Size Effects in Electronic and Catalytic Properties of Unsupported Palladium Nanoparticles in Electrooxidation of Formic Acid

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We report a combined X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and chronoamperometry (CA) study of formic acid electrooxidation on unsupported palladium nanoparticle catalysts in the particle size range from 9 to 40 nm. The CV and CA measurements show that the most active catalyst is made of the smallest (9 and 11 nm) Pd nanoparticles. Besides the high reactivity, XPS data show that such nanoparticles display the highest core-level binding energy (BE) shift and the highest valence band (VB) center downshift with respect to the Fermi level. We believe therefore that we found a correlation between formic acid oxidation current and BE and VB center shifts, which, in turn, can directly be related to the electronic structure of palladium nanoparticles of different particle sizes. Clearly, such a trend using unsupported catalysts has never been reported. According to the density functional theory of heterogeneous catalysis, and mechanistic considerations, the observed shifts are caused by a weakening of the bond strength of the COOH intermediate adsorption on the catalyst surface. This, in turn, results in the increase in the formic acid oxidation rate to CO₂ (and in the associated oxidation current). Overall, our measurements demonstrate the particle size effect on the electronic properties of palladium that yields different catalytic activity in the HCOOH oxidation reaction. Our work highlights the significance of the core-level binding energy and center of the d-band shifts in electrocatalysis and underlines the value of the theory that connects the center of the d-band shifts to catalytic reactivity.

Introduction

Direct formic acid fuel cell (DFAFC) is a convenient energy source for micropower energy devices such as cell phones and/ or laptops and promises to be one of the first small fuel cells on the market.^{1,2} Therefore, major efforts have been made to demonstrate the DFAFC performance and, at the same time, to advance understanding of mechanisms of formic acid electrooxidation processes.^{2–9} The studies reported below concentrate on the formic acid oxidation process on unsupported nanoparticle Pd catalysts, that is, on the active DFAFC anode.¹ Notice that the use of nanoparticle materials in practical electrocatalysis is essential as the nanoparticles guarantee sufficiently high surface-to-bulk atomic ratio and utilization of the noble metal catalyst components economically. As an additional bonus, the nanoparticle electronic properties can be adjusted by controlling the nanoparticle size.¹⁰

In this report, we use electrochemistry and X-ray photoelectron spectroscopy (XPS) to probe the particle size and electronic effects in the formic acid electrooxidation process. We present experimental evidence of the correlation between the electronic properties of unsupported Pd nanoparticles—as they vary as a function of their particle size—and their catalytic activity.

It is generally accepted that the oxidation of formic acid occurs via the dual path mechanism:^{11,12} one path involving a direct carbon dioxide formation and another an inhibiting intermediate formation.¹³ At low potentials, adsorbed CO produced from formic acid decomposition is the inhibiting intermediate.^{12,14,15} Therefore, it is important to understand the CO oxidation behavior at the Pd nanoparticles, as it will be referred to below. At higher potentials, formate intermediate is the poisoning species.¹³ However, no voltammetric signature to the formate species has been assigned, and this essentially XPS and electrochemistry study cannot refer to this intermediate.^{4,11,13} (We did comment on the role of the formate on formic acid electrocatalysis previously.⁴)

In present heterogeneous catalysis research, the density functional theory (DFT) is frequently used to account quantitatively for metal/alloy behaviors in reacting chemical molecules to desired products.^{16–20} In particular, it has been shown theoretically^{17–19} that a change in the adsorbate chemisorption energy scales directly with the change in the metal center of the d-band: lowering of the d-band center results in the decrease

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Figure 1. Representative XPS survey spectra for (a) completely reduced Pd nanoparticles of the 9 nm size and (b) clean Pd(111).

in adsorption energy (or the surface bond strength) of the adsorbate to the substrate. In gas-phase research, the correlation between the metal d-band center, the core-level binding energy, and the catalytic activity is now well-established.^{21–24} Verification of similar correlations in the field of electrocatalysis begins to emerge.^{25,26}

Experimental Section

The electrochemical UHV-XPS (UHV = ultrahigh vacuum) instrument consisting of the main UHV chamber has been described before.^{27,28} (This measuring configuration prevents an exposure of samples to air upon the sample transfer between UHV and an electrochemical cell.) An ESCA M-probe, highresolution multichannel hemispherical electron analyzer (Surface Science Instruments) equipped with a monochromatic Al Ka line, operated at 110 W and a constant pass energy of 25 eV, was used for all XPS measurements. The S-probe version of the 1.36 ESCA software (Fison Instruments) was used, and all XPS spectral peaks reported herein were fitted using a mixed Gaussian-Lorentzian line shape and Shirley baselines. The linearity of the BE scale of the detector was calibrated using Au 4f_{7/2} (84.0 eV), Ag 3d_{5/2} (368.25 eV), and Cu 2p_{3/2} (932.68 eV).²⁹ For the Pd 3d and valence band regions, the exact BE corrections were determined by comparison with the clean Pd(111) surface, assuming that the Pd 3d_{5/2} BE is 384.10 eV and that the Pd Fermi edge is at 0.0 eV.^{30,31}

Pd particles, 9 and 11 nm, were purchased from Sigma-Aldrich and Pd black (40 nm) from Alfa Aesar. A transmission electron microscopy (TEM) instrument, JEOL 2010F, was used to confirm the average size of the nanoparticles. Prior to performing oxidation of formic acid, Pd nanoparticles were immobilized on a gold disk,^{27,32} electrochemically reduced at 0.10 V, and further stabilized at 0.5 V for 20 min. The pretreatment produced a contamination free surface, as demonstrated by the XPS measurements. Figure 1 shows a typical XPS survey for 9 nm Pd nanoparticle surfaces after the pretreatment and XPS from the UHV cleaned Pd(111). Practically identical XPS spectral features in Figure 1 indicate a clean nanoparticle surface system. Furthermore, our XPS for Pd metal and for the Pd nanoparticles do not show any of the features that are associated with formation of PdH_x .³³ The layer of the immobilized Pd nanoparticles was thick enough to completely attenuate the XPS Au substrate signal, which simplifies interpretations of the Pd XPS results. If not stated otherwise, the real surface area of the Pd nanoparticle surface was estimated from the known sample weight multiplied by the value of the sample surface area per gram.

As a reference for the XPS, a MaTeck disk Pd(111) crystal (8 \times 2 mm) was used. The crystal surface was cleaned by multiple cycles of argon ion bombardment and subsequently hot argon ion bombardment, and then the crystal was annealed at high temperature (including annealing in oxygen atmosphere at 10^{-8} Torr), until no impurities were detected by XPS.

Chemicals used were H_2SO_4 (GFS, double distilled from Vycor) and HCOOH (Sigma-Aldrich, Fluka for HPLC) and Millipore water. Ultrahigh purity quality argon and CO gases were supplied by S. J. Smith Welding Supply. Electrochemical measurements were carried out using the Autolab G30 potentiostat in a conventional three electrodes electrochemical cell with platinized platinum gauze as a counter electrode and Ag/AgCl in 3 M NaCl as the reference electrode. All potentials are quoted with respect to RHE, and the experiments were performed at room temperature.

Results and Discussion

Representative, high-resolution transmission electron microscopy (HRTEM) images of the Pd nanoparticles in use are presented in Figure 2. The histograms of the particle size distribution indicate that the average particle sizes are 9 ± 2.5 , 11 ± 3 , and 40 ± 15 nm. Figure 3 shows steady-state cyclic voltammograms (CV) for formic acid oxidation for the three nanoparticle samples in 0.5 M HCOOH in 0.5 M H₂SO₄, at 20 mV/s. The data indicate a low inhibition rate of formic acid oxidation, which is consistent with previous studies with conventional Pd electrodes.^{3,34} Figure 4 shows chronoamperometric current-time plots obtained during formic acid oxidation in a 0.5 M HCOOH + 0.5 M H₂SO₄ solution using the three Pd catalysts at 0.27 V (the same trend was found until E = 0.5V, that is, until the end of utility of Pd as the formic acid oxidation catalyst). Clearly, the 9 and 11 nm Pd nanoparticles display higher activity both at the experiment beginning and after 1 h of reaction. The decay trends are quite similar: ca. 70% of the initial activity remains after 1 h of reaction. After the 1 h, the current density from the 9 and 11 nm Pd nanoparticles is similar, for example, 0.2 mA cm⁻². However, the current density for the 40 nm nanoparticles is lower and is 0.15 mA cm^{-2} (see also the data in Table 1).

Figure 5 shows results from voltammetric CO stripping experiments using a 9 nm nanoparticle sample in 0.5 M H₂SO₄ and at 5mV/s, with the CO stripping peak at 0.89 V. The same CO stripping voltammograms (and the same CO oxidation peak potential) were found for the remaining Pd nanoparticles. Clearly, the CO oxidation on nanoparticle Pd is sample size independent. Since a dependence of the formic acid electrooxidation activity upon reduction in the particle size is found (Figure 4), we conclude that the activity increase is not due to facilitating the CO oxidation process but rather due to the reaction leading to CO₂ formation directly.^{11,12}

The clean and reduced Pd nanoparticle samples were transferred from the electrochemical cell to the XPS chamber Palladium Nanoparticles in Formic Acid



Figure 2. TEM images of the palladium nanoparticles used for this study, along with the statistical results from the analyses of many different regions of the particles. Histograms of the particle size distribution yield average particle sizes of (a) 9 ± 2.5 , (b) 11 ± 3 , and (c) 40 ± 15 nm. A 20 nm scale bar is applied to images (a) and (b) and the 100 nm to image (c).

according to the procedure described in the Experimental Section.^{27,28} The comparison of the core-level Pd 3d XPS spectra shows different electron core-level binding energy (BE) among the samples (the Pd $3d_{5/2}$ data in Figure 6 and in Table 1). Namely, the BE of Pd 3d from the 9 and 11 nm nanoparticles is shifted by ca. +0.2 eV vs the 40 nm sample and the Pd bulk, which is accompanied by the increase in the fwhm by 0.15 eV. (All spectra and current densities were measured at least three times, and the data in Table 1 are the average of three independent measurements.)

Figure 7 shows the XPS valence band (VB) spectra from the three Pd nanoparticle samples and from Pd(111). (The nanoparticle peak heights around $E_{\rm F}$ are scaled to that of Pd(111).) Notice that the broad peak associated with PdH_x at 8 eV³³ is not found. The position of the center of the valence band is given by $\int N(\epsilon)\epsilon d\epsilon / \int N(\epsilon) d\epsilon$, where $N(\epsilon)$ is the DOS or, in our case, the XPS-intensity after background subtraction (Experimental Section). To obtain the valence band centers, we carried out the integration up to 10.0 eV BE with respect to $E_{\rm F}$. The VB center for Pd(111) is 2.49 ± 0.06 and is in good agreement with the value of 2.39 eV obtained from the gradientcorrected DFT periodic slab calculations by Pallassana et al.³⁵ This demonstrates the validity of our method. The largest particles (40 nm) do not show a VB center change vs Pd(111). However, the smallest nanoparticles (9 and 11 nm) exhibit the VB center shift of ca. +0.2 eV vs the Pd bulk. Wertheim et al.³⁶ and also Mason et al.³⁷ reported a trend in the VB-band center shift with decreasing size of Pd clusters (vapor deposited on amorphous carbon substrates) that we now confirm. Clearly,

the direction of the BE shift with particles size is consistent with the shift in the VB center.^{21,22,37,38}

The particle size effect on the metal electronic structure in the particle size range investigated in this study was already observed using metal nanoparticle nuclear magnetic resonance (EC NMR).³⁹ While dealing with Pt³⁹ rather than with Pd, the nanoparticle catalyst was unsupported as is the case here, and the data informed us that the smaller the particle size, the smaller the NMR frequency of "bulk" Pt. That is, the particle size had a strong effect on the bulk Knight shift or on the "bulk" LDOS at the Fermi level. We believe that this relates to the present observation that the bulk electronic properties of the samples measured by XPS are affected by the particle size (Figure 6). More work is necessary to delineate possible correlations between the Knight shift data and the present BE data. However, the advantage in using large nanoparticles such as in this work (ca. 10 nm and larger) is that final state changes in the relaxation and screening of the core holes are not important since the screening is expected to have converged to the bulk limit.^{40,41} Thus, our observed shifts are due to the initial state effect only. Further, as we stated in the Experimental Section, we ruled out the presence of impurities such as dissolved hydrogen or surface carbon as being responsible for the observed BE shifts. Therefore, we propose that the lattice strain is the origin of the BE shifts to higher BE for the smallest Pd particles studied (compared with the larger nanoparticles and the Pd single crystal). However, the lattice strain does not have the same physical origin as the 5-7% lattice strain observed for small particles on inert supports,^{40,42-44} as discussed below.



Figure 3. Cyclic voltammetric curves taken in the positive direction (solid lines) and the negative direction (long dashed lines) for (a) 9, (b) 11, and (c) 40 nm Pd catalysts in 0.5 M HCOOH in 0.5 M H₂SO₄ solution at 20 mV/s.



Figure 4. Formic acid oxidation current densities measured for three sizes of Pd nanoparticles in 0.5 M HCOOH in 0.5 M H₂SO₄ at 0.27 V vs RHE for 1 h reaction time. The current densities shown correspond to Pd catalysts with the size of 9 nm (black line), 11 nm (red line), and 40 nm (blue line). The electrochemically active surface area of the Pd nanoparticle film was estimated from the known sample weight multiplied by the known sample surface area per gram. The plot was constructed after a five adjacent points smoothing procedure was applied.

It is important to correlate the shifts of the XPS BEs for different particle sizes with the electronic structure of the particles since this helps us to relate the XPS to the nanoparticle

TABLE 1: Steady-state Current Density for Formic Acid Oxidation (measured at 1 h, see text), the Center of Valence Band (VB), and the Core-Level Binding Energy (BE) of the Pd 3d_{5/2} Level for Palladium

steady-state chronoamperometric current, XPS peak of Pd 3d _{5/2} , and center of VB band for different sizes of Pd particles			
sample	steady-state CA after 1 h (mA cm ⁻²)	center of VB (eV)	BE of Pd 3d _{5/2} (eV)
Pd (111) ^a	not measured	2.49 ± 0.06	335.10 ± 0.03
Pd (40 nm) ^b	0.15 ± 0.01	2.49 ± 0.06	335.12 ± 0.03
Pd (11 nm) ^c	0.21 ± 0.02	2.59 ± 0.06	335.25 ± 0.03
Pd $(9 \text{ nm})^d$	0.21 ± 0.02	2.64 ± 0.06	335.33 ± 0.03

^{*a*} The data for Pd(111) as a reference for the XPS measurements. ^{*b*} Pd black (particle size = 40 nm). ^{*c*} Pd nanoparticles (11 nm). ^{*d*} Pd nanoparticles (9 nm). The data were obtained from three independent measurements and are given at a 95% confidence level.



Figure 5. Voltammetric CO stripping with Pd nanoparticles (9 nm) in 0.5 M H₂SO₄. The scan rate was v = 5 mV/s. Shown are the first scan (black solid line) starting at 0.13 V and the second scan (red dot line). The electrode was exposed to dissolved CO for 10 min at 0.13 V followed by Ar bubbling for 20 min.

chemistry. To make this correlation, we can bring to bear a system that involves shifts of the BEs of metal nanoparticles supported on inert, typically oxide substrates. Here, it is known that the BEs of supported metal particles shift to lower BE with increasing size ${}^{36,40,45-48}$ by ~ 1 eV. Although the range of sizes of particles on inert supports are typically $\sim 1 \text{ nm}$,⁴⁰ these simpler systems are useful to establish the mechanisms relevant for the BE shifts observed with the size of our present Pd particles. Notice the key findings of Richter et al.⁴⁰ to show that two mechanisms contribute, about equally, to the $\sim 1 \text{ eV}$ BE shift. The first is the final state relaxation that screens the core hole; this relaxation grows in magnitude as the particle size increases. The second is an initial state effect arising from the lattice strain that exists as bond distances are shorter in smaller particles.^{42,43} Furthermore, it was shown that the lattice strain affects the BEs primarily because the d-hybridization changes with the lattice strain.^{40,44} We now use the concept of hybridization to encompass all d-shell chemical bonding effects that act to change the number and character of the d electrons



Figure 6. Representative XPS spectra for the Pd 3d core levels of the completely reduced Pd nanoparticles with the size of (a) 9, (b) 11, and (c) 40 nm and for (d) clean Pd(111). The maximum of the Pd $3d_{5/2}$ peak is used as the measure of the binding energy and is indicated by the vertical lines. The Pd sample reduction was carried out by holding the electrode at 0.1 V vs RHE for 20 min. See also Table 1.

around the XPS ionized atom. Further, there is strong and general evidence that relates the degree of hybridization to shifts of the core-level BEs and to shifts of the d-band center.^{40,44,46,49} The key point is that the d-hybridization is known to affect the XPS BEs for a wide range of cases.^{40,44,46,49} Furthermore, our recent work has established the connection between the lattice strain and the d-hybridization.^{40,44}

The fact that the BE shifts depend on the extent of dhybridization is a very important observation relative to how the BE shifts may reflect the chemical activity of the system. This relationship occurs because d-hybridization which forms stronger bonds between the metal atoms reduces the potential of the metal to form strong bonds with adsorbed reactants. In turn, this change of the adsorbate bond strength to a nanoparticle is, as we discuss below, a key factor for the reactivity. We invoke the lattice strain as the origin of the hybridization and the change of reactivity because of the evidence that the strain leading to a lattice contraction is consistent with an increase of core-level BEs,^{40,41} exactly as we measure for our Pd particles; see Table 1.

To reiterate, the data in Table 1 show that the most active catalyst for the formic acid oxidation is made of the smallest Pd nanoparticles (the increase in the current density is from 0.15 to 0.21 mA cm⁻²). Such smallest Pd nanoparticles (9 and 11 nm) display, at the same time, the highest BE shift and the highest valence band (VB) center downshift with respect to the Fermi level. In other words, the center of the d-band is reduced and the smallest nanoparticles display the highest formic acid



Figure 7. Representative valence band spectra for three Pd nanoparticle samples of the size of (a) 9, (b) 11, and (c) 40 nm and for (d) clean Pd(111). The lines shown were smoothed using a five-points adjacent average on the original lines. The peak heights around E_F of the VB spectra are scaled to that of Pd(111) (see text).

reactivity. Norskov and co-workers^{17–19} have shown that changes in the adsorbate chemisorption energies scale directly with the changes in the center of the catalyst d-band: lowering the d-band center (moving down and away from the Fermi level) results in the decrease in the bond strength of adsorbates (or in their chemisorption energy).

Notice that, for formic acid oxidation to CO_2 , we have the following set of reactions to consider^{4,11,13}

$$\text{HCOOH}_{\text{bulk}} \rightarrow 2\text{H}^+ + 2\text{e}^- + \text{CO}_2 \tag{1}$$

$$\text{HCOOH}_{\text{ads}} \rightarrow (\text{COOH})_{\text{ads}} + \text{H}^+ + \text{e}^-$$
 (2)

$$(\text{COOH})_{\text{ads}} \xrightarrow{\text{rds}} \text{CO}_2 + \text{H}^+ + \text{e}^-$$
 (3)

We believe that the meaning of the experimental and theoretical findings is as follows. The rate of formic acid transformation to CO_2 (reaction 1) is the highest at the surface that is free of (COOH)_{ads}. Since the smallest Pd nanoparticles have the lowest d-band center, they bind the COOH intermediate less strongly (vs larger nanoparticles) and reduce the surface (COOH)_{ads} coverage (reactions 2 and 3). If the limiting step of reaction 3 is avoided because of the low COOH coverage, then higher rates of the direct HCOOH decomposition process to CO_2 via reaction 1 are expected. Notice however that this interpretation is limited to few nanoparticle sizes selected for this project. If using a broader range of Pd nanoparticle sizes will show the rate to maximize at an optimized particle size, ⁵⁰ interpretations involving a volcano behavior will have to be invoked.²⁶

Conclusions

Our measurements demonstrate a Pd particle size effect on the XPS spectra and on the rate of HCOOH oxidation reaction. Due to the size of the nanoparticles in use, only the initial state effect in the XPS measurements has to be considered. We could then provide a line of evidence that the initial state effect results from the lattice strain change that occurs as bond distances are shorter in smaller nanoparticles. Therefore, the lattice strain effect and its electronic-level consequences emerge as the key driving force in the catalysis, at least in reacting HCOOH to CO₂. These electronic-level factors that are affected by the lattice strain change are the core-level binding energies, the related position of the center of the d-band, and the Knight sifts (or local DOS) in the EC NMR measurements.³⁹

To be more specific, we have found that the most active Pd nanoparticle catalyst in formic aid electrooxidation is made of the smallest particles. Such smallest particles display the highest binding energy shift and the highest valence band center downshift with respect to Fermi level, which is consistent with enhancement of the d-band hybridization in small nanoparticles. With the formic acid oxidation mechanism represented by eqs 1-3 (see above), we interpret our data as follows: the lower d-band center results in a decrease in adsorption energy of the formate intermediate that enhances the rate of the HCOOH molecule decomposition via the direct path. This conjecture is consistent with predictions of the modern theory of heterogeneous catalysis concerning the center of the d-band shifts of metal and alloy catalysts in reacting simple organic molecules to products.

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References and Notes

(1) Rice, C.; Ha, S.; Masel, R. I.; Waszczuk, P.; Wieckowski, A.; Barnard, T.; *J. Power Sources* **2002**, *111*, 83.

- (2) Rice, C.; Ha, S.; Masel, R. I.; Wieckowski, A. J. Power Sources 2003, 115, 229.
- (3) Baldauf, M.; Kolb, D. M. J. Phys. Chem. **1996**, 100, 11375.
- (4) Lu, G.-Q.; Crown, A.; Wieckowski, A. J. Phys. Chem. B 1999, 103, 9700.
- (5) Waszczuk, P.; Barnard, T. M.; Rice, C.; Masel, R. I.; Wieckowski, A. *Electrochem. Commun.* **2002**, *4*, 599.
- (6) Zhao, M. C.; Rice, C.; Masel, R. I.; Waszczuk, P.; Wieckowski, A. J. Electrochem. Soc. 2004, 151, A131.
- (7) Ha, S.; Larsen, R.; Masel, R. I. J. Power Sources 2005, 144, 28.
 (8) Zhu, Y. M.; Khan, Z.; Masel, R. I. J. Power Sources 2005, 139, 15
- (9) Larsen, R.; Zakzeski, J.; Masel, R. I. *Electrochem. Solid-State Lett.* 2005, 8, A291.
 - (10) Henry, C. R. Surf. Sci. Rep. 1998, 31, 231.
 - (11) Capon, A.; Parsons, R. J. Electroanal. Chem. 1973, 45, 205.
 - (12) Vela, M. E.; Lezna, R. O.; De Tacconi, N. R.; Arvia, A. J.; Beden,
- B.; Hahn, F.; Lamy, C. J. Electroanal. Chem. 1992, 323, 289.
 - (13) Samjeske, G.; Osawa, M. Angew. Chem., Int. Ed. 2005, 44, 5694.
 (14) Kunimatsu, K.; Kita, H. J. Electroanal. Chem. 1987, 218, 155.

- (15) Corrigan, D. S.; Weaver, M. J. J. Electroanal. Chem. 1988, 241, 143.
 - (16) Hammer, B.; Norskov, J. K. Adv. Catal. 2000, 45, 71.
 - (17) Hammer, B.; Norskov, J. K. Surf. Sci. **1995**, 343, 211.
- (18) Ruban, A.; Hammer, B.; Stoltze, P.; Skriver, H. L.; Norskov, J. K. J. Mol. Catal. A: Chem. **1997**, *115*, 421.
- (19) Mavrikakis, M.; Hammer, B.; Norskov, J. K. *Phys. Rev. Lett.* **1998**, *81*, 2819.
- (20) Greeley, J.; Norskov, J. K.; Mavrikakis, M. Annu. Rev. Phys. Chem. 2002, 53, 319.
- (21) Ganduglia-Pirovano, M. V.; Natoli, V.; Cohen, M. H.; Kudrnovsky, J.; Turek, I. *Phys. Rev. B* **1996**, *54*, 8892.
- (22) Hennig, D.; Ganduglia-Pirovano, M. V.; Scheffler, M. Phys. Rev. B 1996, 53, 10344.
- (23) Rodriguez, J. A. Surf. Sci. Rep. 1996, 24, 223.
- (24) Rodriguez, J. A.; Goodman, D. W. Science 1992, 257, 897.
- (25) Zhang, J. I.; Vukmirovic, M. B.; Xu, Y.; Mavrikakis, M.; Adizic,
 R. R. Angew. Chem., Int. Ed. 2005, 44, 2132.
- (26) Kibler, L. A.; el-Aziz, A. m.; Hoyer, R.; Kolb, D. M. Angew. Chem., Int. Ed. 2005, 44, 2080.
- (27) Lewera, A.; Zhou, W. P.; Vericat, C.; Chung, J. H.; Haasch, R.; Wieckowski, A.; Bagus, P. S. *Electrochim. Acta* **2006**, *51*, 3950.
- (28) Vericat, C.; Wakisaka, M.; Haasch, R.; Bagus, P. S.; Wieckowski, A. J. Solid-State Electrochem. 2004, 8, 794.
- (29) Seah, M. P.; Gilmore, I. S.; Beamson, G. Surf. Interface Anal. 1998, 26, 642.
- (30) Anthony, M. T.; Seah, M. P. Surf. Interface Anal. 1984, 6, 95.
- (31) Wagner, C. D.; Naumkin, A. V.; Kraut-Vass, A.; Allison, J. W.; Powell, C. J.; Rumble, J. R., Jr. *NIST Standard Reference Database 20*, Version 3.4 (Web Version), http://srdata.nist.gov/xps/.
- (32) Waszczuk, P.; Solla-Gullon, J.; Kim, H.-S.; Tong, Y. Y.; Montiel, V.; Aldaz, A.; Wieckowski, A. J. Catal. 2001, 203, 1.
- (33) Bennett, P. A.; Fuggle, J. C. Phys. Rev. B: Condens. Matter Mater. Phys. **1982**, 26, 6030.
- (34) Pavese, A.; Solis, V.; Giordano, M. C. J. Electroanal. Chem. 1988, 245, 145.
- (35) Pallassana, V.; Neurock, M.; Hansen, L. B.; Hammer, B.; Norskov, J. K. *Phys. Rev. B* **1999**, *60*, 6140.
- (36) Wertheim, G. K.; DiCenzo, S. B.; Buchanan, D. N. E. *Phys. Rev.* B 1986, 33, 5384.
- (37) Mason, M. G.; Gerenser, L. J.; Lee, S.-T. Phys. Rev. Lett. 1977, 39, 288.
 - (38) Citrin, P. H.; Wertheim, G. K. Phys. Rev. B 1983, 27, 3176.
- (39) Babu, P. K.; Oldfield, E.; Wieckowski, A.; In Modern Aspects of
- Electrochemistry; Vayenas, C. G., Conway, B. E., White, R. E., Gamboa-
- Adelco, A. E., Eds.; Kluwer Academic Publishers: New York, 2003; p 1.
 (40) Richter, B.; Kuhlenbeck, H.; Freund, H.-J.; Bagus, P. S. *Phys. Rev. Lett.* 2004, 93, 026805.
- (41) Bagus, P. S.; Nelin, C. J.; Kay, E.; Parmigiani, F. J. Electron Spectrosc. Relat. Phen. **1987**, 43, C13.
- (42) Klimenkov, M.; Nepijko, S.; Kuhlenbeck, H.; Baumer, M.; Schlogl, R.; Freund, H.-J. Surf. Sci. **1997**, 391, 27.
- (43) Nepijko, S. A.; Klimenkov, M.; Adelt, M.; Kuhlenbeck, H.; Schlogl, R.; Freund, H.-J. Langmuir 1999, 15, 5309.
- (44) Bagus, P. S.; Wieckowski, A.; Freund, H.-J. Chem. Phys. Lett. 2005, 420, 42.
 - (45) Egelhoff, W. F., Jr. Surf. Sci. Rep. 1987, 6, 253.
 - (46) Mason, M. G. Phys. Rev. B 1983, 27, 748.
 - (47) Wertheim, G. K. Z. Phys. D: At., Mol. Clusters 1989, 12, 319.
- (48) Wertheim, G. K. Z. Phys. B 1987, 66, 53.
- (49) Bagus, P. S.; Illas, F.; Pacchioni, G.; Parmigiani, F. J. Electron Spectrosc. Relat. Phenom. 1999, 100, 215.
- (50) Masel, R. I. *Principles of adsorption and reaction on solid surfaces*; Wiley-Interscience: New York, 1996.