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^{195}Pt NMR of Platinum Electrocatalysts: Friedel−Heine Invariance and Correlations between Platinum Knight Shifts, Healing Length, and Adsorbate Electronegativity

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Abstract: The influence of a series of different ligands (H, O, S, CN$^-$, CO, and Ru), electrochemically adsorbed onto carbon-supported nanoscale Pt particles, has been investigated by ^{195}Pt NMR, in an electrochemical environment. The NMR Knight shifts from atoms in the interior of the particles are invariant to surface ligand adsorption, as expected by the Friedel−Heine invariance theorem. However, the shifts of the surface and subsurface atoms vary over a ~11000 ppm range for the adsorbates investigated. The Knight shifts of the surface and subsurface platinum atoms, obtained by using an NMR layer-model simulation, linearly map the electronegativity of the adsorbate. These observations permit the derivation of a correlation between the "healing length" of the Pt metal, a parameter indicating how fast the bulk metal properties are recovered when moving in from the surface, and the electronegativity of the adsorbate, providing a new probe of electrocatalyst and heterogeneous catalyst surface electronic structure.

Introduction

Understanding how submonolayer adsorbates modify the chemical and physical properties of metal surfaces has long been one of the central themes of surface science,[1] and is of importance in relation to the ability to scientifically engineer metal surface properties for targeted applications, such as enhancing the CO-tolerance of electrocatalysts used in fuel cells[2] or more generally in promoting metal surface catalysis.[3] In this article, we report the first observations of correlations between adsorbate electronegativity and metal surface electronic properties as deduced by metal NMR, specifically, with the ^{195}Pt NMR Knight shift and with the Pt healing length. Our results also provide definitive experimental confirmation of the Friedel−Heine invariance theorem,[4,5] in the context of electrochemical surface science and nanoscale metal particle catalysts.

Experimental Section

The electrode material used was a carbon-black (XC-72)-supported commercial fuel cell grade platinum electrocatalyst having an average particle size of 2.5 nm (E-TEK Inc., Natrick, MA). Chemisorption of different adsorbates was achieved electrochemically. Prior to any electrochemical adsorption, the Pt nanoparticles (ca. 500 mg) were electrochemically cleaned by holding the electrode potential within the double layer region (250 mV vs 3 M NaCl Ag/AgCl reference electrode), which removed surface oxides.[6] Unless otherwise stated, 0.5 M H_2SO_4 was used as the supporting electrolyte. By holding the electrode potential at either the hydrogen evolution (−185 mV) or oxidation region (1120 mV) until the current decayed to a minimal value, a saturated layer of H or O was produced. Chemisorbed CO (ca. 0.6 monolayer) was produced via electrodissociative adsorption of methanol[7] (0.6 M, ACS grade, Fisher Scientific, Fairlawn, NJ); S (ca. 0.9 monolayer) via open potential deposition from a 10 mL Na_2S solution[8] (Alfa AESAR, Ward Hill, MA) and Ru (ca. 0.09 monolayer) via spontaneous deposition[9] from a $RuCl_3$ (Alfa AESAR) solution (1 mL of $RuCl_3$ in 0.1 M $HClO_4$, FGS Chemicals, Columbus, OH). CN$^-$ (ca. 0.7 monolayer) was adsorbed from a basic electrolyte solution at pH 11.2[10] by adding 0.2 M NaCN (Cambridge Isotope Laboratories, Andover, MA) at −310 mV in 0.5 M Na_2SO_4 (ACS grade, EM Science, Gibbstown, NJ). All electrode materials were then rinsed with supporting electrolyte (0.5 M Na_2SO_4 for Pt/CN$^-$) and transferred, together with supporting electrolyte and under argon, to glass ampules which were then immediately flame-sealed. ^{195}Pt NMR spectra were obtained at 8.47 T basically as described previously.[6]

Results and Discussions

We show in Figure 1 a series of point-by-point ^{195}Pt NMR spectra (large solid circles) of the carbon-supported nanoscale electrode materials with and without adsorbates (clean, Ru, H, CO, CN$^-$, S, or O). The solid lines represent fitted spectra based on the NMR-layer-model deconvolution described previously,[11] while the small dots are the variances between the experimental and fitted values. Both the clean-surface spectrum, Figure 1A, and its deconvolution, Figure 1B, have been reported previously,[6] but are shown again here to facilitate discussion.

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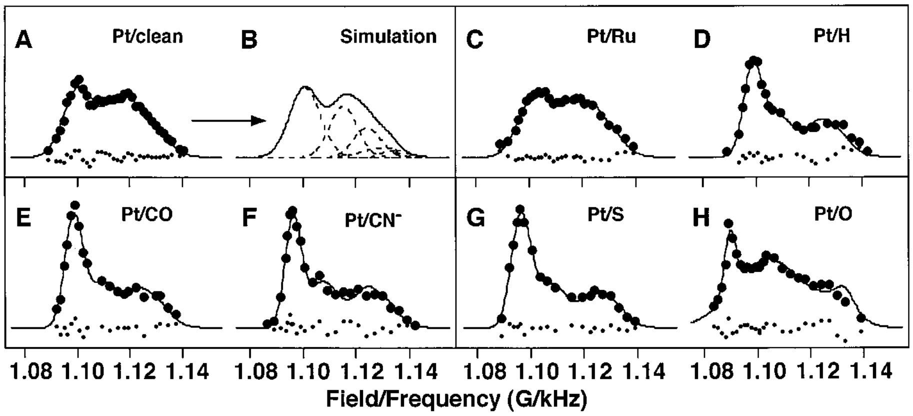

Figure 1. Point-by-point, 8.47 T ^{195}Pt NMR spectra (solid circles) and simulations of 2.5 nm carbon-supported Pt electrocatalysts with and without adsorbates. The solid lines are the NMR layer-model simulations and the small dots are the variances between the experimental and fitted values: (A) Clean surface Pt; (B) simulation of spectrum A; (C) Pt with adsorbed Ru; (D) Pt with adsorbed H; (E) Pt with adsorbed CO; (F) Pt with adsorbed cyanide; (G) Pt with adsorbed S (from Na_2S solution); (H) Pt with adsorbed O (generated electrochemically).

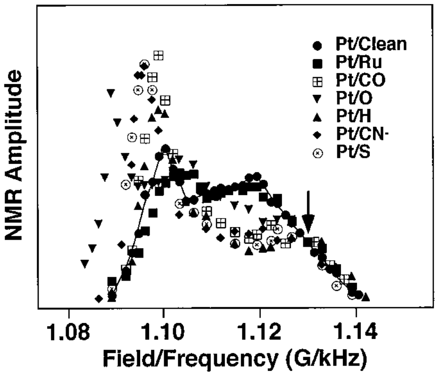

Figure 2. Superimposition of point-by-point, 8.47 T ^{195}Pt NMR spectra from Figure 1, but normalized by equalizing the amplitude at 1.131 G/kHz (indicated by the arrow). The invariance of signals beyond 1.131 G/kHz provides experimental confirmation of the Friedel−Heine invariance theorem. The surface peaks range over ∼11000 ppm.

The peak at 1.100 G/kHz for the clean-surface sample corresponds to atoms at the electrode surface. When moving into the particles, Pt atoms see their electronic environment (i.e., the electronic local density of states, LDOS) gradually recover toward that seen by bulk Pt atoms. That is, the more buried the atom the closer its Knight shift is to that of bulk platinum, 1.138 G/kHz. The experimental spectrum can then be deconvoluted by following the NMR layer model[11] in which the 2.5 nm particle is approximated by an ideal five-layer cubooctahedron.[6] Note that the frequency difference between surface and bulk resonance positions at 8.5 T is some 2.5 MHz, large enough to provide a very convenient spectral visualization of how deep the influence of an adsorbate can go, as shown in Figure 2. The spectra are normalized by equalizing their amplitudes at 1.131 G/kHz, indicated by the arrow. The interesting observation here is that the position of the high-field signal intensity (above 1.131 G/kHz), which is due to Pt atoms within the three innermost layers, is *independent* of adsorbate type. This independence provides direct experimental evidence for the validity of the Friedel−Heine invariance theorem,[4,5] which states that the integral electronic properties at an atom, such as its local density of states (LDOS), are determined primarily by the surrounding medium, within a few electronic wavelengths. This is exactly what is observed: although the chemical identity of the adsorbates is quite varied, their influences, to a very good approximation, do not go beyond their next-nearest neighbors. That is, the high-field signals are invariant toward "boundary" changes.

It is important to point out that the invariance we observed here is in quite a different context to that originally proposed in the Friedel−Heine invariance theorem. A good example[5] to illustrate this point is the ferromagnetically ordred alloy Fe_3Al. In this body-centered cubic alloy, there are two types of iron site: one has eight Fe atoms and the other has 4 Fe and 4 Al atoms as nearest neighbors. The magnetic moments on the former and latter sites are 2.14 and 1.46 Bohr magnetons (μ_B), to be compared with that of pure Fe, 2.2 μ_B. The Friedel−Heine invariance theorem is demonstrated in this case by the fact that the local magnetic moment at the center of a cubic ensemble of iron atoms embedded in an extended Fe_3Al alloy is almost exactly the same as that found in an extended solid iron lattice. The situation is quite different for nanoscale metal particles. Due to the presence of surfaces and the significant reductions in particle volume, the electronic properties at the innermost three layers of the clean-surface Pt particles investigated *are* indeed somewhat different from those of bulk Pt. However, the Fermi level LDOSs still show a remarkable invariance toward changes in surface chemical environment, even though they vary slightly from those of bulk Pt.

In complete contrast to the Friedel−Heine invariance of the electronic properties observed for the innermost platinum particle layers, the surface and subsurface NMR signals undergo major frequency shifts as different chemical species are adsorbed. We show in Figure 1C−H the experimental ^{195}Pt NMR spectra with different adsorbates, together with simulations based on the layer model analysis.[6,11] The NMR layer model assumes that (1) nanoscale platinum particles can be represented by ideal cubooctahedra built up layer-by-layer from a central atom, (2) NMR signals from atoms within a given layer can be approximated by a Gaussian, and (3) the average Knight shift of the nth layer, K_n, which is the center of the corresponding Gaussian, "heals" back exponentially[12] toward the bulk platinum position when moving into the particle from the surface. The relative contribution of each Gaussian is dictated by the fraction of the atoms within the corresponding layer, which can be determined from the size distribution of the sample.

Due to Friedel−Heine invariance, we fixed the NMR parameters (peak position, width, relative intensity) for the three central layers to the clean-surface values, while the surface and subsurface peak positions were allowed to vary. For Pt/O, the

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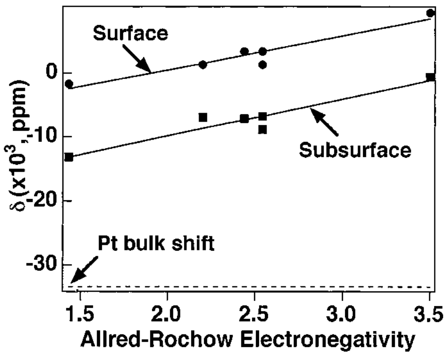

Figure 3. Correlation between surface/subsurface frequency shifts (with respect to the Pt NMR reference H_2PtCl_6) and the Allred−Rochow electronegativity. The dashed horizontal line indicates the Knight shift of bulk platinum atoms. The solid straight lines are linear fits to the surface and subsurface shifts as a function of the electronegativity. Both have R^2 values of ca. 0.92.

position of the third layer was also varied, due to the long healing length in this system, plus the surface peak areas were also varied in some simulations, due to saturation effects caused by longer T_1 values. The surface and subsurface peak positions obtained from these simulations are plotted in Figure 3 as a function of the Allred−Rochow electronegativity[13] of the bonded adsorbate atom (defined as the electrostatic force exerted by the nucleus of the atom on its valence electrons). Remarkably, both the surface and subsurface peak positions map almost linearly the electronegativity of the adsorbate.

According to the layer model analysis,[6,11] the average Knight shift, K_n, of a given layer n, counting inward from the surface ($n = 0$), is expressed as:

$$K_n = K_\infty + (K_0 - K_\infty)\exp(-n/m) \qquad (1)$$

where K_0 is the surface and K_∞ (=3.34%) the bulk Pt Knight shifts, and m is the so-called "healing length" parameter—an indicator of how deep is the influence of the surface on the bulk metal properties. For the subsurface layer, $n = 1$, and one therefore has $K_1 = K_\infty + (K_0 - K_\infty)\exp(-1/m)$. A simple mathematical conversion gives $m = 1/\ln[(K_0-K_\infty)/(K_1-K_\infty)]$. Now, by replacing K_1 and K_0 by the correlation lines shown in Figure 3:

$$K_0\ (\text{ppm}) = (-10.2 + 5.3\chi) \times 10^3 \qquad (2)$$

$$K_1\ (\text{ppm}) = (-21.5 + 5.8\chi) \times 10^3 \qquad (3)$$

m can then be directly expressed as a function of the electronegativity χ:

$$m = 1/\ln[(23.2 + 5.3\chi)/(11.9 + 5.8\chi)] \qquad (4)$$

We plot the healing length (=0.229m, where 0.229 nm is the layer thickness for Pt particles) as a function of the electronegativity, eq 4, in Figure 4. This result clearly shows that *the larger the electronegativity of the adsorbate, the longer the healing length*, i.e., the deeper the influence of the adsorbate goes. It is also interesting to note that the value of the healing length m for hydrogen ($\chi = 2.2$) adsorption obtained via eq 4 is ca. 2.9, which is very close to the $m = 2.6$ value found previously by a detailed layer model analysis.[11] In addition, for the adsorption of the alkali metal elements ($\chi \sim 1$), eq 4 predicts $m \sim 2$, virtually the same m as obtained for clean surface Pt particles in an electrochemical environment.[6] One would therefore expect that alkali adsorption would not significantly change the ^{195}Pt NMR spectrum of small Pt particles after adsorption. This is exactly what has been observed experimentally (in a gas-phase system), which was rather puzzling at the time.[14] These three new experimentally estimated points are also plotted in Figure 4 for comparison with eq 4.

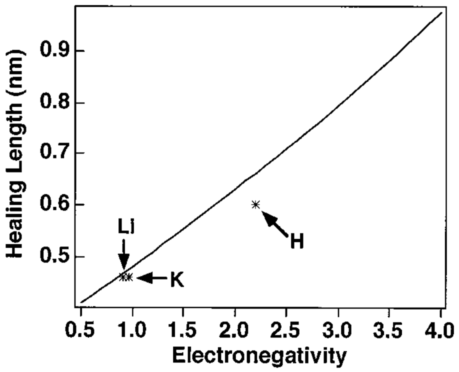

Figure 4. Solid curve showing the relationship between the healing length and electronegativity as determined from eq 4. For comparison, we also show the three experimental points based on previous observations. See the text for details.

In general, the extent of the influence of a surface layer is expected to increase in the following order: metal to semiconductor to insulator. Equation 4 suggests that the larger is the electronegativity of the adsorbate, the less metallic character there is in its bonding to the metal (Pt) surface. This is in agreement with previous NMR observations: protons on Cu/MgO[15] and CO[7] and CN^{-}[10] on Pt gain metallic character, while O adsorption creates nonmetallic sites on Pt surfaces.[16] It is therefore not surprising that for oxygen adsorption our results indicate the involvement of the sub-subsurface layer as well (from spectral simulations).

In summary, the results we have presented above indicate the following when different species are adsorbed onto clean platinum surfaces: First, the ^{195}Pt NMR Knight shifts of the surface and subsurface platinum atoms reflect the electronegativity of the adsorbate in a rather direct and linear way, implying an interesting correlation between the chemical nature of the ligand and the changes in the physical properties of the metal (Pt) substrate it induces. Second, the invariance of the frequency shifts of the more buried Pt atoms (deeper than the 3rd layer) to surface adsorbate electronegativity provides strong evidence demonstrating the applicability of Friedel−Heine invariance of the LDOS in these nanoscale electrocatalyst systems. Such an applicability is a rather interesting extension of the originally proposed Friedel−Heine invariance theorem to nanoscale systems. Third, eq 4 provides a convenient, quantitative way of describing how the chemistry of a surface adsorbate can be related to its influence on the bulk metal substrate.

It seems clear that these correlations will have utility in describing the electronic surface structure of metal catalysts in different chemical environments, leading to useful correlations between electronic properties (Knight shifts, relaxation rates, local density of states, healing length) and more conventional chemical descriptors, such as ligand electronegativity, which

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may be helpful in understanding the electronic structure of metal/adsorbate interfaces and catalytic processes in general

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