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Surface Electrochemistry of CO on Pt(111): Anion Effects

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Abstract

In-situ studies of CO adsorption by surface x-ray scattering (SXS) and Fourier transform infrared (FTIR) spectroscopy techniques are used to create the link between the macroscopic kinetic rates of CO oxidation and the microscopic level of understanding the structure/site occupancy of CO on Pt(111). A remarkable difference in activity was observed between alkaline and acid solutions. In alkaline solution the oxidation of CO proceeds at low overpotential (<0.2 V) by the surface reaction between the adsorbed CO and OH, the latter forming selectively in the hydrogen underpotential potential region at defect sites. In acid solution these sites are blocked by specific adsorption of anions, and consequently in a solution containing Br⁻ the ignition potential is shifted positively by 0.6 V. Anions of supporting electrolytes also have dramatic effects on both the potential range of stability and the domain size of the p(2x2)-3CO structure which is formed at 0.05 V. The stability/domain size of this structure increases from KOH (*ca.* 30 Å between 0.05 <E<0.3V), to $HClO_4$ (*ca.* 140 Å between 0.05 <E<0.6V) to $HClO_4$ + Br⁻ (*ca* 350 Å between 0.05 <E<0.8V). The larger the ordered domains of the p(2x2)-CO_{ad} structure are, the less active the surface is towards CO oxidation.

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INTRODUCTION

Carbon monoxide is the simplest C_1 molecule that can be electrochemically oxidized in a low temperature fuel cell at a reasonable (although not necessarily practical) potential. It thus serves as an important model "fuel" for fundamental studies of C_1 electrocatalysis. Just as in heterogeneous catalysis, the ultimate challenge in electrocatalysis science is to relate the microscopic details of adsorbed states of intermediates to the macroscopic measurement of kinetic rates and thermodynamic state functions. Unfortunately, in the case of surface chemistry of CO on Pt(*hkl*) surfaces, this approach has an intrinsic difficulty. Given that CO adsorption on Pt(*hkl*) at near ambient temperature is an irreversible process, and due to the narrow temperature range available in aqueous solutions, the heat of adsorption of CO cannot be determined at Pt electrodes. One can use, however, the values of thermodynamic functions which are obtained from UHV measurements and test them in the electrochemical system for consistency. Two general features in the energetics of the CO_{ad}/Pt system clearly emerge from the UHV studies: that the heat of adsorption of CO on Pt(*hkl*) is strongly coverage dependent [1] and that the heats of CO adsorption are relatively insensitive to the surface structure of the substrate [2;3]. From these general observations, it was suggested that at the Pt(111)/solution interface the heats of adsorption at saturation coverage of CO_{ad} are close to $\approx 1/3$ of the initial value [4], *e.g.* a heat of adsorption of CO at Pt(111) aqueous electrolytes may vary from $\approx 150 \pm 15$ kJ/mol at low coverages to $\approx 65 \pm 15$ kJ/mol at saturation. Closely following UHV terminology, we proposed that energetically two forms of CO_{ad} species can be distinguished on Pt(111) in an electrochemical environment[5]: *(i)* CO_{ad} with a low heat of adsorption is characterized as the "weakly adsorbed" state, $CO_{ad,w}$, and *(ii)* CO_{ad} with a relatively high enthalpy of adsorption is characterized as the "strongly adsorbed" state, $CO_{ad,s}$. These concepts for CO_{ad} energetics, and the transition from the $CO_{ad,w}$ layer into the $CO_{ad,s}$ state, are the keys to understanding

the relation between reactivity and interfacial structures of CO_{ad} on the Pt(hkl). Independent, non-electrochemical insight into the Pt(111)-CO system was obtained by combination of in-situ structure-sensitive probes, such as scanning tunneling microscopy (STM) [6;7] and surface x-ray scattering (SXS), [8] with in-situ adsorption-site-sensitive probes, such as Fourier transform infrared (FTIR) spectroscopy [6;7;9] and sum frequency generation (SFG) [9]. These studies demonstrated that, although the nature and adsorption site occupancy of CO_{ad} are strongly dependent of applied potential, the mechanism for CO_{ad} oxidation on Pt(111) is independent of electrode potential; $e.g.,$ CO_{ad} reacts with OH_{ad}, species through either non-competitive or competitive Langmuir-Hinshelwood (L-H) type reaction [5]:

$$CO_{ad} + OH_{ad} = CO_2 + H^+ + e^- \tag{1}$$

Furthermore, it was suggested that the kinetics of reaction (1) does not depend only on the surface concentration of CO_{ad} and OH_{ad} species, but is strongly affected by a delicate balance between the coverage of CO_{ad}, OH_{ad} and *anions* from supporting electrolytes [5;10].

In this paper we describe the role of anions in controlling both the kinetics of CO_b electrooxidation on Pt(111) in aqueous electrolytes and the potential range of stability of p(2x2)-3CO structure, which is formed on the Pt(111) surface at low overpotentials. Polarization curves for CO_b oxidation on Pt(111) are compared in alkaline solution, perchloric acid solution, and perchloric acid solution containing Br⁻. The kinetics of CO oxidation were measured by utilizing the rotating disk electrode (RDE) method. Direct information regarding the anion effect on the CO_{ad} structure and site occupancy was obtained from SXS and FTIR measurements. In combination, these three techniques allow to illuminate the development of a new insight into relation between the microscopic details of the Pt(111)-CO_{ad} interface and the kinetics of CO electrooxidation.

2. EXPERIMENTAL

2.1 Electrochemical measurements

Most of the experimental details were described previously [10]. Following the flame annealing-hydrogen (or argon) cooling method, the Pt(111) electrode was transferred into the disk configuration of the RDE. The cleanliness of the transfer and the electrolyte, even under sustained rotation at high rotation rates, were demonstrated in our previous work [11]. For the electrooxidation of dissolved pure CO gas (denoted hereafter as CO_b), the electrolyte was firstly equilibrated for 5 minutes with the respective gas while the electrode potential was held at 0.05 V, and subsequently the positive was scanned (20 mV/s). The kinetics of CO_b oxidation was in three different electrolytes: 0.1 M NaOH, 0.1 M $HClO_4$, and 0.1 M $HClO_4$, + 10^{-2}M Br^-. The reference electrode was a saturated calomel electrode (SCE) at 298 K separated by an electrolyte bridge. However, all potentials are referred to the reversible hydrogen electrode.

2.2 FTIR measurement

FTIR experiments were performed with a Nicolet Magna 850 spectrometer equipped with a MCT detector. The Pt(111) single crystal electrode employed (ca. 4.5 mm in diameter) was prepared by using the method developed by Clavilier [12]. The flame-annealed electrode was rinsed with water and transferred to a spectroelectrochemical cell provided with a prismatic CaF_2 window bevelled at 60º. Once a cyclic voltammogram was recorder in order to check the cleanliness of the electrode surface, the solution was saturated with CO while holding the electrode potential at 0.10 V. Spectra were then collected with p-polarized light and a resolution of 8 cm^{-1} while the electrode potential was swept at 1 mV s^{-1} up to 1.0 V (0.1 M $HClO_4$ and 0.1 M NaOH solutions) or up to 1.2 V (0.01 M $KBr+0.1$ M $HClO_4$). Typically, 10 s were needed to collect 104 interferograms which were co-added to obtain each single beam spectrum corresponding to a potential window of 10 mV. Absorbance spectra were calculated as the ratio –log $(R/R_0$) where R and R_0 are the reflectance values corresponding to the sample and

reference single beam spectra, respectively. Either the spectrum collected at the upper potential limit, i.e. after the oxidative stripping of adsorbed CO, or that obtained at 0.10 V were used as the reference spectrum.

2.3 X-ray scattering measurements

The Pt(111) crystal (miscut <0.2˚) was prepared by annealing in a hydrogen flame and then transferred under electrolyte to the x-ray electrochemical cell [8]. The cell was mounted at the center of a four-circle Huber goniometer on beamline 7-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). SXS measurements were performed using a focused monochromatic x-ray beam of energy 10 keV, defined by slits to be a 1 mm x 1 mm spot at the sample. Diffracted x-rays were measured by a Ge solid state detector after passing through a Soller slit which defined an in-plane resolution of ~0.005 Å^{-1}. The crystal was indexed to the conventional hexagonal until cell for the (111) surface. The adsorption of CO was studied by purging the outer shell of the x-ray cell with CO (99.999% purity) which was then able to diffuse through the polypropylene film trapping the electrolyte and saturate the solution.

3. RESULTS AND DISCUSSION

Recently, we proposed that two potential regions can be distinguished in the current *vs.* potential relationship during CO_b oxidation on Pt(111): a potential region of the electrooxidation *via* the weakly adsorbed state of CO (the so called pre-ignition or pre-oxidation potential region [13,14]) and the potential region of the oxidation *via* the strongly adsorbed state of CO_{ad} (the so called ignition potential region). The ignition potential is the electrochemical analog of ignition temperature for the gas phase oxidation of CO. It is the potential at which the rate becomes entirely mass transfer limited (rate of CO_b diffusion to the surface). Recall that although the nature of CO_{ad} changes with electrode potential, the mechanism for CO_{ad} oxidation on Pt(*hkl*) follows the L-H reaction

mechanism in the entire potential range [5]. Other research groups have proposed different models for CO oxidation. In particular, Bergelin et al., [15;16] suggested that in the pre-ignition potential region CO oxidation cannot proceed through the L-H mechanism, but rather through an Eley-Rideal (E-R) mechanism, $i.e.$ reaction between CO_{ad} and "activated" water molecules in the electrical double-layer. Rather than debate the interpretations here, the interested reader is referred to the original references for details. In this paper, CO oxidation on Pt(111) will be considered to proceed through the L-H mechanism, in which the kinetics is strongly dependent on the delicate balance between the surface coverage of CO_{ad}, OH_{ad} and anions from supporting electrolytes.

3.1 Anion effects on the kinetics of CO_b oxidation

The role of anions in the supporting electrolyte on the kinetics of CO_b electrooxidation can be seen by comparing the polarization curves for CO_b oxidation on Pt(111) in different electrolytes, $e.g.,$ alkaline solution, perchloric acid solution, and perchloric acid solution containing Br^-. Figure 1 shows that the activity of Pt(111) increases in the sequence: $Br^- << HClO_4 << NaOH$. In the latter case, the onset of the pre-ignition region is in what is generally considered to be the H_{upd} potential region (!). If the L-H mechanism is operative, the catalytic activity in the H_{upd} potential region implies that in alkaline solution OH_{ad} is adsorbed even at potentials below ca. 0.2 V (RHE). This would translate into an increase in the Pt-OH_{ad} bond energy by $ca.$ 70-80 kJ/mol, from 136 kJ/mol in acidic solution to $ca.$ 206-216 kJ/mol. We had proposed that adsorption of OH_{ad} with this higher bond energy occurs at the defect/step sites on the Pt(111) surface [10]. The low defect density on this surface explains the relatively low rate of reaction achieved in this potential region. On the Pt(100) surface, where the defect density is high due to the lifting of the reconstruction, the activity in the same potential region is much higher than on Pt(111) [17]. The explanation, therefore, for the remarkable effect of pH on the rate of CO_b oxidation on Pt(hkl) is the "pH dependent" adsorption of OH_{ad} at

defect/step sites. In acid solution at low overpotentials OH_{ad} is most likely excluded from active sites, *e.g.,* the dipole moment at defect/step sites is intrinsically attractive to anions [10]. The fact that in solution containing bromide the ignition potential is shifted ca. 0.6 V positively from one observed in alkaline solution implies that Br⁻ can indeed effectively suppress the adsorption of OH_{ad}. As a consequence, in solution containing bromide a diffusion limiting current is not observed for CO_b oxidation even above 1.1 V. In fact, a close inspection of Figure 1 clearly reveals that in the presence of Br⁻ a *bulk* oxidation of CO is more similar to the stripping voltammetry of CO_{ad} than to characteristic polarization curves for CO_b oxidation in 0.1 M $HClO_4$ and 0.1 M NaOH. The supposition that the active centers are the defect/steps sites is fully consistent with the recent results for the electrooxidation of CO on stepped Pt[n(111)x(111)] electrodes. Lebedeva *et al.,* [18] showed that the onset potential for oxidation of dissolved CO increases in the sequence Pt(553) < Pt(554) < Pt(111).

3.2 Effects of anions on the surface structure of CO_{ad}

Aside from the pioneering STM studies by Villegas and Weaver [6,7], and later studies by our group using SXS [8,9,19], there is very little information about the interplay between the substrate structure and the bonding geometry of the CO_{ad} molecules on Pt(111). In the SXS experiments [8], direct information regarding the CO_{ad} structure on Pt(111) in perchloric acid solution was obtained since the CO_{ad} formed an ordered adlayer with p(2x2) symmetry and the diffraction signal from this structure could be followed as the electrode potential was changed. Valuable complementary information can be obtained from vibrational spectroscopies, such as FTIR and SFG. In this section we describe SXS and FTIR combined studies in application to the atomic-structure of CO_{ad} on Pt(111) in alkaline solution and in acid solution containing Br⁻. For completeness, the original results obtained for the Pt(111)-CO system in perchloric acid are also shown.

In perchloric acid solution, Figure 2, while holding the potential at 0.05 V and with a continuous supply of CO to the x-ray cell, a diffraction pattern consistent with a p(2 x 2) symmetry was observed [8], which is in a good agreement with previous STM results [6]. Figure 2a shows that the potential range of stability of the p(2 x 2)-3CO phase, with a CO coverage of 0.75 ML, is strongly affected by the oxidation of a *small* fraction (15 %) of the saturation coverage. With a constant overpressure of CO in the x-ray cell, the SXS experiments revealed a *reversible* order-disorder transition of the p(2 x 2)-3CO structure, with the p(2 x 2)-3CO structure re-forming as the potential was slowly (1 mV/s) swept below 0.2 V, Figure 2a. Besides the p(2x2) structure, markedly different CO_{ad} unit cells were found in STM measurements. For example, depending on the electrode potential and the surface coverage of CO_{ad}, Oda et al. observed either complex CO structures or the $(\sqrt{3} \times \sqrt{3})R30°$ structure [20], which was previously observed in ex-situ measurements [21;22]. On the other hand, above 0 V (vs SCE) in solution containing CO Villegas and Weaver found a $(\sqrt{19} \times \sqrt{19})R23.4°$ structure [6]. At potentials below 0.2 (vs. SCE), after the removal of solution-phase CO, another CO adlayer structure with the $(\sqrt{7} \times \sqrt{7})R19.1°$ symmetry was also reported from the latter authors [6]. Although a careful search was made to find diffraction peaks due to domain structures based on either the $\sqrt{3}$ symmetry or the $(\sqrt{19} \times \sqrt{19})R23.4°$ and $(\sqrt{7} \times \sqrt{7})$ phases, such superlattice CO_{ad} peaks were not found in SXS measurements at any partial pressure of CO and at any surface coverage by CO. It was concluded, therefore, that the p(2 x 2)-3CO structure is the only structure present with *long-range order* [8]. A rocking scan through the (½, ½, 0.2) position is shown in Figure 3b together with the fit of a Lorentzian lineshape (solid line) to the data. From the width of this peak and from the result of similar fits to other p(2 x 2) reflections a coherent domain size in the range of 80-120 Å for the CO adlayer was deduced [5;8]. The derived structural model is shown schematically in Figure 3, which consists of three CO molecules per p(2 x 2) unit cell. It is important to note, however, that besides the symmetry of the ordered CO structure, SXS measurements were unable to provide

information about the real sites occupancy in the unit cell. Closely following ref.[6], these information are obtained from FTIR measurements.

Fig.2c shows a set of the absorbance spectra referred to the single beam spectrum collected at 1.0 V. As previously described by different authors [23-26] characteristic C-O stretching bands near 2070 and near 1780cm^{-1}, corresponding to a-top and three-fold hollow CO respectively, predominates in the spectra obtained at potentials below 0.50 V. At higher potentials, the three-fold hollow band is replaced by a new C-O stretching band at ca. 1840 cm^{-1} that can be related to the presence of bridge-bonded CO. Plots for the integrated intensity of the observed C-O stretching bands as a function of the electrode potential are summarized in Figure 2b. Comparison of the potential dependent intensity changes for the three-fold and bridge CO bands with the SXS [9] data suggests that the three-fold hollow band is related to the (2x2)-3CO structure whereas the loss of this ordered structure is reflected by the appearance of the bridge-bonded CO band. Based on the analysis of the C-O vibrational spectra obtained for a series of stepped surfaces with (111) terraces, the p(2x2)-3CO structure in CO-saturated $HClO_4$ solution is also sensitive to the two-dimensional long-range order of the Pt(111) [25] surface.

At this point it should be recalled that changes of the band intensities for adsorbed CO with potential as plotted in Figure 2b must be interpreted with caution. Qualitatively, and in agreement with refs. [6;9] we can conclude that the order-disorder transition in the CO adlayer is mirrored by the disappearance of CO_{ad} from the three-fold hollow sites, and the relaxation of the remaining CO_{ad} into a combination of bridge sites and a-top sites. However, whereas the intensity of the a-top band at saturation coverage is higher than that of multi-coordinate CO, examination of the real-space model of the p(2 x 2)-3CO structure in Figure 3, shows that about 1/3 of the CO_{ad} occupy a-top sites, and 2/3 are in three-fold hollow sites. The stronger a-top signal observed with IR spectroscopy can be explained by "intensity stealing" by which the higher-frequency a-top mode gains intensity over the lower frequency hollow-site mode [27]. Quantitation of the intensity

changes to fractional coverages can only be done with modeling of the dipole coupling, and even then would entail assumptions about the CO_{ad}-CO_{ad} coordination as the coverage changes [27].

Another point that can be clarified from the in-situ infrared experiments performed with the CO-covered Pt(111) electrode is that of the relation between the loss of the (2x2) structure and the onset of CO oxidation. Recall that comparison of the SXS and voltammetric data suggested that the disordering transition is governed by electrooxidation of a relatively small amount of CO_{ad}, *ca*. 15% [5]. This can be confirmed from Fig.2a, which provides a quantitative measure of CO_2 formation from the asymmetric O-C-O stretch at 2343 cm^{-1}. To obtain this plot, the same set of single potential spectra used to obtain the difference spectra in Fig.2c was now referred to the reference spectrum collected at 0.10 V. Compared with Figure 2b, CO_2 production occurs simultaneously with the binding site occupancy change, indicating that structural transformation in the CO_{ad} layer is triggered by oxidative removal of CO_{ad}, as in equation 1. Interestingly, the CO_2 plot shows two (positive) slopes: the low-CO_2 slope between 0.5 V and 0.7 V corresponds to the pre-ignition region were disappearance of the three-fold hollow sites is observed in Figure 2b, and the high CO_2-slope above 0.7 V that is related to the oxidation of a-top and bridge CO_{ad} in the ignition potential region. Point of inflection in the CO_2 slope may correspond to the "ignition potential", which is defined in section 3.1. Therefore, linking macroscopic and macroscopic characterization of the Pt(111)-CO system, the macroscopic terminology of $CO_{ad,w}$ may correspond microscopically to a saturated CO_{ad} layer consisting of three CO molecules per p(2x2) unit cell located in a-top and three-fold hollow sites. Figure 2 shows that oxidation of the CO_{ad} in the three-fold hollow sites and relaxation of the remaining CO_{ad} into bridge sites and a-top sites disrupts the long-range ordering in the remaining adlayer, as the Bragg peak intensity for the p(2 x 2)-3CO structure decreases rapidly in this potential region (Figure 2c). The characterized microscopically as "relaxed" CO_{ad} adlayer with

substantial alternation in binding site geometry from predominantly three-fold hollow to bridge sites can be linked macroscopically to the strongly adsorbed state of CO_{ad} that is oxidized in the ignition potential region.

Figures 4 and 5 show that the anions in the supporting electrolyte do affect the stability of the p(2 x 2)-3CO structure. Combined SXS/FTIR data for the Pt(111)-CO_{ad} system in alkaline solution (Figure 4) and in perchloric acid solution containing Br^- (Figure 5) are representative examples. Clearly, in alkaline solution the oxidation of CO (production of CO_3^{2-} in Figure 4a) begins as low as at 0.3 V, concurrent with the loss of CO_{ad} at three-fold hollow sites (band at 1733 cm^{-1} in the spectra shown in Fig.4c) and the development of CO_{ad} at bridge sites (band at ca. 1804 cm^{-1}) , Figure 4b. Note that the observation of the C-O stretching bands at lower wavenumbers than in Fig.2c is related to the lower surface potential in alkaline solutions 24 [24]. The oxidation of CO at very low potentials in alkaline solution reduces the potential range of the stability of the p(2 x 2)-3CO structure, 0.05-0.35 V in KOH *versus* 0.05 – 0.6 V in $HClO_4$. We argued in reference [10] and in the previous section on kinetics of CO oxidation that CO_{ad} is oxidatively removed by OH_{ad} adsorbed at the defect/step sites on the Pt(111) surface. The adsorption of OH onto these sites is facile in alkaline solution, and consequently the production of CO_3^{2-} is observed even in the H_{upd} potential region. In solution containing Br^-, however, these defect/step sites are blocked with Br_{ad}, thus the potential stability of the p(2 x 2)-3CO structure and CO_2 prodution is extended to higher potential than even in perchloric acid solution, see Figure 5. This figure also shows that the complete stripping of the CO adlayer remaining on the Pt(111) surface once the (2x2) structure disappears is shifted towards more positive potentials. In this way, the bridge bonded CO band is observed in a relatively broad potential region between 0.70 and 0.90 V. As in perchloric acid, CO_2 plot in Figure 5a shows two positive slopes that can be related to the oxidation of CO_{ad} the pre-ignition and ignition potential regions. Note that in alkaline solution the

transition from the pre-ignition to the ignition potential region is less clear from the plot of CO_3^{2-} intensity which is shown in Figure 4a.

Finally, it is also worth mentioning that besides tuning the fine balance between a-top and multifold coordinated CO_{ad}, the domain size of the CO_{ad} structure is significantly affected by the nature of anions. Figure 3 shows rocking scans through the (1/2,1/2,0.2) position measured at 0.05 V in three different electrolytes. The solid lines are fitted Lorentzian lineshapes to the data, and from these data and from other measured reflections (a total of nine symmetry independent reflections [8]) a domain size in the range 30-350 Å was calculated. The domain size of the p(2 x 2)-3CO structure increases from KOH (*ca.* 30 Å), to HClO$_4$ (*ca.* 140 Å) to HClO$_4$ + Br$^-$ (*ca* 350 Å), *i.e.,* the less active the surface is towards CO_{ad} oxidation, the larger the ordered domains of the p(2 x 2)-3 CO structure was observed in SXS measurements. A self-consistent explanation for this result is that both the stability and domain size of the ordered CO_{ad} adlayer is determined by the potential dependent competition between OH_{ad} and spectator anions for the defect/step sites on the Pt(111) surface [10].

4. CONCLUSIONS

In-situ studies of CO adsorption by surface x-ray scattering (SXS) and Fourier transform infrared (FTIR) spectroscopy have been used to create the link between the macroscopic kinetic rate of CO oxidation and the microscopic level of understanding the structure/site occupancy of CO on Pt(111). A remarkable difference in activity was observed between alkaline and acid solutions. In alkaline solution, the oxidation of CO proceeds at low overpotential (<0.2 V) between the adsorbed CO and OH, the latter forming selectively in hydrogen underpotential region at defect sites. In acid solution these sites are blocked by specific adsorption of anions, and consequently in solution containing Br$^-$ the ignition potential is shifted by 0.6 V positively. The anions of supporting electrolyte have also dramatic effects on the potential range of stability and the

domain size of the p(2x2)-3CO structure, which is formed at 0.05 V. The stability/domain size of this structure increases from KOH (*ca.* 30 Å between 0.05 <E<0.3V), to $HClO_4$ (*ca.* 140 Å between 0.05 <E<0.6V) to $HClO_4$ + Br^- (*ca* 350 Å between 0.05 <E<0.8V), the larger the ordered domains are, the less active the surface is towards CO oxidation.

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FIGURE CAPTIONS

Figure 1. Potentiodynamic CO_b oxidation current densities on Pt(111) in 0.1 M $HClO_4 + 10^{-2}$ M Br$^-$; 0.1 M $HClO_4$; and 0.1 M KOH. Sweep rate 20 mV/s. Rotation rate 900 rpm.

Figure 2. . **(a)** Potential-dependent stability of the p(2x2)-3CO_{ad} structure on Pt(111) in 0.1 M $HClO_4$ in CO-saturated solution, and CO_2 production as a function of electrode potential (data extracted from FTIR measurement) during the oxidation of CO_{ad}. **(b)** Integrated intensities for CO_{ad}-atop, CO_{ad}-multi and CO_{ad}-bridge on Pt(111) as a function of electrode potential in CO-saturated 0.1 M $HClO_4$ solution. **(c)** FTIR spectra obtained during progressive oxidation of CO_{ad} on Pt(111) in 0.1 M $HClO_4$ from the initial potential, *ca.* E=0.05 V. Each spectrum, displayed as relative reflectance (ΔR/R), was acquired from 100 interferometer scans at the range potential indicated, rationed to the corresponding spectrum obtained at the final potential, *ca.* E=0.9 V.

Figure 3. Rocking scans through the (½, ½, 0.2) reciprocal lattice position, where scattering from the p(2x2)-3CO structure is observed, for (a) 0.1M $HClO_4 + 10^{-2}$ M Br$^-$, (b) 0.1 M $HClO_4$ and (c) 0.1 M KOH. The solid lines are fits of a Lorentzian lineshape to the data which give a coherent domain size for the p(2x2) structure of 350 Å, 130 Å and 30 Å in (a), (b) and (c) respectively. Also shown is a schematic picture of the p(2x2)-3CO structure. The symmetry of the unit cell ad the site f occupancy are deermined from SXS and FTIR measurements, respectively.

Figure 4. **(a)** Potential-dependent stability of the p(2x2)-3CO$_{ad}$ structure on Pt(111) in 0.1 M NaOH in CO-saturated solution, and CO$_3^{2-}$ production as a function of electrode potential (data extracted from FTIR measurement) during the oxidation of CO$_{ad}$. **(b)** Integrated intensities for CO$_{ad}$-atop, CO$_{ad}$-multi and CO$_{ad}$-bridge on Pt(111) as a function of electrode potential in CO-saturated 0.1 M NaOH solution. **(c)** FTIR spectra obtained during progressive oxidation of CO$_{ad}$ on Pt(111) in 0.1 M NaOH from the initial potential, *ca.* E=0.05 V. Each spectrum, displayed as relative reflectance (ΔR/R), was acquired from 100 interferometer scans at the range potential indicated, rationed to the corresponding spectrum obtained at the final potential, *ca.* E=0.9 V.

Figure 5(a) Potential-dependent stability of the p(2x2)-3CO$_{ad}$ structure on Pt(111) in 0.1 M HClO$_4$ + 10^{-2} M Br$^-$ in CO-saturated solution, and CO$_2$ production as a function of electrode potential (data extracted from FTIR measurement) during the oxidation of CO$_{ad}$. **(b)** Integrated intensities for CO$_{ad}$-atop, CO$_{ad}$-multi and CO$_{ad}$-bridge on Pt(111) as a function of electrode potential in CO-saturated solution. **(c)** FTIR spectra obtained during progressive oxidation of CO$_{ad}$ on Pt(111) in 0.1 M HClO$_4$ + !0^{-2} M Br$^-$ from the initial potential, *ca.* E=0.05 V. Each spectrum, displayed as relative reflectance (ΔR/R), was acquired from 100 interferometer scans at the range potential indicated, rationed to the corresponding spectrum obtained at the final potential, *ca.* E=0.9 V.