Structure–property–activity correlations of Pt-bimetallic nanoparticles: 
A theoretical study

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\section*{A R T I C L E   I N F O}

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\section*{A B S T R A C T}

A novel modeling approach based on FEFF8 calculations is developed to study the relationships between the atomic structure, electronic property, and oxygen reduction reaction (ORR) activity of Pt\textsubscript{3}M nanoparticles (NPs) in combination with experimental results. We have developed a representative cluster model of Pt\textsubscript{3}M (M = Cr, Mn, Fe, Co, Ni) NPs, namely Pt\textsubscript{3}M\textsubscript{NPs}, based on experimental X-ray absorption spectroscopy (XAS) data, and demonstrated that the calculated Pt surface d-band center \(\epsilon_d\) can be directly related to the ORR catalytic enhancement trends exhibited by Pt\textsubscript{3}M NPs in cathode catalysts. The correlations between \(\epsilon_d\) and cluster morphology parameters such as the Pt–Pt bond distance \(d_{\text{MNP}}\) (strain effects), the Pt–M bond distance \(d_{\text{MNP}}\) (interlayer ligand effects), and the choice of specific element M (pure ligand effects) are established. The results show that strain effects play a dominant role in downshifting \(\epsilon_d\) for late 3d elements, and ligand (pure ligand plus interlayer strain) effects can either upshift or downshift \(\epsilon_d\) relative to Pt depending on the near-surface morphology. The implications of the complex nature of ligand effects are discussed. This modeling approach complements the XAS technique in understanding structure–property–activity relationships of PtM NPs, and the understanding established here can be used to provide a fundamental basis for the improvement of existing cathode catalysts.

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1. Introduction

The structure–property–activity correlations of well-characterized Pt bimetallic alloys have been established by Stamenkovic’s [1,2] (on ordered extended surfaces) and Norskov’s [3,4] (theoretical calculations). Their work demonstrates the crucial role played by subsurface M atoms in shifting the Pt surface d-band center \(\epsilon_d\), and how this alters the oxygen binding energy \(\Delta E_o\) of the modified Pt surface to accelerate the sluggish oxygen reduction reaction (ORR). Both \(\epsilon_d\) and \(\Delta E_o\) have been directly correlated to ORR kinetics with a general consensus of a volcano type behavior based on choice of alloying element, and regarded as good descriptors of the activity of PtM alloys [4,5]. It has also been postulated that the ORR mechanism established for bulk Pt alloy surfaces is applicable to understand the activity of supported Pt-bimetallic NPs, which are known to exhibit specific ORR activities 2–5 times higher than that of Pt [6,7]. However, accurate structure–property–activity correlations of Pt\textsubscript{3}M NPs are stymied due to the more complex nature of such NPs, and the generally poor characterization of their physical and electronic structure.

X-ray absorption spectroscopy (XAS) has long been used to study supported Pt\textsubscript{3}M NP catalysts, since it offers unique insights into electrode processes by providing simultaneously, electronic and short-range (atomic scale) structural information on the catalysts under in situ and operando conditions including ORR [6,8–10]. By studying a series of Pt\textsubscript{3}M NP catalysts using in situ XAS, Mukerjee et al. stated that the enhanced ORR activities of Pt\textsubscript{3}M NPs were related to the modified Pt–Pt bond length and Pt d-band vacancies [6,8]. These studies and those reported later [9,11,12] correlated these parameters to (a) the onset potential of water activation for atop and sub-surface oxides, (b) affinity for molecular oxygen binding as a function of potential and presence of surface adsorbed moieties, and (c) the self-segregation of the alloying element as a function of potential and concomitant surface adsorbed species. Later, the \(\Delta \mu\) XANES (X-ray absorption near edge structure) technique pioneered by Ramaker et al. extended the XAS technique from a bulk-averaging structural technique (e.g. extended X-ray absorption fine structure (EXAFS)) into a surface adsorbate sensitive technique [13,14]. They demonstrated that the \(\Delta \mu\) technique...
could provide adsorbate coverage and specific adsorption site information [15–17], when a representative cluster model is used to interpret the experimental $\Delta \mu$ data [18]. Accordingly, they showed that the activity trend for Pt$_3$M and Pt NPs tracks with the OH coverage for small compression strain, confirming the role of OH on inhibiting the Pt$_3$M ORR activity [2, 19], and suggests that the in situ obtained OH coverage might serve as a reasonable predictor of Pt$_3$M ORR activity. Although, in situ measurements can now provide OH coverage, concomitant in situ measurement of $\Delta \mu$ for Pt$_3$M NPs is not possible via XAS or any other technique available today. Alternatives such as measurement of $d$-band vacancy are possible and have been reported earlier [6, 8], however its accurate link to $d$-band center is debatable.

Since the structural and surface adsorption information has been obtained from the EXAFS and $\Delta \mu$ XANES data using FEFF calculations, it is logical to also calculate the electronic properties using the same FEFF code, and thereby establish the structure–property–activity correlations. However, no such efforts have been reported primarily for two reasons: the limitation of previous FEFF versions for estimating electronic properties accurately; and more critical, the lack of a reliable representative cluster model for the Pt$_3$M NPs. Other theoretical methods such as density functional theory (DFT) have been used to calculate $\epsilon_d$, but DFT is similarly limited by the lack of a good reliable cluster model. The strong relationship between FEFF and XAS, and its success in providing structural information, and more recently even adsorbate information via the $\Delta \mu$ technique, makes FEFF the theoretical method of choice in this work.

Strain and ligand effects caused by the second metal in PtM alloys have been widely used to correlate structural and electronic properties, and to explain the enhanced ORR activity of PtM catalysts in comparison to Pt [20–22]. The role of strain effects in shifting the Pt $d$-band has been unambiguously demonstrated [23–25]. In brief, a compressive-strain increases the Pt–Pt $d$-orbital overlap, leading to a broadening and downshift of the $d$-band energy; on the other hand, tensile-strain decreases the $d$-orbital overlap, resulting in a narrowing and upshift of the $d$-band. According to the simple model developed by Hammer and Nørskov [26, 27], a downshift/upshift of $\epsilon_d$ weakens/strengthens the overall binding energy of simple adsorbates such as H, O, and CO to the Pt surface. However, it should be noted that Dimakis et al. showed the modification of the bind energy of CO to the Pt surface is primarily due to the changed exchange repulsion between them instead of Pt $d$-band shift using cluster and periodic DFT [28, 29].

In contrast, the understanding of electronic ligand effects has been controversial, partly due to the difficulty in separating ligand and strain effects experimentally. Using in situ XAS, Mukerjee et al. indicated that conventional PtM NPs have higher $d$-band electron vacancies in comparison with Pt NPs, and attributed that to charge transfer from Pt to M [6, 8]. As the electron filling decreases, the Fermi level shifts downward, resulting in an upshift of the $d$-band center relative to the Fermi level [30], which is opposite to the compressive-strain effects. However, Watanabe et al. [31] argued that the electron transfer must occur from Co to Pt since Pt has a higher work function than Co, and therefore the higher $d$-orbital electron vacancies found on Pt should be explained by re-hybridization of the $d$-band as well as the sp-band [32–34]. The resultant modification of the work function leads to an upshift of the Fermi level, and thus an opposite downshift of the Pt 4f$_{7/2}$ core level and $d$-band center as determined by X-ray photoelectron spectroscopy (XPS). In this case ligand effects would be additive to the convoluted compressive-strain effects. Similarly, Nørskov et al. also proposed that the ligand effects between Pt$\{1\ 1\ 1\}$ and subsurface $3d$ transition elements cause a downshift of the Pt $d$-band using DFT calculations, but they reported that there was no significant charge transfer between Pt and M, and the Pt $d$-band filling remains unaffected [21]. It is apparent that different techniques lead to distinctly different understanding of ligand effects. Thus an understanding of the role of ligand effects has been elusive.

In this work, a representative cluster model for Pt$_3$M NPs, namely Pt$_{10}$M$_{15}$, is constructed based on the experimental EXAFS data. This cluster is then used for calculating the Pt electronic properties (e.g., electronic filling, Fermi level, $d$-band center, etc.), which in return are consistently related to the experimental OH coverage and activity of Pt$_3$M NPs. This cluster is then used as a starting point to study strain and ligand effects separately and jointly to elucidate their roles in modification of the surface electronic properties of Pt. Other important effects that might influence the PtM NP surface properties, such as ensemble effects [35], and adsorbate–adsorbate lateral repulsive effects [9], are not included in these calculations. Detailed changes in the Pt $d$-band center $\epsilon_d$ have been monitored along with the changes of Pt–Pt bond distance $d_{\text{MPP}}$, Pt–M bond distance $d_{\text{PM}}$, and specific element M. The results are compared to the corresponding experimental or DFT theoretical results to verify the validity of the representative cluster and the proposed modeling approach. This is the first trial of FEFF8, that we are aware of, for calculating $\epsilon_d$ and other electronic properties that correlate the structure and activity of Pt$_3$M NPs. We believe FEFF8 can be used as a first step toward predicting the electronic properties of bimetallic systems and thereby reduce the need for more expensive DFT calculations.

2. Computational details

2.1. FEFF8 calculations

FEFF8 is an ab initio real space multiple-scattering (RSMS) code for simultaneous calculation of XAS spectra and electronic structure [36, 37]. The latest version of FEFF8, which includes full multiple scattering self consistent field (SCF) calculations of the potentials, is capable of providing electronic structure information, including local densities of states (LDOS) based on an all-electron, real space relativistic Greens function formalism. It thus gives a reasonably accurate Fermi level position and number of s, p, and d orbital electrons (the f-orbital fillings are omitted here due to their negligibility and contribution), and also accounts for charge transfer. The code used in this work was an author–customized version of FEFF8, which extends the independent number of potentials up to 19 (from 8) and the number of points in the LDOS calculations from the default (84) to 400, and therefore enables us to perform calculations on larger more complicated clusters. The default Hedin–Lundqvist self-energy was used. The LDOS were calculated without the presence of a screened core-hole (NOHOLE card) since the one-particle calculations for d-elements without a core-hole usually agrees better with experimental data, even for XAS experiments, so certainly for ground state properties, we do not want a core hole present [38]. The d-band center $\epsilon_d$ was calculated as the first moment of the LDOS referenced to the Fermi level, and the mean squared $d$-band width $W_d^2$ was calculated as the second moment.

2.2. Pt$_{10}$M$_{15}$ cluster

In this work, Pt$_3$M NPs are considered because supported Pt$_3$M NP catalysts are frequently the catalyst of choice in fuel cells. The in situ XAS data of Pt$_3$Ni/C and Pt/C NPs as cathode catalysts within an operando fuel cell are used as references to build the representative clusters [22]. The physicochemical properties of bimetallic NPs mainly depend on: (1) the composition; (2) the shape; (3) the particle size; (4) the atomic distribution, (5) the bond lengths; and (6) the architecture [10, 39]. An ideal representative cluster should closely reproduce all these properties.
In the surface morphologies must be considered as it is directly related to the ORR activity. The so-called ‘sandwich’ near surface structure of polycrystalline Pt3M and Pt3M NPs, where segregation of Pt to the surface has occurred, has been reported to be thermodynamically stable and exhibit enhanced ORR activity [2,40,41]. Thus this structure is mainly focused on here.

Taking all the factors under consideration, the cluster Pt19Ni6, as shown in Fig. 1, is proposed to optimally represent Pt3Ni NPs. The balls in blue and orange represent Pt and Ni atoms, respectively. The top layer contains only Pt atoms to mimic the pure Pt(1 1 1) surface, and the middle layer has 3 Ni atoms inside and 9 Pt outside. In the bottom layer, 3 Pt and 3 Ni atoms are uniformly distributed. Similarly, the same cluster with all the Ni atoms replaced by Pt (and thus, Pt25) is used to represent Pt/C NPs. The XAS absorbing atom (from which the calculated results are collected) is the central atom in the top layer unless noted otherwise. The model thus retains the bulk Pt3M stoichiometry. The shape of this cluster can be regarded as about half of a geometrically closed cuboctahedron structure containing 55 atoms. This polyhedral cluster, characterized by a structural magic number, is proposed to be energetically most stable [42], especially for the 3d elements Co and Ni [43].

In order to mimic the sandwich structure, it is critical to define the atoms in the surface or subsurface appropriately. In this work, they are identified by their first shell coordination numbers (CNs). The absorbing atom in the Pt25 cluster with 9 nearest surrounding atoms is regard as a surface atom, while the three nearest atoms underneath with 12 surrounding atoms are considered as subsurface atoms. The argument of using CNs to identify atoms on or beneath the surface in FEFF8 is further examined by comparing their d-band vacancies, which can be quantitatively determined by XAS. Fig. 2 shows the calculated Pt L2 (inset) and L3 XANES spectra of the surface and subsurface atom, respectively. Assuming the d-band vacancy for Pt atoms in the subsurface (CN = 12) is equal to that of Pt foil (CN = 12), 0.3 [44], the calculated d-band vacancy of the surface atom (absorbing atom, CN = 9) is 0.327 following the method developed by Mansour et al. [45]. This value is extremely close to 0.329 [6], the experimental value for a ~3 nm diameter Pt/C particle when the corresponding averaged CN is estimated by Benfield’s method [46] at a.c. 9.6. The high consistency between the experimental and calculated d-band vacancy further validates the identification of the atoms on or beneath the surface. Thus the sandwich structure, which cannot be modeled by using a smaller under-coordinated cluster [15], is reproduced in the Pt19Ni6 cluster.

As listed in Table 1, the CNs of the surface Pt and subsurface Ni atoms are close to the experimental results from in situ EXAFS fitting for the Pt3Ni/C NPs [22]. The experimental Pt–Pt bond length (dPt-Pt), 2.70 Å, is achieved by setting the lattice constant of the cluster at 3.81 Å; and then the three Ni atoms in the second layer are brought closer to the absorbing atom to give the experimental Pt–Ni bond length (dPtNi), 2.65 Å. It is worth mentioning that these dPtNi and dPtNi bond distances are typical values reported for many Pt3M NPs (within ±0.02 Å) [9,22,47], and thus are used here as representative values. In this way, the physical properties of Pt3Ni/C, determined experimentally from EXAFS, are mimicked with a reasonable Pt19Ni6 cluster. Similarly, the experimental results reported for Pt/C NPs in the same work, 2.75 Å for the bond length and 8.7 for the CNs, can be modeled with a Pt25 cluster with the same bond length.

It should be noted that although the structural parameters of the simple cluster model are close to the experimental results, the model is certainly much less complicated than the real catalysts. Therefore, the aim of this approach is not to reproduce the absolute values of the electronic properties quantitatively, but instead to evaluate how the electronic properties are modified when changing the structural parameters so as to explore the structure/property correlations within similar systems like PtM.

### Table 1

Comparison between the coordination numbers for Pt and Pt3Ni NPs (EXAFS experimental fitting results reported by us previously [22]) and those for Pt25 and Pt19Ni6 clusters.

<table>
<thead>
<tr>
<th></th>
<th>CN_{PtNi}</th>
<th>CN_{Pt25}</th>
<th>CN_{Pt3Ni}</th>
<th>CN_{Pt19Ni6}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>8.7</td>
<td>9</td>
<td>6.1</td>
<td>6</td>
</tr>
<tr>
<td>Pt25</td>
<td></td>
<td></td>
<td>3.4</td>
<td>3</td>
</tr>
<tr>
<td>Pt3Ni</td>
<td></td>
<td></td>
<td>8.9</td>
<td>9</td>
</tr>
<tr>
<td>Pt19Ni6</td>
<td></td>
<td></td>
<td>3.7</td>
<td>3</td>
</tr>
</tbody>
</table>
reported the $\varepsilon_d$ of polycrystalline Pt$_3$Ni to be about 0.2 eV lower than that of Pt [2]. The consistency between the calculated and experimental results suggests that Pt$_{19}$Ni$_6$ can indeed serve as a representative cluster for Pt$_3$Ni NPs.

The above cluster is then utilized to study a series of Pt$_3$M bimetallics. The electrochemical and XAS data from Pt$_3$M/C NPs reported previously are referred to for discussion [6,9]. As presented in Fig. 3, the calculated $\varepsilon_d$ of Pt$_{19}$M$_6$ increase when the second metal M moves from C to Ni, but all of them are still lower than that of Pt$_{25}$. The OH coverage of the Pt$_3$M and Pt NPs shows the same trend [9], which effectively validates the predicted $\varepsilon_d$ trend, since the higher the $\varepsilon_d$, the higher the filling of the antibonding states, and thus the stronger the Pt$-$O(H) interactions [23]. Moreover, the direct correlation between the OH coverage and the activities of these catalysts has been demonstrated by Ramaker et al. [9]. Therefore, the calculated $\varepsilon_d$ can be directly correlated to the activity of Pt$_3$M/C NPs (lower $\varepsilon_d$ corresponding to higher activity) as presented in Fig. 3. The property/activity correlation suggests that the ORR enhancement mechanism for Pt$_3$M NPs is not fundamentally different from extended PtM surfaces, i.e., a lowering of the Pt surface $\varepsilon_d$ by alloying with M reducing the OH poisoning of the Pt free sites.

Here, the excellent agreement between the experimental results and calculations is not the most significant point. Rather, we stress that we have a representative cluster model for Pt$_3$M NPs guided by XAS experimental data, and the trend in calculated $\varepsilon_d$ using FEFF8, in combination with the trend in in situ OH coverage can be directly related to the activity trend of Pt$_3$M NPs, which can thus serve as the best guide for narrowing the choice of the second metal M for future studies on Pt based bimetallic alloys.

Since the calculated $\varepsilon_d$ based on the Pt$_{19}$M$_6$ cluster model is a good descriptor of the ORR activity of Pt$_3$M NPs, the same model is used as the starting point for the analysis of strain and ligand effects to establish the correlations between the structural and electronic properties. Although ligand and strain effects are usually convoluted in PtM NPs, it is of particular interest to study them individually to elucidate their roles in modifying the electronic properties of Pt. FEFF8 program allows full freedom of the cluster structure (i.e. atom site and composition), thus a separation of these two effects is theoretically feasible.

3.1. Strain effects

Besides the Pt$_{25}$ cluster model, two other cluster models are also included to eliminate possible artificial results arising from the simplified models, and to examine the coordination number (CN) impact on the electronic properties as well. As shown in Fig. 4, the left cluster is the well-known Janin’s cluster (Pt$_6$), which has been widely used for $\Delta\mu$ analysis [49]. The middle one is the smallest geometrically closed cuboctahedron structure containing 13 atoms (Pt$_{13}$), which tends to form dense fcc packing due to the electron deficient metallic bonding [50–52]. The rightmost one is the Pt$_{25}$ cluster model. The original Pt$-$Pt bond length for all three clusters is set to be 2.75 Å, the same as that of real Pt/C NPs with ca. 2.5 nm particle size [53]. The XAS absorbing atoms for each model are labeled “A”.

In order to single out strain effects in a calculation, all the atoms in the models are set to Pt. The corresponding LDOS for different bond lengths calculated by FEFF8 are presented in Fig. 5, and the electronic properties are listed in Table 2 (only the results obtained from the Pt$_{25}$ cluster are given since the results from the other two clusters are not essentially different, and the Pt$_{25}$ cluster is the most realistic). As clearly seen, the band broadenings and those portions furthest from the Fermi level shift down more. As a result, the density of states at the Fermi Level, which was previously used in correlation with chemical properties, does not change significantly with bond distance $d_0$. Rather, the contraction of $d_0$ leads to a lower and broader $d$-band, in good agreement with the results reported by Nørskov et al. using DFT calculations [23,24] and the experimental results reported by Strasser et al. [20]. The $\varepsilon_d$ or $W_d$ as a function of $d_0$ for all three clusters is presented in Fig. 6. As seen, both $\varepsilon_d$ or $W_d$ are nearly linearly correlated with $d_0$, which makes it possible to predict the more experimentally difficult to measure $\varepsilon_d$ from the easily experimentally measured $d_0$. For Pt$_3$M NPs, the typical $d_0$ is $\sim$2.70 Å, corresponding to $\sim$0.3 eV downshift of $\varepsilon_d$ compared to Pt NPs ($d_0 = 2.75$ Å). This value is comparable to the experimental values reported for polycrystalline Pt$_3$M [2], implying strain effects play an important role in modifying the Pt surface electronic properties. Although this nearly linear correlation has not been confirmed experimentally thus far, alternatively, a linear correlation between $\varepsilon_d$ and $\Delta E_\alpha$ was reported, and DFT
calculations have shown that both \( d_0 \) and \( \varepsilon_d \) have a linear correlation with \( \Delta E_{\text{S}} \), indirectly supporting our calculated results [3,23,24].

Fig. 6 also shows that the \( d\text{-band} \) properties strongly depend on the CNs, as exhibited by the dependence on cluster size. This is usually not a concern for bulk alloys, but has to be considered for NPs with under-coordinated atoms at the surface. XAS is one of the few techniques that can determine CNs quantitatively, and FEFF8 can yield reliable results for electronic properties as a function of cluster size or CNs [38]. As shown in Fig. 6, the absorbing atom in the largest cluster (Pt25) has the lowest and broadest \( d\text{-band} \), which can be ascribed to its highest CN (9). According to the tight binding theory, higher CN leads to larger matrix element \( V_{ij} \) due to the hybridization of more wave functions of the valence electrons, which in turn leads to a broader \( d\text{-band} \) [23]. Furthermore, although the absorbing atoms in Pt6 and Pt13 have the same CNs (5), the latter has a lower and broader \( d\text{-band} \), indicating the influence of higher shell atoms on the band properties. Accordingly, it has been shown that the dependence of the catalytic activity on the cluster size is well correlated with the average CN of metallic NPs [54,55]. In addition, the atoms at corners, edges, and defect sites adsorb oxygenated species more strongly than atoms located on the planes of the NP, consistent with the corresponding lower CNs of these corner/edge sites. Recently, the \( \varepsilon_d \) and \( W_d \) trends as a function of the CNs of Au NPs have been systematically studied by Visikovskiy et al. [56], and the results are in good agreement with our calculations. Moreover, we notice that the slopes of the lines in Fig. 6 decrease with particle size. This indicates that strain effects are weaker for atoms having smaller CNs.

Other than \( \varepsilon_d \), core-level binding energies (BE) have often been chosen as a good indicator of electronic structure changes because they are more easily obtained experimentally. Again, a nearly linear correlation between the contraction of \( d_0 \) and \( E_f \) is shown in Fig. 7, and a \( \sim 5\% \) contraction of \( d_0 \) leads to a positive shift in \( E_f \) of \( \sim 0.5\text{ eV} \), corresponding to an opposite downshift of the core-level binding energies (BE) [31]. Experimentally, Richter et al. reported a nearly linear correlation between BE and lattice constant \( a_0 \) of Ni and Cu NPs, and a \( \sim 5\% \) contraction of \( a_0 \) leads to a \( \sim 0.5\text{ eV} \) shift of BE [57], in good agreement with our calculations. This shift of BE has been generally related to the gain or loss of electrons by the atom, or \( d\)-orbital hybridization, etc. [58]. As listed in Table 2, the charge transfer, or the sum of \( s \), \( p \), and \( d \) electrons (total electrons) remains unchanged with reduction of bond distance, thus a shift of \( E_f \) (or BE) due to charge transfer can be ruled out. On the other hand, the slight decrease of \( d\text{-band} \) filling with contraction of \( d_0 \) (Fig. 7) strongly suggests that the \( E_f \) shift is caused by hybridization, which promotes intra-atomic charge transfer from the compact \( d\text{-band} \) into a more diffuse \( sp\text{-band} \). The hybridization increases strongly for shorter \( d_0 \) since shorter bond distances favor an increased bonding

**Table 2**

Calculated Pt \( d\text{-band} \) properties\(^a\) as a function of Pt–Pt bond length in the Pt25 cluster.

<table>
<thead>
<tr>
<th>( R_{\text{Pt-Pt}} ) (Å)</th>
<th>( E_f ) (eV)</th>
<th>( \varepsilon_d ) (eV)</th>
<th>( W_d ) (eV)</th>
<th>Charge transfer (e/atom)</th>
<th>( d ) electrons (e/atom)</th>
<th>Total electrons (e/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>−7.02</td>
<td>−2.71</td>
<td>3.16</td>
<td>0.10</td>
<td>8.43</td>
<td>9.90</td>
</tr>
<tr>
<td>2.77</td>
<td>−6.94</td>
<td>−2.91</td>
<td>3.37</td>
<td>0.13</td>
<td>8.41</td>
<td>9.88</td>
</tr>
<tr>
<td>2.75</td>
<td>−6.91</td>
<td>−3.03</td>
<td>3.50</td>
<td>0.13</td>
<td>8.40</td>
<td>9.88</td>
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<tr>
<td>2.70</td>
<td>−6.68</td>
<td>−3.35</td>
<td>3.85</td>
<td>0.12</td>
<td>8.36</td>
<td>9.88</td>
</tr>
<tr>
<td>2.65</td>
<td>−6.53</td>
<td>−3.71</td>
<td>4.24</td>
<td>0.13</td>
<td>8.33</td>
<td>9.88</td>
</tr>
</tbody>
</table>

\(^a\) \( E_f \): Fermi level; \( \varepsilon_d \): \( d\text{-band} \) center; \( W_d \): root means-squared (rms) \( d\text{-band} \) width; charge transfer: the fraction of electron transferred from the absorbing atom to other atoms; total electrons: the sum of \( s \), \( p \), and \( d \) electrons.

Fig. 5. Calculated Pt surface \( d\text{-band} \) DOS for different Pt–Pt bond lengths. The dashed vertical line represents the Fermi Level. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 6. (a) Effects of relative change in bond length \( d/d_0 \) on the rms \( d\text{-band} \) width of Pt (top), and the \( d\text{-band} \) center of Pt (bottom) for the three clusters. \( d_0 \) is the original Pt–Pt bond length 2.75 Å. Red, green, and blue diamonds correspond to the Pt6, Pt13, and Pt25 clusters, respectively. The gray dashed lines are drawn as guides to the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
participation of the compact d-orbitals, and the resultant increase of d-band width (Wd) is listed in Table 2.

Overall, the nearly linear correlations between d0, εd, and Ef (or BE) as demonstrated experimentally are perfectly reproduced by the FEFF8 calculations, which also accounts for the effect of the CN, affirming its effectiveness in studying strain effects. This makes in situ XAS, in combination with FEFF8 calculations, a promising technique to study dealloyed PtM NPs, for which the exceptional ORR activities were mainly attributed to isolated strain effects [7,59,60]. Recently, we found the ORR activity trend within dealloyed PtM NPs can also be understood through the Pt–Pt bond distance and the OH coverage obtained by in situ XAS [61].

3.2. Ligand effects

By restricting the bond lengths of a Pt19M6 cluster to be the same as those of the unstrained Pt25, 2.75 Å, “geometric” strain effects are entirely eliminated and electronic “ligand effects” are thus isolated. It is worth noting that the “ligand effects” defined here are different from those in Ref. [21]. In that work, ligand effects still include the strain effects arising between the surface and subsurface (termed as interlayer strain effects here) as pointed out in their later work [23]. To avoid ambiguity, the ligand effects noted herein without any strain effects are named as pure (electronic) ligand effects. The “ligand effects” including interlayer strain effects are mimicked here by reducing the bond distance between the Pt atoms on the surface and the subsurface M atoms dPM from 2.75 Å to 2.65 Å, while the dPM on the surface is maintained at 2.75 Å. In this way, the Pt electronic properties modified by strain effects, interlayer strain effects, and pure ligand effects, can be respectively related to dPM, dPM, and element specific M, all of which can be readily determined by XAS.

The Pt band properties governed by ligand effects (i.e., fixed dPM = 2.75 Å, dPM = 2.65 Å but with changing M) are listed in Table 3. A decrease in the number of Pt d electrons and total electrons with M, indicates that charge is transferred from the surface Pt d-orbitals to the M atoms below. Correspondingly, the Ef of Pt in Pt19M6 is lower than that of Pt25. The charge transfer from Pt to M observed here is consistent with the increased Pt d-band vacancy previously reported for Pt3M NPs [6,8]. On the contrary, DFT calculations show that the charge transfer is generally from M to Pt [62] or negligible [21], supported by the smaller work function or electronegativity of these 3d elements compared to that of Pt. In spite of the contradiction in charge transfer sign, the absolute magnitude of the charge transfer is found to be modest (<0.1 electrons/atom) for both FEFF8 and DFT calculations, and widely reported for many bimetalllic systems [34,63,64]. Considering that all of the theoretical calculations are based on simplified models that are much less complex than the real Pt3M alloys used in fuel cell applications, and the calculations also employ various approximations, the accuracy of the predicted charge transfer is unclear. Experimentally, it is also not clear to what extent the charge transfer magnitude within bimetalllic alloys is significant [63]. Therefore, the charge transfer in PtM alloys is still inconclusive, but the modest scale of the charge transfer can safely concluded.

Although the charge transfer, number of Pt d electrons, or Fermi level Ef of Pt19M6 is different from that of Pt25, the differences between them are trivial. On the other hand, a clear trend of εd or Wd with M is obtained (listed in Table 3). These trends can be directly observed in the corresponding LDOS as presented in Fig. 8. As seen, when M moves from Cr to Ni, the intensity of the peak (–2 to 0 eV) closest to the Fermi Level increases, and the other two peaks shift closer to the Fermi Level. Consequently, Wd gets narrower and εd gets closer to the Fermi level. These results clearly show that it is the entire d-band, not just a certain fraction of it that gets modified by ligand effects; thus εd or Wd, which is the first or rms second moment of the entire band that provides a more general picture regarding the electronic properties of alloys. Moreover, Nørskov et al. has shown that the interactions between adsorbates and transition metal surfaces also involve the entire d-band [3]. Therefore, compared to Ef, d-band vacancy, or the density of states at Fermi Level etc., εd or Wd appears to be a more appropriate descriptor of electronic properties to bridge the structure and activity correlation of PtM alloys.

The εd changes resulting from “ligand” effects are essentially determined by the pure ligand and interlayer strain effects simultaneously. As shown in Fig. 9(a), the Pt d-band center εd, when including only pure ligand effects (i.e., fixed dPM = 2.75 Å and dPM = 2.75 Å with only the component M atom changing – red line), shifts up as the subsurface metal M moves from Cr to Ni. This trend arises because of the decreasing M atom characteristic radius going left to right in the periodic table, and is related to the spatial extent of the d-orbitals [65]. The higher εd of Pt19M6 compared to that of Pt25 is also consistent with a second trend in the M radius, which increases from top to bottom among transition metals in the periodic table [65]. Accordingly, the downshift of εd with M moving from Ni to Pt is shown in Fig. 9(b). Therefore, pure ligand effects
upshift $\epsilon_d$ with the shift increasing as the M atom radius decreases. Upon including just the interlayer strain effects by reducing the $d_{\text{PM}}$ from 2.75 Å to 2.65 Å (i.e., pure ligand + interlayer strain), the $\epsilon_d(s)$ of Pt$_{19}$M$_6$ (pink line) moves down. Upon including all strain effects by reducing $d_{\text{PM}}$ from 2.75 Å to 2.70 Å and $d_{\text{PM}}$ from 2.75 Å to 2.65 Å (black line in Fig. 9(a) and as in Fig. 3), the $\epsilon_d(s)$ of Pt$_{19}$M$_6$ moves down further. The difference between the red and black lines (the effect of strain) in nearly constant with M because the two strain effects are the same for all M since we used the same incremental decrease in $d_{\text{PM}}$ and $d_{\text{PM}}$ for all M, as guided by the experimental EXAFS results. This is not surprising since the original bond length of all the M metals is almost the same (2.49 ± 0.01 Å), and thus the bond lengths across Pt$_M$ alloys should be very close according to Vegard’s law. Apparently the strain effects are much less sensitive to the changing M atom radius than the ligand effects.

All of these trends, as discussed earlier, are in excellent agreement with the trends in the OH coverage and ORR activity found for the same catalysts. Therefore, we propose that the ORR activity of this group of Pt$_M$ NPs tracks mainly to the intrinsic property of the M: the characteristic radius. In parallel developments, the experimental $\epsilon_d$ of polycrystalline Pt$_3$M measured by ultraviolet photoemission spectroscopy [2] shows exactly the same trend, directly supporting our argument. However, the extension here to NPs is particularly important for tailoring advanced catalysts with the desired activity.

To evaluate the interlayer strain effects more quantitatively, the interlayer strain $S_{IL}$ can be expressed as:

$$S_{IL} = \frac{d_{\text{PM}} - d_{\text{PM}}^{\text{std}}}{d_{\text{PM}}^{\text{std}}} \times 100$$

where $d_{\text{PM}}$ is as defined above, and $d_{\text{PM}}^{\text{std}}$ is the interlayer Pt–Pt bond distance in unstrained Pt (2.75 Å here). The $\epsilon_d(s)$ of Pt$_{19}$M$_6$ as a function of $S_{IL}$ is presented in Fig. 10. As shown, when $S_{IL} = 0$ (pure ligand effects), the $\epsilon_d(s)$ of Pt$_{19}$M$_6$ are all higher than that of unstrained Pt$_{25}$ (gray dashed line), and shift down with the decrease in $S_{IL}$ (interlayer strain effects). The crossing point, where the interlayer strain effects counterbalance the pure ligand effects, shifts from $\sim -0.5\%$ to $\sim -4.5\%$ $S_{IL}$ as M changes from Cr to Ni. Thus the two opposing effects together, pure ligand effects plus interlayer strain effects, can either upshift or downshift $\epsilon_d$ relative to Pt depending on which effects win out. The experimental value of $d_{\text{PM}}$ in Pt$_M$ NPs, 2.65 Å (or $-3.6\%$ $S_{IL}$), corresponds to an insignificant $\epsilon_d$ shift for the late 3d elements like Fe, Co, or Ni as clearly shown in Fig. 10. These results suggest that the “ligand” (pure + interlayer strain) effects for the late 3d elements are trivial, and thus the shift of $\epsilon_d$ is mainly caused by the “bulk” strain effects. On the other hand,
the $S_{II}$ value obtained from geometric optimization of DFT calculations is usually $\leqslant -10\%$ for Pt(1 1 1) slabs containing subsurface M compared to pure Pt(1 1 1) slabs, thus it is not surprising that ligand effects were found to be shifting $\varepsilon_d$ downwards in that work [21].

Although this work mainly focuses on the ligand effects caused by subsurface M as discussed above, it is worth considering the ligand effects caused by M atoms on the surface as well (hereafter referred to as in-plane ligand effects). To simulate these effects, the Pt$_{12}$M$_6$ cluster model is modified by rearranging the three M atoms from the sublayer to the top layer, and locating them around the central atom symmetrically with $d_{PM}$ set to be 2.75 Å or 2.65 Å as above. The in-plane ligand effects are determined by the particular M (in-plane pure ligand effects) and the in-plane $d_{PM}$ (in-plane intra-layer strain effects) simultaneously. The in-plane pure ligand effects upshift $\varepsilon_d$ in the same way as the pure ligand effects from the subsurface M, and are counteracted by the in-plane intra-layer strain effects, which is also characterized by the parameter $S_{II}$ referred to as interlayer strain above. As expected, the in-plane ligand effects are similar to the ligand effects caused by subsurface M because the interaction between Pt and M is essentially independent of bond orientations.

It should be noted that the $S_{II}$ defined in Eq. (1) is relative to the unstrained Pt NPs. However, the surfaces of Pt$_x$M NPs are generally under some lateral strains even without M present in the near-surface region due to the mismatch between Pt in the outer shell and the Pt$_x$M in the core; and the strain effects can have an effective range of up to more than 5 Pt layers [25]. Therefore, the in-plane $S_{II}$ must be defined using the in-plane $d_{PM}$, which is shorter than that of unstrained Pt NPs (2.75 Å). Accordingly, the in-plane intra-layer strain effects are relatively weaker than the interlayer strain effects. As a consequence, the in-plane ligand effects caused by the late 3d elements generally upshifts the Pt surface $\varepsilon_d$. This would suggest that in-plane ligand effects lead to a stronger interaction between Pt and simple adsorbates on surface. However, adsorbate-adsorbate lateral repulsive effects caused by the M atoms on the surface also exist, and the repulsive effects have been demonstrated to decrease the bond strength between Pt and simple adsorbates [9,66]. Thus the in-plane ligand effects and lateral repulsive effects counteract each other, and the nature of the adsorbate and its coverage may determine which one wins. Indeed, Gauthier et al. [67] observed an increasing Pt–CO bond strength on PtCo(1 1 1) with increasing number of Co neighbors on the surface, and attributed this to the release of the surface strain caused by the in-plane surrounding Co atoms. They therefore concluded that the in-plane ligand effects dominated the CO–CO lateral repulsive effects. This finding for CO–CO repulsive effects, if also true for OH–OH repulsive effects, would suggest that it is better to maintain a pure Pt surface on PtM catalysts so as to reduce the binding energy of OH that poisons Pt sites for the ORR.

On the other hand, it is known that a Pt dominated surface under lateral strain will significantly relax outward unless some M exist in the subsurface region [52,67]. Accordingly, the $S_{II}$ caused by subsurface M atoms is more negative relative to that in the absence of subsurface M, and thus the interlayer strain effects are relatively stronger. As a result, the ligand effects caused by the late 3d elements in the subsurface region downshifts the Pt surface $\varepsilon_d$. Using DFT calculations, Xu et al. showed that the Pt atoms in the Pt skin with Co immediately underneath in PtCo(1 1 1) have much lower interlayer separation (∼0.1 Å) and $\varepsilon_d$ (∼0.2 ev) than those of the Pt atoms without Co underneath [62]. Experimentally, Gauthier et al. observed that the Pt atoms in PtCo(1 1 1) appearing highest (largest distance to the subsurface) bind Co most strongly, and their DFT calculations revealed that the surface Pt atoms with less than two Co neighbors in the subsurface layer relax outwards and thus have the highest $\varepsilon_d$ [67]. All these results underscore the importance of subsurface M in suppressing the outward relaxation of the Pt surface. Therefore, despite the fact that the late 3d M elements in the subsurface do not shift $\varepsilon_d$ greatly, subsurface M atoms are still desired.

In summary, the ligand effects caused by subsurface or surface M atoms in Pt$_x$M NPs can downshift or upshift $\varepsilon_d$, relatively, to the pure Pt surface under lateral strain. As a direct result, a pure Pt surface with an M dominated subsurface is most favorable in terms of downshifting $\varepsilon_d$ and weakening Pt–adsorbate bond strengths. Assuming the Pt–OH bond strength is on the high side of the volcano plot in pure Pt [5], and therefore poisons Pt sites, such downshift will give a better ORR activity by moving toward the maximum in the volcano plot.

Experimental results have shown that for most part this conclusion is true. Annealing PtM alloys at high temperature, resulting in Pt enrichment in the surface compensated by M enrichment in the subsurface, has been widely demonstrated as a promising method to enhance the ORR activity [1,2,4,6,68]. In addition, PtM NPs with an ordered structure having an L1$_0$ or L1$_2$ onion-type (shell-wise) alternating arrangement of Pt or M layers shows unusually high ORR activity compared to PtM NPs with a disordered structure [69–71]. However, other work with dealloyed Pt$_x$M (M = Co or Ni) NPs have shown that catalysts with an abundance of percolated particles (i.e. with multicores and open holes) and having M atoms at or near the surface have similar activities to those with no M atoms on the surface [72,73]. Further, NPs with M atoms at the surface or just subsurface are not likely to be sufficiently durable, as such M atoms can easily be removed entirely or at least move from the subsurface to the surface with oxidation, where their ligand effects can change from helpful to detrimental. Thus, after considering both the durability and ORR activity aspects, thicker Pt skins of more than one monolayer appear to be preferable. Nevertheless, this work shows that the rational design of advanced catalyst requires a full knowledge of the structure–property–activity relationships.

4. Conclusions

In the present study we have established quantitative structure–property–activity relationships for Pt$_x$M NPs using FEFF8 calculations in combination with experimental results. A representative cluster model of Pt$_x$M NPs, Pt$_{12}$M$_6$, has been developed based on the experimental EXAFS data, and the corresponding Pt surface $d$-band center $\varepsilon_d$ is demonstrated to provide a very general picture of the electronic properties in relating the structure and ORR activity of Pt$_x$M NPs. The high consistency between the $\varepsilon_d$ trend, the OH coverage trend, and the activity trend of Pt$_x$M NPs explains the enhanced ORR activity of Pt$_x$M NPs compared to Pt; namely, it can be attributed primarily to OH inhibition caused by the downshift of $\varepsilon_d$. The correlation between $\varepsilon_d$ or other electronic properties and the structural properties accessible to XAS results, such as $d_{PM}$, $d_{PM}$, and M, etc. are then related to elucidate the roles of strain and ligand effects in modification of the Pt surface electronic properties.

We find that both $\varepsilon_d$ and $E_f$ are nearly linearly correlated with bond distance, and that the shift of $E_f$ can be attributed to the intratomic charge transfer from the compact $d$-band into a more diffuse $sp$-band. We show that the strain effects play a dominant role in downshifting $\varepsilon_d$, especially for the late 3d elements, underscoring the importance of an M-rich core to compress the in-plane $d_{PM}$. Ligand effects consist of two opposing effects: pure electronic ligand effects and interlayer (or intra-layer for in-plane Pt–M interactions) strain effects, and together these can either upshift or downshift $\varepsilon_d$ depending on which effect is more significant. The fact that a pure Pt surface supported on an M dominated subsurface structure is favored for activity enhancement, is essentially determined by this complex nature of ligand effects. The
success of our theoretical approach, as demonstrated here, makes it a good complement to the XAS technique in understanding the structure–property–activity relationship of supported bimetallic Pt–M nanoparticles. The application of this approach can be extended toward many other topics involving bonding interactions between transition metal elements.

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