

DEMS study on the nature of acetaldehyde adsorbates at Pt and Pd by isotopic labelling

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Received: 28 September 2006 / Revised: 26 February 2007 / Accepted: 2 March 2007 / Published online: 27 June 2007
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Abstract The formation of acetaldehyde adsorbates on Pt and Pd has been studied applying cyclic voltammetry and differential electrochemical mass spectrometry (DEMS). The adspecies were isolated on the metal surface at selected adsorption potentials (E_{ad}) applying a flow cell procedure under potential control, and the anodic stripping were performed for each E_{ad} . For Pt, two different contributions were established during oxidation: one at $E < 0.80$ V and the second in the range 0.80–1.50 V in the Pt oxide region. For Pd, the voltammetric profile resembles that for the oxidation of adsorbed CO. DEMS experiments have shown that CO₂ was the sole electro-oxidation product in both cases. The oxidation of each C atom in acetaldehyde adsorbates has been distinguished using the isotopic-labelled aldehyde ($^{12}CH_3^{13}CHO$) in DEMS experiments at selected E_{ad} . It was observed that, on Pt, acetaldehyde molecules loose part of the CH₃ groups during adsorption at $E_{ad} < 0.40$ V, whereas the CHO groups are easily oxidized at $E_{ad} > 0.40$ V. Therefore, both C₁ and C₂ species are present on the surface, and their yields depend on E_{ad} . On the contrary, on Pd, most of the CH₃ groups are lost during adsorption at all E_{ad} , and the main adsorbed species seems to be CO_{ad}.

Keywords Acetaldehyde adsorbates · DEMS · Cyclic voltammetry · Isotopic labelling

Dedicated to Prof. Dr. Teresa Iwasita on the occasion of her 65th birthday in recognition of her numerous contributions to interfacial electrochemistry.

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Introduction

Acetaldehyde can be considered a model for C₂ organic compounds in electro-catalytic systems, especially for the understanding of the mechanism of aldehydes oxidation and breaking of C–C bonds. But the interest is also related to its formation during ethanol oxidation, a target compound in fuel cells. In this context, it has to be considered that for ethanol oxidation at Pt-based electrodes (for example, [1–7]), the low efficiency towards oxidation to CO₂ is due to the presence of parallel reactions with the production of acetaldehyde and acetic acid. Recently, it has been proved that for concentrated ethanol solution, the pathway producing the aldehyde becomes predominant [8, 9].

Although ethanol oxidation has been widely investigated, scarce studies can be found concerning the electro-reactivity of acetaldehyde, and these refer mainly to Pt [3–6, 10–13]. It has been reported that the amount of CO₂ evolved during electro-oxidation at Pt in the range 0.01–1 M is almost constant, suggesting that in this reaction pathway, the amount of adsorbate limits the production of the gas [10]. Only CO_{ad} was detected from in situ infrared spectroscopy in the presence of bulk acetaldehyde [4–6], but other adspecies have been established from the spectra obtained after application of a flow cell procedure [12].

According to these results, the oxidation of the residues is the crucial path for the production of CO₂, and therefore, the nature of the adspecies is relevant for the oxidation mechanism and C–C scission. In the present paper, differential electrochemical mass spectrometry (DEMS) is applied to study the electro-oxidation of acetaldehyde adsorbates isolated at Pt after a flow cell procedure. Isotopic labelling of acetaldehyde ($^{12}CH_3^{13}CHO$) allows distinguishing between the C atom containing the CHO group and that with the CH₃ group, through the production

of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. Moreover, fragmentation during adsorption can be also analyzed from the integration of the corresponding mass signals.

Finally, the experiments were also performed with Pd and compared with Pt. We have previously reported a DEMS study on the electro-oxidation of acetaldehyde on Rh [13, 14], but to our knowledge, no similar spectroscopic research has been performed on the reactivity at Pd.

Materials and methods

General Solutions were prepared from Millipore-MilliQ* water and analytical grade reagents. 0.02 M CH_3CHO (Merck p.a.) was used as working solution for adsorption experiments in 0.1 M HClO_4 (Merck p.a.) as base electrolyte. Isotopic-labelled acetaldehyde ($^{12}\text{CH}_3^{13}\text{CHO}$, MSD Isotopes, ^{13}C 90%) was employed for DEMS. All experiments were carried out in electrochemical flow cells at room temperature under Ar (99.998%) atmosphere.

The working electrodes were whether a Pt/Pd foil (1.6–2.2 cm^2 real area, 0.5 cm^2 geometric area) for cyclic voltammetry or a porous Pt/Pd layer sputtered on a microporous polytetrafluoroethylene (PTFE) membrane for DEMS experiments (10–20 cm^2 real area, 0.8 cm^2 geometric area, see later). The electrochemical cells were completed with a plate or a wire of platinized Pt as counter electrode and a reversible hydrogen electrode in the supporting electrolyte as reference. All potentials in the present paper are referred to this value.

DEMS The DEMS system consists of an electrochemical cell directly attached to a vacuum chamber containing the quadrupole mass spectrometer (Balzers QMG 112) with a Faraday cup detector. The working electrode was a porous layer sputtered onto a PTFE membrane (Scimat, 200/40/60). This membrane forms the interface between the electrochemical cell and the ionization chamber of the mass spectrometer. The experimental setup allows the simultaneous detection of mass spectrometric cyclic voltammograms (MSCVs) for selected mass-to-charge ratios (m/z) and cyclic voltammograms (CVs) at a scan rate of $\nu = 0.01 \text{ V s}^{-1}$. Details of this method have been given elsewhere [15–17]. Both working electrodes were activated in the supporting electrolyte solution by potential cycling at 0.01 V s^{-1} , between the onset for hydrogen and oxygen evolution in the case of Pt, and between 0.20 and 1.40 V in the case of Pd.

Adsorption procedure Acetaldehyde was adsorbed on Pt/Pd at controlled adsorption potentials (E_{ad}) in the range 0.07–

0.70 V for Pt and 0.15–0.07 V for Pd. Then, the anodic stripping of the isolated adspecies was performed. The complete experimental procedure consists of the following steps:

1. Adsorption. The potential was set at E_{ad} in the supporting electrolyte during the anodic scan until the current reaches a stationary value and the acetaldehyde solution was introduced in the cell during 10 min.
2. Elimination of bulk acetaldehyde. Subsequently, the solution was completely replaced by pure base electrolyte under potential control at E_{ad} . To ensure a total electrolyte replacement, about 10 times the volume needed to fill the electrochemical cell was allowed to flow through.
3. Stripping of the adlayer. Acetaldehyde residues were oxidized through the application of a positive-going potential scan starting from E_{ad} up to the anodic limit at a scan rate of 0.05 and 0.01 V s^{-1} for cyclic voltammetry and DEMS, respectively. For the latter experiments, CVs and MSCVs for CO_2 were simultaneously recorded.

Determination of K^* The DEMS system was calibrated following the procedure described in [15] using CO (99.999%) as a probe molecule. The value of K^* (the constant of the mass spectrometer) can be evaluated using the expression:

$$Q_M = (K * A Q_1) / n$$

where A is the faradaic efficiency of the reaction and n the number of electrons involved in the reaction per molecule of the product. Q_1 and Q_M are the faradaic charge and the ion charge associated with the fragments of the product reaching the mass analyzer, respectively. For CO, its electrochemical oxidation yields CO_2 ($n=2$) in a single potential cycle with a faradaic efficiency of 100%. With the value of K^* , n can be calculated for the adsorbed species obtained from acetaldehyde.

Results and discussion

Adsorption on Pt

Adsorption experiments were performed on polycrystalline Pt in the potential range $0.07 \leq E_{\text{ad}} \leq 0.60 \text{ V}$ from 0.10 V each 0.05 V. The anodic stripping of the adspecies is given in Fig. 1. First, it is remarkable that, opposite to the adsorption of saturated alcohols, acetaldehyde adsorbs on Pt highly covered with hydrogen; that is, acetaldehyde is able to displace H_{ad} during adsorption. On the other hand,

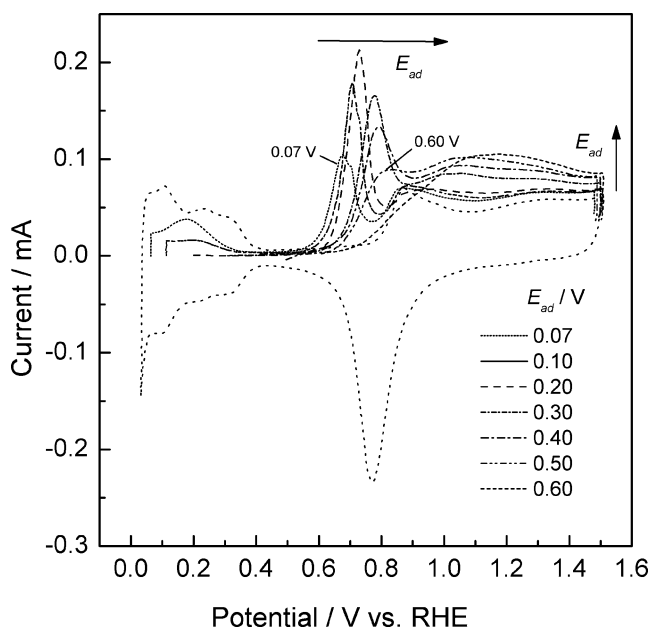


Fig. 1 Anodic stripping of acetaldehyde adsorbates formed on Pt in 0.1 M HClO₄ at the values of E_{ad} indicated in the figure. $\nu=0.05$ V s⁻¹; area=1.6 cm². (Dotted line) CV in the supporting electrolyte

two different oxidation regions are clearly defined in the CVs. One is located at $E < 0.80$ V in the double layer region, where a peak is defined in the same potential region for CO_{ad} oxidation. This peak shifts positively with increasing E_{ad} , but the charge involved passes through a maximum at $E_{ad}=0.20$ V and then decreases. The second contribution is a broad feature located in the Pt oxide region, which increases with E_{ad} .

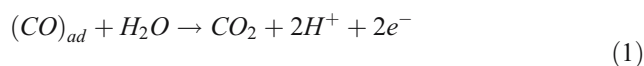
DEMS studies in the same conditions have shown that the sole oxidation product from acetaldehyde adsorbates is CO₂. Three E_{ad} were selected, which are representative for the changes in the shape of the anodic features with E_{ad} . CVs and corresponding MSCVs for $m/z=44$ ([CO₂]⁺) at $E_{ad}=0.10, 0.40,$ and 0.60 V can be seen in Fig. 2. For the most negative E_{ad} , the first contribution in the MSCV attains a peak at 0.62 V, and the second is weak, but a maximum is apparent at 1.03 V. The ion current for $E_{ad}=0.60$ V displays only the second feature with the maximum at the same potential. Finally, in the case of $E_{ad}=0.40$ V, both contributions are important, the first peak shifted to 0.69 V.

The experiments were repeated at the selected adsorption potentials with isotopic-labelled acetaldehyde (¹²CH₃¹³CHO). Thus, it is possible to follow the oxidation of the CH₃ (mass signal for $m/z=44, [^{12}\text{CO}_2]^+$) and CHO groups (mass signal for $m/z=45, [^{13}\text{CO}_2]^+$). Furthermore, the integration of both ion currents (σ_{45} and σ_{44}) is proportional to the amount of each group in the adsorbed layer (it should be the same if both C atoms remain at the surface). From these values, it is possible to establish the loose part of these groups during adsorption. All ionic

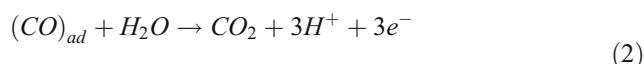
charges obtained from the MSCVs and charge ratios, as well as n values (number of electrons per CO₂ molecule formed during the oxidation), are summarized in Table 1.

The MSCVs for $m/z=44$ and 45 are given in Fig. 3. It has to be mentioned that the mass signals have been corrected assuming that 10% of acetaldehyde was not isotopic labelled (see “Materials and methods”).

It is clearly shown that for $E_{ad}=0.10$ V, the adsorbate mainly originates from the CHO as the intensity of the signal $m/z=44$ is much lower ($\sigma_{45}/\sigma_{44}=4.6$, see Table 1). Moreover, the oxidation occurs below 0.80 V and resembles that for CO_{ad} oxidation. Accordingly, the value of $n=2.6$ at this E_{ad} is between those corresponding to (CO)_{ad} ($n=2$) and (COH)_{ad} ($n=3$).



$$n = 2/1 = 2$$



$$n = 3/1 = 3$$

In previous DEMS studies, methane was established at $E < 0.20$ V during potential cycling in an acetaldehyde

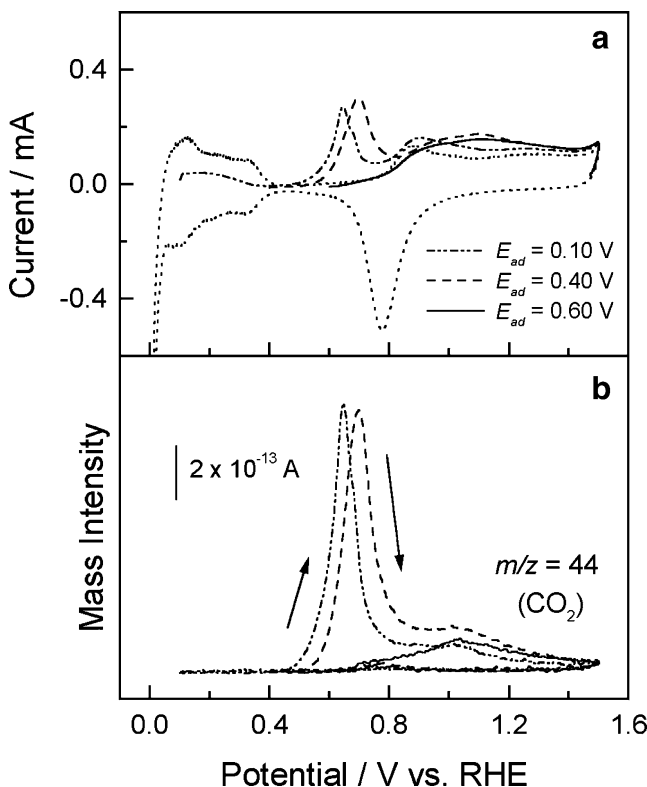


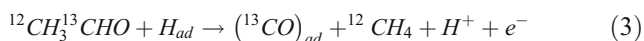
Fig. 2 Anodic stripping of acetaldehyde adsorbates formed from ¹²CH₃¹³CHO on Pt at $E_{ad}=0.10, 0.40,$ and 0.60 V. **a** CVs and **b** MSCVs for CO₂ ($m/z=44$). $\nu=0.01$ V s⁻¹; $A=18.8$ cm². (Dotted line) CV in the supporting electrolyte (0.1 M HClO₄)

Table 1 Charge densities obtained from the MSCVs for the signals $m/z=44$ ($^{12}\text{CO}_2$) and $m/z=45$ ($^{13}\text{CO}_2$) from Fig. 3 for Pt and Fig. 6 for Pd

E_{ad}/V	$10^{13} \sigma_{\text{CO}_2}/\text{C cm}^{-2}$		σ_{45}/σ_{44}	n
	$m/z=45$	$m/z=44$		
Platinum				
0.10	4.1	0.88	4.6	2.7
0.40	2.9	3.1	0.9	3.2
0.60	0.76	1.5	0.5	3.7
Palladium				
0.20	11.3	0.85	13.2	1.9
0.40	11.4	1.0	11.4	2.0
0.60	6.6	1.1	6.0	1.9

Values of n at selected E_{ad}

containing solution [3, 13]. Therefore, the following adsorption reaction is confirmed:



It is concluded that in this potential region, dissociation of acetaldehyde takes place (at least in part) favored by the presence of H_{ad} .

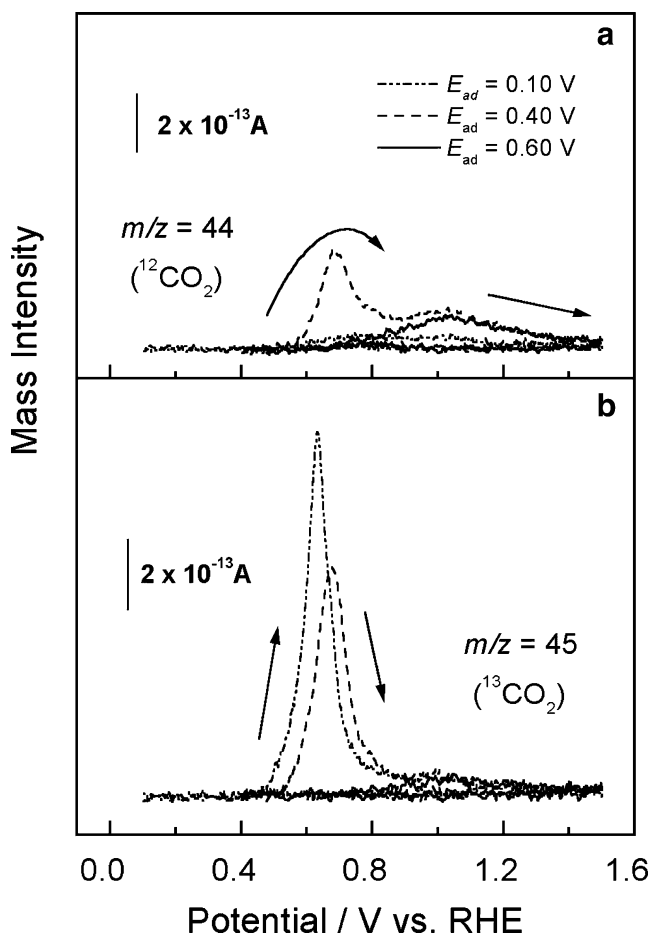
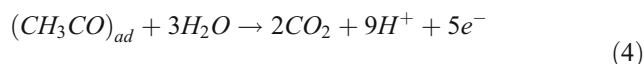
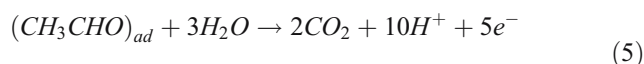


Fig. 3 MSCVs recorded during the anodic stripping of acetaldehyde adsorbates formed from $^{12}\text{CH}_3^{13}\text{CHO}$ on Pt. MSCVs for **a** $m/z=44$ ($^{12}\text{CO}_2$) and **b** $m/z=45$ ($^{13}\text{CO}_2$). Same conditions as Fig. 2

In the case of $E_{ad}=0.60$ V, the ratio $\sigma_{45}/\sigma_{44}=0.5$ indicates that at this potential, part of the CHO groups is already oxidized to CO_2 during adsorption, and then, CH_3 groups prevail on the surface. The value of n at this E_{ad} is 3.7, which confirms the presence of more hydrogenated adsorbates [as examples, n values for $(\text{CH}_3\text{CO})_{ad}$ and $(\text{CH}_3\text{CHO})_{ad}$ oxidation are 4.5 and 5, respectively].



$$n = 9/2 = 4.5$$



$$n = 10/2 = 5$$

Only at $E_{ad}=0.40$ V, the ion charge for both CO_2 signals is similar (see Table 1). Therefore, dissociation during adsorption seems to be less important at this E_{ad} . It should be noticed that both signals for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ contribute to the current associated to the first peak. This result implies that both CHO and CH_3 groups could be oxidized at potentials below the Pt oxide region.

Adsorption on Pd

CVs for the electro-oxidation of adsorbed acetaldehyde on polycrystalline Pd in the range $0.15 \leq E_{ad} \leq 0.70$ V can be seen in Fig. 4. Except for $E_{ad}=0.60$ V, in all cases, the adsorbate describes a sharp peak around 0.90 V with inhibition of the Pd oxide formation. These curves resemble

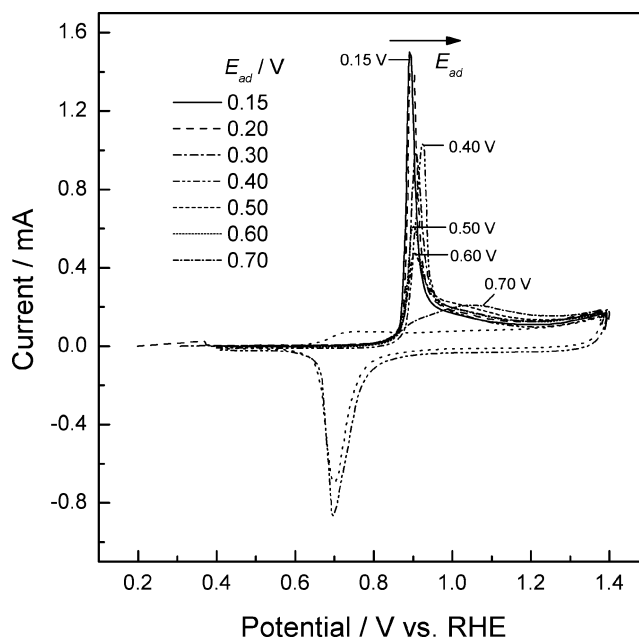


Fig. 4 Anodic stripping of acetaldehyde adsorbates on Pd in 0.1 M HClO_4 formed at the values of E_{ad} indicated in the figure. $\nu=0.05$ V s^{-1} ; area=2.6 cm^2 . (Dotted line) CV in the supporting electrolyte

that for CO_{ad} stripping. The amount of adsorbed species as well as the peak intensity decrease with E_{ad}. However, the shift in the peak position is small. At E_{ad}=0.70 V, the peak at 0.90 V is no more apparent, and a broad contribution centered at 1.06 V is developed. The amount of adsorbate at this E_{ad} is drastically decreased, probably due to the lack of CH₄ production during adsorption at this potential and the direct oxidation of the CHO group to CO₂. Then the adspecies is mainly related to the CH₃ which needs more positive potentials for the oxidation.

As in the case of Pt, only CO₂ is detected from DEMS experiments (Fig. 2). Selected E_{ad} for DEMS were 0.20, 0.40, and 0.60 V (0.20 was chosen instead of 0.10 V to avoid hydrogen absorption at Pd). MSCVs for m/z=44 in Fig. 2b show that the amount of CO₂ involved in the peak (in the potential range 0.70–1.00 V) diminishes with increasing the adsorption potential, but the yield at E > 1.00 V is independent on E_{ad}.

After calibration of the mass spectrometer, the values of n at the three potentials approximates 2, which is the value expected for the oxidation to CO₂ of a monolayer CO_{ad} (reaction 1). Accordingly, it is concluded that reaction (3) is the main process in the whole potential range.

The experiments with ¹²CH₃¹³CHO demonstrate this fact. Thus, the main contribution to the total CO₂ signal in

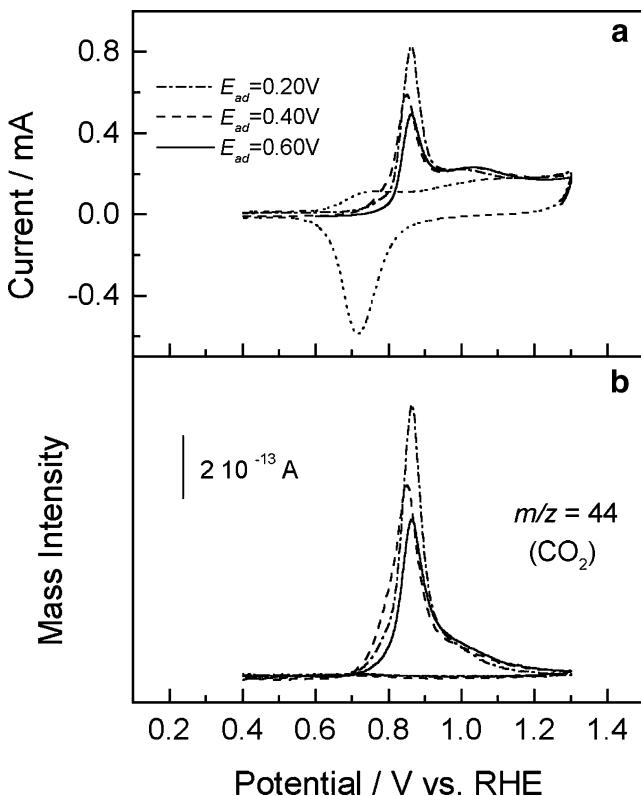


Fig. 5 Anodic stripping of acetaldehyde adsorbates formed from ¹²CH₃¹²CHO on Pt at E_{ad}=0.20, 0.40, and 0.60 V. **a** CVs and **b** MSCVs for CO₂ (m/z=44). ν=0.01 V s⁻¹; A=15.8 cm². (Dotted line) CV in the supporting electrolyte (0.1 M HClO₄)

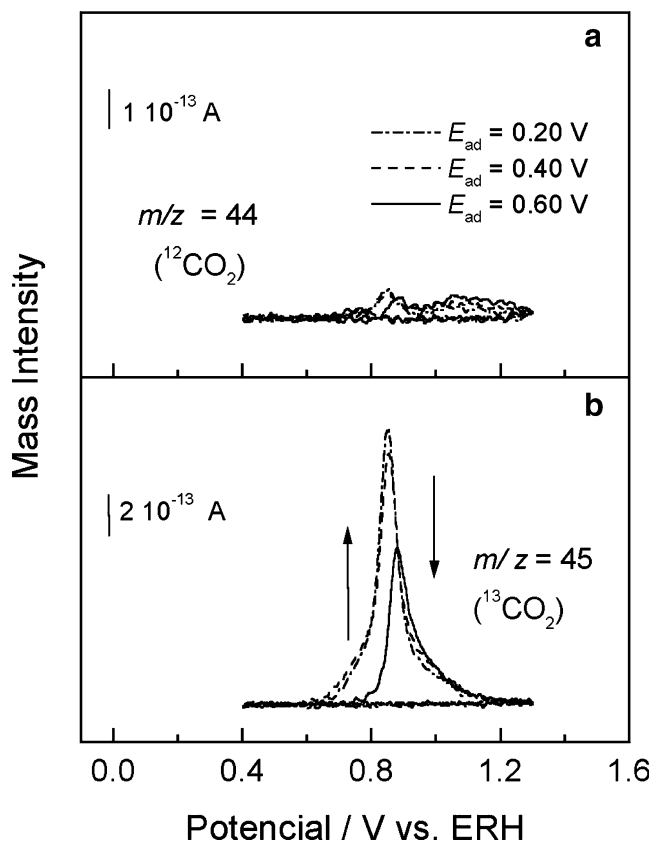


Fig. 6 MSCVs recorded during the anodic stripping of acetaldehyde adsorbates formed from ¹²CH₃¹³CHO on Pd. MSCVs for **a** m/z=44 (¹²CO₂) and **b** m/z=45 (¹³CO₂). A=12.3 cm². Same conditions as Fig. 5

Fig. 5b is related to the production of m/z=45 ([¹³CO₂]⁺) (see Fig. 6b). This ion current follows the CV in Fig. 5a. The intensity of the signal for m/z=44 ([¹²CO₂]⁺) in Fig. 6a is very small (the ratio σ₄₅/σ₄₄ is high at all adsorption potentials, although it decreases with E_{ad}), and in this case, a broad contribution between 0.80 and 1.30 V is apparent. These results indicate that the origin of the species on the surface is the CHO group and only traces of CH₃ remains adsorbed, the latter increasing with E_{ad}.

Comparison between both metals let us establish that Pd can break the C–C bond much easily than Pt, but both C atoms cannot be oxidized. The C atom from the CHO remains on the surface as CO_{ad} and that from the CH₃ is lost during adsorption as methane [18]. In the case of Pt, the fragmentation of the molecule after reaction (3) occurs only at E_{ad}<0.20 V, and at more positive potentials, the adsorbate maintains both C₂. For E_{ad}>0.60 V oxidation of the CHO group can occur at Pd and Pt.

Conclusions

Acetaldehyde adsorbates on Pt and Pd can be isolated on the metal surfaces applying a flow cell procedure. Cyclic

voltammetry combined with online mass spectrometric detections (DEMS) are appropriate techniques to follow the changes in the adsorbed layer with E_{ad} . Isotopic labelling of aldehyde ($^{12}CH_3^{13}CHO$) enables to study the oxidation of each C atom. At Pt, the oxidation takes place in two stages: first, a peak develops at $E < 0.80$ V, in the same potential region for the oxidation of CO_{ad} on this metal; and then, a broad contribution is apparent up to the upper limit of the scan. For $E_{ad} = 0.20$ and 0.60 V, fragmentation of acetaldehyde occurs during the production of methane from the CH_3 group at the former potential and oxidizing the CHO group at the latter. At $E_{ad} = 0.40$ V, both C_2 atoms are retained on the surface. The main contribution for the faradaic current at $E < 0.80$ V is related to the CHO group whereas that at $E > 0.80$ V is due to the CH_3 group.

In the case of Pd, the adsorption in the potential range 0.20 – 0.60 V implies the rupture on the C–C bond in the molecule, with the production of high amounts of methane and adsorption of CO from the CHO group in acetaldehyde.

Acknowledgements Financial support from MEC (MAT2005-06669-C03-02 and NAN2004-09333-C05-04, Feder, Spain) is acknowledged. J.A. S-C. and O. G-V. thank Cajacanarias for the fellowship.

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