In situ FTIRS study of ‘reduced’ CO₂ on columnar-structured platinum electrodes in different acid media

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Abstract

In situ Fourier transform infrared spectra (FTIRS) of species related to ‘reduced’ CO₂ (r-CO₂) adsorbates formed on columnar-structured Pt electrodes in aqueous 0.5 M HClO₄, 0.5 M H₂SO₄ and 0.5 M H₃PO₄ at 25°C are presented. From spectral, electrochemical and electrode topography data, the appearance of different types of complex adsorbates involving CO₂, H_{ad}, multi, bridge-, and linearly bonded CO has been concluded. The influence of anions on the CO adsorbate adsorption band is tentatively interpreted through changes in the water-electrolyte structure caused by different types of anions. © 1997 Elsevier Science S.A.

1. Introduction

The adsorption of CO₂ on Pt electrodes takes place in the H-atom electroadsorption potential range, leading to adsorbates usually called ‘reduced’ CO₂ adsorbates (hereafter denoted as r-CO₂ adsorbates) [1–23]. Authors of all works agree that CO₂ adsorption on Pt results from a CO₂–H-atom interaction, although there are different interpretations regarding the stoichiometry and properties of the adsorbed species. These adsorbates are of a particular interest for understanding the kinetics and mechanism of CO₂ electroreduction reactions as well as the electrooxidation of some organic molecules.

According to mass spectrometry data, the stoichiometry of r-CO₂ adsorbates on Pt corresponds to COH occupying three adsorption sites and requiring the removal of three electrons to be oxidized [7,12,24], although radiotracer and transient electrochemical techniques data lead to COOH as the stoichiometric composition of the r-CO₂ adsorbate [25]. Otherwise, previously reported EMIRS data of r-CO₂ adsorbates showed that CO_{ad} was one important species [26], but it was suggested that other species could also be present on the Pt surface in acid solutions.

On the other hand, CO-adsorbates formed on columnar-structured Pt (hereafter denoted as cs-Pt) electrodes in acid solutions [27,28] suggested that the poisoning effect by CO-adsorbates for this type of electrodes was less than on smooth Pt. This conclusion was in a fair qualitative agreement with a slightly greater electrocatalytic activity of cs-Pt electrodes for CO-adsorbate electrooxidation [29]. Nevertheless, the changes in EMIRS were much greater than those observed from electrochemical data. These ambiguous conclusions could be the result of the Pt surface heterogeneity, which possibly induces the formation of several forms of r-CO₂ adsorbates on Pt. The possibility of preparing cs-Pt electrodes, i.e., Pt electrodes with a defined rough topography [30–32], and the development of in situ FTIRS spectroscopy, a technique which, when used under the SPAIRS variant, avoids the possible changes at the electrochemical interface caused by electrode potential modulation, offer the possibility of a further investigation of CO₂ adsorbates on Pt in acid solution. In situ FTIRS has been recently used to investigate the formation of r-CO₂ surface complexes on smooth Pt electrodes in acid electrolytes [33].

Columnar-structured Pt electrodes can be produced easily by electroreduction of Pt hydrous layers of different thicknesses [30]. The cs-Pt structure was characterized by combining scanning tunneling microscopy imaging (STM) and electrochemical data [29,34]. Under appropriate prob-

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ing conditions, the cs-Pt surface can be described as a self-affine surface fractal [31]. This means that the accessibility of a particular adsorbate to the entire electrode surface should depend not only on the adsorbate–substrate and adsorbate–adsorbate specific interactions, but also on the adsorbate cross-section and irregularity size distribution at the surface [32]. The average irregularity size of these electrodes as seen through STM imaging is in the 10–15 nm range, i.e., the average irregularity size at the surface is much smaller than the wavelength of the light beam employed in IR spectroscopy.

For small size adsorbates such as H- and O-adatoms [34], CO- [29], and r-CO₂ adsorbates [17,19–21], the entire cs-Pt electrode surface, including the inner parts of the columns, becomes fully accessible. Thus, the evaluation of the roughness factor for this type of electrode becomes possible by means of conventional voltammetry [35].

This work is devoted to investigating the behaviour of r-CO₂ adsorbates on cs-Pt electrodes in various acid solutions aiming to enhance surface effects on the formation and reactions of adsorbed species, as well as to evaluate the influence of electrode roughness on spectrochemical data related to the electrodecomposition of r-CO₂ adsorbates on Pt.

2. Experimental

Columnar-structured (cs) Pt electrodes were prepared by the electrochemical technique already described in previous publications [17,30], which includes the accumulation of a Pt hydrous oxide layer by applying to the electrode a fast periodic potential routine, and then electroreducing the oxide layer by means of a slow linear potential scan. The roughness factor of the electrode, ρ , was evaluated as the ratio between the corresponding H-adatom voltammetric charge per cm² of active surface area and the calculated 210 $\mu\text{C cm}^{-2}$ charge involved in the formation of a full H-adatom monolayer at a smooth Pt electrode. For this study, two different cs-Pt electrodes were employed, with $\rho = 7$ and $\rho = 80$, respectively. Both electrodes exhibited, at low magnification, a homogeneous aspect and good reflectance.

The cs-Pt electrode was mounted in the spectroelectrochemical cell, which was equipped with a CaF₂ IR transparent window. The cell was completed with a Pt wire counterelectrode and a hydrogen reference electrode (RHE) in the same solution (potentials in the text are given in the RHE scale). The following aqueous electrolyte solutions were used: 0.5 M HClO₄, 0.5 M H₂SO₄ and 0.5 M H₃PO₄, prepared from concentrated acid (Merck suprapur) and Millipore-Milli-Q water.

Experimental measurements were made as follows: the solution was deoxygenated by N₂ bubbling and a voltammogram at the potential sweep rate $v = 0.05 \text{ V s}^{-1}$ was taken to check the system purity and to determine the

value of ρ . Subsequently, CO₂ was bubbled through the cell while holding the working electrode potential at a selected potential value, $E_{\text{ad}} \leq 0.29 \text{ V}$, during 30 min, thus achieving saturation coverage by adsorbate species when $E_{\text{ad}} \leq 0.20 \text{ V}$. Before commencing the spectroscopic measurement, CO₂ was removed from the solution by bubbling N₂ for 30 min while still holding the potential at E_{ad} . Then, the electrode was pushed against the optical window so that it remained in contact with a thin layer of electrolyte.

Two experimental procedures were employed to obtain IR data, namely, SPAIRS (single potential alteration infrared reflectance spectroscopy) [36] and SNIFTIRS (subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy) [37–39].

With SPAIRS, a series of spectra resulting from either 512 or 2048 interferograms, to increase the signal-to-noise ratio, were collected during the voltammetric sweep at a very slow rate, at successive potentials E . Results were displayed as $\Delta R/R = (R_{E_2} - R_{E_1})/R_{E_1}$, with $E_2 > E_1$. Different subtractions of spectra were made, depending on the choice of the reference spectrum (R_{E_1}).

With SNIFTIRS, modulation between two switching potentials A and B was made. 128 interferograms were accumulated and Fourier transformed alternatively at each potential, 50 times. The total time for the process was 20 min, and data were displayed as the ratio $\Delta R/R = (R_A - R_B)/R_B$.

The electrochemical set-up consisted of a LB 81 Wenking potentiostat, a Hi-tek waveform generator and a BD90 X-Y recorder. The Fourier transform infrared spectrometer was a Bruker IFS 66v which was modified for beam reflection upon the electrode surface with an angle of incidence of 65°. The beam path was under vacuum to avoid the interference of atmospheric water and CO₂ signals. Either *p*- or *s*-polarized IR light was employed. A N₂ cooled Infrared Associates HgCdTe detector was used. All measurements were made at $25 \pm 2^\circ\text{C}$.

3. Results and discussion

3.1. Cyclic voltammetry results

Anodic stripping voltammograms of CO₂-containing adsorbates formed at $E_{\text{ad}} = 0.05$, 0.20 and 0.29 V, were run at $v = 0.5 \text{ mV s}^{-1}$ simultaneously to the acquisition of spectra. Fig. 1 refers to $E_{\text{ad}} = 0.05 \text{ V}$. For the three acid media, these voltammograms show a multiplicity of anodic current peaks in the region 0.38–0.80 V. The electrooxidation starts at ca. 0.38 V in 0.5 M HClO₄, 0.42 V in 0.5 M H₃PO₄ and 0.45 V in 0.5 M H₂SO₄ solution. The two components of the oxidation peak are more clearly distinguishable in aqueous 0.5 M HClO₄ ($E_{\text{pI}} = 0.57 \text{ V}$, $E_{\text{pII}} = 0.62 \text{ V}$), while in aqueous 0.5 M H₂SO₄ and 0.5 M H₃PO₄ the second component is shown only as a shoulder at the

Fig. 1. Voltammograms obtained simultaneously to the acquisition of spectra. $\nu = 0.5 \text{ mV s}^{-1}$; $\rho = 80$; $E_{\text{ad}} = 0.05 \text{ V}$. Current densities are referred to the Pt electrode area before the cs-Pt preparation. Acid medium: (A) 0.5 M HClO_4 ; (B) 0.5 M H_2SO_4 ; (C) 0.5 M H_3PO_4 .

positive side of the main peak which occurs at ca. 0.63 and 0.615 V, respectively (Table 1).

The adsorbate anodic stripping is completed at 0.66 V in aqueous 0.5 M HClO_4 and at ca. 0.75 V in the other two acid media. This is an indication that, in aqueous 0.5 M HClO_4 , there is a narrow potential window where the electrode surface is free from both organic adsorbates and oxygen-containing species.

3.2. SPAIRS study

SPAIR spectra were taken for cs-Pt electrodes ($\rho = 7$ and $\rho = 80$) in the three acid media using p - and s -polarization, after CO_2 adsorption at $E_{\text{ad}} = 0.05, 0.20$ and 0.29 V . For $E_{\text{ad}} = 0.29 \text{ V}$ only strongly adsorbed H-atoms are produced in the base electrolyte. Adsorption is very slow at this potential, and saturation coverage with r- CO_2 adsorbates is not attained for the adsorption time employed in our experiments, i.e., measurements at $E_{\text{ad}} = 0.29 \text{ V}$ correspond to low adsorbate coverage values.

3.2.1. General description of spectra

Fig. 2 shows SPAIR spectra (p -polarization) obtained after CO_2 adsorption at 0.05 V in 0.5 M H_2SO_4 solutions. Qualitatively similar spectra are obtained in 0.5 M HClO_4 and 0.5 M H_3PO_4 solutions. Spectra are displayed as $\Delta R/R$, and have been calculated using as reference the spectrum at 0.05 V, R_{E_1} . Accordingly, a band correspond-

ing to a species appearing at E_1 and absent at E_2 , would result in the $\Delta R/R$ spectrum as a monopolar upwards-going band, whereas a species that exists only at E_2 results in a monopolar downwards-going band. Otherwise, a species which is present both at E_1 and E_2 , results in a bipolar band, because of the expected wavenumber shift with potential of adsorbed species [37–39].

At first sight, the spectra like those of Fig. 2 show the appearance of bands in the wavenumber ranges of CO_{ad} (2100 to 1850 cm^{-1}), CO_2 (ca. 2345 cm^{-1}), water (ca. 1640 cm^{-1}) and anions (1250 to 1000 cm^{-1}). There are no obvious bands for other types of species such as HCOOH , HCHO , $\cdot\text{COOH}$, $\cdot\text{CHO}$, COH , etc., which could be related to r- CO_2 adsorbates, or to their subsequent redox forms. A striking feature of spectra like those depicted in Fig. 2 is the very strong intensity of the CO_2 band, as compared to that of CO_{ad} .

3.2.2. Adsorbed CO spectra

Among the most significant spectral bands found in this work are those corresponding to CO adsorbates. These adsorbates are present at negative potential values with respect to the main voltammetric oxidation peak, and the corresponding bands generally shift with potential. For studying the intensity and position of these bands, it is convenient to use a reference spectrum R_{E_1} , in which the CO adsorbate bands no longer exist. Spectra of CO_{ad} species produced at $E_{\text{ad}} = 0.20 \text{ V}$ in a 0.5 M H_2SO_4 solution, where $E_1 = 0.90 \text{ V}$ and where E_2 was changed from 0.20 to 0.80 V, are shown in Fig. 3. Analogous spectra are obtained when working in 0.5 M HClO_4 and 0.5 M H_3PO_4 solutions.

The main CO_{ad} band, at ca. 2050 cm^{-1} , appears as a monopolar asymmetrical band, irrespective of the solution composition and the value of ρ . This band corresponds to CO linearly bonded to the surface (CO_L) and its asymmetry increases with ρ . This fact suggests the existence of different states for CO_L , probably associated with different

Table 1

Peak potentials, measured on cyclic voltammograms ($\nu = 0.5 \text{ mV s}^{-1}$), for the electrooxidation of r- CO_2 adsorbates formed at three different adsorption potentials, in three different acid solutions

Acid medium	$E_{\text{ad}} (\text{V}_{\text{RHE}})$	$E_{\text{pl}} (\text{V}_{\text{RHE}})$	$E_{\text{ph}} (\text{V}_{\text{RHE}})$
HClO_4	0.05	0.57	0.62
	0.20	0.58	0.62
	0.29	0.58	0.625
H_2SO_4	0.05	0.63	shd
	0.20	0.65	shd
	0.29	0.65	shd
H_3PO_4	0.05	0.615	shd
	0.20	0.625	shd
	0.29	0.595	shd

shd denotes that the peak is observed only as a shoulder.

Fig. 2. SPAIRS at various potentials of 'reduced' CO_2 adsorbates at a cs-Pt electrode ($\rho = 80$) in $0.5 \text{ M H}_2\text{SO}_4$. $E_{\text{ad}} = 0.05 \text{ V (RHE)}$; spectral subtraction with spectrum obtained at 0.05 V (RHE) ; p -polarization; potential as follows: (a) 0.17 V , (b) 0.37 V , (c) 0.47 V , (d) 0.57 V , (e) 0.67 V , (f) 0.77 V , (g) 0.87 V , (h) 1.07 V , (i) 1.27 V and (j) 1.47 V . Spectra B are the same as A, but with the Y scale expanded 10 times.

types of adsorption sites at the substrate surface, which are related to the various surface crystallographic orientations (polyorientation).

The band near 1870 to 1850 cm^{-1} can be attributed to multibonded CO (i.e., noted CO_m). This band is of a lower

intensity and it is more difficult to observe than that of CO_l . Its presence is also evident in spectra like those given in Fig. 2. In general, the greater the contribution of the CO_m band, the lower the value of E_2 and the greater the value of ρ .

Fig. 3. SPAIRS at various potentials of 'reduced' CO_2 adsorbates at cs-Pt electrodes of $\rho = 7$ (A) and $\rho = 80$ (B) in $0.5 \text{ M H}_2\text{SO}_4$. $E_{\text{ad}} = 0.2 \text{ V (RHE)}$; spectral subtraction with spectrum obtained at 0.90 V (RHE) ; p -polarization; potential as follows: (a) 0.2 V , (b) 0.3 V , (c) 0.4 V , (d) 0.5 V , (e) 0.6 V , (f) 0.7 V , (g) 0.8 V , (h) 0.2 V , (i) 0.1 V , (j) 0 V , (k) 0.1 V , (l) 0.2 V , (m) 0.4 V , (n) 0.6 V , (o) 0.8 V .

Fig. 4. SPAIRS at various potentials of 'reduced' CO_2 adsorbates at a cs-Pt electrode ($\rho = 80$) in 0.5 M H_2SO_4 , s -polarization; $E_{\text{ad}} = 0.05$ V (RHE); spectral subtraction with spectrum obtained at 0.05 V (RHE); potential as follows: (a) 0.17 V, (b) 0.37 V, (c) 0.47 V, (d) 0.57 V, (e) 0.67 V, (f) 0.77 V, (g) 0.97 V, (h) 1.07 V, (i) 1.37 V. Spectra B is the same as A, but with a 10 times enlarged Y scale.

3.2.3. Effect of s - and p -polarized light

SPAIRS measurements with p -polarized light at a perfectly smooth surface provide information about both adsorbed species and species in solution, whereas measurements with s -polarized light supply data only about species in solution. However, s -polarized spectra obtained with cs-Pt electrodes (Fig. 4) also show bands that can be assigned to adsorbed species. Thus, the CO_L band, although smaller in intensity than in p -polarized spectra, is undoubtedly present in all experiments run with s -polarized light. This effect was also found to be present when using a smooth Pt electrode (not columnar-structured), but only as very small bands. Therefore, the presence of the more accentuated band due to adsorbed species in the s -polarized spectra on cs-Pt electrodes should be an effect of the topography of such electrodes, and not a defect in the s -light coming from the polarizer. Seemingly, these spectroscopic data would indicate that the so-called 'surface selection rule' [37–39] is no longer applicable for adsorbed species at cs-Pt. The reason why this happens is at present known. Further investigations will follow to give an explanation for this effect.

The CO_L s - and p -polarization band intensity ratio (I_s/I_p) for all the electrolytic media, the adsorption potentials, and the ρ values are given in Table 2. The I_s/I_p ratio, which should be ideally zero for $\rho = 1$, corresponds to finite figures, which decrease with ρ , for cs-Pt electrodes.

3.2.4. Anion effect on the CO_L absorption band

The position of the CO_L band shifts with the applied potential. When these adsorbates are formed on smooth Pt directly from dissolved CO in solution, it is well known that the wavenumber shift of the corresponding absorption band is about $+30 \text{ cm}^{-1} \text{ V}^{-1}$ [40,41]. However, when CO_L is formed from r-CO_2 on cs-Pt, the wavenumber vs. potential plot yields a straight line also (Fig. 5) but the slope of this line is always less than $+30 \text{ cm}^{-1} \text{ V}^{-1}$.

Table 2

Band intensity ratio (I_s , polarization)/(I_p , polarization) for CO_L at different ρ , E_{ad} values and acid media

Acid medium	ρ	E_{ad} (V _{RHE})	I_s/I_p ^a
HClO_4	7	0.05	0.24
	80	0.05	0.48
	80	0.20	0.39
	80	0.29	0.38
H_2SO_4	7	0.05	0.25
	80	0.05	0.35
	80	0.20	0.25
	80	0.29	0.28
H_3PO_4	80	0.05	0.47
	80	0.20	0.47
	80	0.29	0.38

^a I_s = CO_L band intensity in s -polarization; I_p = CO_L band intensity in p -polarization.

(Table 3). This value depends slightly on ρ and on the nature of the acid medium, and the smallest slopes in this work are always obtained in aqueous 0.5 M HClO₄.

Furthermore, it should be noted that the wavenumber of the CO-adsorbate IR band is about 20–25 cm⁻¹ lower than that expected for a full surface coverage by r-CO₂ [42]. Thus, there is a chemical shift due to the presence of co-adsorbates that act reversely and competitively to the Stark effect. Besides, the fact that the slope decreases as ρ increases suggests that the anion-substrate interaction is enhanced as ρ is increased.

Another interesting feature derived from the comparison of spectra run in the three electrolytic media (Fig. 5), is that the wavenumber of the CO_L band in aqueous 0.5 M H₂SO₄ is about 3–4 cm⁻¹ higher than that in other acids. This wavenumber shift, even if its magnitude is weak, is seen consistently whatever the experimental conditions (Fig. 5). Therefore, from these spectral data, one can conclude that there is a definite anion effect on the adsorbate properties and structure.

3.2.5. CO_L and CO₂ bands intensities

A band at 2343 cm⁻¹ corresponding to CO₂ starts to appear in the spectra at a potential value that coincides with the initiation of the voltammetric oxidation peak. Simultaneously, the CO_L band diminishes, and finally disappears completely at ca. 0.7 V, or even slightly earlier in aqueous 0.5 M HClO₄. Considering the experimental

Fig. 5. Wavenumber vs. electrode potential plots for the CO_L signal. Acid medium: □ — — — HClO₄; ○ - - - H₂SO₄; ● - - - H₃PO₄. (A) $\rho = 7$, $E_{ad} = 0.05$ V; (B) $\rho = 80$, $E_{ad} = 0.05$ V; (C) $\rho = 80$, $E_{ad} = 0.2$ V.

Table 3

Slopes of the linear wavenumber vs. potential plots for the CO_L absorption band resulting for different ρ , E_{ad} and acid media

Acid medium	ρ	E_{ad} (V _{RHE})	Slope (cm ⁻¹ V ⁻¹)
HClO ₄	7	0.05	22
	80	0.05	16
	80	0.20	18
H ₂ SO ₄	7	0.05	24
	80	0.05	20
	80	0.20	25
H ₃ PO ₄	7	0.05	24
	80	0.05	19
	80	0.20	20

procedure, and the fact that no other reduced species could be detected, one comes to the conclusion that CO₂ can be produced only by oxidation of CO_{ad}, whose major form is CO_L, or by release of weakly adsorbed CO₂.

According to Leung and Weaver [43,44], the extinction coefficient for CO₂ is about 1.5 times that of CO_L. Thus, their band intensities should be in roughly the same ratio, provided that their surface concentrations are about the same. However, the experimental data show a CO₂ band intensity much larger than that of CO_L (Table 4). Their intensity ratio increases by a factor close to 10 in going from $\rho = 7$ to $\rho = 80$ for the three electrolytic media, i.e., the ratio increases according to the real surface area of the working electrodes.

Some results obtained on smooth Pt under the same experimental conditions used in the present work were taken from the literature [33] and included in Table 4 for the sake of comparison. One can observe that these results approach the ideal situation. It is interesting to note that, for ex-Pt, the absolute value of the CO_L band intensity increases with ρ , but that it is far from a direct proportionality. In aqueous 0.5 M H₂SO₄ and at $E_{ad} = 0.05$ V for instance, it changes from 0.20 for $\rho = 1$ (smooth Pt) to 0.45 for $\rho = 80$.

Conversely, a much larger dependence on ρ is observed for the CO₂ band intensity, even if this intensity value cannot be accurately determined because CO₂ produced along the anodic stripping diffuses away from the electrode surface to the bulk of the solution. There is always a small amount of CO₂ that 'escapes' before it can be detected spectroscopically. Although the CO₂ band intensity might be somewhat smaller than that expected if all CO₂ produced could be detected, there is a rough proportionality between the intensity of the band and the increase of ρ . Values of q_{ox} , the oxidation charge density resulting from the voltammograms taken simultaneously with the spectroscopic measurements, are also summarized in Table 4. In all cases the values of q_{ox} are directly proportional to ρ , as already reported in previous publications [17,19–21].

Table 4

CO_L and CO₂ *p*-polarized band intensity ratio and *q*_{ox}, the total voltammetric oxidation charge density, resulting for different *ρ*, *E*_{ad} and acid media

Acid medium	ρ	E_{ad} (V_{RHE})	I_{COL} ^a	I_{CO_2} ^a	I_{CO_2}/I_{COL} ^a	q_{ox} ($mC\ cm^{-2}$) ^b	q_{ox}/ρ ($mC\ cm^{-2}$)
HClO ₄	7	0.05	0.27	0.99	3.7	1.66	0.23
		0.20	0.31	1.54	5.0	1.71	0.25
		0.29	0.28	1.25	4.5	0.82	0.11
	80	0.05	0.40	15.4	38	15.7	0.19
		0.20	0.47	17.0	36	16.2	0.20
		0.29	0.34	14.3	42	13.2	0.17
H ₂ SO ₄	1 ^c	0.08	0.20	0.28	1.4	—	—
		0.20	0.27	0.41	1.5	—	—
	7	0.05	0.31	1.41	4.5	1.51	0.22
		0.20	0.33	1.41	4.3	1.54	0.22
		0.29	0.21	0.91	4.3	1.33	0.19
	80	0.05	0.45	20.3	45	16.2	0.20
		0.20	0.52	21.6	42	16.7	0.21
		0.29	0.23	12.8	56	13.3	0.17
	H ₃ PO ₄	7	0.05	0.21	0.86	4.1	1.36
0.20			0.31	0.91	2.9	1.36	0.19
0.29			0.08	0.65	8.1	1.04	0.15
80		0.05	0.45	17.7	39	16.0	0.20
		0.20	0.46	17.5	38	17.0	0.21
		0.29	0.12	8.61	72	9.0	0.11

^a *I*_{COL}: CO_L band intensity; *I*_{CO₂}: CO₂ band intensity. Both are given in absorbance units.^b Charge density referred to the electrode area 'before' the cs-Pt preparation process (smooth Pt substrate).^c Smooth Pt data taken from the original spectra of Ref. [33], for a Pt electrode of the same area as the apparent electrode area used in this work.

Interestingly, it can be seen in the same table that the ratios *q*_{ox}:*ρ* at *E*_{ad} = 0.05 V and *E*_{ad} = 0.20 V always lead to a nearly constant value, close to 0.21 mC cm⁻², i.e., the reference charge associated to a one-electron process for a

full monolayer at a smooth surface (*ρ* being ideally 1). In other words, as two electrons are exchanged for the electrooxidation of CO_L species, the corresponding coverage can be estimated as very close to *θ* = 0.5 irrespective of

Fig. 6. SNIPTIRS of 'reduced' CO₂ adsorbates at a cs-Pt electrode (*ρ* = 7) in 0.5 M HClO₄ (A), 0.5 M H₂SO₄ (B) and 0.5 M H₃PO₄. *p*-polarization; *E*_{ad} = 0.05 V (RHE); potential modulation between: (a) 0.05 and 0.35 V (RHE); (b) 0.15 and 0.45 V (RHE); (c) 0.25 and 0.55 V (RHE), and (d) 0.35 and 0.65 V (RHE).

the roughness of the surface. However, when the adsorption potential is more positive, $E_{ad} = 0.29$ V, the ratios $q_{ox} : p$ tend to decrease, due to the decrease of the coverage itself, but also possibly to a proportionally more important contribution of CO_B or CO_m species.

3.3. SNIFTIRS results

The SNIFTIRS technique is particularly useful for studying adsorbed species involving potential-dependent absorption bands. Accordingly, adsorbates can be detected much more clearly with SNIFTIRS than with SPAIRS, provided that no decomposition of the adsorbate takes place during potential modulation [39].

3.3.1. Comparison of SNIFTIRS data obtained with the three electrolytic media

SNIFTIR spectra after adsorption at 0.05 V obtained in the three acid media for different modulation limits are shown in Fig. 6. No CO_2 bands can be observed in these spectra, except for aqueous 0.5 M $HClO_4$ for the 0.25–0.55 V modulation range. In contrast, very clear CO_{ad} bands related to three different kinds of adsorbed species can be seen. The most intense band, at ca. 2050 cm^{-1} , is assigned to CO_L , and the band at ca. 1850 cm^{-1} corresponds to CO_m . SNIFTIR spectra show the band at ca. 1850 cm^{-1} better defined than with SPAIRS. Finally, the presence of a weak band at ca. 1960 cm^{-1} , presumably due to bridge bonded CO (CO_B), can also be observed.

The fact that there are no 'carbonyl' bands within the 1800 to 1600 cm^{-1} range, confirms that the strong band seen with SPAIRS at ca. 1640 cm^{-1} is due only to the H_2O -deformation mode $\delta(HOH)$. A similar conclusion can be drawn from results by Aramata et al. [45].

As far as the role of anions is concerned, these results show that the ClO_4^- ion band depends strongly on E , whereas this dependence is hardly seen for HSO_4^-/SO_4^{2-} ions, and it is definitely not observed for those ions coming from aqueous H_3PO_4 .

3.3.2. Influence of the spectral accumulation time

The usual procedure in SNIFTIRS is to accumulate series of 128 interferograms alternately at each potential limit, repeating the process 50 times. Thus, to determine the $\Delta R/R$ ratio, R_A and R_B are obtained by averaging, respectively, 50 spectra obtained at potentials A and B . This process takes about 20 min to complete, and occasionally significant differences between spectra obtained at the beginning and at the end of the experiment were noticed. These differences are missed in the averaging process and, for this reason, it was convenient to calculate $\Delta R/R$ at three stages of the measurement. Results obtained through this procedure are displayed in Fig. 7. A different number of spectra at each limit has been averaged, i.e., 10 in Fig. 7a (total acquisition time ca. 4 min), 25 in Fig. 7b (ca. 10 min), and 50 in Fig. 7c (ca. 20 min).

Fig. 7. SNIFTIRS of 'reduced' CO_2 adsorbates at a Cs-Pt electrode ($p = 7$) in 0.5 M $HClO_4$ and during the spectral accumulation: (a) after 4 min of accumulation (averaging), (b) after 10 min of accumulation, (c) after 20 min of accumulation; p -polarization; $E_{ad} = 0.05$ V (RHE); potential modulation between 0.15 and 0.45 V (RHE).

The modulation limits were fixed between 0.15 and 0.45 V because, in aqueous 0.5 M $HClO_4$, 0.45 V is just the limit at which $r\text{-}CO_2$ adsorbates anodic stripping commences, as seen from voltammetry. Thus, the total intensity of CO_{ad} bands diminishes slightly with the accumulation time, which means that a small amount of adsorbate is oxidized without readsorbing. But the most interesting feature of these results is that I_{pp} , the peak to peak intensity, remains about the same for CO_m , whereas it decreases with time for CO_L . Two different interpretations can be advanced for this fact; namely, (a) CO_L is more easily oxidized than CO_m , i.e., CO_L 'disappears' before CO_m , or (b) CO_m is easier to oxidize than CO_L , but the CO_m surface coverage remains constant (steady state) due to a fast adsorbate rearrangement process at the surface that can be represented as $CO_L \rightarrow CO_m$. These two explanations account, in principle, for the experimental results, but the second one appears to be more consistent with the CO_L and CO_m adsorption energies, and with the well-known fact that, at low coverage, it is the CO_m form that prevails.

3.4. Influence of the nature of anions

The influence of anions at different potentials on the adsorbed layer structure can be followed on spectra like those depicted in Fig. 2 for aqueous 0.5 M H_2SO_4 solutions and the analogous ones in 0.5 M $HClO_4$ and 0.5 M H_3PO_4 solutions. For each medium, the nature of partici-

Table 5

Reference IR bands for anions in the 1000–1300 cm^{-1} wavenumber range

Electrolyte	ν (cm^{-1})	Reference
HClO_4^-	1119	[46]
HClO_4 , aq	1117	This work, Fig. 8
HSO_4^-	1160–1200	[47–52]
SO_4^{2-}	1060	[47–52]
H_2SO_4 , aq	1084, 1160–1290	This work, Fig. 8
H_2PO_4^-	1030–1090 cm^{-1}	[53]
H_2PO_4^-	1077, 1153 and 1256	[54]
HPO_4^{2-}	1050–1070	[53]
PO_4^{3-}	1050–1100	[53]
H_3PO_4 , aq	1010, 1165 and 1250	[54]
H_3PO_4 , aq	1032, 1075, 1128, 1249	This work, Fig. 8

pating species (neutral or ionic) can be deduced from the location of their IR absorption bands [46]. Table 5 gives the characteristic wavenumbers of the different species that can be present in the electrolytic media. There are rather large discrepancies between wavenumbers and the band assignments given by authors for ionic species, especially for bisulfate and sulfate species. References are just given here without comment, as their discussion is beyond the scope of this work. Data given in Table 5 for bands due to aqueous acid components correspond to transmission spectra of aqueous acid solutions obtained in the same thin-layer spectroelectrochemical cell (see Fig. 8).

Two main potential dependent changes are generally seen in the band intensity of anions. Thus, in aqueous 0.5 M HClO_4 , the main species in solution is the ClO_4^- anion, whose absorption band appears at ca. 1117 cm^{-1} . Striking

intensity changes of this band take place at ca. 0.60 V, where the substrate is free from CO_{ad} species, and at ca. 0.97 V, where the adsorption of oxygen-containing species becomes significant.

Otherwise, in aqueous 0.5 M H_2SO_4 , the dominating anion in solution is HSO_4^- , with absorption bands at ca. 1200 and 1050 cm^{-1} , in agreement with the expected dissociation of H_2SO_4 in aqueous solution and previous spectroscopic work [47–53], although a minor contribution of SO_4^{2-} ion can also be noticed from the band at ca. 1100 cm^{-1} . In this medium, anion band intensity changes are observed at ca. 0.67 V and ca. 0.97 V [54].

Finally, spectra run in aqueous 0.5 M H_3PO_4 indicate a large contribution of non-neutral H_2PO_4^- species through the band at ca. 1180 cm^{-1} . Obviously, several ionic species are present, as shown by various small potential dependent bands in the 1100–1000 cm^{-1} range. A first band intensity change at ca. 0.65 V can be hardly seen, and a second band intensity change takes place at ca. 0.95 V.

From these results, it can be concluded that the first change in anion band intensity takes place exactly at the potential of the second voltammetric oxidation peak. This peak is well defined in aqueous 0.5 M HClO_4 and appears as a shoulder in other electrolytic media. Consequently, the first adsorbate electrooxidation stage does not imply a change of anion concentration close to the surface. Therefore, these results seem to indicate that the two electrooxidation voltammetric peaks of r-CO_2 adsorbates would be related, the first one to the electrooxidation of CO species in a 'surface complex', whereas the second one involves the electrooxidation of adsorbed hydrogen atoms forming part of the 'surface complex'. On the other hand, the fact that both voltammetric and spectroscopic measurements show a r-CO_2 -adsorbate electrooxidation that starts at a lower potential in aqueous 0.5 M HClO_4 , provides further support to the influence of anions in the formation of these adsorbates.

The second anion band intensity change observed in all media at about 0.95 V is undoubtedly related to the initiation of Pt surface oxide formation [55].

3.5. The nature of adsorbates

From a comparison of SPAIRS and SNIFTIRS data, adsorbates formed on Pt in an acid solution through the interaction of CO_2 with H-adatoms can be qualitatively described as adsorbates of a common nature, irrespective of the solution composition.

According to previously reported EMIRS data on smooth Pt surfaces [26], large quantities of CO_{ad} species are formed during the adsorption of CO_2 in acid media, and in this case no other bands due to carbonyl species (HCOOH , $\cdot\text{COOH}$, HCHO , $\cdot\text{CHO}$, etc.) were detected. This work confirms that different CO_{ad} species are actually produced by interaction of r-CO_2 with the Pt surface.

Fig. 8. Infrared reference spectra of different aqueous media: (a) HClO_4 , (b) H_2SO_4 and (c) H_3PO_4 .

Fig. 9. SPAIRS at various potentials of 'reduced' CO_2 adsorbates at a cs-Pt electrode ($\rho = 7$) in $0.5 \text{ M H}_3\text{PO}_4$, $E_{\text{ad}} = 0.05 \text{ V (RHE)}$; spectral subtraction with spectrum obtained at 0.05 V (RHE) ; p -polarization; potential as follows: (a) 0 V , (b) -0.03 V , (c) -0.12 V , (d) -0.20 V , (e) -0.12 V , (f) -0.03 V , (g) 0 V , (h) 0.05 V , (i) 0.20 V , (j) 0.40 V , (k) 0.60 V , (l) 0.80 V and (m) 1.00 V .

Among these species CO_L is dominant, whereas a minor contribution of CO_m (and presumably CO_H) species can be observed, in agreement with recent SNIFTIRS results [56]. It should also be noted that CO_L itself seems to be engaged in several types of adsorption sites as shown by the low wavenumber component of the band at ca. 2030 cm^{-1} , particularly when ρ , the electrode roughness factor, is increased.

The question of whether other adsorbed species could be formed but not be spectroscopically detected is still open to discussion. A possible answer to the absence of carbonyl bands would be that the applied potential was always insufficiently negative to yield reduced products involving these IR absorption bands, as the lowest negative potential in most cases was generally of about 0 V (RHE) . To test this idea, the following experiment was performed. The value of E_{ad} was first set at 0.05 V to form the r-CO_2 adsorbates. Then, the potential was stepwise shifted negatively down to -0.20 V ; at this potential the hydrogen evolution reaction proceeds at the entire electrode surface. Finally, the potential was moved positively up to 1.00 V . As the corresponding spectra (Fig. 9) showed no evidence of subsidiary bands, it could be concluded that this tentative explanation is inadequate.

The slightly different characteristics of the CO_L bands in the three different media can be, in principle, assigned to a specific influence of the anion on the adsorbate structure. This means that anions are somewhat involved in

the structure of adsorbed complexes. Seemingly, the strongest influence on the CO_{ad} band is due to the presence of ClO_4^- ions. Otherwise, the influence of aqueous H_2SO_4 or H_3PO_4 media is rather similar. This behaviour resembles the influence of the anionic composition of the solution on the voltammetric features of CO_{ad} -species, as discussed elsewhere [17,19–21,29]. The anion influence on the characteristics of the CO_L band can be interpreted either by a direct anion adsorption on the electrode surface, which induces a change in the surface energy distribution at adsorption sites, or by an anion-promoted structural change of the electrolyte solution, which reflects on the adsorbate structure itself.

It is well-known that aqueous ClO_4^- ions are weakly adsorbed on Pt, as compared to those ionic species resulting from aqueous H_2SO_4 or H_3PO_4 . This fact is consistent with the electrooxidation of r-CO_2 adsorbates in aqueous 0.5 M HClO_4 starting at lower potentials than in both aqueous $0.5 \text{ M H}_2\text{SO}_4$ and $0.5 \text{ M H}_3\text{PO}_4$, and leading to two distinguishable electrooxidation voltammetric peaks.

The results of this work suggest that the anion effect does not involve a predominantly anion-surface direct interaction, 'but interactions among anions and adsorbate complexes'. This assumption is supported by the fact that for r-CO_2 adsorbate formation, H -atoms produced by H_3O^+ electroreduction are required, and also by the ability of ions resulting from aqueous H_2SO_4 and H_3PO_4 solutions to modify the proper structure of water in the solution through hydrogen bonding, in contrast to HClO_4 solutions. Accordingly, the structure of adsorbed complexes would depend on the electrolyte composition [57,58] as expected, for instance, from Samoilov's theory for water-containing inorganic complexes [59]. Nevertheless, this first explanation for the influence of anions on the infrared spectra of r-CO_2 adsorbates still deserves further experimental work, and should be considered as a first attempt to explain the effects found.

3.6. Poisoning phenomena

Data clearly show that the quantity of CO_2 resulting from voltammetry is much greater than the quantity of CO_{ad} that is spectroscopically detected (Table 3). Thus, for $\rho = 80$, the $\text{CO}_2:\text{CO}_\text{L}$ ratio is about 40, whereas for $\rho = 7$ it is about 4. In principle, there are two possible explanations for these results; namely, either a large portion of CO_{ad} species is hidden in voids of the cs-Pt structure and it becomes spectroscopically undetectable, or another adsorbed species which is also electrooxidized to CO_2 rather than CO_{ad} , is present at the electrode surface. Considering the preceding discussion, the second possibility seems to be rather unlikely. If this were the case, then the increase of ρ leading to an increase in the apparent concentration of adsorbates should make the detection of any new adsorbed species much easier, in the same way as it does for

CO₂. But this is definitively not the case, whatever the experimental conditions. In contrast, the Pt columnar structure, which is known to have a 10–15 nm irregularity size, is sufficiently open for the penetration of CO₂ species and subsequent formation of surface complexes upon adsorption to be allowed at the overall electrode surface. Therefore, it seems that CO_{ad} is regularly produced at the inner walls of the columnar structure, but the penetration depth of the infrared beam indicates that only those species located at or near to column tips are spectroscopically detected. Otherwise, when the applied potential becomes sufficiently positive, CO_{ad} species are electrooxidized and, then, a relatively large quantity of CO₂ is released from the rough electrode surface.

From the preceding discussion, which is based on a more complete knowledge of the cs-Pt structure, it follows that, in contrast to previous conclusions, the poisoning effect due to CO_{ad} on rough Pt is comparable to that already found for smooth Pt electrodes, as a large fraction of CO_{ad} species, which is present at the cs-Pt surfaces, is spectroscopically missed.

3.7. Further aspects of the anodic stripping of r-CO₂ adsorbates

The multiplicity of current peaks related to the anodic stripping voltammogram is consistent with the formation of different r-CO₂ adsorbates. In turn, the differences between those r-CO₂ adsorbates may result from the participation in CO₂ reduction of two kinds of hydrogen atoms: those which are embedded [60] or those that become simply adsorbed on the Pt electrode surface. The presence of different current peaks cannot be explained only by means of thermodynamic arguments, but could also be the consequence of an influence of the electrolyte composition (particularly the influence of anions) on the kinetics of the electrooxidation reaction of the r-CO₂ adsorbates.

4. Conclusion

There is no evidence of either CHO_{ad} [18] or COOH_{ad} [23] adsorbates, at least under the experimental conditions reported in this work. The adsorbate structures proposed from the analysis of spectral and electrochemical data could be given in terms of a simple COH adsorbed stoichiometry. However, no spectral features to justify either COH or COOH adsorbate structures were found. The appearance of COOH-adsorbed species appears to be the result of a rather prolonged prepolarization time [23]. Presumably, COOH_{ad} species can be considered as precursors for CO₂ electroreduction on electrocatalytically active metals [61].

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