Site specific co-adsorption at Pt(335) as probed by infrared spectroscopy: Structural alterations in the CO adlayer under aqueous electrochemical conditions

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Experiments probe the effect of hydrogen co-adsorption on the infrared spectral features of carbon monoxide adsorbed at Pt(335) {Pt(S)-[4(111)×(100)]} under aqueous electrochemical conditions. Using intermediate CO coverages, where it is possible to discern infrared spectral features for CO bound terminally (atop) at edge sites and at terrace sites, the present experiments observe greater alterations in the atop CO population at the step edge compared to the atop CO population on the terrace plane when hydrogen is co-adsorbed under aqueous electrochemical conditions. These findings suggest that hydrogen is preferentially adsorbed at step sites on the Pt(335) surface plane and they coincide with what has been revealed by recent UHV experiments which probed the effect of co-adsorbing oxygen at Pt(335) in the presence of a partial CO monolayer.

INTRODUCTION

In the study of surface catalytic processes, there is considerable interest in exploring adsorption and reactivity at the high index surface planes of crystalline materials. The structure of these surfaces is well defined on the atomic level and the periodic step and kink sites serve to model the defects that are thought to be of central importance in practical catalytic systems.

Using the experimental methods available to ultrahigh vacuum (UHV) surface science, early work in this area probed the structure and stability of some of the high index surface planes of platinum[1-3] and aimed to examine the influence of step and kink sites on molecular adsorption and reactivity.[3-7] In recent experiments, the stepped Pt(335) {Pt(S)-[4(111)×(100)]} surface plane was used as a model to examine the surface catalyzed oxidation of carbon monoxide (CO) under UHV conditions.[5,6] This work showed how it was possible to derive a molecular level model of the surface catalytic reaction site on the basis of infrared reflection-absorption spectra. By working at intermediate CO coverages, where it was possible to discern vibrational bands assignable to modes of CO bound terminally (atop) at sites on the terrace and sites on the step edge, it was shown that co-adsorbing oxygen at low temperatures displaced CO dipoles at the step edge and forced them to occupy vacant sites on the terrace plane. Then, by acquiring vibrational spectra while warming the sample to catalyze CO oxidation, it was shown that atop CO at terrace sites is oxidized preferentially as compared to atop CO at edge sites. A molecular model of the catalytic reaction site placed oxygen in bridging coordination environments in the (100) surface plane of the step edge and reacting CO molecules on the (111) terrace plane along the bottom of the step.[5,6]

In the present report, we use infrared reflection-absorption spectroscopy (IRAS) to show that similar alterations in the site occupancy of CO at Pt(335) ensue when hydrogen is co-adsorbed under aqueous electrochemical conditions. This effect is somewhat more complicated than what occurs in the presence of co-adsorbed oxygen, as co-adsorbing hydrogen causes a fraction of the terminal CO population to move into bridging sites.[7-10] However, the results of the present experiments indicate that these hydrogen induced adlayer structural transformations are most extensive at the step edge. These findings are consistent with electrochemical experiments that show a close correspondence between the number of step sites on the Pt(S)-[n(111)×(100)] surface planes and the charge passed during hydrogen adsorption.[11] They are also important in advancing knowledge of the relationship between reactive surface processes under electrochemical and UHV conditions.[8,12]

EXPERIMENT

All procedures employed in undertaking the reported spectroscopic experiments have been described in detail.[7] The Pt(335) single crystal disk (7 mm diameter by 2 mm thick)[7] was obtained from the Cornell University Materials Preparation Facility. The orientation was confirmed in our laboratory by x-ray back diffraction. The flame annealing method used to clean and order the platinum (335) surface plane prior to spectroscopic experiments is as described in Ref. 7, except that the disk was cooled in an argon atmosphere over ultra pure water[13] rather than in pure hydrogen gas. IRAS experiments were performed with the platinum disk in a three electrode electrochemical cell constructed from Kel-F and fitted with a calcium fluoride trapezoidal window. A platinum ring counter electrode and saturated calomel reference electrode were employed. The potential of the Pt(335) working electrode
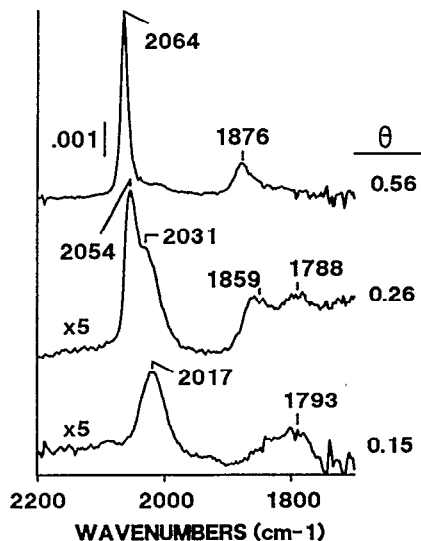
FIG. 1. IRAS spectra of CO adsorbed at Pt(335) under aqueous electrochemical conditions. Spectra were recorded in 0.1M HClO$_4$ with the electrode at a potential of +0.1 V vs SCE. Spectra were recorded as a function of CO surface coverage [assuming $\theta_{max}=0.67$ (Ref. 19)]. (Compared to the spectrum corresponding to $\theta=0.56$, spectra corresponding to $\theta=0.15$ and $\theta=0.26$ have been enlarged by a factor of 5).
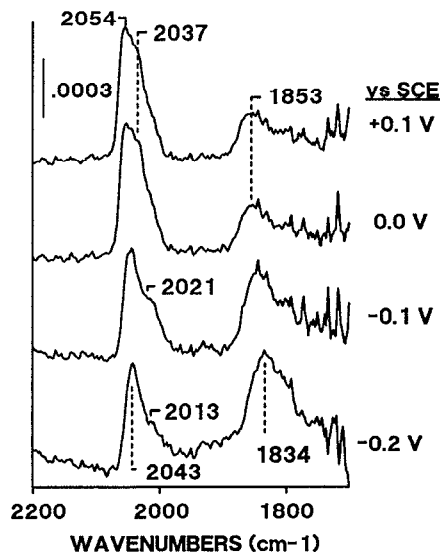

FIG. 2. IRAS spectra of CO adsorbed at Pt(335) recorded as the potential was stepped in sequence from −0.2 to +0.1 V (vs SCE). The CO surface coverage corresponds to $\theta=0.34$. Spectra were recorded with the Pt electrode in 0.1M HClO$_4$.

was controlled using a Pine model AFRDE4 potentiostat. All potentials are reported with respect to the saturated calomel electrode (SCE).

CO adlayers were formed by dosing under potential control from electrolyte solutions containing dilute levels ($\sim4\times10^{-5}M$) of dissolved CO.[7,14,15] In recording the reported spectra, the electrode was held at the indicated potential while 1024 interferograms were co-added, signal averaged, and then Fourier transformed to give a (sample) single beam spectrum. A reference single beam spectrum was collected at the end of each experiment by stepping the potential to +0.6 V (vs SCE), where adsorbed CO is removed from the electrode on account of its oxidation to CO$_2$. Absorbance spectra were computed from the ratio of the sample and reference single beam spectra. Electrolyte solutions were prepared from perchloric acid (Baker Ultrex) using distilled water that was further purified by using a Barnstead Nanopure cartridge system followed by oxidation processing under ultraviolet irradiation (Barnstead Organic-pure). Infrared spectra were collected using a Digilab FTS-40 infrared spectrometer equipped with a narrow band Mercury Cadmium Telluride (MCT) detector. Spectral resolution was 4 cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows coverage dependent IRAS spectra of CO at Pt(335) under aqueous electrochemical conditions. Spectra were obtained with the electrode held at +0.1 V, in the so-called classical double-layer region, where water is believed to be the predominant co-adsorbed species. Spectral features appear that are assignable to CO adsorbed at sites of terminal (2017–2064 cm^{-1}) and twofold bridging (1788–1876 cm^{-1}) coordination. Compared to

infrared spectra obtained under UHV conditions, spectra in Fig. 1 show the expected coverage dependent features characteristic of CO site-occupancy alterations and dipole-coupling interactions.[5–7,16–19] At the lowest coverage [Fig. 1(a)], the vibrational bands for terminal (atop) CO and for bridging CO appear at 2017 and 1793 cm^{-1}, respectively. Accounting for differences in the surface potential between the UHV and the aqueous electrochemical environment,[7,8,20] these low coverage spectral features appear at energies that are consistent with CO occupancy at Pt(335) edge sites.[5–7,16–19] At intermediate coverages [Fig. 1(b)], the band for atop CO broadens and shifts to higher energy (2054 cm^{-1}) and a shoulder appears on the low energy side (2031 cm^{-1}). The main peak and its shoulder are assignable to atop CO at terrace and step sites, respectively.[5–7,16–18] Near saturation [Fig. 1(c)], the spectral features narrow. For atop CO under these conditions, the single vibrational feature at 2064 cm^{-1} is assignable to CO at terrace sites;[5–7,16–18] the edge atop CO spectral feature cannot be distinguished on account of coupling interactions with terrace CO dipoles.[16–18] For the bridging feature at 1876 cm^{-1}, our earlier work[7] showed that this band is assignable to CO at sites on the Pt(335) step edge, and that it appears at the expense of the terrace CO bridging feature through interactions which couple edge and terrace CO dipoles.

The effect that co-adsorbing hydrogen has on the CO vibrational features is shown in Fig. 2. These spectra are for the intermediate coverage condition shown in Fig. 1(b), where it is possible to discern atop CO at edge and terrace sites. IRAS spectra shown in Fig. 2 were collected as the potential was stepped in sequence from −0.2 V, where hydrogen is the predominant co-adsorbed species to +0.1 V, where water is the predominant co-adsorbed species. As expected,[7–10] the CO site occupancy is predomi-
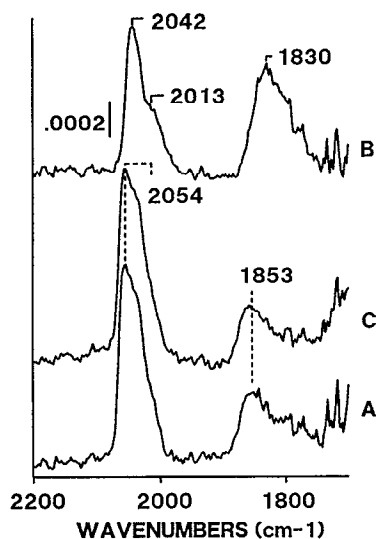
FIG. 3. IRAS spectra of CO adsorbed at Pt(335) recorded as the potential was stepped from +0.1 V (A) to −0.2 V (B), and then back to +0.1 V (A). The CO surface coverage corresponds to $\theta=0.34$. Spectra were recorded with the Pt electrode in $0.1M$ $HClO_4$.

nantly bridging at potentials in the classical hydrogen adsorption region (−0.2 to −0.05 V), and shifts toward increased atop coordination at potentials in the classical double-layer region (0.0 to +0.1 V). What is unexpected is that the alterations in atop CO population are greater for CO at the step edge than for CO at the terrace. For example, the edge CO feature is barely discernable at −0.2 V (2013 cm^{-1}) but appears as a weak shoulder (2021 cm^{-1}) following partial hydrogen desorption at 0.1 V. At potentials in the double-layer region, the features for atop edge (2037 cm^{-1}) and atop terrace (2056 cm^{-1}) CO have nearly equal intensity. That these potential induced adlayer transformations are reversible is demonstrated by spectra shown in Fig. 3, which were obtained as the potential was stepped from 0.1 to −0.2 V and then back to 0.1 V [Figs. 3(a)–(c)].

SUMMARY

In conclusion, we find that for a partial monolayer of CO at Pt(335), co-adsorbing hydrogen under aqueous electrochemical conditions alters the site occupancy of atop CO at the step edge to a greater extent than atop CO

on the terrace plane. This behavior is consistent with what IRAS experiments have observed for a partial CO monolayer at Pt(335) when oxygen is co-adsorbed under UHV conditions.[5,6] These results support models of the electrochemical environment which suggest that hydrogen is adsorbed at the step edge of Pt(S)-[$n(111)\times(100)$] surface planes[11] and they advance knowledge concerning the structure of the aqueous electrochemical environment.

[1] B. Lang, R. W. Joyner, and G. A. Somorjai, Surf. Sci. 30, 440 (1972).
[2] D. W. Blakely and G. A. Somorjai, Surf. Sci. 65, 419 (1977).
[3] G. A. Somorjai, Chemistry in Two Dimensions: Surfaces (Cornell, Ithaca, NY, 1981).
[4] M. A. Henderson, A. Szabo, and J. T. Yates, Jr., J. Chem. Phys. 91, 7245 (1989), and references therein.
[5] J. Xu, P. Henriksen, and J. T. Yates, Jr., J. Chem. Phys. 97, 5250 (1992).
[6] J. Xu and J. T. Yates, Jr., J. Chem. Phys. 99, 725 (1993).
[7] C. S. Kim, W. J. Tornquist, and C. Korzeniewski, J. Phys. Chem. 97, 6484 (1993).
[8] S.-C. Chang and M. J. Weaver, J. Phys. Chem. 95, 5391 (1991).
[9] R. Zenobi, J. Xu, and J. T. Yates, Jr., Surf. Sci. 276, 241 (1992).
[10] D. Hodg, M. Tushaus, and A. M. Bradshaw, Surf. Sci. 207, L935 (1988).
[11] A. Rodes, K. El Achi, M. A. Zamakhchari, and J. Clavilier, J. Electroanal. Chem. 284, 245 (1990).
[12] D. Zurawski, M. Wasberg, and A. Wieckowski, J. Phys. Chem. 94, 2076 (1990).
[13] M. E. Gamboa-Aldeco, E. Herreo, P. S. Zelenay, and A. Wieckowski, J. Electroanal. Chem. 348, 451 (1993).
[14] S.-C. Chang and M. J. Weaver, J. Chem. Phys. 92, 4582 (1990).
[15] S.-C. Chang and M. J. Weaver, J. Phys. Chem. 94, 5095 (1990).
[16] B. E. Hayden, K. Kretzschmar, A. M. Bradshaw, and R. G. Greenler, Surf. Sci. 149, 394 (1985).
[17] F. M. Leibsle, R. S. Sorbello, and R. G. Greenler, Surf. Sci. 179, 101 (1987).
[18] D. K. Lambert and R. G. Tobin, Surf. Sci. 232, 149 (1990).
[19] J. S. Luo, R. G. Tobin, D. K. Lambert, G. B. Fisher, and C. L. DiMaggio, Surf. Sci. 274, 53 (1992).
[20] In comparing vibrational spectra of species adsorbed under aqueous electrochemical and UHV conditions, it is important to note that the substantially lower surface potentials found in the electrochemical environment shift the C–O stretching vibrational frequency to lower energy and make bridging coordination geometries more favorable (see Ref. 8 for a review).