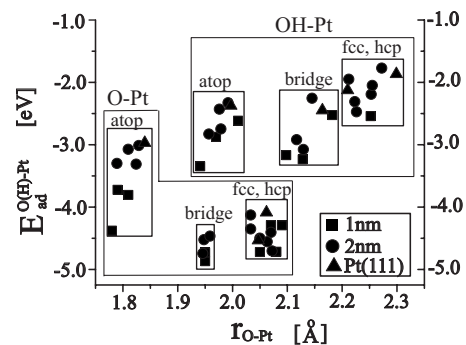


FIG. 3. Chemisorption energies of O and OH as a function of bond length with Pt.

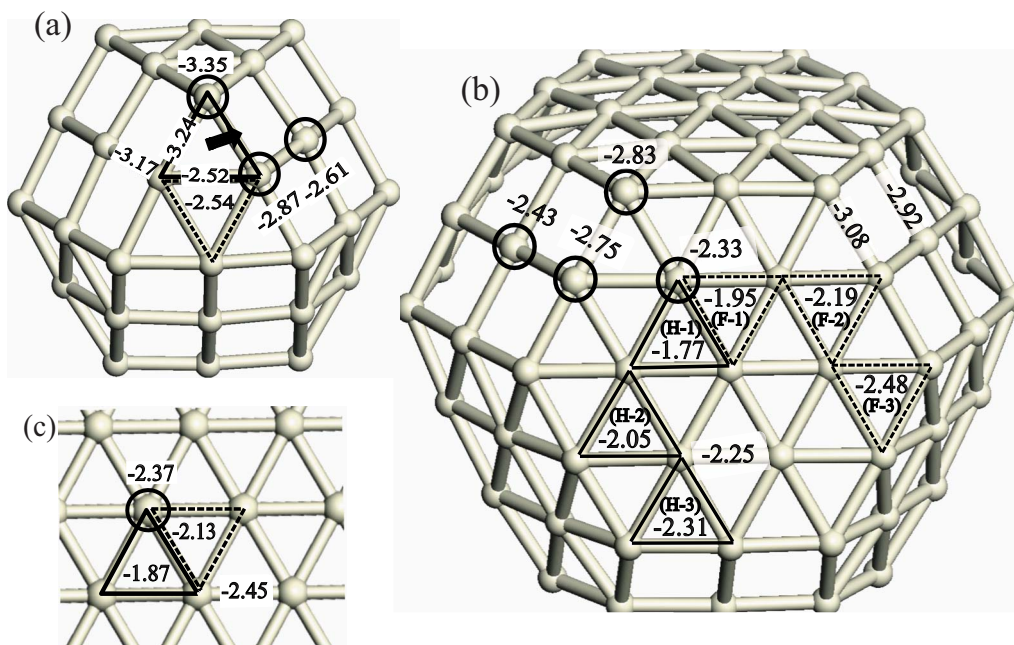


FIG. 4. (Color online) Chemisorption energies of OH at various sites of the Pt model systems: (a) 1 nm and (b) 2 nm clusters and (c) Pt(111) surface. Solid (dashed) triangles denote hcp (fcc) sites. The OH group at an hcp site on the (111) facet of the 1 nm cluster is unstable and moves to the bridge site (marked by a solid arrow).

–2.33 eV at the (111) facet [A(111), Z=9] to –2.83 eV at a vertex (AV, Z=6). These differences in adsorption energy of OH are smaller than for O (Table II). This may be due to the fact that the OH group binds, in general, less strongly as O and H already form a stable bond.

Figure 3 also shows the Pt-O bond length for Pt-OH. While there is a general increase in energy for Pt-OH (decrease in adsorption energy) as the bond length increases, the bond length is again largely controlled by the type of adsorption site.

IV. ANALYSIS AND DISCUSSION

The results presented in the previous section indicate that the effect of particle size and local surface structure on the

chemisorption energies of O and OH is substantial. These two factors are, in fact, strongly coupled since the equilibrium shape of a nanoparticle depends considerably on its size.⁴³ Hence, it may not be easy to decouple the two effects with experimental measurements which would provide quantities that entangle the effect of both factors. First-principles DFT method, however, enables us to approach the task in a more or less systematic way probing the energy of adsorption at every site.

A. Effect of surface structure (coordination number) of adsorption site

An overall trend we observe is that the adsorption energy increases as the Pt atom(s) involved in the adsorption be-

TABLE II. The strongest and weakest adsorption sites and their adsorption energies for O and OH in the three Pt model systems. The energy difference (ΔE) is given between the two sites.

Adsorbate	Model system				
			1 nm	2 nm	Pt(111)
O	Strongest adsorption	Site	BE(1,0)	BE(1,0)	F-1
		Energy	–4.87	–4.74	–4.54
	Weakest adsorption	Site	A(100)	A(111)	A(111)
		Energy	–3.72	–3.01	–3.08
	ΔE (eV)		–1.15	–1.73	–1.46
OH	Strongest adsorption	Site	AV	BE(1,0)	B(111)
		Energy	–3.35	–3.08	–2.45
	Weakest adsorption	Site	F-1	H-1	H-1
		Energy	–2.52	–1.77	–1.87
	ΔE (eV)		–0.83	–1.31	–0.58

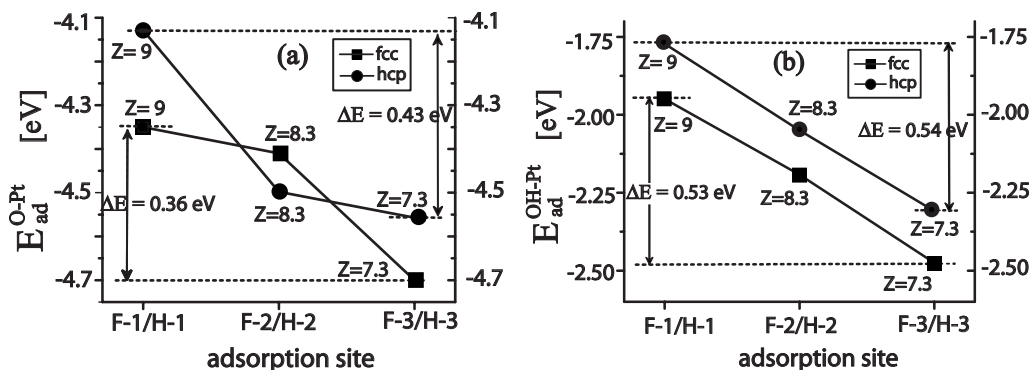


FIG. 5. The chemisorption energies of (a) O and (b) OH at fcc and hcp sites on the (111) facet on the 2 nm cluster. The position of adsorption site is numbered with decreasing coordination and can be located on Figs. 2 and 4.

comes less coordinated by other Pt. This can be very clearly observed in Fig. 5 which shows the chemisorption energies of O and OH on the 2 nm Pt particle for three fcc and hcp sites with different amounts of undercoordinated atoms. As the boundary atoms are considerably undercoordinated compared to those in the center of the facets, the adsorption energy increases as the adsorption site moves toward the boundaries of the surface facet. The magnitude of this variation with coordination (≈ 0.4 eV for O and ≈ 0.5 eV for OH) must have dramatic consequences on the range of oxygen pressures or electrochemical potentials at which nanosized Pt oxidizes. The variation with coordination is stronger than the

bulk fcc/hcp adsorption energy difference since the hcp site containing a vertex Pt attracts O and OH more strongly than an fcc site in the center of the (111) facet.

Figure 6 shows the effect of Pt coordination for adsorption on the atop and bridge positions of the 1 and 2 nm particles. The chemical adsorption energies at the atop and bridge sites vary by as much as 0.9 eV (O-Pt) and 0.7 eV (OH-Pt) for a 1 nm Pt particle and about 0.3 eV (O-Pt) and 0.8 eV (OH-Pt) in the 2 nm particle. Therefore, the effect of coordination number on the chemisorption energy at the atop and bridge sites is even more substantial than for the high symmetry fcc and hcp sites.

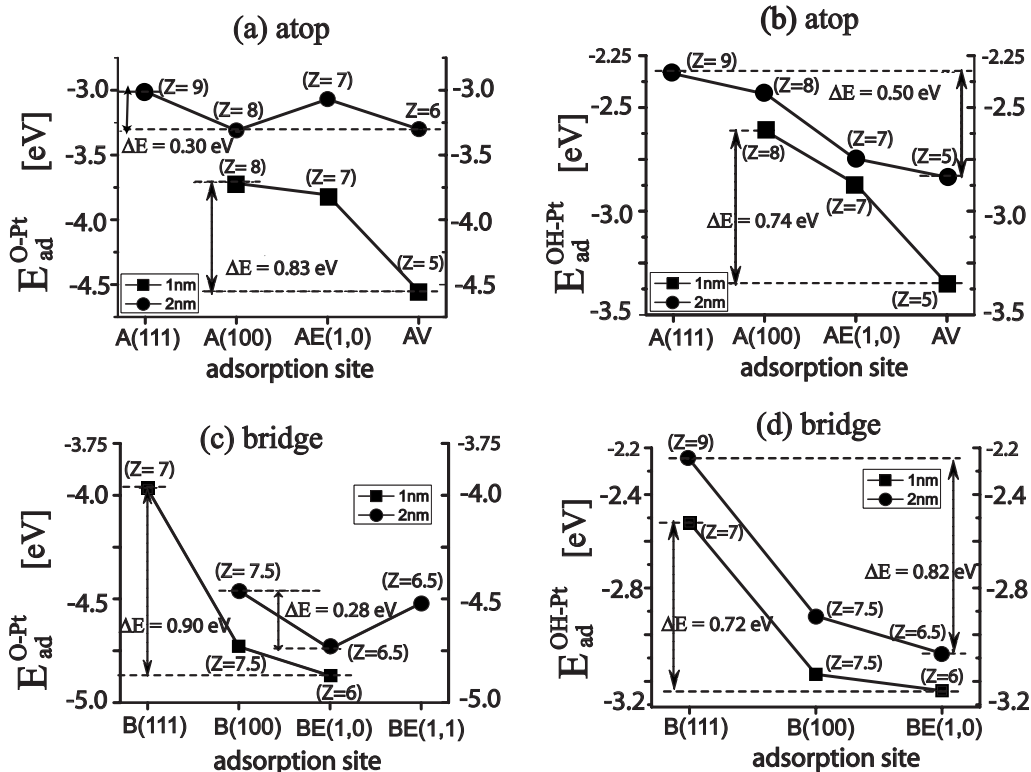


FIG. 6. Effect of coordination number on the chemisorption energy of O and OH at [(a) and (b)] atop and [(c) and (d)] bridge sites of the two Pt nanoparticle model systems. Note that oxygen atom is not stable at the bridge site of the (111) facet [B(111)] in the 2 nm particle.

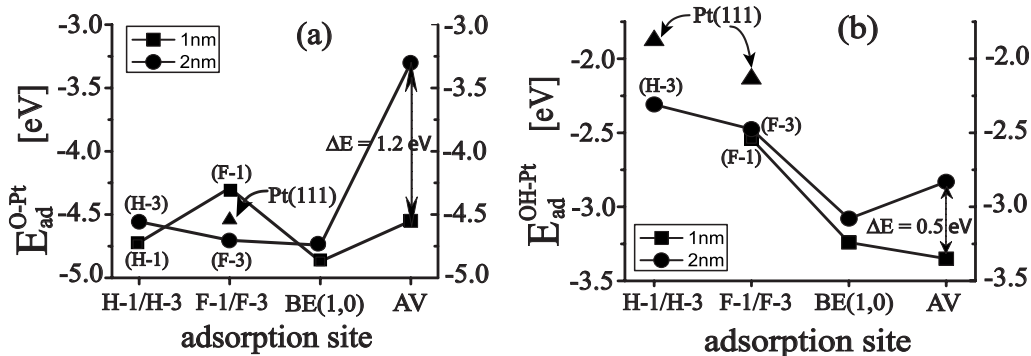


FIG. 7. Comparison of chemisorption energies of (a) O and (b) OH on sites with similar coordination in the nanoparticles and the (111) bulk surface. OH at the hcp site on the (111) facet (H-1) of the 1 nm Pt cluster is unstable and moves to the bridge site.

B. Effect of a particle size

In Figs. 5 and 6, we showed the effect of Pt coordination on the adsorption energy for different sites on a particle of fixed size. With Fig. 7, we try to investigate whether there is an intrinsic particle size effect on the adsorption energy even for sites with similar coordination but on a different particle size. Figure 7 shows chemisorption energies of O and OH on the three Pt model systems as a function of Pt particle size for a given adsorption site. We attempted to pick corresponding sites on each particle with the same coordination as much as possible. Since all the Pt atoms on the (111) facet of a 1 nm cluster are on the edges or vertices, they are compared to the chemical adsorption energies of O and OH on similar edges or vertices of the 2 nm cluster. Hence, the energy differences shown in Fig. 7 are largely induced by the effect of particle size. For reference, the chemisorption energies of O and OH on a Pt(111) bulk surface are also presented. As the results in Fig. 7 show, O and OH bind more strongly to the 1 nm particle (except for the fcc site). The largest size effect for both O and OH occurs for binding at the atop vertex site (~ 1.2 eV). The adsorption energy for O(OH) on the bridge site varies by 0.06 eV (0.16 eV). Hence, particle size effects are the most pronounced at the atop vertex.

C. Electronic structure effects

The previous sections demonstrate that both coordination environment and particle size of Pt significantly affect its chemical ability to adsorb O and OH. One may ask whether this variation of chemisorption energy can be described by a simple underlying parameter or physical change. Hammer and Nørskov previously suggested a model that relates chemisorption to the location of the d -band center (ϵ_d) of the transition metals.¹ Figure 8 shows chemisorption energies of O and OH on the three Pt model systems as a function of the unadsorbed d -band center of the Pt located at the adsorption sites. The solid (dashed) lines denote linear fits of the chemical adsorption energies of O (OH) to the d -band center of Pt at the adsorption site. The chemisorption energies at the atop and bridge sites vary more than at the fcc and hcp sites for the same amount of the d -band center change. This clearly indicates that the d -band center is not the only variable that controls the adsorption energy. Actually, it may not at all be

a relevant variable when change in particle size and coordination occurs. While the d -band center shift correlates with the overall variation of the chemisorption energies, a unique relation with the d -band center is not present.

D. Discussion

The chemisorption energies of O and OH vary considerably between the Pt(111) surface and 1 and 2 nm particles. Only some sites near the center of the (111) facet on the 2 nm show similar adsorption energies to the Pt(111) bulk surface, as shown in Fig. 9. While we find that on the bulk surface the fcc site is the most stable adsorption site, in agreement with previous work,^{38–40} oxygen adsorption is strongest in bridge sites on the edges of the 2 and 1 nm particles. For both particles, the maximal adsorption energy is stronger than on the bulk surface. The adsorption energies in the fcc and hcp sites of the nanoparticles are distributed above and below the bulk surface value, with adsorption getting stronger as the site is closer to the edge of the surface.

For OH adsorption, the effects of particle size are more dramatic. For OH in dilute concentration, as is the case in our supercell, the most stable sites on the bulk (111) surface are bridge and atop sites, in agreement with earlier works.^{28,42} At higher concentration of OH, experiments indicate that adsorption shifts to the atop position.⁴⁴ The adsorption energy for OH in both positions increases dramatically in the 2 nm particle (Fig. 4) going up by more than half an eV. This trend continues in the 1 nm particle where the atop site becomes the most stable site with almost an eV higher adsorption energy. The fcc and hcp positions, which are typically not favored for OH, also increase in adsorption energy when the particle becomes smaller, though the effect is less pronounced than for the lower coordinated edge and vertex sites. These results enforce the notion that to estimate the surface reactivity of nanoscale Pt catalyst, a relevant Pt model system is important, and bulk values may be less relevant than previously thought.

While the d -band center has been successfully used to explain the variation of adsorption energy with chemistry under identical surface geometry,¹⁵ it does not capture most of the variation we find between different sites and particle size (Fig. 8). While there is an overall trend that the adsorp-

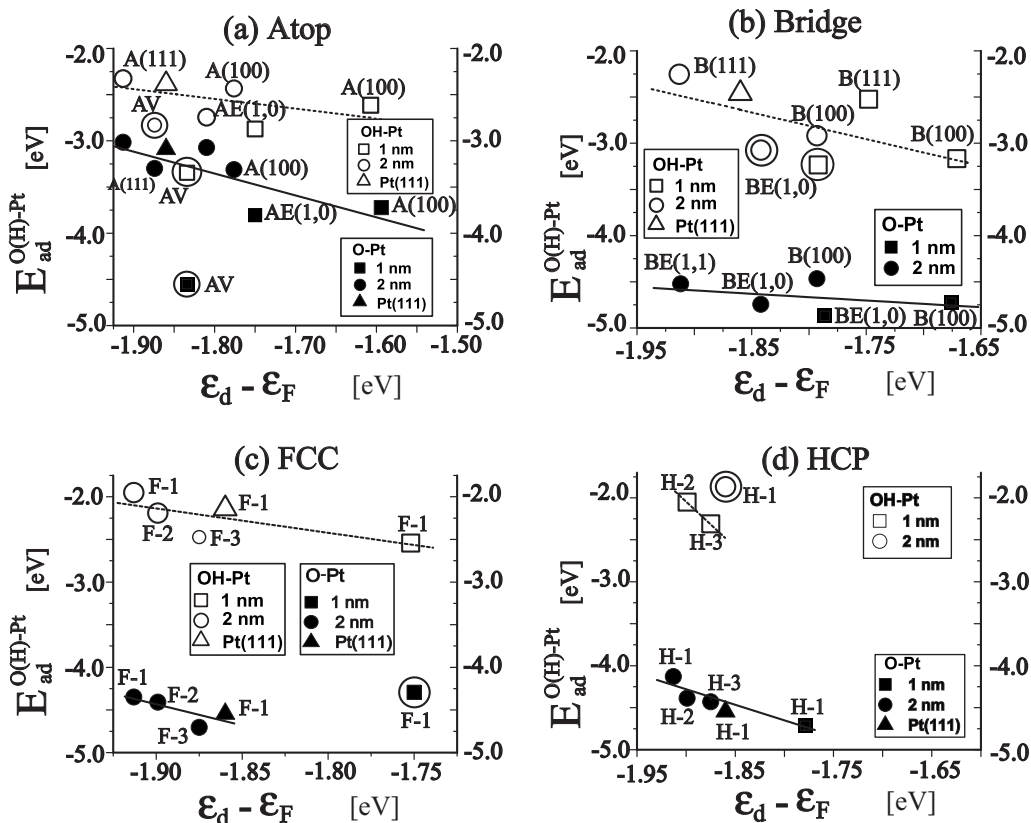


FIG. 8. Chemisorption energies of the O and OH on the three model systems as a function of the d -band center at the adsorption site. The solid (dashed) lines are a linear fit of adsorption energy of O (OH) to d -band centers for each site: (a) atop, (b) bridge, (c) fcc, and (d) hcp. The site which shows a large deviation is marked by a circle.

tion energy increases as the d -band center moves closer to the Fermi level, the adsorption energies seem to be largely controlled by long-range coordination effects. This can be best observed by comparing the adsorption energy of a given type of site at different positions on the nanoparticle, as, for example, presented in Fig. 5. As the site gets closer to the edge of the surface, the adsorption energy increases. This position dependence is what one would expect from a bond saturation argument, which is often applied to explain the variation of bond strength with coordination in metals.⁴⁵⁻⁴⁷ the Pt atoms near the edge of the surface have less neighbors,

thereby increasing the bond strength of each species they are bonded with. Anderson and co-workers have used similar arguments, pointing at the excess charge that builds up on corner atoms as an indication that electrophilic species will adsorb stronger.^{46,47}

The effect of coordination seems more pronounced for the atop and bridge positions than for the fcc and hcp positions which explains why the adsorption energy of OH varies more with particle size than that of oxygen. It is possible that as the adsorbed species binds with less Pt atoms (as in the atop position), it is much more sensitive to the extent to

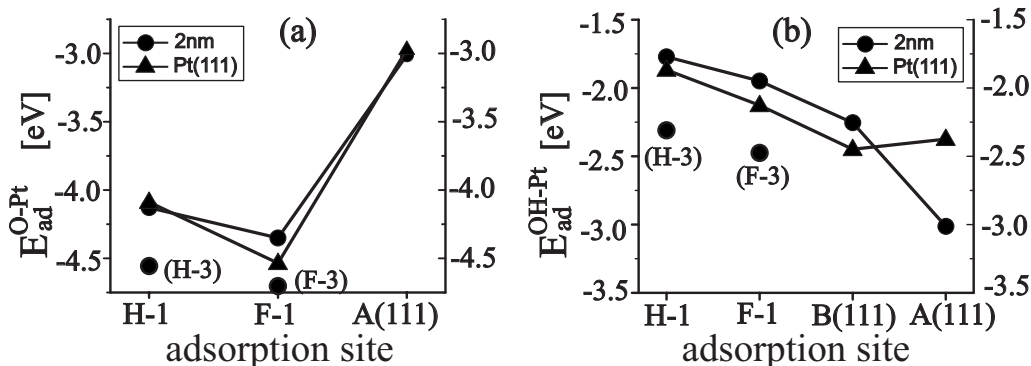


FIG. 9. Chemisorption energy of (a) O and (b) OH on the (111) facets of the 2 nm cluster and on the Pt(111) surface as a function of adsorption site.

which that Pt atom is bonded with other Pt atoms.

While, in general, the adsorption energy on the 1 nm particle on equivalent sites is higher than on the 2 nm particle, this trend is reversed for the fcc(111) site. This peculiarity occurs because the surface facets on the 1 nm particle have a significant curvature in order to reduce the total surface area of the particle. This causes the distance between nearest neighbor Pt atoms to be longer on the surface of the 1 nm particle (2.85 Å before O adsorption) than on the 2 nm particle (2.7 Å before O adsorption). This bond elongation reduces the extent to which adsorbed oxygen can simultaneously hybridize with all three Pt atoms defining the site.

Understanding how the variations of the adsorption energy with particle size affect catalysis is complex and depends on the precise role of the adsorbed species (O and OH in this study) in the catalytic process and on the change in adsorption of other relevant species. It is now generally accepted that the specific CO oxidation rate increases as the particle size decreases.^{8,48,49} Mayrhofer *et al.*⁸ attributed this to the stronger OH adsorption on smaller particles which provides the oxidant for CO. Our finding of a stronger OH adsorption would certainly corroborate this finding. The situation when Pt is used as a cathode for the oxygen reduction reaction is more complex. Watanabe *et al.*⁵⁰ argued that there is no effect of particle size on the rate of the ORR (oxygen reduction reaction), but that the mean particle spacing on the support is the more relevant variable though his findings have been disputed by Giordano *et al.*⁵¹ and Takasu *et al.*⁵² Similarly, Yano *et al.*⁵³ measured the ORR catalytic activity and the ratio of peroxide (H₂O₂) formation for particles 1.6, 2.6, and 4.8 nm in diameter. By using NMR analysis for ¹⁹⁵Pt located at surfaces of the Pt nanoparticles, they found that the electronic structure does not change with particle sizes, from which they suggested that the ORR activity does not change with Pt particle size. Mayrhofer *et al.*⁸ on the other hand, argue that the rate of the ORR will decrease with decreasing particle size since stronger OH adsorption removes sites for oxygen adsorption.

Recently, other investigations have pointed at the importance of undercoordinated sites on nanoparticles. Narayanan and El-Sayed^{54,55} systematically investigated how the shape and particle size affect the catalytic activity of Pt nanoparticles: they found that the surface activity of Pt is significantly sensitive to the number of undercoordinated sites, such as edges and vertices. More recently, Tian *et al.*⁵⁶ synthesized a tetrahedral Pt nanocrystal and observed it to have enhanced catalytic activity for the electro-oxidation of small organic molecules. They rationalized this finding on the basis of the large number of undercoordinated sites on high index facets.

Our results indicate that adsorption on nanoparticles is significantly different than on flat bulk surfaces and quanti-

tative results from bulk studies may be less relevant to nanoparticle catalysis than previously thought. While we find, in general, that the adsorption energies increase as the particle size decreases, consistent with a lack of bond saturation of the Pt atoms in small particles, the magnitude of the effect varies substantially with the type of site. Adsorption in low coordination, such as on the atop or bridge positions, changes much more significantly with particle size than adsorption energies in the higher symmetry hcp and fcc sites. How particle size will affect the adsorption of a species will therefore depend on the position in which it adsorbs. Hence, given that the catalytic activity depends on the outcome of competitive adsorption between species, there may be no general trend to predict how the catalytic activity of reactions changes with particle size. However, clever engineering of both the shape and size of catalyst particles, thereby optimizing the adsorption strength and number of adsorption positions for all the relevant species involved, could, in principle, be used to design better catalyst, though such a study would require the evaluation of considerably more species than what has been presented in this paper.

Our results indicate that Pt nanoparticles may undergo oxidation (reduction) reaction at different external conditions than bulk Pt metal. According to our calculated chemisorption energies of O and OH, the smaller 1 nm Pt cluster will form surface oxide much more easily than the 2 nm and bulk Pt(111) surface. For very small clusters Pt_nO_m of only a few atoms (in the range of $n=1-3$), a similar result was pointed out by Xu *et al.*⁵⁷ Our results indicate that the stronger affinity to oxygen persists even in a 2 nm Pt particle.

V. CONCLUSION

We investigated the effect of particle size and local surface structure on the adsorption of O and OH on Pt. We found that adsorption energies of O and OH are sensitive to the coordination number and size of the Pt particles in some case changing by as much as 1 eV from the bulk to the 1 nm particle. Low-coordinated sites show a much stronger sensitivity to the particle size and surface structure than other sites. Although an electronic structure model such as the *d*-band center theory captures some overall tendencies of chemical reactivity as a function of Pt size and adsorption site, there is considerable deviation from this model at the vertex or edge sites.

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