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and Scanning Tunneling Microscopy

by

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**ATOMIC-LEVEL STRUCTURE AND DYNAMICS OF ORDERED
METAL ELECTRODES AS PROBED BY INFRARED SPECTROSCOPY
AND SCANNING TUNNELING MICROSCOPY**

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Some recent applications of in-situ surface infrared spectroscopy and scanning tunneling microscopy (STM) to the adsorption and reaction of small molecules on monocrystalline metal surfaces in electrochemical environments are outlined, with emphasis on the structural effects. Carbon monoxide adsorption and electrooxidation on low-index platinum, rhodium, and iridium surfaces in aqueous solutions as well as nonaqueous media are considered in comparison with the behavior of metal surfaces in ultrahigh vacuum. The combined use of FTIR and STM for the deduction of atomic-level CO adlayer structures is noted for Rh(111) and Rh(110). Real-time FTIR coupled with simultaneous or parallel voltammetric measurements yields molecule-specific information concerning the electrooxidation mechanisms of several small organic molecules on various low-index platinum, rhodium, and bismuth-modified platinum surfaces. The acquisition of structural and dynamical information for potential-induced surface reconstruction on low-index gold electrodes by means of atomic-resolution STM is also outlined.

INTRODUCTION

Infrared reflection-absorption spectroscopy (IRAS) has proved to be viable at metal-solution as well as metal-ultrahigh vacuum (uhv) interfaces (1). This in-situ approach can provide detailed information on surface composition and bonding not only for stable systems, but also for intermediate and product species formed in electrochemical processes. The advent of commercial Fourier transform infrared (FTIR) spectrometers in conjunction with thin-layer optical geometries enables real-time information to be obtained for surface species, and also for solution-phase compositional changes accompanying irreversible electrochemical reactions (2).

Although the majority of surface electrochemical applications of IRAS have involved polycrystalline surfaces, the last few years have

seen a growing number of applications of this technique to ordered monocrystalline electrodes. While various adsorbates have been examined, emphasis has been placed on carbon monoxide (3). This is because of the unusual sensitivity of the C-O stretching frequency (ν_{CO}) to the surface coordination geometry and local environment, and the availability of detailed vibrational studies undertaken for CO on monocrystalline metal surfaces in uhv. These factors make CO a uniquely suitable choice with which to compare structural effects upon adsorbate binding between related electrochemical and uhv surface environments (3,4).

In mechanistic electrochemical studies, IRAS can provide some information on the nature of the adsorbed reaction intermediates or poisons involved. For instance, it was found that adsorbed CO formed by chemisorption of small organic molecules constitutes a common inhibitor (and sometimes a possible reaction intermediate) for their electrooxidation at metal-aqueous solution interfaces (5). Detailed examination of these systems at monocrystalline surfaces offers important opportunities for investigating the role of surface crystallographic orientation on electrocatalytic processes as part of the overall issue of surface structure-reactivity relationships in heterogeneous catalysis.

We have recently been utilizing an experimental procedure that employs a single-potential sweep or step during the Fourier transform data acquisition. This tactic, which we have dubbed "single-potential alteration infrared spectroscopy" (SPAIRS) (6,7), can yield quantitative information on irreversible potential-induced compositional changes for adsorbates and in the thin-layer solution (8). A particular virtue of SPAIRS is that it can be coupled directly with simultaneous voltammetric sweep measurements, thereby aiding the molecular interpretation of the latter (6-8).

Another topic of major importance in surface science is elucidating the atomic structures formed at ordered monocrystalline metal surfaces, both in the absence and presence of adsorbates. Knowledge of such structures, and their sensitivity to system conditions, is crucial to our understanding of surface crystallographic effects in adsorption, catalysis, and so on. Scanning tunneling microscopy (STM) is an especially promising in-situ probe in this regard since it can observe directly real-space surface structure with atomic resolution; in particular, it can yield remarkably detailed potential-dependent information on surface reconstruction.

In this conference paper, we review some recent FTIR and STM studies in our laboratory performed on single-crystal surfaces in electrochemical environments. Outlined in the following section are FTIR examinations of adsorption and electrooxidation of CO on low-index platinum, rhodium, and iridium surfaces in both aqueous and non-aqueous media, and pertinent comparisons between electrochemical and metal-uhv interfaces. Described in the third section are studies on electrooxida-

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tion of small organic molecules on low-index platinum and rhodium surfaces by means of SPAIRS in conjunction with voltammetry, and the effects of predosed bismuth on these reactions. The last two sections summarize the combined use of IRAS and STM to elucidate CO adlayer structures, and the application of STM to explore potential-dependent reconstruction at ordered Au(100)-, (110)-, and (111)-aqueous interfaces.

FTIR STUDIES ON ELECTROOXIDATION OF ADSORBED CO ON LOW-INDEX PLATINUM, RHODIUM, AND IRIIDIUM SURFACES

The results for Pt(111), (100), (110), Rh(111), (100), (110), and Ir(111) in aqueous electrolytes are detailed in refs. 3, 4, 9-15. The form of the electrochemical infrared spectra in the C-O stretching (ν_{CO}) region, especially the relative intensities of the characteristic terminal and twofold bridging ν_{CO} bands, tends to be most similar to spectra obtained at the metal-uhv surfaces at high CO coverage, θ_{CO} , and at relatively positive electrode potentials. Altering the potential, E , in the negative direction on most electrodes at high θ_{CO} favors increasingly CO binding in bridging rather than terminal sites, especially on the rhodium surfaces. Bridging CO coordination is also favored increasingly at most electrochemical interfaces towards lower θ_{CO} (3,4).

The ability to vary externally the metal-solution potential difference, ϕ_a^M , is a unique feature of electrochemical systems. At metal-uhv interfaces, on the other hand, the interfacial potential ϕ_v^M (denoted experimentally by the work function $e\phi_v^M$ (16)) is predetermined by the chemical and physical properties of the system: the bulk metal, the surface crystallographic orientation, and the adlayer composition. It is valuable to establish a connection between the "surface potentials" that characterize a given metal interface in electrochemical and uhv environments, respectively. Most simply, we can define an electrode potential E_o^M given by (3a,17)

$$E_o^M = \phi_v^M - E_K(\text{ref}) \quad [1]$$

At E_o^M , the overall potential drop across the electrochemical and uhv interfaces is the same (9,18). The "absolute reference electrode potential" $E_K(\text{ref})$ converts the electrode potential E to the vacuum reference scale appropriate for ϕ_v^M (17,19,20). It is profitable to compare the spectroscopic properties of CO at a given metal-solution interface held at an electrode potential E_o^M that corresponds to the work function $e\phi_v^M$ of the related metal-uhv surface containing the same CO coverage (3,4,18).

A commonly observed, yet striking, characteristic of metal-solution interfaces is that the vibrational frequencies of adsorbed CO depend significantly on the electrode potential. The frequency-potential (ν -E) dependencies at fixed adsorbate coverage and site occupancy, while often termed "Stark tuning", may arise from potential-dependent surface bonding (21) as well as from electrostatic field (first-order Stark) phenomena (22). Since the potentials that characterize the uncharged anhydrous metal-uhv interfaces are substantially (ca 0.5-1 V) more positive than the onset potentials for CO electro-oxidation in aqueous media, an extrapolation of the electrochemical results to potentials appropriate for the corresponding uhv interfaces is necessary. This procedure has been applied to terminal coordinated CO in saturated adlayers on Pt(111), (100), (110), and Rh(111) (3,4). For Pt(111), (100), and Rh(111), this analysis yields self-consistent results, indicating that the lower ν_{CO}^t values that are observed in the electrochemical versus uhv environments arise primarily from the less positive potentials that characterize the former interfaces.

There are various theoretical models to account for such ν_{CO} frequency-potential dependencies. Variations in electrode potential may be expected to influence adsorbate frequencies, both as a consequence of changes in the local electrostatic field (Stark effect) and from alterations in the adsorbate-metal bonding (21-29).

As already noted, marked potential-induced changes can occur in the adsorbate coordination geometry. At high θ_{CO} , potential-induced site conversion between terminal and bridging coordination, favoring increasingly bridging CO at low potentials, has been observed on Pt(111) (14,30), Pt(100) (10,31,32), Rh(111) (14), and Rh(100) (14). Comparison between corresponding aqueous electrochemical and uhv systems indicates that the observed differences in CO site occupancy in these two kinds of systems can again be rationalized in terms of the differing surface potentials characterizing these two types of interfacial environment. The "atom superposition and electron delocalization molecular orbital" (ASED-MO) theory developed by Anderson can predict such potential-induced site occupancy shifts for electrochemical systems (26,29). Physically, this coordination shift can be considered to be triggered by the increased extent of $d\pi - 2\pi^*$ back donation occurring at low potentials (i.e., at more negative surface charges) given that such charge transfer is more extensive for bridging versus terminal CO coordination.

As mentioned above, a limitation of aqueous media is that the occurrence of CO electrooxidation restricts the range of electrochemical surface potentials to values substantially (ca 0.5-1 V) below those encountered at the metal-uhv interfaces. This difficulty can be circumvented by the use of nonaqueous solvents, which often provide a much wider range of potentials in the negative as well as positive directions. Recently in our laboratory, potential-dependent infrared spectra for saturated CO adlayers have been measured on ordered low-

index platinum and rhodium surfaces in five nonaqueous solvents: acetonitrile, dimethylformamide, dichloromethane, tetrahydrofuran, and methanol, with various supporting electrolytes (33,34).

It was found that the CO saturation coverages at these metal-nonaqueous interfaces is virtually the same as that obtained at metal-aqueous interfaces. The form of the infrared spectra at the Pt(110)- and (111)-nonaqueous interfaces is similar to those obtained for the aqueous systems. Although the nonaqueous media used span a wide range of dielectric and solvating properties, the potential-dependent ν_{CO} frequencies and site occupancies display a remarkable insensitivity to the solvating medium in the presence of a given supporting electrolyte cation. The data also allow a direct comparison to be made between the CO spectral properties on Pt(110) and (111) in these nonaqueous electrochemical environments with corresponding uhv results at the same surface potential, enabling the role of the double layer on the adlayer structure to be further delineated. Significantly divergent $\nu_{\text{CO}} - E$ plots are obtained with different tetraalkylammonium electrolyte cations, with cation of larger radius yielding smaller $\nu_{\text{CO}} - E$ slopes (33,34). These divergences can be understood in terms of cation-induced variations in the inner-layer potential profile; the intersection point [ca 1.0 V vs SCE for Pt(111) (33)] corresponds to the potential of zero charge, where the free-charge contribution to ϕ_s^M will disappear.

FTIR STUDIES ON ELECTROOXIDATION OF SMALL ORGANIC MOLECULES ON LOW-INDEX PLATINUM, RHODIUM AND BISMUTH-MODIFIED PT(111) AND (100) SURFACES

The electrooxidation kinetics of formic acid, methanol, and ethanol in 0.1 M HClO₄ on ordered Pt(111) (35), (100), (110) (36), and Rh(111) (37) surfaces were examined by means of coupled SPAIRS-voltammetric measurements. The crystal-face-dependent morphology of the voltammograms obtained on three low-index platinum surfaces certifies the strong sensitivity of the electrochemical kinetics to the surface crystallography. For formic acid electrooxidation, CO₂ is the exclusive product with high coverages ($\theta_{\text{CO}} \geq 0.7$) of terminally bound CO being formed on Pt(100) and (110) that inhibit severely the reaction at low overpotentials during the positive-going sweep. The more facile kinetics observed on Pt(111) under the same reaction conditions are consistent with the observed low coverage of CO and other chemisorbed poisons. For methanol electrooxidation, only low or moderate CO coverages ($\theta_{\text{CO}} \leq 0.3$), with CO bound predominantly in the terminal configuration, were obtained on all three platinum faces (36). While the sum of hydrogen and CO coverage ($\theta_{\text{H}} + \theta_{\text{CO}}$) for methanol on Pt(111) is comparable to that for adsorbed hydrogen or saturated CO adsorption alone, the ($\theta_{\text{H}} + \theta_{\text{CO}}$) values for methanol on both Pt(100) and Pt(110) faces are significantly below those expected on this basis, indicative of the presence of additional adsorbed species, either chemisorbed

poisons or reaction intermediates (36). Unlike formic acid and methanol electrooxidation, ethanol undergoes predominantly partial oxidation to form acetaldehyde and acetic acid (35). In addition to low coverages of CO, direct spectroscopic evidence for chemisorbed poisons was obtained from their electrooxidation to CO₂. On Pt(111), ethanol undergoes primarily four-electron oxidation to acetic acid. On Pt(100) and (110), in contrast, acetic acid formation is inhibited almost entirely at potentials below where electrooxidation of chemisorbed poisons to CO₂ occurs, two-electron ethanol oxidation to acetaldehyde dominating under these conditions (35,36).

High coverages ($\theta_{\text{CO}} \geq 0.4$) of adsorbed CO are formed during electrooxidation of formic acid, methanol, and ethanol on ordered Rh(111), as detected from a band at ca 1880-1890 cm⁻¹ at the most negative potentials (-0.25 to 0.05 V vs SCE). As for solution CO adsorption, this is replaced by a band at 2030-2040 cm⁻¹ at more positive potentials (37). These two features are assigned to C-O vibrations, ν_{CO} , associated with CO adsorbed in bridging and terminal coordination geometries, respectively. The former configuration is apparently engendered by hydrogen coadsorption. For cyclic voltammetric potential excursions to ≤ 0.6 V vs SCE, the adsorbed CO formed by dissociative reactant chemisorption undergoes complete electrooxidation only during the reverse portion of the potential sweep, at ca 0.4 V. This inability to remove adsorbed CO on ordered Rh(111) appears to be at least partly responsible for the observed weakly electrocatalytic properties of this surface for organic electrooxidations. The production of CO₂ even from formic acid does not commence in earnest on Rh(111) until CO is removed during the reverse scan. The electrooxidation of methanol and ethanol on ordered Rh(111) is extremely sluggish, yielding only small amounts of CO₂. Unlike rhodium-uvf interfaces, then, these unmodified rhodium-aqueous interfaces exhibit poor electrocatalytic activity. This is probably due to the onset of anodic oxide formation at low potentials, inhibiting organic electrooxidation.

To address the issue of the effect of surface modification by foreign metal adatoms, the influence of predosed bismuth upon the electrooxidation of formic acid and methanol on Pt(111) and (100) (38), and ethylene glycol on Pt(111) (39), in 0.1 M HClO₄ was also examined by means of voltammetry combined with real-time infrared spectroscopy. Bismuth can be readily adsorbed irreversibly on platinum electrode surfaces from separate dilute Bi³⁺ solutions, giving well-defined redox cyclic voltammograms which can be used to quantify the bismuth coverage (40). In addition, bismuth is very inert for chemisorption of many chemically interesting small molecules and has an electronegativity similar to platinum; this makes bismuth-modified platinum an excellent model bimetallic catalyst to study "ensemble effects" (41).

Formic acid electrooxidation rates are enhanced substantially (up to 30-40 fold) in the presence of bismuth on Pt(100) (38). This enhancement is due primarily to the attenuation in the degree of CO

poison formation as discerned from FTIR. The CO formation, which reaches near-saturation coverages in the absence of bismuth (*vide infra*), is essentially eliminated for bismuth coverages above ca 0.2. The production of terminal CO is triggered by the onset of formic acid oxidation, suggesting that it forms from a reactive intermediate. The bismuth-induced electrocatalysis of formic acid oxidation observed on Pt(111) apparently also arises in a similar manner, although the major poison in this case is not adsorbed CO (38). These electrocatalytic influences of bismuth are consistent with the occurrence of an "ensemble effect", whereby poison formation is suppressed to a markedly greater degree than is the reactive precursor. In contrast, the electrooxidation rates of methanol on Pt(100) and especially Pt(111) are diminished in the presence of predosed bismuth. The terminal CO coverages formed during methanol electrooxidation also correlate directly with the variation in the reaction rates induced by altering either the reactant concentration or the bismuth coverage. These results suggest that CO can act as a reaction intermediate for methanol electrooxidation under these conditions.

Ethylene glycol provides an example of a simple difunctional reactant which yields several solution species upon electrooxidation. On Pt(111) and bismuth-modified Pt(111), two major oxidation products, oxalic acid and CO₂, are formed via distinct reaction pathways (39). The presence of predosed bismuth adatoms significantly alter the selectivity of the model electrocatalyst in that the production of CO₂ increases monotonically with the bismuth coverage at the expense of the oxalic acid yield (39). These results suggest that larger ensembles of contiguous active sites are required for the partial oxidation of ethylene glycol to form oxalic acid than for exhaustive electrooxidation to yield CO₂.

COMBINED STM-FTIR EXAMINATIONS OF CO ADLAYER STRUCTURES

While infrared spectroscopy can yield detailed insight into adsorbate binding geometries and average local environments, little real-space information is afforded by this technique. In suitable cases, however, it has recently become apparent that the latter type of information, even with atomic resolution, can be obtained with STM. The advent of in-situ STM along with IRAS therefore offers new opportunities to extract detailed structures for electrochemical adlayers by employing the two techniques in tandem. While structural analysis along these lines has been undertaken for some time for metal-uHV surfaces by means of low-energy electron diffraction (LEED), such information for in-situ electrochemical systems has been largely unavailable previously.

We have recently undertaken a detailed in-situ STM-IRAS study for saturated CO adlayers on Rh(111) in aqueous solution (42). This system was chosen since it is known from IRAS data to undergo a sharp structur-

al transition at -0.1 V from chiefly bridging to primarily terminal coordination, the latter occurring towards higher potentials (4,12). At potentials above where adsorbed CO electrooxidation proceeds (ca 0.3 V), STM images of the hexagonal close-packed Rh surface atoms are obtained. At lower potentials, where the saturated CO adlayer is present, markedly different STM images were observed that reflect the spatial properties of the adlayer rather than the substrate (42).

Significantly, distinctly different images are obtained over potential ranges that match closely the high- and low-potential IRAS data. In the former potential region, an adlayer structure having a (2×2) -3CO symmetry is obtained. Of the three distinguishable STM spots within the unit cell, the two "brighter" components (i.e., those associated with more efficient electron tunneling) are identified with near-atop CO's, and the weaker component with bridging CO, by comparison with the IRAS data. At lower potentials, a $(3 \times \sqrt{3})$ -4CO structure is discerned. Again by comparison with the corresponding IRAS data, only a single CO in the unit cell is identified as atop, the remaining 3CO's being present in asymmetric and symmetric bridging sites.

A similar STM-IRAS study has also been performed for CO on Rh(110). Unlike Rh(111), the Rh(110)/CO does not feature a structural transition over the available potential range, a mixture of atop and bridging CO coordination being evident from IRAS (4). The corresponding STM images exhibit a (4×3) -12CO unit cell. While the CO coverage for this structure is unity, in agreement with electrochemical and infrared data, the adsorbate spacing is somewhat incommensurate with the underlying substrate, yielding an ordered array exhibiting a mixture of asymmetric atop and bridging coordination geometries (43).

It is fair to note that the extraction of atomic-resolution adlayer structures having such unprecedented detail in this fashion will be limited by several factors, especially the need to maintain immobility of the adsorbate over the relatively long timescales (0.1-20s) required to obtain an STM image. Nevertheless, in carefully selected cases the combined use of STM and IRAS would appear to have a bright future.

STM STUDIES OF POTENTIAL-DEPENDENT RECONSTRUCTION AT ORDERED LOW-INDEX AU-AQUEOUS INTERFACES

The reconstruction of ordered Au(100) (44), (110) (45), and (111) (46) surfaces in aqueous 0.1 M HClO₄ as a function of electrode potential has been studied recently in our laboratory by in-situ STM. The results demonstrate the remarkable degree of atomic detail that can be obtained for the substrate at ordered electrochemical surfaces.

For Au(100), below ca -0.25 V vs SCE, the square planar (1×1)

surface lattice reconstructs to form corrugated quasi-hexagonal domains. Multiple distinct, yet related, structures are formed that resemble those postulated from diffraction measurements. The first structure (labeled here I) features prominent single strings of close-packed gold atoms, typically $14(\pm 1)$ atoms long, with each string separated by a distance ($14.5 \pm 0.5 \text{ \AA}$) commensurate with a five-atom gold spacing. The parallel strands of atoms are staggered so to form a quasi-hexagonal close-packed layer. Since six gold atoms are present in the unit cell dimension normal to the strand direction, the buckled surface layer exhibits a 20% increase in atomic density compared with the unreconstructed substrate. The second structure (II) exhibits similar chains of gold, but with a pair of equal intensity strings separated by 4.5–4.6 Å in place of the single strands seen in structure I. These corrugations were observed in both possible (90°) directions ($[0\bar{1}1]$ and $[011]$) along the square planar (1×1) lattice.

For Au(110), lowering the potential to -0.3 V vs SCE yields images consisting primarily of parallel atomic strands spaced $8 \text{ \AA}$ apart, i.e., having (1×2) symmetry with respect to the unreconstructed surface. While the (1×2) structure exhibits an atomic density commensurate with the usual "missing-row" model, the images suggest that significant relaxation of both top- and second-layer atoms occurs. Instead of having equivalent pairs of atom rows at either side of the central $[1\bar{1}0]$ furrows as in the conventional missing-row structure, one of these rows in each unit cell is shifted by half of the atomic distance along the $[1\bar{1}0]$ direction. Three-atom wide ribbons, lying along the $[1\bar{1}0]$ direction, are seen to provide the basic building blocks of the reconstruction; these units also yield "added-row" domains of ($1 \times n$) symmetry, where $n = 3$ or higher.

For Au(111), when the potential is lowered from 0.1 V to -0.3 V vs SCE, the original unreconstructed hexagonal close-packed (1×1) structure is seen to be overlaid with corrugations appearing as parallel pairs of broad "lines" running in a $[11\bar{2}]$ direction, i.e., at an angle midway between a pair of intersecting close-packed atomic rows. The distance across the corrugated pairs (in the $[1\bar{1}0]$ direction) is $63(\pm 3) \text{ \AA}$. Twenty-three gold atoms are observed in this unit cell dimension instead of 22 for the unreconstructed surface. The atomic rows in the $[1\bar{1}0]$ direction are displaced sideways by distances up to ca $1.0 \text{ \AA}$ in the channels between the row pairs, consistent with an alteration from fcc to hcp stacking within this region, thereby yielding strictly a $(\sqrt{3} \times 22)$ unit cell designation. The reconstruction appears to be triggered preferentially in regions close to terrace edges. Not only the $(\sqrt{3} \times 22)$ atomic reconstruction, but also the longer-range superstructures, formed at this electrochemical interface are seen to be remarkably similar to those observed previously by STM on clean Au(111) in ultrahigh vacuum (47,48).

The reconstruction at these Au-aqueous interfaces can be lifted by altering the electrode potential to relatively positive values, so that

the potential-induced reconstruction appears to be largely reversible. However, the rates of reconstruction are markedly faster on Au(110) compared with Au(100) and (111), occurring over ca 2-10s and 5-10 min., respectively. Reconstruction on all these three low-index Au-aqueous interfaces occurs at potentials below the potential of zero charge. This suggests that excess electronic charge density at the metal interface provides a major driving force for reconstruction, which is in harmony with theoretical predictions for low-index noble metal surfaces (49).

In conclusion, surface FTIR and STM are proving to be powerful techniques for examining surface structures and their relevance in electrocatalysis at ordered metal-solution interfaces, especially in providing microscopic information to supplement the inherently macroscopic data provided by voltammetry and other electrochemical techniques. There is, therefore, good reason to expect surface FTIR along with STM to contribute increasingly to the study of surface electrocatalytic as well as adsorption phenomena in the future.

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