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COMMUNICATIONS

Dual Reactivity of Step-Bound Carbon Monoxide during Oxidation on a Stepped Platinum Electrode in Alkaline Media

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The "active site" is one of the central ideas but also one of the most elusive concepts in heterogeneous catalysis.[1] On a catalytic metal surface, low-coordination step, corner, and edge sites are often considered to be active sites for many catalytic reactions because of their enhanced ability (relative to that of highly coordinated terrace sites) to bind catalytic intermediates.

A frequently adopted strategy for studying the role of defects in heterogeneous catalysis is to use stepped single-crystal surfaces in which the orientation of the step differs from that of the mostly close-packed (111)-type terrace.[2] Employing such tactics, it has been demonstrated that steps of (110) orientation are active sites in the electrooxidation of carbon monoxide adsorbed on stepped platinum single-crystal electrodes in acidic media.[3,4] It is generally assumed that the active OH species, formed by the reaction $H_2O + * \leftrightarrows OH_{ads} + H^+ + e^-$, adsorb at low-coordination "defect" sites preferentially over terrace sites and react with adsorbed CO according to $CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + e^- + 2*$.[3−7] However, it has remained unclear whether every combination of CO_{ads} and OH_{ads} near a step is equally reactive or whether a differential reactivity still exists. Using a similar strategy in UHV, Xu and Yates[8] deduced that the most active combination for CO oxidation is CO on the terrace reacting with O in the step edge. For the electrocatalytic CO oxidation in acidic media, the mobility of adsorbed CO was concluded to be too high to render an unequivocal demonstration of such an effect feasible.[4,9]

Recently, we studied the same CO adlayer electrooxidation reaction on stepped Pt electrodes in alkaline media.[10] Surprisingly, the mobility of CO_{ads} turns out to be much lower in alkaline media than in acidic media. The reason for this reduced mobility has not yet been fully clarified, but our current understanding suggests that is related to the coadsorption of the CO oxidation product in alkaline media (i.e., carbonate). This low effective mobility of CO_{ads} affords the possibility of looking in more detail into the dynamics of the CO oxidation process, especially into the possible differential reactivity of step-bound CO. All of the experimental methods used to obtain the results described below are identical to those in ref 10.

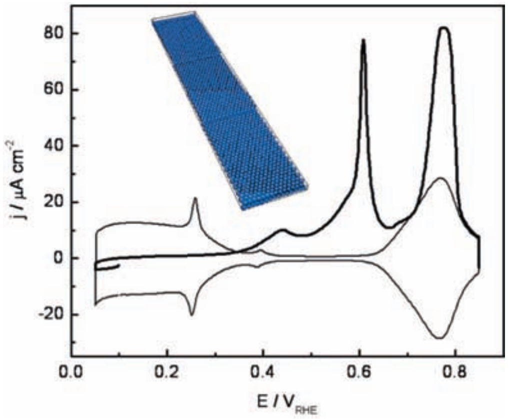

Figure 1. Blank (thin solid line) and CO stripping (thick solid line) voltammograms for Pt(15 15 14) in 0.1 M NaOH (sweep rate 20 mV s^{-1}, $E_{ad} = 0.1$ V vs RHE).

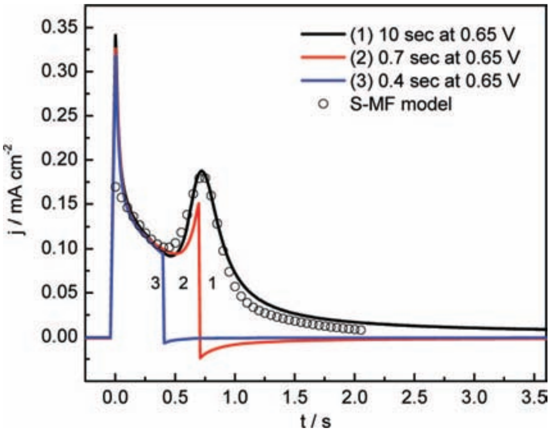

Figure 2. Current transients for CO oxidation on Pt(15 15 14) in 0.1 M NaOH ($E_{ad} = 0.1$ V). The step potential was 0.65 V applied during (1) 10, (2) 0.7, and (3) 0.4 s. Open circles are the fit to the S-MF model, with $k_s = 1.5\ s^{-1}$, $k_t = 12\ s^{-1}$, $A = 1.133 \times 10^{-4}$ mC cm^{-2}, $B = 4.18 \times 10^{-4}$ mC cm^{-2}, and $C = 7 \times 10^3$. For a detailed explanation, see the text.

Figure 1 shows the blank voltammetry of the stepped Pt(15 15 14) electrode under consideration in this communication, together with the stripping voltammetry of a saturated CO monolayer adsorbed at $E_{ad} = 0.1$ V (vs RHE). The three stripping peaks observed at 0.44, 0.60, and 0.77 V have been ascribed to CO oxidation at kinks (or step defects), steps, and terraces, as follows from the consistency of the peak charges with the surface structure of the single crystal.[5,10] The charge corresponding to the peaks depends on the scan rate, suggesting a low but finite mobility of CO_{ads}, as discussed in detail in our previous paper.[10] Figure 2 shows the chronoamperometric transient obtained for a potential step from 0.1 to 0.65 V. Steps to other potentials give similar results. The open circles in Figure 2 are a fit to the curve labeled "1", which was stopped at $t = 10$ s. The fitting equation is $j(t) = Ak_s \exp(-k_s t) + BCk_t \exp(-k_t t)/[1 + C \exp(-k_t t)]^2$, where k_s and k_t are the rate constants for CO oxidation at the step and terrace, respectively, and A, B, and C are constants depending only on the initial conditions. The first term on the right-hand side of this equation for the current transient has recently been derived[11] for a one-dimensional instantaneous nucleation and growth mechanism for CO oxidation, but it could in principle also reflect an oxidation mechanism between CO and OH that does not imply competitive adsorption; the second term is the well-known mean-field expression for CO oxidation.[12] The fit is quite reasonable, although the initial part of the transient seems to have an additional faster exponential decay right at the beginning. A detailed analysis of the model

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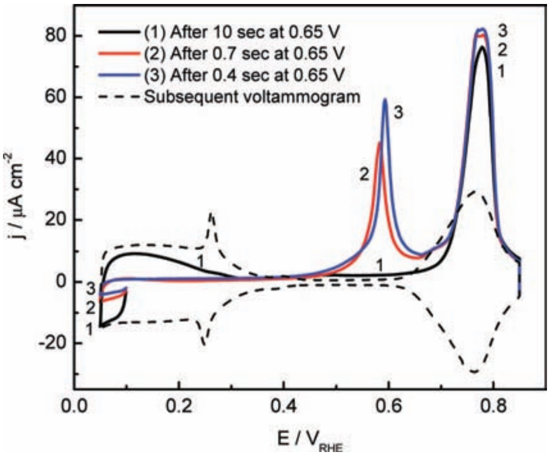

Figure 3. CO stripping voltammograms after the chronoamperometric transients depicted in Figure 2 and the subsequent cyclic voltammogram (dashed line) for Pt(15 15 14) in 0.1 M NaOH (sweep rate 20 mV s^{-1}). The previous step potential was 0.65 V over (1) 10, (2) 0.7, and (3) 0.4 s.

(referred to as the S-MF model) and the fitting of the transients will be left for a future paper.

Significantly, and in agreement with the above mathematical model, all of the experimental transients on Pt(15 15 14) [as well as on Pt(111), Pt(554), and Pt(553)] display an exponential current decay before the main oxidation peak. Such an exponential decay has not been observed during CO$_{ads}$ chronoamperometric oxidation in acidic media.[4] Our suggestion is that it is due to the oxidation of CO$_{ads}$ adsorbed initially along the steps and step defects. The exponential decay is not due to double-layer charging, as this is expected to be much faster. To demonstrate that CO$_{ads}$ is indeed oxidized in the initial exponentially decaying part of the transient, we conducted the following experiment. The transient was stopped at three different times [0.4, 0.7, and 10 s (see Figure 2)], after which the potential was stepped back to 0.1 V. Next, a stripping voltammogram was recorded, first scanning negatively until 0.05 V to probe the entire hydrogen region and then scanning positively up to 0.85 to oxidize off all of the remaining CO$_{ads}$. When the transient was discontinued at 0.4 s (the curve labeled “3” in Figure 2), i.e., close to the minimum in the transient, it was observed that all of the CO$_{ads}$ corresponding to the kink and defect step sites had been oxidized off (see Figure 3a), as well as a significant fraction of the CO$_{ads}$ near the step, whereas the peak corresponding to the CO$_{ads}$ oxidation on the terrace had essentially the same charge as that for the full monolayer oxidation. When the transient was discontinued at 0.7 s, in the rising part of the transient (the curve labeled “2” in Figure 2), the subsequent stripping voltammogram (Figure 3b) showed that the peak corresponding to step oxidation had decreased more, whereas the charge corresponding to the terrace oxidation had decreased only very slightly. The blockage of the hydrogen region also suggested that at 0.7 s, most of the CO on the terrace had not reacted yet. After 10 s (the curve labeled “1” in Figure 2), the subsequent stripping voltammogram exhibited two interesting features. First of all, in the hydrogen region, it was observed that a significant fraction of terrace sites had become available for hydrogen adsorption, but the characteristic peak at 0.26 V ascribed to hydrogen adsorption at the step sites[10,13] was still completely blocked, suggesting the adsorption of CO there (we considered it less likely that carbonate was blocking hydrogen adsorption on steps, as transfer to an acidic solution, in which carbonate should be much less stable, still displayed blocking of the “hydrogen step” sites). However, in the CO stripping curve, only the peak attributed to CO$_{ads}$ oxidation on the terrace was observed.

From these results, the following picture of CO$_{ads}$ oxidation on a stepped Pt electrode emerges. The CO adsorbed near the bottom (or at one side) of the step is the most reactive CO on the surface. When the steps are activated by application of a positive potential, these CO react first. The sites made available in this process are characterized as “terrace” sites for hydrogen adsorption. The CO adsorbed on top (or on the other side) of the step is strongly bound and reacts last. When this CO reacts, it is oxidized by OH$_{ads}$ on the terrace, at least in alkaline media. The sites made available in this process are characterized as “step” sites for hydrogen adsorption. The argument for assuming this type of CO to sit on top of the step is based on DFT calculations for CO adsorption on a stepped surface, in which it was found that the most strongly adsorbed CO is the one that coordinates to a bridge site on top of the step.[14,15] Moreover, the results suggest that the main peak observed in the chronoamperometry is primarily due to terrace-adsorbed CO being oxidized in the step, following the well-known competitive adsorption mechanism,[4,12] rather than to oxidation on the terrace itself. Clearly, it would be desirable to observe OH on steps and terraces spectroscopically, but such an experiment remains a challenge.[16]

Our experiment provides an illustration of the “dual” role of the step site in catalyzing the CO$_{ads}$ electrooxidation reaction on Pt in alkaline media: CO approaching the step from the bottom is the most reactive, whereas CO sitting on top of the step is the least reactive CO on the surface and reacts with OH$_{ads}$ on the terrace. It shows that the “active site”, both in heterogeneous catalysis and in electrocatalysis, remains a complex concept, as “active sites” may lead to enhanced *as well as* reduced activity, depending on which side of the active site the reaction intermediates are adsorbed.

Acknowledgment. This work was funded by The Netherlands Organization for Scientific Research (NWO) through a “VICI” Grant awarded to M.T.M.K.

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JA9009869