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CO Adsorption on Ru-Modified Pt(100) Surfaces: Infrared Reflection Absorption Studies in Ultrahigh Vacuum

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The mode of bonding of CO to Ru-modified Pt(100) surfaces prepared by chemical vapor deposition was investigated using infrared reflection absorption spectroscopy (IRAS) in ultrahigh vacuum (UHV). Spectra recorded in the CO stretching region for freshly prepared $Ru(\theta_{Ru}$ ca. 0.52)/Pt(100) exposed to saturation coverage of CO displayed, in addition to a rather weak peak ascribed to CO bound to bridging sites, a single asymmetric peak centered at ca. 2092 cm^{-1}. Statistical analyses of IRAS spectra recorded in experiments in which a $Ru(\theta_{Ru}$ ca. 0.52)/Pt(100) surface was annealed sequentially to 650 K for ca. 2.5 h prior to a saturation exposure of CO yielded two peaks at 2100 cm^{-1} and 2092 cm^{-1} with a clearly identifiable isosbestic point, characteristic of a quantitative conversion of one type of species into the other. This behavior has been attributed to a thermally induced surface incorporation of Ru into Pt, as has been shown with low-energy ion-scattering spectroscopy (LEIS) for other Ru-modified low-index single-crystal Pt surfaces (Davies et al. *Electrochim. Acta* **1998**, *44*, 1181), which effectively enriches the surface with Pt while reducing the Ru coverage.

Introduction

Bimetallic Pt/Ru surfaces have been shown to display exceptional activity for methanol oxidation[1-7] and increased CO tolerance for hydrogen oxidation in electrochemical environments.[8-10] Indeed, both Ru-modified Pt[1-5,11] and Pt-modified Ru[8] have been examined as potential electrode materials. A more detailed comparison between the affinity of CO, the strongly bound intermediate, to these two types of bimetallic surfaces is of interest to determine whether the nature of the substrate, either Pt or Ru, plays a role in governing the overall electrocatalytic performance. Carbon monoxide adsorption on these bimetallic Ru−Pt surfaces has been investigated in ultrahigh vacuum (UHV) by vibrational spectroscopy[12] and temperature-programmed desorption (TPD)[3,12-16] and also in electrochemical environments.[1-5,7-12,14,17-23] Particularly relevant to the present

contribution is the work of Schlapka et al.,[12] who examined the Pt surface redistribution induced by annealing of Pt-modified Ru(001) using scanning tunneling microscopy (STM), as well as the binding of CO to such surfaces by infrared reflection absorption spectroscopy (IRAS). This investigation extends our earlier X-ray photoelectron spectroscopy (XPS) and TPD studies of CO adsorption on Ru-modified Pt(100) surfaces prepared by chemical vapor deposition[13] to include IRAS in UHV for monitoring the mode of bonding of CO. As will be shown, this vibrational probe makes it possible to identify relative changes in the Ru/Pt surface composition induced by repeated annealing, by comparing the relative magnitudes of the integrated areas under the two peaks observed, which are attributed to Pt(100) and Ru-modified sites.

Experimental Section

The Pt(100) single crystal used for these measurements was mounted on a variable temperature (110−1270 K) liquid

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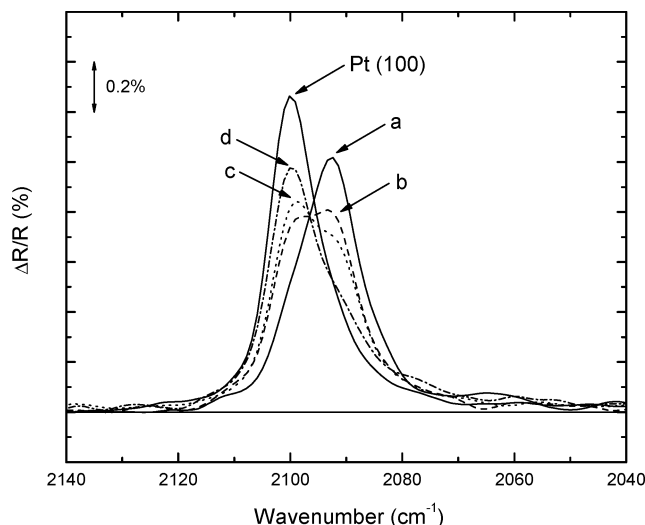**5848** *J. Phys. Chem. B, Vol. 108, No. 19, 2004*

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Figure 1. IRAS spectra for a Ru-modified Pt(100) ($\theta_{Ru} = 0.52$) prepared by the procedures specified in the Experimental Section. The Ru-modified Pt(100) first annealed for 20 min at 650 K and then exposed to CO to achieve saturation coverage at 130 K (curve a). The corresponding spectra of identical annealing/CO exposure experiments run in sequence for the same Ru/Pt surface are given in order in curves b−d in this same figure. Also shown in this plot is the spectrum of CO on pristine Pt(100) recorded under otherwise identical conditions.

nitrogen-cooled cryostat mounted on a UHV chamber (base pressure from mid 10^{-11} to ca. 1×10^{-10} Torr) equipped with IRAS, Auger electron spectroscopy (AES), XPS, and low-energy electron diffraction (LEED) described in detail elsewhere.[24] Bimetallic Ru/Pt surfaces were prepared by first cleaning the Pt(100) crystal with cycles of Ar$^+$ sputtering and annealing to 1073 K in an O$_2$ atmosphere (ca. 1×10^{-8} Torr). The Pt(100) crystal was characterized by XPS and then dosed with trisruthenium dodecacarbonyl, Ru$_3$(CO)$_{12}$, using procedures developed in our laboratory.[13] As specified in that article, a few Ru$_3$(CO)$_{12}$ crystals are placed in a copper boat collimator assembly mounted on a transfer arm and stored under a dry Ar atmosphere in another independently pumped auxiliary chamber while not in use. For the actual deposition, this latter chamber was evacuated, the gate valve that connects to the main UHV chamber was opened, and the tip of the boat-collimator was placed ca. 1.5 cm from the surface of the clean Pt(100) crystal cooled to ca. 130 K to allow Ru$_3$(CO)$_{12}$ vapors to condense on the surface while monitoring the deposition process with time-resolved IRAS. After deposition, the Ru$_3$(CO)$_{12}$ layer was decomposed by irradiating the sample with X-rays, while simultaneously heating the sample to ca. 650 K. After turning the X-ray source off, the sample was annealed at ca. 650 K in an O$_2$ atmosphere (ca. 1×10^{-8} Torr) for 5 min, and then XPS spectra were recorded to check for carbon and oxygen impurities. Ru coverages, θ_{Ru}, quoted in this work, were calculated based on the homogeneous attenuation model[25] and, therefore, cannot be generally correlated with actual surface coverages (see below).

For a typical experiment, freshly prepared bimetallic Ru/Pt surfaces were first cooled to 133 K, then flash-annealed to ca. 650 K, and subsequently allowed to cool back to 133 K before exposure to CO. The latter was effected using a gas leak valve (Varian) allowing for control of the partial pressure of CO in the low 10^{-11} Torr range. The partial pressure of CO during the runs was monitored using an ionization gauge, while recording real time IRAS spectra at ca. 20 s intervals. As is customary, IRAS data were displayed in the form $\Delta R/R = (R_{sam} - R_{ref})/R_{ref}$, where R_{ref} and R_{sam} in this case represented the

IRAS spectra of the surface before and after exposure to CO. After each CO adsorption experiment, the bimetallic Ru/Pt surface was annealed at ca. 650 K for 2.5 h, including 6 min at ca. 650 K in an O$_2$ atmosphere (1×10^{-8} Torr) to remove residual carbon. Although measurements were performed over the range $0.24 < \theta_{Ru} < 0.73$ and a range of CO exposures, only results obtained for $\theta_{Ru} = 0.52$ and saturation CO coverage will be reported in this work. Infrared features attributed to CO adsorption on sites generated by the presence of Ru were identified by subtracting, from the recorded spectra, contributions due to CO on pristine Pt(100), for which the IRAS spectrum at 130 K displayed an atop CO stretching band at 2100 cm^{-1}, in excellent agreement with data reported by other groups for the same surface under very similar conditions.[26]

Results and Discussion

Shown in Figure 1, curve a, is the IRAS spectrum of a Ru-modified Pt(100) ($\theta_{Ru} = 0.52$) prepared by the procedures specified in the Experimental Section, which was first annealed for 42 min at 650 K and then exposed to CO to achieve saturation coverage at 130 K. The corresponding spectra for the same Ru/Pt surface following identical annealing/CO exposure experiments run consecutively are given in sequence in curves b through d in this same figure. As clearly indicated, these curves show a well-defined isosbestic point at 2096 cm^{-1}, providing strong evidence for a quantitative conversion of one type of site into the other. A statistical analysis of these data was performed in terms of a component at 2100 cm^{-1} due to CO on pristine Pt(100) extracted directly from the IRAS spectra of CO adsorbed under the same conditions on the Ru-free Pt-(100) surface and a second peak attributed to CO adsorption on Ru-modified sites (see Figure 2). The dotted and dashed lines in each of the panels in this figure represent best fit components attributed to CO adsorbed linearly on Pt(100) sites (2100 cm^{-1}) and on Ru-modified sites (2092 cm^{-1}), respectively. As shown in Figure 3, the integrated area of these two peaks normalized by the average total area under the composite feature is consistent with a monotonic decrease in the Ru-modified sites (or equivalently an increase in the Pt(100) sites) from 80% down to 25%. In harmony with the presence of the isosbestic point, and within the uncertainties of this analysis, the sum of the two contributing peaks was constant for all four runs (see solid squares in Figure 3). Also shown in this figure (see right ordinate, open squares) is the amount of Ru determined from the XPS data for each of the Ru/Pt(100) surfaces, which was found to be virtually constant for the specimen following each annealing/CO adsorption cycle. As shown by the elegant low-energy ion-scattering (LEIS) work of Hayden and co-workers for both Pt(111)[27] and Pt(110),[28,29] Ru does incorporate into the Pt surface region for temperatures much lower 650 K, leading to a net decrease in the Ru coverage and, thus, a corresponding Pt surface enrichment. Both the IRAS and LEIS data underscore the limitations of XPS for the determination of true surface coverages for Ru-modified Pt surfaces. Further support for this model is provided by the earlier data reported by Lamouri et al., who monitored a surface Pt enrichment (Ru depletion) by TPD for which the low-temperature desorption peak attributed to Ru-modified sites decreased (and that corresponding to Pt sites increased) as the time of annealing of the bimetallic Ru/Pt surface was increased.

In summary, the IRAS results obtained in this study afford a means of monitoring changes in the surface composition of Ru-modified Pt surfaces induced by thermal annealing, which serves to complement information derived from TPD. As shown by
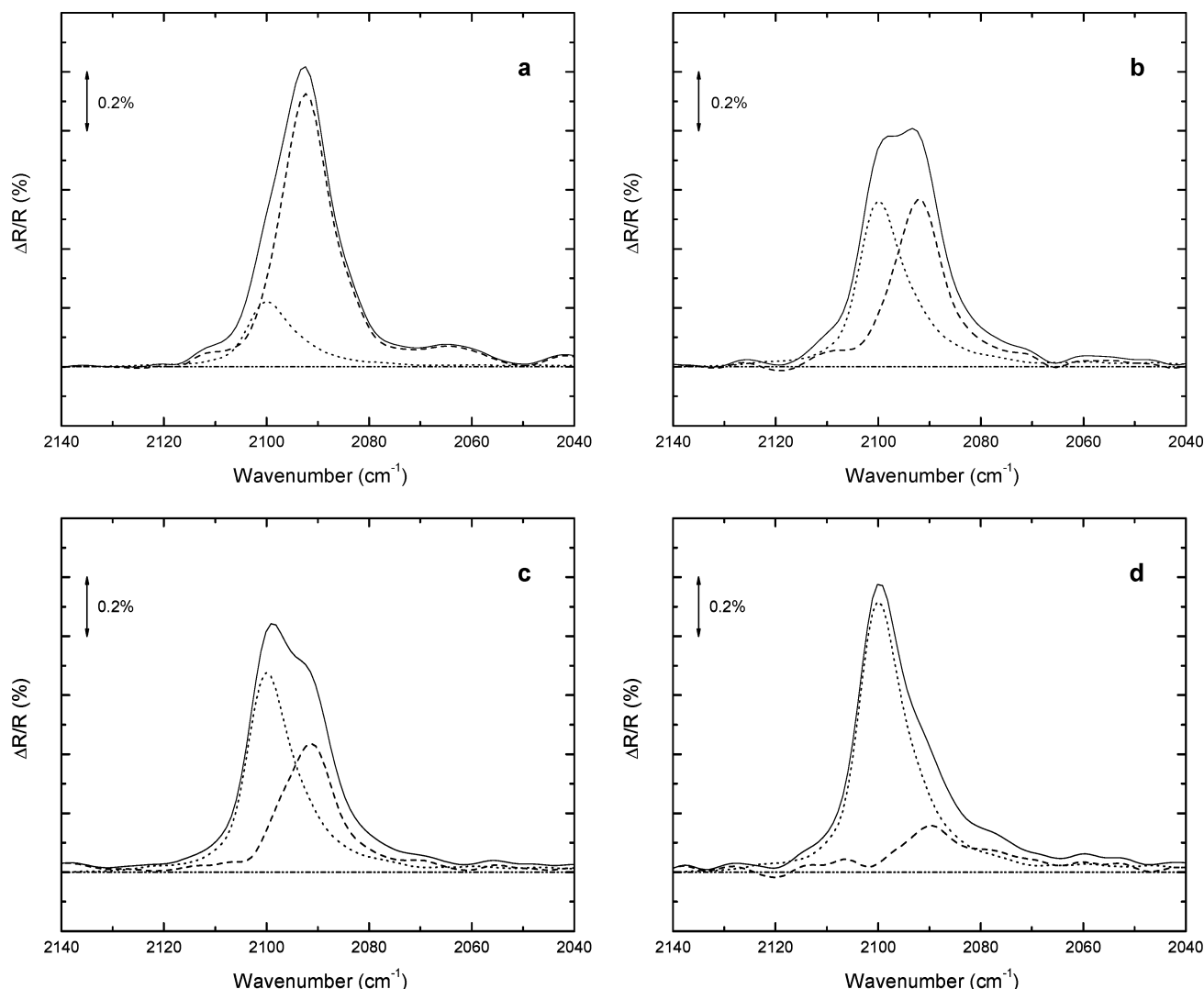
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Figure 2. IRAS spectra of a Ru-modified Pt surface ($\theta_{Ru} = 0.52$) exposed to CO to achieve saturation coverage at 130 K (solid line, panel a). The dotted and dashed lines represent the components attributed to CO on Pt(100) sites (2100 cm^{-1}) and on sites induced by Ru deposition (2092 cm^{-1}), respectively. The corresponding spectra in panels b–d display similar IRAS spectra obtained following heating of the CO-dosed Ru-modified surface in panel a to 650 K for 2.5 h and subsequent exposure of the resulting surface to CO to achieve saturation coverage at 130 K in sequence (see text for details). The contributions from each of the two types of sites derived from a statistical analysis (see text) are given in Figure 3.
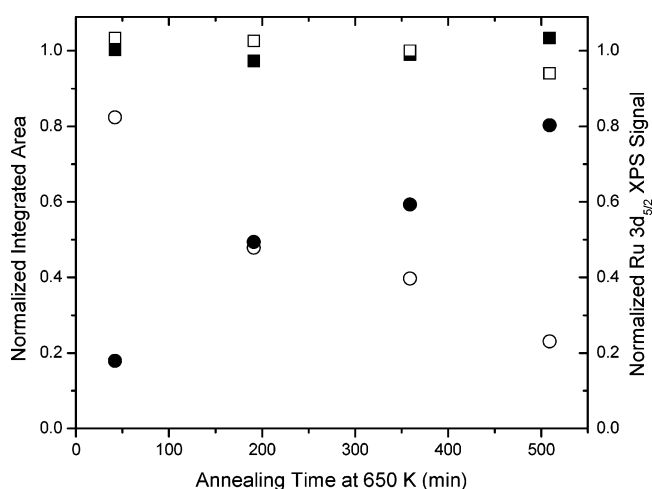

Figure 3. Plots of the integrated area (IA) of the peaks centered at 2100 cm^{-1} (●) and 2092 cm^{-1} (○) and the sum of the IA for these two features normalized by the averaged sum over the four measurements obtained from the data in Figure 2 (■). Also shown in this plot (see right ordinate) are the areas of the 3d$_{5/2}$ Ru XPS peaks normalized by the average obtained for the four surfaces (□).

the data presented in this work and in agreement with earlier observations,[27–30] annealing to high temperature, ca. 650 K, induces a gradual incorporation of Ru into the surface, as reflected by the decrease in the integrated areas of the CO stretching peak ascribed to CO adsorbed on a Ru-induced site and a corresponding increase in the analogous feature attributed to CO bound to pristine Pt sites on the Ru-modified surface. Evidence that such a conversion is quantitative was obtained on the basis of the presence of a clearly defined isosbestic point.

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