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Oxidation of CO on hydrogen-loaded palladium

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Abstract

The oxidation of CO adsorbed on the surface of palladium electrodes loaded with different amounts of hydrogen was studied by single potential alteration infrared reflectance spectroscopy (SPAIRS). In the absence of hydrogen, only CO_2 was detected during anodic oxidation of CO. Adsorption of CO in the presence of hydrogen in palladium led to a more negative onset of its electrooxidation, and the formation of other products, such as ethanol and formaldehyde, as well as CO_2. The results indicate that hydrogen occluded in palladium contributes to the displacement of carbon monoxide from the interface; this may assist in the continual electrooxidation of organic compounds at palladium electrodes.

1. Introduction

The development and use of fuel cells with direct electrochemical oxidation of low molecular weight organic fuels has been severely limited by poisoning of electrocatalysts [1], primarily due to the strong adsorption of CO produced during the organic fuel oxidation, precluding further adsorption and oxidation of the organic fuel. One possible route for extending the turnover of the electrocatalyst, is that of introducing a chemical reaction capable of desorbing the CO strongly attached to the surface. Palladium, being an excellent electrocatalyst for organic fuel electrooxidation [2] and the reduction of protons [3], is also able to store and release substantial amounts of hydrogen [4], which may be useful in diminishing the strong adsorption of CO on the surface of the electrocatalyst during the course of the electrooxidation reaction, thus alleviating the effects of poisoning. The electroadsorption of CO on palladium has been actively studied by electrochemical ([5–8] and references cited therein), i.r. spectroscopy [9–14], surface-enhanced Raman spectroscopy (SERS) [13] and potential-modulated reflectance spectroscopy (PMRS) [15] techniques.

Czerwinski [8] has studied the adsorption and oxidation of CO on to Pd deposits at several adsorption potentials, indicating the possibility of effects due to hydrogen absorption on the adsorption and oxidation of CO. Ayers and Farley [16, 17] reported insertion of hydrogen at one side of a bipolar palladium electrode, and its discharge at the anodic side to assist in the reduction of CO_2 to methanol, formaldehyde and formic acid. With a similar procedure, but reducing CO_2 on the cathodic side, Yoshitake et al. [18] and Ohkawa et al. [19] reported formation of carbon monoxide, formic acid, methane and hydrogen. Assuming that CO is involved as adsorbed intermediate in the reduction of CO_2 [18], these reports indicate, on the basis of the principle of microscopic reversibility, the possibility of assisting the oxidation of C_1 organic fuels to CO_2 by reaction of CO with hydrogen occluded in the Pd lattice, as supported by the results presented in this paper.

2. Experimental details

Most of the details concerning the experimental procedures and instrumentation used have been reported by other workers (e.g., [20–22]). The Fourier transform infrared spectrometer used for single potential alteration infrared reflectance spectroscopy (SPAIRS) studies was a Bruker–IBM IR 98-4A instrument, with globar source and InSb detector, at 8 cm^{-1} resolution, with an EG&G PAR 173 potentiostat and an EG&G PAR 175 waveform generator. The working electrode was a polycrystalline Pd (99.99%) disc of 0.71 cm^2 exposed area. All potentials are referred to the saturated calomel electrode (0.242 V vs NHE) used, and all measurements were carried out at room temperature. Pretreatment of the Pd electrode before each SPAIRS experimental run consisted in flame-annealing and protecting with I_2 [23] prior to immersion in 0.1 M $HClO_4$ solution, where adsorbed iodine was exchanged with CO at 0.0 or

−0.7 V, followed by electrochemical CO oxidation. Typical voltammetric response of palladium electrodes in $HClO_4$ solution [24] were obtained between −250 and 1200 mV after the treatment described. Perchlorate absorbs in the spectral region of interest, thus electrochemical and i.r. measurements were taken in argon-deareated aqueous (Millipore) 0.1 M NaF solutions in a thin layer of electrolyte ($\sim$10 μm), after pushing the working electrode against the CaF_2 optical flat window at the bottom of the electrochemical cell. CO (99.99%, Matheson) was used throughout the study. The spectra are expressed as $-\log(R_{\mathrm{sample}}/R_{\mathrm{ref}})$, where R_{sample} and R_{ref} are the signals at the sample and reference potentials, respectively. The latter were the signals obtained at the initial sweep potentials, (i.e., 0.0 or −0.7 V), as described below. With this convention formation and consumption of species originate positive and negative bands, respectively. All experiments were carried out at a sweep rate of 1 mV s^{-1}.

3. Results

Results obtained from two kinds of experiments will be described:

(i) *Hydrogen-free palladium in the presence of CO.* Maintaining the working electrode under potentiostatic control at 0 V, CO was bubbled through the working solution for 2 min, followed by Ar bubbling for 5 min to displace CO from solution, but not from the electrode surface. After producing the thin layer cell configuration necessary to perform the SPAIRS measurements, these were obtained, with the spectrum acquired at 0 V taken as reference.

(ii) *Hydrogen-loaded palladium in the presence of CO.* The palladium electrode was deliberately loaded with different amounts of hydrogen by holding it at −0.700 V in 0.1 M NaF solution during various times; then, while maintaining potentiostatic control, CO was bubbled for 2 min, followed by Ar for 5 min, after which the SPAIRS measurements were initiated. The cathodic charge passed through the working electrode prior to the SPAIRS experiments was determined with a digital coulometer and taken as a measure of the hydrogen load. The spectrum acquired at −0.7 V was taken as reference.

Figure 1 shows the result obtained from experiment (i). A bipolar band centred at 1900 cm^{-1}, due to shift of the stretching frequency of bridge adsorbed CO with the electrode potential [10], is observable at low potentials (cf., for example, spectra at 75 and 130 mV in Figure 1), turning into an increasingly negative peak at more positive potentials, indicating the displacement of CO from the interface up to 350 mV, then remaining constant at more positive potentials. A positive peak

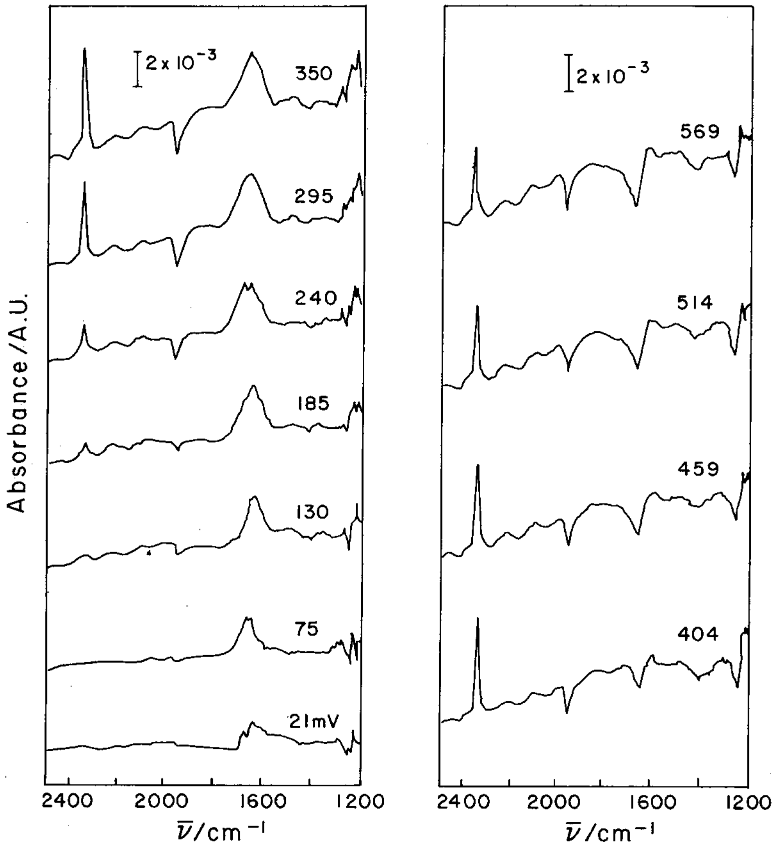


Fig. 1. SPAIRS spectra of hydrogen-free palladium electrode in contact with 0.1 M NaF solution, at the potentials indicated in mV, after adsorption of a monolayer of CO. Initial potential: 0 mV. Sweep rate: 1 mV s^{-1}.

at 2345 cm^{-1}, due to CO_2, starts growing at 130 mV, attaining maximum intensity at 300 mV and decreasing at more positive potentials. The positive band around 1640 cm^{-1} is due to absorption by water [25] and is also present in experiments with other electrolytes, such as $NaPF_6$ and $NaClO_4$ (not shown).

A result of an experiment of the second kind, obtained occluding in Pd 0.1 C (1.0×10^{-6} mole) of hydrogen, is shown in Figure 2. The bipolar band at 1900 cm^{-1} between −615 and −501 mV becomes a negative peak from −385 to −214 mV, remaining constant at more positive potentials. Positive peaks at 1400 and 2865 cm^{-1} start growing from −501 mV, attaining maximum intensities at −214 mV, the former completely disappears at potentials more positive than about 71 mV and at higher potentials becomes negative. Another positive band at 1465 cm^{-1}, a doublet, starts developing at 129 mV, shifting to 1473 cm^{-1} (just noticeable at the 8 cm^{-1} resolution used) at 759 mV. Finally, the positive peak of CO_2 formation at 2345 cm^{-1} starts growing at −43 mV, becoming more intense as the potential increases. The assignment of the bands, at 1400, 1465, 2345 and 2865 cm^{-1}, not observed in experiments carried out under conditions in which hydrogen sorption was deliberately excluded, will be discussed below.

Figure 3 shows the result obtained with a considerably increased amount of occluded hydrogen, 2.15 C (2.2×10^{-5} mol). The initially bipolar band at 1900 cm^{-1} becomes a negative peak that increases up to −113 mV and remains constant at more positive potentials; that at 1400 cm^{-1} first increases with potential, but then decays and does not appear at potentials positive to about −169 mV. The 2345 cm^{-1} peak appears at −284 mV and increases with potential up to 534 mV. In contrast with the results shown in Figure 2, peaks at 2865 and 1465 cm^{-1} were not observed at high loading of Pd with H.

The intensities of the 2345 cm^{-1} peaks obtained at various loadings with occluded hydrogen are shown as a function of the potential in Figure 4. In the absence of H, the amount of CO_2 increases rapidly from 0 V and peaks at 300 mV, decaying at more positive potentials. Upon loading with 1.0×10^{-6} or 2.2×10^{-5} mol of hydrogen, formation of CO_2 starts at progressively more negative potentials and increases over a considerably wider potential range.

4. Discussion

The spectra obtained in the absence of occluded hydrogen (cf. Figure 1) show features related to the oxidation of CO at increasing potentials. The negative signal at 1900 cm^{-1} indicates the decreasing presence of CO at the interface from 185 mV onwards, coincident with the appearance of the peak at 2345 cm^{-1} due to

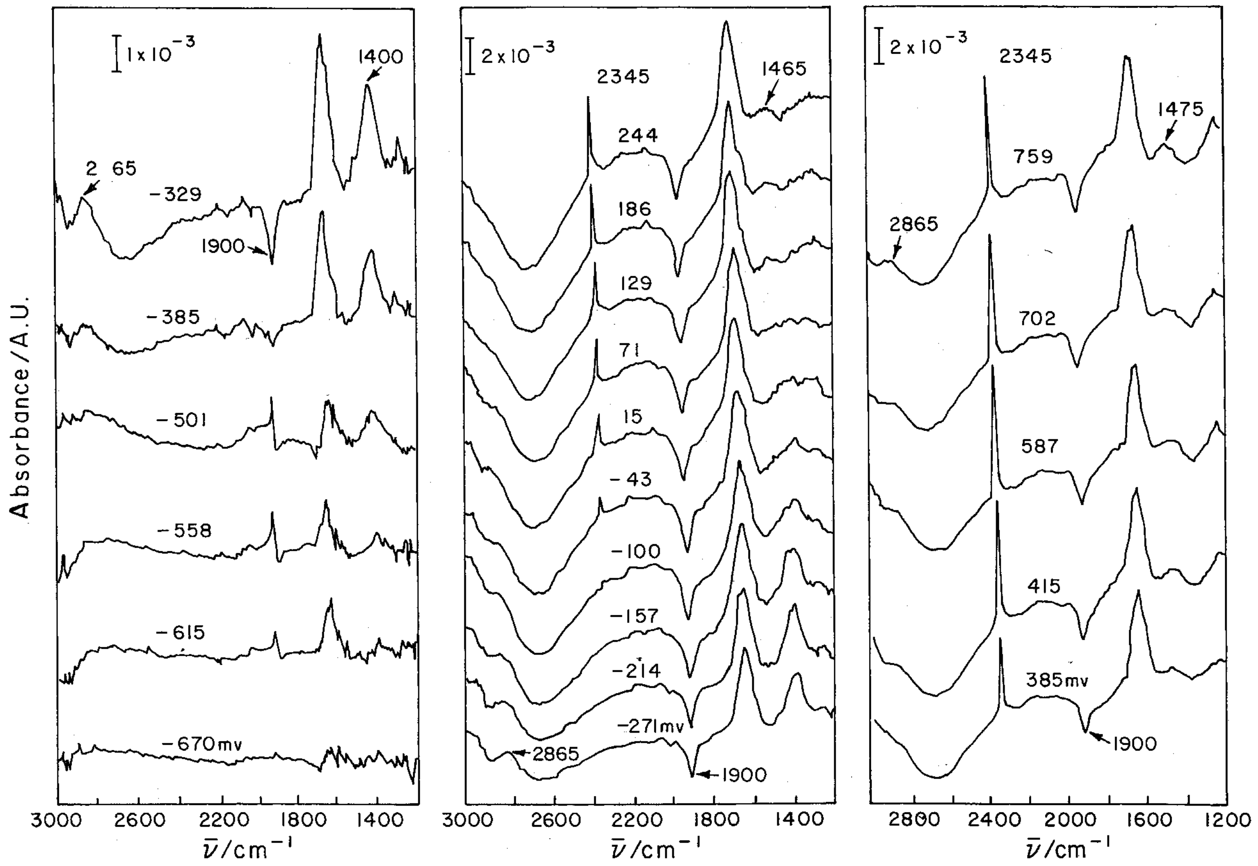


Fig. 2. SPAIRS spectra of palladium electrode loaded with 0.1 C (1.0×10^{-6} mol) hydrogen, in contact with 0.1 M NaF solution after adsorption of a monolayer of CO. Initial potential: −700 mV. Sweep rate: 1 mV s^{-1}. See text for further details.

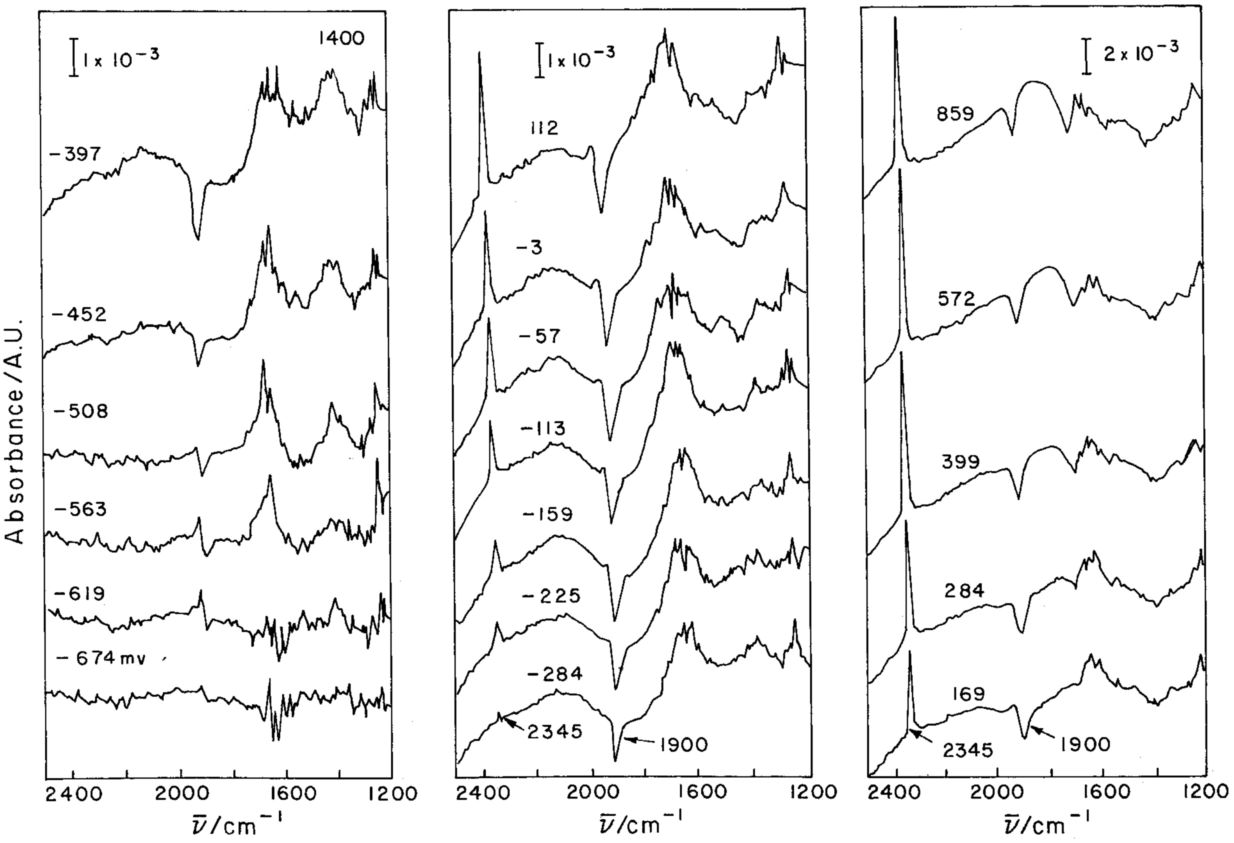


Fig. 3. SPAIRS spectra of palladium electrode loaded with 2.15 C (2.2×10^{-5} mol) hydrogen, in contact with 0.1 M NaF solution after adsorption of a monolayer of CO. Initial potential: −700 mV. Sweep rate: 1 mV s^{-1}. See text for further details.

CO_2 [21]. Constant intensity of the 1900 cm^{-1} negative peak due to exhaustion of CO at the interface, and decreasing intensity of the 2345 cm^{-1} positive peak beyond 350 mV, due to CO_2 diffusion in solution, indicates that conversion of CO to CO_2 is completed at about 350 mV.

Figures 2 and 3 show differences when CO adsorption is carried out concurrently with hydrogen absorption at −0.7 V, as compared with CO adsorption in its absence at 0 V. At the onset of the potential sweep, the absorption band related to CO at 1900 cm^{-1} [10] is present. This band was not observed in experiments with the potential for CO adsorption restricted to 0 V in order to exclude the presence of hydrogen on the electrode, in which lower coverages with adsorbed CO were attained.

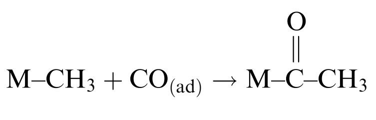
Apart from differences in the band related to CO adsorption and its conversion into CO_2 upon oxidation at higher potentials, the spectra obtained in the presence of hydrogen occluded in palladium show bands corresponding to the presence of additional species at the interface. The strong signals at 1400 and 2865 cm^{-1} grow concurrently with potential as the presence of CO at the interface decreases, and are indicative of the formation of CH_3—CO [26] and C—H (sp^3 hybridisation) bonds during CO oxidation, instead of CO_2, as in the absence of H occluded in palladium. Upon electrooxidation of CO from the interface, the intensity of the 1400 cm^{-1} band decreases down to zero at 71 mV in the presence of H. Methanol and formaldehyde are produced during reduction of CO_2 in aqueous phase with hydrogen occluded in palladium [18], and chromatographic analysis of reaction products during CH_4 electrooxidation on hydrogen loaded Pd shows the presence of CH_3OH, CH_3CH_2OH and $(CH_3)_2CHOH$ [27]. Thus, the rise of the CH_3 band is possibly due to formation of methyl groups through reaction of chemisorbed CO with occluded hydrogen,

$$CO_{(ad)} + 2\,H^{\cdot} \rightarrow H_2CO_{(ad)} \qquad (1)$$

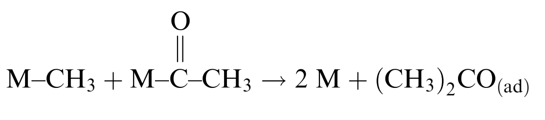
$$H_2CO_{(ad)} + 2\,H^{\cdot} \rightarrow CH_3OH_{(ad)} \qquad (2)$$

$$CH_3OH_{(ad)} + H^{\cdot} \rightarrow M\text{–}CH_3 + H_2O \qquad (3)$$

while formation of higher hydrocarbon chains is produced during hydrogenation of CO on metal catalysts, for example, as in the Fischer–Tropsch process [28], by insertion of adsorbed alkyl groups into carbonyl,



$$M\text{–}CH_3 + CO_{(ad)} \rightarrow M\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_3 \qquad (4)$$



$$M\text{–}CH_3 + M\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_3 \rightarrow 2\,M + (CH_3)_2CO_{(ad)} \qquad (5)$$

where M is a site on the surface, leading to formation of other species such as alcohols by further reaction with occluded hydrogen,

$$(CH_3)_2CO_{(ad)} + 2\,H^{\cdot} \rightarrow (CH_3)_2CHOH \qquad (6)$$

and giving rise, for example, to the band observed at 1465 cm^{-1} at high potentials. This band appears as a doublet, it is then likely that the growth of the chain is in this case symmetric, the doublet arising from $-CH_3$ gem dimethyl absorption from isopropyl alcohol. The 2865 cm^{-1} and 1465 cm^{-1} bands were observed under conditions of low hydrogen flux, as discussed below. At higher hydrogen load, these reaction products of CO with occluded H may quickly abandon the surface and, hence, not seen. In contrast, at high hydrogen load, a negative band at about 1700 cm^{-1} was observed at potentials above 284 mV (cf. Figure 3), indicating the disappearance of aldehyde or ketone species, formed by chemical reaction between CO and occluded H as indicated in Equations 1–6, and being electrooxidized to CO_2 at higher potentials, in agreement with the observed increase of the CO_2 band. In all cases, CO_2 is formed at sufficiently positive potentials, although significantly favoured in the presence of occluded hydrogen.

In the absence of occluded hydrogen, an abrupt rise of the CO_2 absorption band with potential obtains (cf. Figure 4) due to reaction of $CO_{(ad)}$ with $OH_{(ad)}$, the latter originated from water oxidation on the surface [29],

$$H_2O \rightarrow OH_{(ad)} + H^+ + e^- \qquad (7)$$

$$CO_{(ad)} + OH_{(ad)} \rightarrow COOH \qquad (8)$$

$$COOH \rightarrow CO_2 + H^+ + e^- \qquad (9)$$

In the presence of occluded hydrogen (cf. Figures 2 and 3), the CO_2 absorption band appears at lower potentials, does not rise abruptly, and its intensity depends on the amount of hydrogen occluded in the electrode. At these lower potentials, the coverage of the electrode surface by $OH_{(ad)}$ is negligible and conversion of $CO_{(ad)}$ to CO_2 occurs through an alternative route, involving participation of occluded hydrogen but not $OH_{(ad)}$ (cf. Equation 1),

$$H_2CO_{(ad)} + H_2O \rightarrow CO_2 + 4\,H^+ + 4\,e^- \qquad (10)$$

Thus, the presence of hydrogen in palladium induces a negative shift in the onset potential for CO oxidation. Considering that, in the presence of hydrogen, CO electrooxidation begins through eqn. (1), and that in the absence of hydrogen a 0.75 coverage of CO gives rise to 0.0114 A.U. of CO_2 [30], the amount of hydrogen consumed by reaction with chemisorbed CO was estimated. These amounts are given as fractions of the hydrogen occluded in palladium in Table 1. Given that the duration of the experiments, including hydrogen loading, CO adsorption and oxidation, was about 30 min, the average penetration depth of the occluded

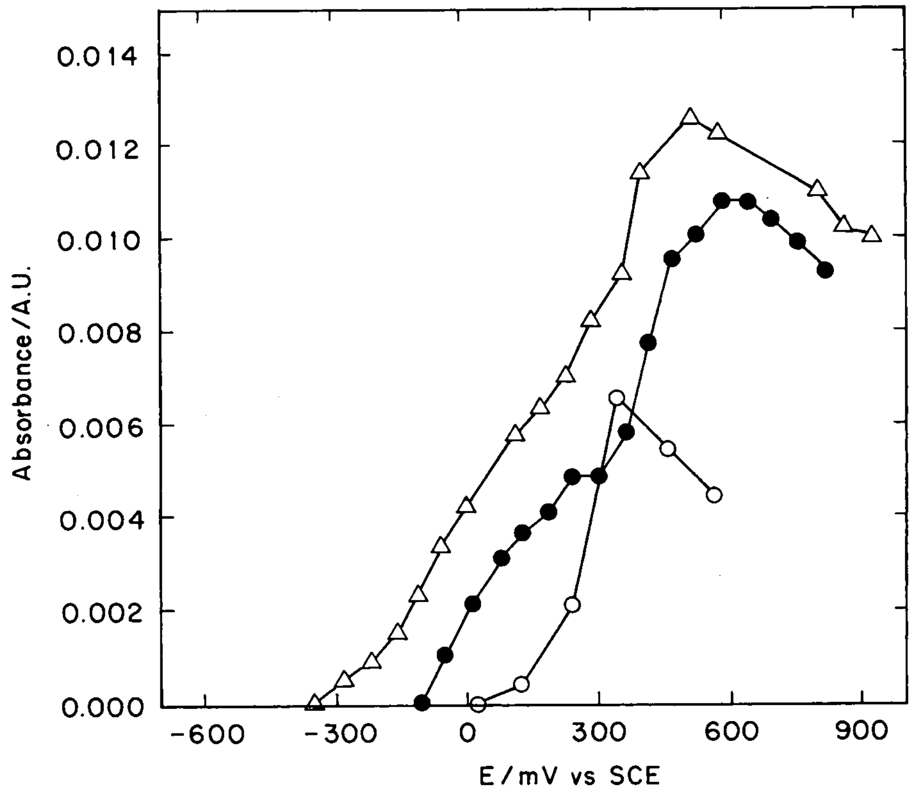


Fig. 4. Amount of CO_2 produced as a function of electrode potential, on palladium electrodes loaded with 0.0 (○), 0.1 (●) and 2.2 (△) C of hydrogen.

Table 1. Fraction of hydrogen used for displacement of $CO_{(ad)}$ from the interface

Hydrogen load		Hydrogen used for CO displacement		%
Charge/C	Amount/mol	Charge/C	Amount/mol	
0.10	1.0×10^{-6}	1.8×10^{-4}	1.8×10^{-9}	0.18
2.15	2.2×10^{-5}	2.1×10^{-4}	2.2×10^{-9}	0.01

hydrogen, estimated from $\langle \Delta x \rangle^2 = 2Dt$, where $D \approx 10^{-7}$ cm^2 s^{-1} [31, 32] is the diffusion coefficient of H in Pd, is about 0.02 cm, from which the H/Pd ratios may be estimated as about 0.001 and 0.03 for the experiments involving 0.1 and 2.15 C of hydrogen load, respectively. Given that the upper limit for the α phase is H/Pd = 0.015 [4], it follows that the first experiment corresponds to H/Pd in the α phase, while it is likely that the second may correspond to the β phase. In either case, large excesses of occluded hydrogen were available for reaction with CO. At sufficiently positive potentials with respect to the hydrogen electrode, the flux of hydrogen through the electrode/solution interface becomes independent of the electrode potential; nonetheless, its flux depends upon the amount of hydrogen occluded. Thus, the more hydrogen occluded, the more negative is the onset potential for CO_2 production.

5. Conclusion

CO adsorbs irreversibly on palladium and interferes with the electrooxidation of organic compounds. In the absence of occluded hydrogen, CO_2 was the sole oxidation product detected. The oxidation of CO on palladium commences at significantly more negative potentials in the presence of hydrogen, leading to products other than CO_2, such as higher alcohols.

The results described in this work indicate that hydrogen occluded in palladium contributes to the displacement of carbon monoxide from the interface, leading to the formation of CO_2 as well as other oxidation products, at lower potentials than required in its absence. The release of hydrogen may thus provide a viable route for lowering the surface concentration of adsorbed CO, permitting the continual oxidation of organic compounds at the palladium surface, as we will report elsewhere [33].

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