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Catalytic oxidation of maleic and oxalic acids under potential control of platinum catalysts

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Abstract

The oxidation of maleic and oxalic acids in diluted aqueous solutions and with platinum catalysts under potential control was studied with the purpose of defining the influence of potential on the catalytic activity. This control was achieved either by an external device or was spontaneously established in the presence of the reactants. The effect of the composition and of the pH was also investigated.

Oxalic acid can be oxidized in mild experimental conditions (T=333 K, $P_{O_2} \leq 1$ bar) and at potential values of the catalyst comprised between 0.7<E<1.8 V/RHE with a maximum catalytic activity at 1.3 V/RHE. The catalytic oxidation of this compound under external control of catalyst potential occurs following the same mechanism as the electrocatalytic oxidation. Oxalic acid is weakly adsorbed and its oxidation is inhibited by strongly adsorbed anions.

Maleic acid needs more severe experimental condition to be oxidized (T=383 K, $P_{O_2} = 1$–5 bars) and catalyst potentials in the range of 0.4≤E<1.1 V/RHE. In the same potential range an active adsorbed species was detected.

The catalytic oxidation of maleic acid follows the same mechanism with and without external control of catalyst potential which should be different from the mechanism of the electrocatalytic oxidation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic oxidation; Electrocatalytic oxidation; Maleic acid; Oxalic acid; Catalyst potential

1. Introduction

The potential of a metal catalyst is an important parameter which can affect its oxidation state, surface structure and electronic properties, thus defining the adsorption properties [1,2] and consequently the activity and selectivity of this catalyst. In the field of heterogeneous catalysis few works deal with this topic [3–9]. Vayenas et al. [3,4] studied numerous catalytic oxidations under the control of catalyst potential, in high temperature gas–solid systems, and found a promotion of the catalytic activity and selectivity. More recently, Mallat et al. [5,6] and Marin et al. [7] investigated the deactivation of platinum catalysts, in aqueous phase oxidation of alcohols, by measuring the catalyst potential. These authors reported that the overoxidation of catalysts could account for their deactivation [5–7].

In our laboratory, the role of the catalyst potential in the liquid phase catalytic hydrogenation of C=C and C≡C bonds has been investigated. It has been found [8,9] that the catalytic activity depends on the catalyst

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potential independently of the way of potential control (by a potentiostat or spontaneous setting up in the presence of reactants) and of the origin of active hydrogen species (gaseous hydrogen or protons). Moreover, it has been shown that only weakly bound hydrogen species are active in hydrogenation of C=C and C≡C bonds, and in addition, the catalytic selectivity of platinum can be changed by monitoring the catalyst potential [8,9].

This work has been extended to the study of the catalytic oxidation of maleic and oxalic acids under control of the catalyst potential.

Small carboxylic or dicarboxylic acids (such as formic, maleic and acetic acids) are intermediate products of the catalytic oxidation of benzenic compounds present in wastewaters [10,11]. Although numerous studies were devoted to the catalytic (or electrocatalytic) oxidation of different water pollutants [10–20], most of them were carried out with oxide catalysts and only a minor part of them concerns noble metal catalysts [11,15,17,20]. However, the use of noble metals allows to avoid the leaching which was observed in the case of composite oxide catalysts and some recent works [11,15,20] have shown that platinum and ruthenium carbon supported catalysts can be efficient for the oxidation of different carboxylic acids.

In this paper, the effect of the potential of platinum catalysts on their activity in oxidation of dilute solutions of maleic acid and oxalic acid is presented. Moreover, different other parameters, as the composition and the acidity of the solution, are discussed.

2. Experimental

A platinized platinum wire (Lyon-Alemand-Louyot, 99.995%) was used as a model catalyst. A large active platinum area, equal to about 800 cm^2, was obtained by electrochemical deposition of platinum [21].

The organic compounds studied were: maleic acid (Fluka pour analyses >99%) and oxalic acid (Aldrich >99%). Different aqueous solvents were used and prepared with suprapure acids and with different mineral salts of high purity. Ultrapure water (of a resistivity equal to 18 MΩ·cm) was used for the preparation of the solutions.

A classical three-electrode reaction cell was used for the in situ characterization of platinum surface. For catalytic oxidations at controlled potentials the counter-electrode compartment was separated from the reaction compartment by a Nafion® membrane (type 417 Aldrich) in order to avoid the migration and the electrochemical reaction of the organic compound on the counter electrode. The measured or applied potentials, given in this work, are referred to the hydrogen electrode (RHE) in the same supporting electrolyte.

Oxalic acid can be oxidized under mild experimental conditions (333 K, $P_{O_2} \leq 1$ bar), whereas maleic acid needs more severe conditions to be oxidized (383 K, $P_{O_2} = 1$–5 bar). For this purpose a special electrochemical autoclave has been designed allowing to measure or to control the potential of a platinum catalyst and to clean and characterize its surface in situ.

Before each experiment, the platinum surface was cleaned by electrochemical potential cycling between 0 and 1.5 V/RHE, with a scanning velocity v=50 mV s^{-1}, as it is classically proposed [22]. This treatment can induce some reconstruction of the polycrystalline platinum surface, but it is less important than in the case of monocrystalline platinum surfaces [22–24]. Nevertheless, the reproducibility of catalytic activities was checked before each experiment by measuring the activity in standard conditions. Then, the effective surface area of the platinum catalyst was evaluated in situ by linear potential sweep cyclic voltammetry (LPSCV) [22]. This evaluation is based on the measurement of the quantity of electricity, Q_H^0, exchanged during the underpotential adsorption or the desorption of a monolayer of hydrogen, following the reaction:

$$H^+ + e^- \leftrightarrows H_{ads} \quad (1)$$

2.1. Experimental methods

The oxidation of maleic and oxalic acids has been studied in aqueous media as a function of the potential of platinum catalysts.

Three experimental methods were used in order to monitor the catalyst potential.

1. In the presence of the organic reactant (C=10^{-3} M) and of gaseous oxygen, at different pressures, the potential of the catalyst is sponta-

neously established (mixed potential) and measured. In this case a classical catalytic oxidation occurs.

2. The potential of the catalyst is controlled by an external device (a potentiostat) in the presence of the organic reactants and in the absence of gaseous oxygen (under a nitrogen stream), the water being the source of active oxygen. In this case a classical electrocatalytic oxidation occurs.
3. The potential of the catalyst is controlled by a potentiostat in the presence of the organic reactants and also of gaseous oxygen. This experimental method is called catalytic oxidation under control of the catalyst potential.

The catalytic activities, obtained according to these three methods, were compared at different potentials of the catalyst. They were determined as follows: the progress of the reaction was followed by the measurement of the organic reactant concentration as a function of the time. At appropriate intervals, an aliquot of the reaction mixture was withdrawn and the acid concentration was determined by high performance liquid chromatography (HPLC) analysis, with a Biorad Aminex HPX 87H or a Bondapack BD C18 column. A UV–Vis detector, with a 230 nm wavelength, coupled with an integrator, was used, that allowed the detection of very small acid concentrations ($<10^{-6}$ mol l^{-1}). Fig. 1 represents an example of the type of obtained curve. A linear decrease of Ln C/C_0 versus time according to a straight line was observed for maleic acid concentration, that is characteristic of an apparent reaction order equal to one versus acid concentration. From the slope of this curve, corresponding to the rate constant of the reaction, the activity at t=0 of the catalyst is calculated. In the case of oxalic acid, the initial activity was determined by tracing the tangent on the curve $C=f(t)$, at t=0. In all cases the error percentage on the calculated activity can be estimated to 10%.

2.2. *Determination of diffusion rates of reactants*

The diffusion rate of gaseous oxygen was evaluated by the measurement, in the same experimental conditions as the studied reactions, of maximum diffusion currents corresponding to the electrocatalytic reduction of oxygen, following the reaction (in an acid solution):

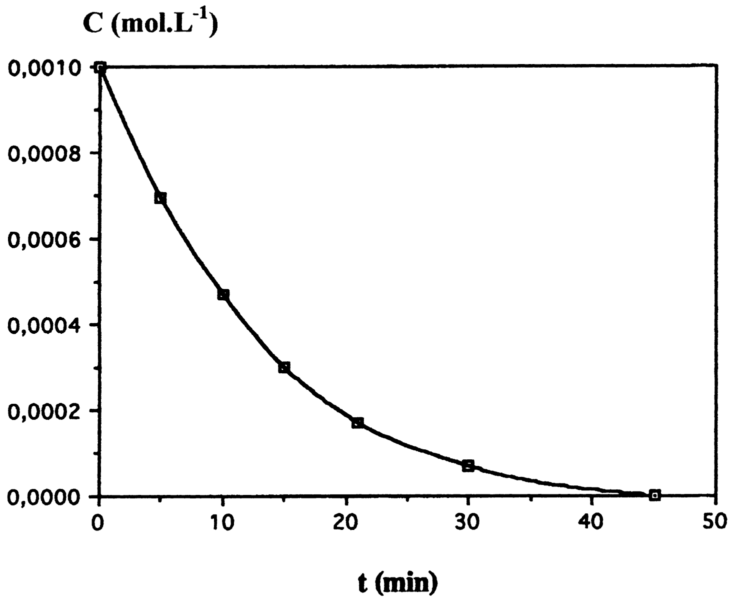

Fig. 1. Evolution of oxalic acid concentration versus time during a catalytic oxidation reaction (333 K, P_{O_2} = 1 bar, 10^{-3} M oxalic acid, 0.25 M $HClO_4$, pH=0.5).

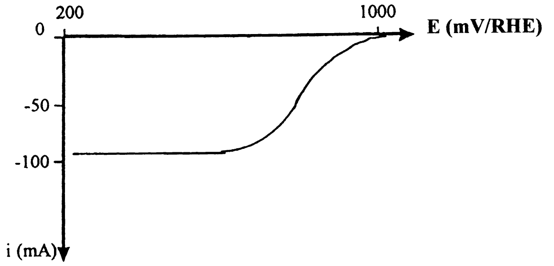

Fig. 2. Stationary current–potential curve associated to the electrocatalytic reduction of oxygen (P_{O_2} = 1 bar, 0.5 M H_2SO_4 aqueous solution, T=299 K, platinized platinum electrode).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

Indeed, at high potentials, on the $i=f(E)$ curve (Fig. 2), a limiting current i_L appears, which is approximately equal to the maximum diffusion current ($i_L \approx i_{diff}$) [25]. Then the diffusion rate of oxygen, r_{diff}, can be determined:

$$r_{diff} = \frac{i_{diff}}{nFS}$$

with n=4, F=96500 C and S=real surface area of platinum (in order to compare to catalytic activities).

The evaluation of the oxygen diffusion rate was carried out with different oxygen pressures, in the same experimental conditions as the oxidation reactions of maleic and oxalic acids. The obtained values were higher than the oxidation rates of these compounds.

For example, for $P_{O_2} = 1$ bar and T=333 K, the oxygen diffusion rate, r_{diff}, was found equal to 1.6×10^{-8} mol min cm^2, whereas the oxidation rate of oxalic acid r_{ox} was equal to 1.8×10^{-9} mol min^{-1} cm^{-2}.

A rough estimation of the diffusion rate of oxalic acid can be performed by comparing the oxidation rates obtained in pure catalytic oxidation with $P_{O_2} \approx$ 1 bar (a=6×10^{-10} mol min^{-1} cm^{-2}) and in electrocatalytic oxidation at a potential E (1350 mV/RHE (a=24×10^{-10} mol min^{-1} cm^{-2}) corresponding to the maximum of the activity versus potential curve (Fig. 4(a)). From this comparison, it can be concluded that the diffusion rate of this compound should be larger than the catalytic oxidation rate with $P_{O_2} = 1$ bar by a parameter equal to or higher than 4.

Concerning maleic acid, a determination of the diffusion rate of this compound, with C=10^{-3} mol l^{-1} at T=299 K, was carried out in a previous work [26] and was found equal to 2×10^{-9} mol min^{-1} cm^{-2}. According to this result and taking into account the difference of the surface roughness (in this work, the surface roughness was lower than in [26] by a parameter equal to 10–15), the difference of the reaction temperature (in this work T=383 K and in [26] T=299 K) and an activation energy of diffusion reaction equal to 5–10 kJ mol^{-1}, the diffusion rate of maleic acid could be evaluated and found equal to about 3×10^{-8}–5×10^{-8} mol min^{-1} cm^{-2}. This value is higher, by a parameter equal to 20–30, than the maximum oxidation rate of this compound (see Table 2).

3. Results and discussion

The results obtained following the three experimental methods described in Section 2.1 are presented separately, for maleic and oxalic acids.

3.1. Oxidation of maleic acid

Some preliminary experiments were first carried out in mild experimental conditions ($T \leq 353$ K, $P_{O_2} \leq 1$ bar), in a classical glass reactor (cf. Section 2). However, the platinized Pt catalyst was not active in such experimental conditions. A fast poisoning of platinum surface can explain this result, as it can be deduced from the fast decrease of oxidation currents obtained at imposed potential values near E=1 V/RHE (in the potential region where oxidation currents appear at 299 K) [27]. Moreover, a previous study on maleic acid adsorption on platinum has demonstrated that different adsorbed species should be involved at 299 K and at temperatures higher than 343 K [27]. Indeed, at ambient temperatures, an associative strong adsorption of this unsaturated compound occurs as it is shown by the displacement of adsorbed hydrogen (Fig. 3(a)) and according to [2,27,32–42,44]. Yet, at 343 K, the existence of an oxidation transient current during the adsorption of maleic acid (at a controlled potential E_{ad}=350 mV/RHE) allows to assume a new type of adsorption (as for example a dissociative or destructive adsorption of this compound) [27]. The appearance of a new oxidation peak on the platinum voltammogram in the pre-

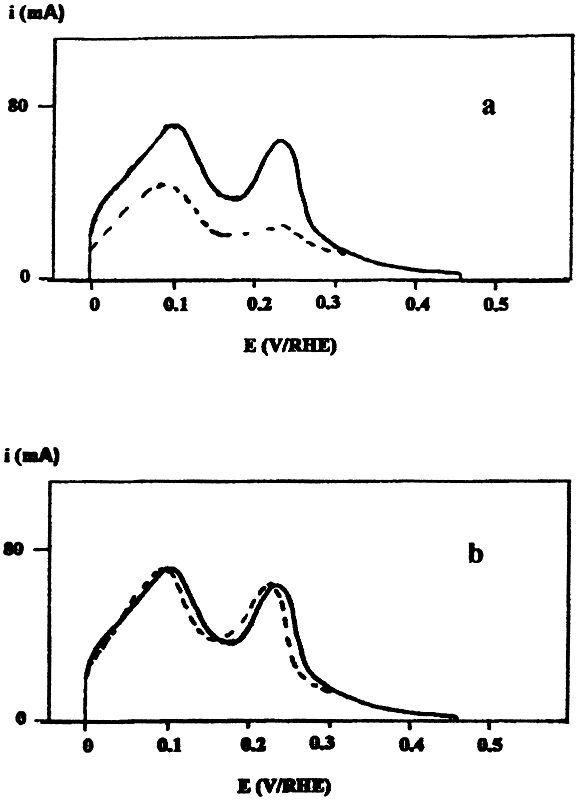

Fig. 3. Voltammogram of platinized platinum associated to the desorption of hydrogen, in the absence (———) and in the presence (- - -) of adsorbed organic compound: (a) maleic acid; (b) oxalic acid (C=10^{-3} M, 299 K, 0.5 M H_2SO_4, 50 mV/s).

sence of adsorbed maleic acid at higher temperatures ($T \geq 343$ K), corroborates this statement [27].

In order to investigate the oxidation of maleic acid in more severe experimental conditions and control the catalyst potential, a special autoclave was designed and constructed, allowing to introduce three electrodes: a platinized Pt catalyst used also as a working electrode, a Pt counter electrode and a reference electrode (AgCl/Ag). At a temperature higher than 373 K and an oxygen pressure higher than 1 bar, in an acid solution, a sintering of the platinized platinum catalyst was observed. In order to avoid the problem of a large variation of the catalyst surface during experiments, the catalyst was sintered by ageing before the first experiment. Then the initial surface of 800 cm^2 was decreased to attain a stabilized value of 50 cm^2. Furthermore, it was verified that the activity of the catalyst for a reference experiment ($P_{O_2} = 5$ bar, T=383 K) and the platinum surface area were constant along the experimental set.

The oxidation of maleic acid was performed successfully according to the three experimental methods presented previously (cf. Section 2.1), at 383 K, with a maleic acid concentration equal to 10^{-3} M, in a 0.5 M H_2SO_4 aqueous solution, in the absence and in the presence of gaseous oxygen with $1 < P_{O_2} \leq 5$ bars.

During the oxidation reaction a partial isomerization of maleic acid in fumaric acid occurred (approximately 10%). No other compounds, produced by a partial oxidation of maleic acid (as glyoxylic, oxalic, formic and acetic acids), were found in the liquid phase, as it was verified by HPLC in appropriate analysis conditions. Consequently, it was supposed that the oxidation of maleic acid was complete and led to the formation of CO_2 in agreement with [28]. On the other hand, it was verified that the fumaric acid cannot be oxidized in the experimental conditions used, thus allowing to evaluate directly the evolution of the isomerization of maleic acid by the evolution of the fumaric acid concentration versus time. The rate of consumption of maleic acid being equal to the sum of the rates of oxidation and isomerization of this acid, it is possible to calculate its oxidation rate after correction by the isomerization rate. For example, Table 1 reports the primary results obtained in a classical catalytic oxidation of maleic acid at 383 K with $P_{O_2} = 1$ bar.

The results of the oxidation reaction, performed according to the three experimental methods

Table 1
Evolution of maleic and fumaric acid concentrations during oxidation of maleic acid (333 K, $P_{O_2} = 1$ bar, total pressure 4 bar, in 0.5 M H_2SO_4)

t (min)	0	10	30	135	158	202	400
C(maleic) (10^3 mol l^{-1})	1.1	1.07	1.05	1	0.965	0.92	8.18
C(fumaric) (10^3 mol l^{-1})	0	0.0048	0.0117	0.031	0.0412	0.0459	0.061

Table 2
Evolution of the activity of platinized platinum catalyst (in mol min^{-1} cm^{-2}) as a function of the potential (10^{-3} M maleic acid, T=383 K, in 0.5 M H_2SO_4) according to three experimental methods

E (mV/RHE)	424	524	585	737	1100
Method 1	–	–	12.8×10^{-10}	10×10^{-10}	–
Method 2	11.3×10^{-10}	14.8×10^{-10}	–	–	0
Method 3	3.4×10^{-10}	3.4×10^{-10}	–	–	0

Method 1: catalytic oxidation with different oxygen pressures.
Method 2: catalytic oxidation at different imposed potential with $P_{O_2}=5$ bar.
Method 3: electrocatalytic oxidation (absence of O_2).

explained in Section 2.1, as a function of the catalyst potential, are summarized in Table 2. As it is shown in this table, the maleic acid is oxidized in a potential range lower than 1100 mV/RHE with a maximum of activity observed around 500 mV/RHE, the activity being equal to zero at 1100 mV/RHE.

Similar activities were obtained in catalytic oxidation with and without potential imposition, indicating that the same mechanism is involved in these two experimental processes, whereas a different mechanism occurs in the electrocatalytic oxidation.

Indeed, in the last case, a pure electrochemical oxidation mechanism can be proposed, following the global reaction:

$$H_4C_4O_4 + 4H_2O \rightarrow 4CO_2 + 12H^+ + 12e^- \quad (3)$$

In this reaction, the oxidation could occur either via a direct electron transfer between the platinum, the ‘‘active’’ organic species and the water, or via oxygen adsorbed species, like $(OH)_{ads}$ as proposed by Johnson and Gilmartin [28] and Bockris et al. [29].

In the case of the pure catalytic oxidation, the potential was spontaneously established at $E\approx700$ mV and $E\approx550$ mV/RHE for P_{O_2} equal to 5 and 1 bar, respectively, and remained constant during the reaction.

At these potential values the gaseous oxygen is reduced following reaction (2). The establishment of these mixed potentials can be explained by the occurrence of an oxidoreduction process following reactions (2) and (3), the overall reaction being (4):

$$3O_2 + 12e^- + 12H^+ \rightarrow 6H_2O \quad (2)$$

$$H_4C_4O_4 + 4H_2O \rightarrow 4CO_2 + 12e^- + 12H^+ \quad (3)$$

$$H_4C_4O_4 + 3O_2 \rightarrow 4CO_2 + 2H_2O \quad (4)$$

A negative order in oxygen is observed and can be explained by a too much high oxygen coverage comparatively to the coverage by active organic species [2,5–7]. However, the oxygen adsorption region on the platinum voltammogram begins at potentials E>0.7 V/RHE, even at high temperature [27,39]. Probably, it could be assumed that some loosely adsorbed oxygen species would be active in this reaction as in the case of glucose and gluconic acid oxidation [30] and not the strongly bound oxygen species corresponding to the voltammetric curves and associated to the reactions:

$$H_2O + Pt \rightarrow Pt(OH)_{ad} + H^+ + e^- \quad (5)$$

$$H_2O + Pt \rightarrow PtO_{ad} + 2H^+ + 2e^- \quad (6)$$

In the case of the catalytic oxidation with control of the potential (in the presence of O_2) similar results as in pure catalytic oxidation were obtained suggesting that a similar mechanism should occur (Table 2).

On the opposite side, much lower activities were obtained in pure electrocatalytic oxidation (in absence of O_2) indicating the occurrence of a different mechanism and/or the formation of ‘‘poison’’ adsorbed intermediates, as in the case of formic acid [31].

3.2. *Oxidation of oxalic acid*

A preliminary study of the adsorption of oxalic acid on platinum (by electrochemical techniques) in an acid solution showed that this compound does not cause a decrease of the quantity of adsorbed hydrogen [39], as it happens generally in the case of a strong adsorption of unsaturated organic compounds [27–29,32–42]. Indeed, the adsorption of this compound induces only a shift of voltammetric peaks associated to the adsorption of hydrogen towards more negative potentials (Fig. 3(b)). This result confirms the weak or reversible or ''anion-like'' adsorption of oxalic acid on platinum found by other authors [43,44]. It is why, in addition to the effect of potential the effect of the composition of the solution (nature of supporting electrolyte) and of its pH on the oxidation of oxalic acid were studied.

3.2.1. *Effect of the pH and of the composition of the solution on the oxidation of oxalic acid*

The catalytic activities of platinum in oxidation of oxalic acid depend on the pH of the solution and are higher at pH=0.5 than at pH=2.5 (with the exception of HCl and KCl) (Table 3). Moreover, a very low activity ($a=10^{-11}$ mol/min cm^2) was obtained at a pH=9 (with a borax buffer), and at a pH=13 the catalyst was inactive.

In addition, this reaction is quite inhibited by the presence of chloride anions and more favoured in the presence of ClO_4^- and HSO_4^-, the platinum activity being higher in the case of perchloric acid than in sulfuric acid, at a pH=0.5 (Table 3).

In a solution of pH=2.5, the highest activity was obtained in pure water pointing out that the presence of any supporting electrolyte induces a decrease of the catalytic activity.

The obtained catalytic activities can be classified as follows:

$$\text{at pH} = 0.5: \quad a_{(HClO_4)} > a_{(H_2SO_4)} > a_{(HCl)}$$

$$\text{at pH} = 2.5: \quad a_{(H_2O)} > a_{(LiClO_4)} = a_{(NaClO_4)} = a_{(K_2SO_4)} > a_{(KCl)}$$

These results can be explained by a weak or reversible or ''anion-like'' adsorption of oxalic acid on platinum [43,44], occurring in competition with the adsorption of other anions, as HSO_4^- and Cl^-. Moreover, the activity does not depend on the nature of the cation (Table 3).

Indeed, Horanyi et al. [44] studied the adsorption of oxalic acid and of different anions by radiochemical and electrochemical techniques and showed that oxalic acid is more weakly adsorbed than Cl^- and has a similar adsorbability as HSO_4^-.

It can be inferred from the comparison of this order with our results that the catalytic activity of platinum for the oxidation of oxalic acid is all the higher as the anions present in the solution are more weakly adsorbed on the platinum surface.

The decrease of activities with increasing pH can be explained by the dissociation of oxalic acid taking into account the values of dissociation constants of this acid ($K_1=5.9\times10^{-2}$ and $K_2=6.4\times10^{-5}$). The obtained results suggest that the reactivity of $HCOO{\cdot}COO^-$ should be lower than that of the undissociated acid. The very low activity found at a pH=9 ($a=10^{-11}$ mol/min cm^2) and the absence of activity at pH=13 suggest that the dianion $^-OOC \cdot COO^-$ should be the least reactive species.

3.2.2. *Effect of the potential of the catalyst on the oxidation of oxalic acid*

The oxidation of oxalic acid was studied following the three experimental methods described previously (cf. Section 2.1).

Fig. 4(a) and (b) represents the evolution of the activity of platinum for this reaction as a function of catalyst potential. The oxidation of oxalic acid begins at 0.7 V/RHE with an increasing activity, which attains a maximum at 1.3 V/RHE ($a=2.5\ 10^{-9}$ mol/

Table 3
Effect of pH and of solvent composition on the catalytic oxidation rate of oxalic acid ($T=333$ K, $P_{O_2}=1$ bar, $C_{AO}=10^{-3}$, supporting electrolyte: acid or salt ($C=0.25$ M))

pH =0.5		pH =2.5	
Supporting electrolyte	Activity $\times10^9$ (mol min^{-1} cm^{-2})	Supporting electrolyte	Activity $\times10^9$ (mol min^{-1} cm^{-2})
		H_2O	4.1
$HClO_4$	5.7	$LiClO_4$	2.7
		$NaClO_4$	2.8
H_2SO_4	4.9	K_2SO_4	2.9
HCl	$\approx10^{-3}$	KCl	0.2

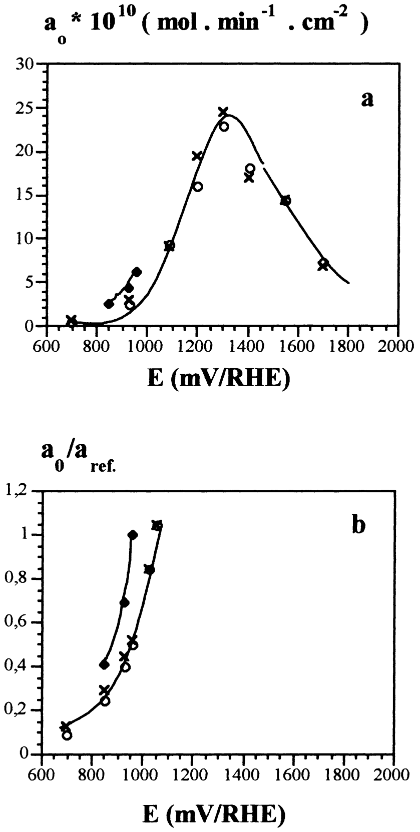

Fig. 4. Comparison of the platinized platinum activity for the oxalic acid oxidation according to the three methods: (○) electrochemical oxidation (under N_2); (×) catalytic oxidation under controlled potential (under O_2); (◆) classical catalytic oxidation with different oxygen partial pressures (spontaneously established potential). (a) Intrinsic activity; (b) relative activity (0.5 M H_2SO_4, oxalic acid 10^{-3} M, 333 K).

min cm^2) and then it decreases reaching a value equal to 1×10^{-10} mol/min cm^2 at 1.7 V/RHE (Fig. 4(a)).

In Fig. 4(b) the relative activity of the catalyst, a_0/a_{ref}, is expressed, a_0 being the activity measured at given experimental conditions and a_{ref} being the reference activity of the catalyst obtained for a partial oxygen pressure equal to 1 ($P_{O_2} = 1$ bar) and corresponding to a mixed potential of the catalyst equal to 934 mV/RHE.

It is clear that the activity of the catalyst in pure catalytic oxidation measured at a given potential is higher by a parameter of 2 than the activities of electrocatalytic oxidations (in absence O_2) and of catalytic oxidations at imposed potentials (in presence of O_2), the last two activities being equal (Fig. 4(b)). Similar results were obtained in a $HClO_4$ solution. However, it should be emphasized that the imposition of a potential equal to 1300 mV/RHE by a potentiostat allows to multiply the activity by 4 (Fig. 4(a)) in comparison to classical catalytic oxidation with $P_{O_2} = 1$ bar.

The obtained results suggest that the catalytic oxidations at imposed potentials occur according to the same mechanism as the pure electrocatalytic oxidations. Different mechanisms were proposed in [45–50] for the electrochemical oxidation of oxalic acid involving the participation of $(OH)_{ads}$ active species or the direct transfer of two electrons from the oxalic acid molecule towards the electrode. However, as this reaction occurs at potentials where (OH) is adsorbed on the electrode, the most probable mechanism is that proposed by Inzelt and Szetey [50]:

$$H_2O \rightarrow (OH)_{ads} + H^+ + e^- \qquad (5)$$

$$H_2C_2O_4 \rightarrow (H_2C_2O_4)_{ads} \qquad (7)$$

$$(H_2C_2O_4)_{ads} + (OH)_{ads} \rightarrow (HCO_2)_{ads} + CO_2 + H_2O \qquad (8)$$

$$(HCO_2)_{ads} \rightarrow CO_2 + H^+ + e^- \qquad (9)$$

A different mechanism, involving active oxygen species produced probably by a dissociative adsorption of gaseous oxygen on platinum should occur in the case of a pure catalytic oxidation, as, for example:

$$O_2 \rightarrow 2O_{ads} \qquad (10)$$

$$2H_2C_2O_4 \rightarrow 2(H_2C_2O_4)_{ads} \qquad (7)$$

$$2(H_2C_2O_4)_{ads} + 2O_{ads} \rightarrow 4CO_2 + H_2O \qquad (11)$$

However, loosely bound oxygen [30] could also be active as it was assumed previously in the case of maleic acid (see Section 3.1).

4. Conclusion

The purpose of this study was to evaluate the effect of an external control of a platinum catalyst in oxidation of maleic and oxalic acids in diluted aqueous solutions. This process was compared with classical catalytic oxidation and electrocatalytic oxidation at different potential values spontaneously established and imposed, respectively.

Different results were obtained for these two carboxylic acids.

In the case of maleic acid similar activities (at a given potential) were obtained in catalytic oxidation with and without external potential control, implying the same mechanism. This mechanism should be different from the one governing the electrocatalytic oxidation, since lower activities were obtained in this case.

The oxidation of maleic acid requires temperatures higher than 343 K, oxygen pressure $1 \leq P_{O_2} \leq 5$ bar and potential values $0.3<E<1.1$ V, which favour the formation of the active adsorbed species, as it was shown in a previous study [27].

Oxalic acid can be oxidized in milder experimental conditions (333 K, $P_{O_2} \leq 1$ bar) and at higher catalyst potentials: $0.7<E<1.8$ V/RHE. Similar activities in function of catalyst potential were obtained in catalytic oxidation of this compound with external potential control (in presence of O_2) and in electrocatalytic oxidation (in absence of O_2). However, these activities were lower than those obtained in classical catalytic oxidation (at a given catalyst potential). Yet, it should be emphasized that by applying an external potential equal to 1.3 V/RHE, the activity was multiplied by a factor of 4 in comparison with the activity obtained in a classical catalytic oxidation with an oxygen pressure equal to 1 bar.

Furthermore, the activity of platinum in catalytic oxidation of oxalic acid, depends on the composition and pH of the solution and especially on the presence of strongly adsorbed anions. This behaviour can be explained by the weak, ''anion-like'' adsorption of this compound [43,44], conversely to maleic acid which is strongly adsorbed [27]. This result can have a practical application on the catalytic oxidation of organic pollutants present in wastewaters.

In conclusion, the platinum catalyzed oxidation of carboxylic acids, in diluted aqueous solutions, depends on several parameters: temperature, composition and acidity of the solution, oxygen source (O_2 or H_2O) and catalyst potential. The ensemble of these parameters can affect the nature of active species and define the catalytic activity. Moreover, the control of the catalyst potential provides a convenient means to adapt the surface properties to the kinetic requirements of a reaction.

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