Mechanistic aspects of methanol oxidation on platinum-based electrocatalysts[†]

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Abstract

An understanding of the overall mechanism of the electrooxidation of methanol is of considerable interest in relation to the optimization of the direct methanol fuel cell. This paper describes in detail the different steps in the oxidation of methanol on platinum-based electrocatalysts with the identification of the key adsorption steps and of the different intermediates involved. From these fundamental studies, it is shown how it is possible to design multimetallic electrocatalysts for the electrooxidation of methanol under experimental conditions suitable for fuel cell application.

1. Introduction

Methanol is one of the most promising fuels for fuel cells, especially if it can be oxidized directly and completely to carbon dioxide. However, this direct electrooxidation is difficult in a potential range suitable for use in a direct methanol fuel cell (DMFC). The challenge is to enhance the kinetics of the electrocatalytic oxidation of methanol at low potentials by avoiding or limiting the poisoning phenomena observed with pure platinum. Such enhancement can only be obtained by modification of the structure and the nature of the electrode, and such a modification can be proposed only in relation to the overall reaction mechanism, which should be known. However, even after more than thirty years of fundamental studies, the mechanism of the oxidation of methanol is still not well understood, a factor which is hindering the development of DMFC [1, 2 and references therein]. The purpose of this paper is, firstly, to focus on the main mechanistic facts widely accepted with Pt and Pt–Ru electrodes and, secondly, to discuss the consequences for the structure and the composition of optimized multimetallic platinum-based anodes for the direct oxidation of methanol.

2. Experimental details

The determination of the mechanisms of an electrocatalytic reaction requires information not only on the activity of the electrode, but also on the nature of the different species involved, including adsorbed species, intermediate and final products.

The following discussion concerning the mechanism is based on the experimental work recently carried out in the author's laboratory, and also by many other groups [1–9]. It is not the purpose of this paper to describe in detail these experiments, but to emphasize the main results in relation to the identification of the key steps in the overall mechanism.

The trimetallic electrodes were obtained by coelectrodeposition, under potentiostatic conditions, of the metals from corresponding metallic salt solutions, into a conducting polymer matrix (polyaniline) obtained by electropolymerization [10–12, 19]. The activity of the electrodes was estimated by cyclic voltammetry or chronopotentiometry. However, the breakthrough in the understanding of the mechanism of methanol electrooxidation was obtained after the identification of the different adsorbed species by *in situ* infrared reflectance spectroscopy [1–5, 13, 14]. Such techniques allow monitoring of the different adsorbed species and their coverages under electrochemical conditions. After the results obtained during the last 20 years, the nature of the different adsorbed species is now known, at least for species present on the electrode surface during a period compatible with the recording of infrared spectra (a few seconds with modern equipment) [1–4].

3. Discussion

The overall reaction involved in a direct methanol fuel cell can be expressed by the equation:

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$$CH_3OH + 3/2\,O_2 \rightarrow CO_2 + 2\,H_2O \quad \text{with}$$
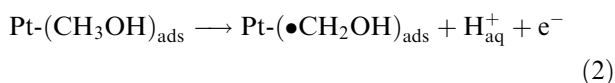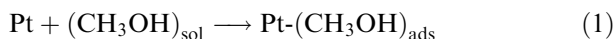$$\Delta G = -702\,\text{kJ}\,\text{mol}^{-1}$$
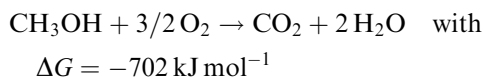
The standard reversible potential of such a cell, $E_r^\circ = 1.21\,\text{V}$ vs SHE, is very close to that of a hydrogen–oxygen fuel cell (e.g., 1.23 V). The anodic potential, E_a°, under standard equilibrium conditions, can be easily calculated from thermodynamic data. A value of 0.016 V vs SHE is obtained, which means that, thermodynamically, methanol can be oxidized at very low potentials. However, it is well known that methanol is only oxidized at potentials greater than 0.5 V, in acid medium on a platinum electrocatalyst. This is due to the slow electrooxidation kinetics, which lead to high overpotentials. But, as methanol electrooxidation is a complex reaction involving the transfer of six electrons, it is clear that the overall mechanism is complex and, consequently, that a detailed knowledge of the different steps is necessary to identify the rate determining step responsible for the 'poison formation'.
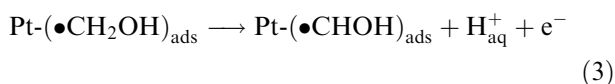
For the elucidation of the reaction mechanism, knowledge of the following items are vital: (i) identification of the reaction products and determination of the electrode kinetics of the different reactions, (ii) identification of all the adsorbed intermediate species, and their distribution on the electrode surface, and (iii) identification of the electrode kinetics of the intermediate steps in the overall mechanism and correlation with the structure and composition of the electrocatalyst surface.

The first step in the reaction is the adsorption of the methanol molecule immediately followed by its dissociation into several adsorbed species. These different species are themselves transformed through several further reactions into more strongly adsorbed species, responsible for the poisoning.
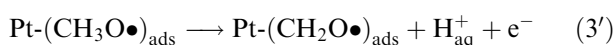
These different reactions can be summarized as followed:

$$Pt + (CH_3OH)_{sol} \longrightarrow Pt\text{-}(CH_3OH)_{ads} \tag{1}$$

$$Pt\text{-}(CH_3OH)_{ads} \longrightarrow Pt\text{-}(\bullet CH_2OH)_{ads} + H_{aq}^+ + e^- \tag{2}$$

or

$$Pt\text{-}(CH_3OH)_{ads} \longrightarrow Pt\text{-}(CH_3O\bullet)_{ads} + H_{aq}^+ + e^- \tag{2'}$$

$$Pt\text{-}(\bullet CH_2OH)_{ads} \longrightarrow Pt\text{-}(\bullet CHOH)_{ads} + H_{aq}^+ + e^- \tag{3}$$

or

$$Pt\text{-}(CH_3O\bullet)_{ads} \longrightarrow Pt\text{-}(CH_2O\bullet)_{ads} + H_{aq}^+ + e^- \tag{3'}$$

$$Pt\text{-}(\bullet CHOH)_{ads} \longrightarrow Pt\text{-}(\bullet CHO)_{ads} + H_{aq}^+ + e^- \tag{4}$$

or

$$Pt\text{-}(CH_2O\bullet)_{ads} \longrightarrow Pt\text{-}(\bullet CHO)_{ads} + H_{aq}^+ + e^- \tag{4'}$$

The different adsorbed species formed during steps 2 to 4 or 2′ to 4′ have been detected by *in situ* infrared reflectance spectroscopy [1, 4]. After Reactions 4 or 4′, the formyl-like species $(\bullet CHO)_{ads}$ is spontaneously dissociated on pure platinum according to the reaction:

$$Pt\text{-}(\bullet CHO)_{ads} \longrightarrow Pt\text{-}(\bullet CO)_{ads} + H_{aq}^+ + e^- \tag{5}$$

The strongly adsorbed CO species formed during this step was clearly identified as the main poisoning species blocking the electrode active sites. Reaction 5 is fast and is the main reason for the rapid poisoning phenomena observed on pure platinum [1, 3, 4].

Thus, a crucial step in the reaction mechanism is the formation of the intermediate $(\bullet CHO)_{ads}$, which can be considered either as an active intermediate, leading directly to the final oxidation product, or as the precursor to the poisoning species. The kinetics of the further desorption and/or oxidation of this formyl-like species is the key step in the overall mechanism.
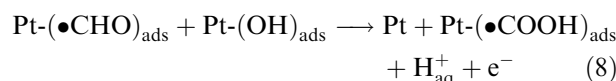
The oxidation of this species requires the presence of OH species arising from the dissociation of water according to the reaction:

$$Pt + H_2O \longrightarrow Pt\text{-}(OH)_{ads} + H_{aq}^+ + e^- \tag{6}$$
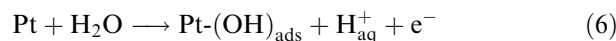
leading to the surface reaction responsible for the formation of carbon dioxide

$$Pt\text{-}(\bullet CHO)_{ads} + Pt\text{-}(OH)_{ads} \longrightarrow 2\,Pt + CO_2 + 2H_{aq}^+ + 2e^- \tag{7}$$
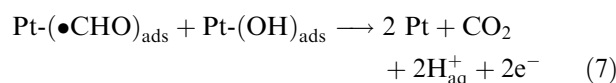
One other reaction has also been observed:

$$Pt\text{-}(\bullet CHO)_{ads} + Pt\text{-}(OH)_{ads} \longrightarrow Pt + Pt\text{-}(\bullet COOH)_{ads} + H_{aq}^+ + e^- \tag{8}$$

then leading also to the formation of carbon dioxide through the reaction:

$$Pt\text{-}(\bullet COOH)_{ads} \longrightarrow Pt + CO_2 + H_{aq}^+ + e^- \tag{9}$$

On the other hand, at more positive potentials, the poisoning species (adsorbed CO) can be oxidized through the reactions:

$$Pt\text{-}(\bullet CO)_{ads} + Pt\text{-}(OH)_{ads} \longrightarrow 2\,Pt + CO_2 + H_{aq}^+ + e^- \tag{10}$$

or

$$Pt\text{-}(\bullet CO)_{ads} + Pt\text{-}(OH)_{ads} \longleftrightarrow Pt + Pt\text{-}(\bullet COOH)_{ads} \tag{11}$$
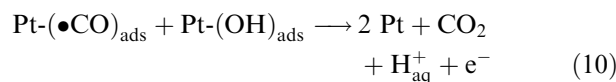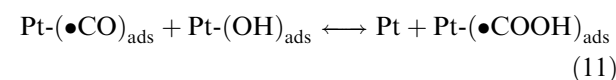
followed by Equation 9.

This mechanism, described by Reactions 1 to 11, takes into account the formation of all the products detected: CO_2 from steps 7, 9 or 10, formation of formaldehyde

after steps 3 or 3′ and 4 or 4′, and formation of formic acid after the steps 8 or 11.

In acid medium, platinum appears to be only the electrocatalyst suitable for the dissociation of the methanol molecule by breaking the C–H bonds during the adsorption steps, at low temperature. Unfortunately, as seen above, this dissociation leads spontaneously to the formation of CO, and due to its strong adsorption on Pt, this species is an electrocatalyst poison for the subsequent steps in the overall reaction of methanol electrooxidation.

The adsorption properties of the platinum surface must be modified to improve the kinetics of the overall reaction. Two different consequences can be envisaged from this modification: prevention of the formation of the strongly adsorbed species, or increase in the oxidation kinetics at lower potentials. This modification will have an effect on the kinetics of steps 7 and 8 instead of step 5 in the first case, and of step 10 in the second case.

The rate-determining step (rds) of the reaction on platinum is the oxidation of adsorbed CO with adsorbed hydroxyl species coming from the water dissociation, i.e. step (10). The current density, j, of the methanol electrooxidation can be expressed as

$$j = nFk\theta_{res}\theta_{OH} \exp\left(\alpha n_{rds}\frac{FE}{RT}\right) \tag{12}$$

where θ_{res} and θ_{OH} are the coverages of the adsorbed residues of methanol and in hydroxyl groups (arising from water dissociation), n and n_{rds} are the numbers of electrons involved in the overall reaction and in the rate determining step, respectively; k is the rate constant, F the faradaic constant, α the transfer coefficient and E the electrode potential. The coverages of methanol adsorbed residues and of hydroxyl species can be expected to depend on the electrode potential. However, in the case of adsorbed CO on platinum, the CO_{ads} coverage is high and relatively constant over a large potential range. Thus, the current density versus potential relation is mainly dependent on the coverage of adsorbed OH. As a consequence, the first approach to improve the overall kinetics is to increase the adsorbed OH coverage at low potentials. Adding to platinum a second metal on which water is more easily dissociated at lower potentials can achieve this.

As discussed above, several kinds of adsorbed species may be simultaneously present on the electrode surface. The different species and their degrees of coverage on the Pt surface depend on the electrode potential and also on the nature and structure of the electrode surface. The crystallographic structure of the platinum electrode surface plays a key role in the distribution of the different adsorbed species leading to important differences in the activity observed with the low index planes of platinum [1, 5, 6].

For the sake of simplicity, if only two types of adsorbed species deriving from methanol dissociation, CO_{ads} and CHO_{ads}, are considered, the overall mechanism can be described by the following general scheme [1, 6]:
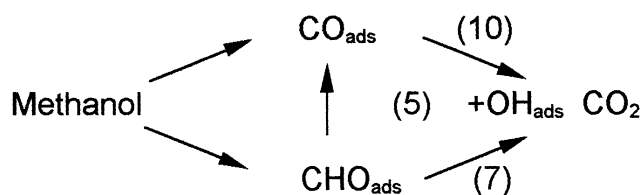
with $\theta_{CO} + \theta_{CHO} + \theta_{OH} = 1$. The current density, j, is then given by the following equation:

$$j = nF(1 - \theta_{CO} - \theta_{CHO})\left[k_{10}\theta_{CO}\exp\left(\alpha_{10}n_{10}\frac{FE}{RT}\right)\right.$$
$$\left. + k_7\theta_{CHO}\exp\left(\alpha_7 n_7\frac{FE}{RT}\right)\right] \tag{13}$$

where k_i, α_i and n_i are the corresponding parameters for steps 7 and 10, respectively. According to this simple model, an optimized electrocatalyst would have a θ_{CO} value as low as possible, and θ_{CHO} and θ_{OH} each being equal to 0.5, at low potentials. As it is impossible to avoid the formation of adsorbed CO on pure platinum, it is obvious that at least a second metal is necessary to fulfill the conditions of optimal coverage in the main adsorbed species.

Ruthenium is recognized to be the most efficient second component to enhance the electrooxidation of methanol on platinum [1, 4, 7–9, 14–17]. The presence of ruthenium increases the possibility of having adsorbed OH species on the electrode surface at low potentials, which results in the possible oxidation of the adsorbed intermediate species in this potential range. In addition, the presence of ruthenium minimizes the formation of the CO poisoning species, as shown by IR reflectance spectroscopy, which reveals that the amount of adsorbed CO, formed from methanol dissociation, is considerably higher on pure platinum than on platinum–ruthenium catalyst. For a $Pt_{0.9}–Ru_{0.1}$ alloy, the amount of linearly adsorbed CO is very small (Figure 1), suggesting a low coverage by the poisoning species.

By observing the potentials at which the CO_2 IR absorption band appears, it is possible to conclude that the oxidation of both $(CHO)_{ads}$ and $(CO)_{ads}$ species occurs at much lower potentials on a Pt–Ru alloy electrode than on pure platinum. Even though there remain some discrepancies, various studies have concluded that an optimum atomic composition around 15 to 20 at % in ruthenium gives the best results for the oxidation of methanol [7, 14]. This composition is different from that for the oxidation of dissolved CO (around 50 at % Ru), confirming a different superficial distribution of the adsorbed species [14].

The mechanism discussed above for pure platinum should be modified due to the promoting effect of ruthenium and can be described as a bifunctional mechanism. The adsorbed OH are formed both at
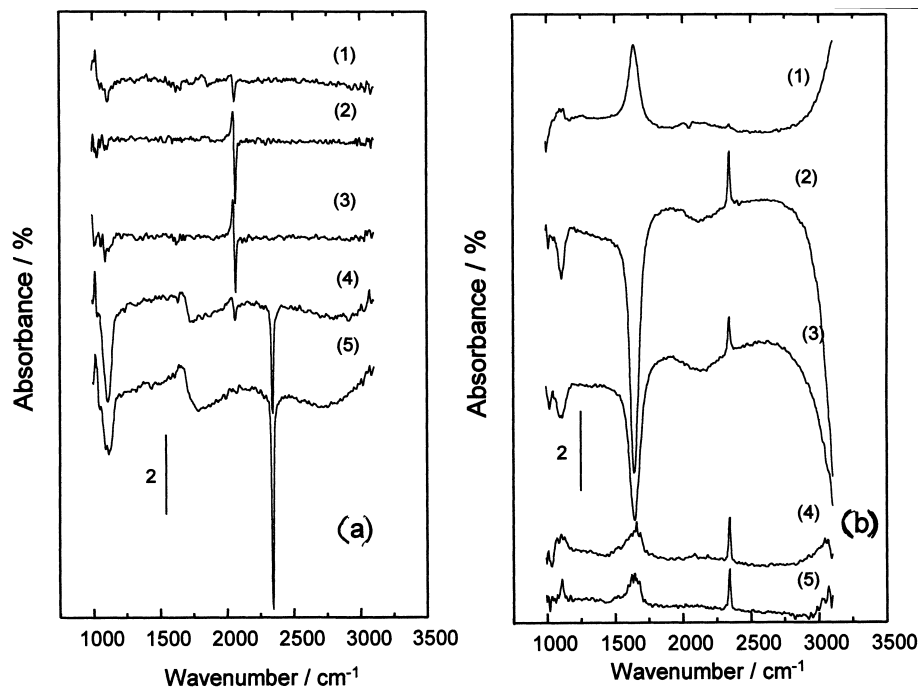
Fig. 1. SNIFTIRS of the adsorbed intermediates formed during the oxidation of 0.1 M CH$_3$OH in 0.5 M HClO$_4$ on a smooth Pt electrode (a) and a smooth Pt$_{0.9}$Ru$_{0.1}$ bulk alloy (b). Modulation potential amplitude 0.3 V; mid-potential (V vs RHE): (1) 0.37, (2) 0.47, (3) 0.57, (4) 0.67, (5) 0.77.

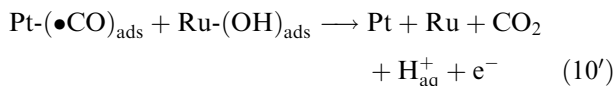platinum sites (Reaction 6), and at ruthenium sites in a lower potential range according to

$$Ru + H_2O \longrightarrow Ru\text{-}(OH)_{ads} + H_{aq}^+ + e^- \quad (6')$$

Then, the oxidation of formyl like species can occur either by Reaction 7 or by Reaction 7′:

$$Pt\text{-}(\bullet CHO)_{ads} + Ru\text{-}(OH)_{ads} \longrightarrow Pt + Ru + CO_2$$
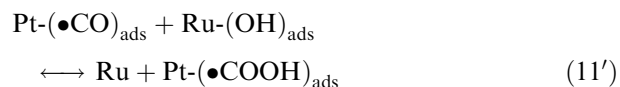$$+ 2H_{aq}^+ + 2e^- \quad (7')$$
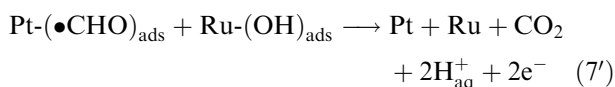
The rate of Reaction 7′ is higher than that of Reaction 7, mainly at lower potentials.

No oxidation of methanol was observed on pure ruthenium and consequently the absence of (•CHO)$_{ads}$ on ruthenium sites is confirmed [14]. However, adsorption of CO was observed on a ruthenium electrode from solution containing dissolved CO [14]. The adsorbed CO observed on a Pt–Ru electrode during the adsorption of methanol may arise mainly from the dissociation of methanol at platinum sites, followed by the migration of such CO species towards the neighboring ruthenium sites. Then, the removal of adsorbed CO, mainly present at platinum sites, by oxidation with adsorbed OH, may occur in two ways: at platinum sites according to Reaction 10, or 11 followed by 9, and at ruthenium sites according to Reaction 10′:
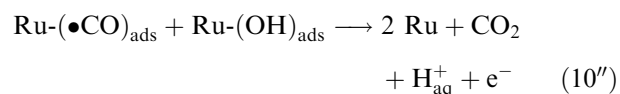
$$Pt\text{-}(\bullet CO)_{ads} + Ru\text{-}(OH)_{ads} \longrightarrow Pt + Ru + CO_2$$
$$+ H_{aq}^+ + e^- \quad (10')$$

or Reaction (11′):

$$Pt\text{-}(\bullet CO)_{ads} + Ru\text{-}(OH)_{ads}$$
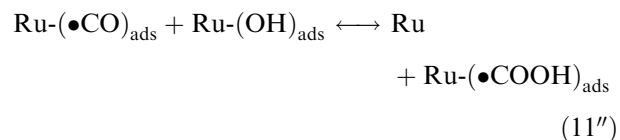$$\longleftrightarrow Ru + Pt\text{-}(\bullet COOH)_{ads} \quad (11')$$

followed by Reaction 9.

The rates of steps 10′ and 11′ are higher than those of the corresponding steps 10 and 11 with pure platinum.

Due to the presence of some adsorbed CO species at ruthenium sites by migration of these species from platinum sites, the following reactions can also occur:

$$Ru\text{-}(\bullet CO)_{ads} + Ru\text{-}(OH)_{ads} \longrightarrow 2 Ru + CO_2$$
$$+ H_{aq}^+ + e^- \quad (10'')$$

or Reaction 11″:

$$Ru\text{-}(\bullet CO)_{ads} + Ru\text{-}(OH)_{ads} \longleftrightarrow Ru$$
$$+ Ru\text{-}(\bullet COOH)_{ads}$$
$$(11'')$$

followed by reaction similar to Reaction 9.

From the description of the mechanism of the oxidation of methanol given above, it is clear that modification of the adsorbed OH coverage is vital to the improvement of the overall oxidation rate. However, at this point, two questions are asked: (a) 'Is Pt–Ru really the best electrocatalyst?' and 'What is the stability of such a bimetallic electrode?'; (b) 'Is it possible to
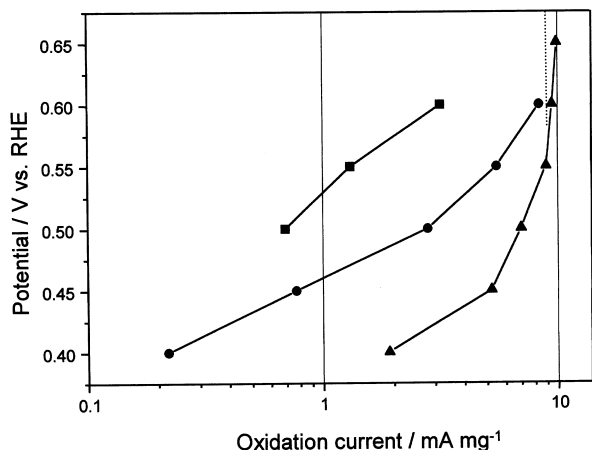
Fig. 2. Comparison of the activity of Pt, Pt–Ru and Pt–Ru–Mo particles for the oxidation of 0.1 M methanol in 0.1 M perchloric acid. Currents recorded after 30 min at each potential. Key: (■) PAni/Pt, (●) PAni/Pt–Ru and (▲) PAni/Pt–Ru–Mo.

consider other bimetallic and multimetallic electrodes, which exhibit higher activity for methanol oxidation?'.

An optimized electrocatalyst for methanol oxidation should have several properties: the possibility to dissociate the methanol molecule, the ability to favor the presence of a sufficient concentration of adsorbed oxygenated species at its surface at low potentials, and the easy removal of poisoning species. One and even two metals cannot fulfill all these conditions. Various components are necessary: (a) platinum for the dissociation of methanol, (b) ruthenium for the adsorption of (OH) at low potentials, and (c) a third metal the role of which could be to avoid or to limit the formation of adsorbed CO, and to increase the superficial concentration of adsorbed OH.

The challenge is then to find a third component which fulfills at least partially this third characteristic. Among the metals able to play such a role, molybdenum seems to be a good candidate, as shown by the results of preliminary experiments given in Figure 2. Molybdenum was proposed 35 years ago as a promotor of methanol electrooxidation on platinum [18], but if Mo is associated with Pt and Ru, the improvement observed is obvious, by comparison to an optimized platinum-ruthenium electrode. This improvement is greater at low potentials, which confirms that the presence of adsorbed OH species is the key point. However, with an electrode containing three metals, the problem of its stability is crucial with the difficulty of maintaining its composition and its structure stable. In the case of the presence of molybdenum, it was observed that the conditions of

preparation of such multimetallic electrodes are important, mainly in relation to the nature of the oxide species present at the surface. Labile OH species are necessary, as pointed out above, but with an easily corrodible metal, such as molybdenum, the main difficulty is to avoid the formation of more oxidized phases which lead to totally inactive electrodes. A complete study of the properties of such multimetallic electrode is necessary, with characterization of the electrocatalyst particles to observe their stability. This study is discussed in another paper [19].

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