ON THE ELECTROCATALYTIC ACTIVITY OF PtAu BIMETALLIC SYSTEMS IN HIGHLY CONCENTRATED METHANOL SOLUTIONS

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ABSTRACT

The electrocatalytic behavior of Pt and PtAu bimetallic electrodes of bulk composition of 20, 40, 60 and 80 at.% is studied in 0.5 M solution of H$_2$SO$_4$ in dried CH$_3$OH and 0.5 M solution of H$_2$SO$_4$ in CH$_3$OH:H$_2$O in a ratio of 1:1. Cyclic voltammetry is applied varying the potential ranges studied and the scan rate applied. The experiments are performed at four temperature values in the interval from 293.2 K to 323.2 K. The data obtained show that O-H bond scission occurs preferably in the first medium leading to formation of formaldehyde and formic acid, while sequential C-H rupture takes place in the second one to yield CO$_{ads}$. The apparent activation energy of the process is found to decrease in both media with Au bulk increase till about 60 at. %. It is concluded that the amount of water present controls the pathway of methanol transformation while alloying favors predominantly the kinetics of the process through its effect on the surface susceptibility to poisonous intermediates.

Keywords: methanol electrooxidation, electrocatalysis, PtAu bimetallic systems, water presence effect, mechanistic pathways.

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INTRODUCTION

The electrocatalytic oxidation of methanol, carbon monoxide and formic acid is a field of study of widespread practical and fundamental interest given its importance to fuel-cell technology [1]. It is so because methanol is one of the most promising fuels for a fuel cell yielding CO$_2$ and six electrons per a methanol molecule:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}$$

(1)

The reaction above has a favorable thermodynamic potential and can theoretically allow a fuel cell output close to that of a hydrogen-based fuel cell. But the formation of surface poisoning species and soluble intermediates lowers the overall efficiency expected. Carbon monoxide is identified as the primary poisoning species [2-5], while formic acid and formaldehyde are formed as intermediate products [6-9]. It is now generally accepted [8-12], that the oxidation of methanol proceeds through a direct pathway involving the formation of formaldehyde and formic acid and an indirect pathway via adsorbed CO. It is suggested that the structure sensitive decision between the parallel pathways is determined by the initial dehydrogenation step, i.e. the breaking of the O-H and C-H bond, respectively. It is reported [12] that the direct pathway requires an ensemble size of between 3-4 Pt atoms, whereas the indirect or the secondary one which is much less structure sensitive requires 1-2 metal atoms. It is evidenced [10] that in sulfuric acid media the oxidation of methanol on Pt (111) shows a preference for the direct oxidation pathway. The explanation is based on the assumption that the strongly adsorbing (bi)sulfate anions decrease the number of the available “ensemble sites” required for the dissociative adsorption of methanol via C-H bond cleavage, i.e. the surface presence of
insufficient ensemble sites provides O-H bond scission resulting in soluble intermediates formation. The relative rate of the indirect oxidation pathway can be increased by introducing [10] of steps in the (111) terraces most probably because of the anion adlayer disruption.

Binary Pt-based electrocatalysts have been found to circumvent some of the major problems referring to incomplete methanol oxidation at low potentials and poisonous species formation. Secondary metals are believed to enhance the oxidation reactivity and to moderate the poisonous intermediates effect by decreasing the number of adsorption sites for CO due to geometrical hindrance in accordance with the third-body or ensemble effect, supplying oxygen-containing species to adjacent Pt surface sites following the bi-functional mechanism of electrocatalysis, shifting Pt d-band and hence modifying this metal electronic structure. PtAu alloys anodic behavior has been studied in a number of oxidative reactions [13-18 for an illustration]. Their high electrocatalytic activity has been well recognized in an alkaline medium and the synergistic effect observed has been attributed to the alloying electronic effect. A certain catalytic activity observed [16] in an acidic medium has been attributed to the third-body effect preventing a reaction auto-inhibitor formation, but it is generally accepted that PtAu alloys have no catalytic activity in an acidic medium because of the lack of a considerable OH surface coverage. PtAu surface alloys and/or Pt-Au nanoparticles on different substrates are of current interest in the context of electrocatalytic methanol oxidation [19-24] because of the unique catalytic properties of Au at nanoscale sizes for CO oxidation [25,26], the development of more reaction-effective surface structures of Pt-modified Au nanoparticles [24], the effect of alloying on the alteration of the major methanol oxidation route [21], the lower price and the greater availability of Au than that of Pt [26]. All studies carried out so far imply that PtAu nanoparticle catalysts are potentially viable candidates for use in fuel cells under a number of conditions. There are some issues that require further elucidation. One of these is connected with the miscibility gap of Pt and Au known for bulk bimetallic PtAu systems [14] and the understanding of this phenomenon operation at the nanoscale under different temperatures. This in turn refers to the ability of controlling the phase properties and hence manipulating the catalytic activities of the bimetallic systems considered.

Methanol is not only a perspective fuel. Being an organic solvent of well outlined physical and chemical properties [27] it finds wide application in electrosynthesis and as an additive or a component modifying the properties of different nonaqueous media and room-temperature ionic liquids [28, 29]. The behavior of Pt in methanol electrooxidation in absence of any traces of water [30-33] differs substantially from that already discussed above. In absence of any chemisorption and subsequent dehydrogenation the rate of the overall anodic process is determined by:

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}^+ + e$$

(2)

The methoxy radicals formed interact to yield formaldehyde or CO and CH$_3$OH:

$$\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH}$$

(3)

$$4 \text{CH}_3\text{O} \rightarrow \text{CO} + 3 \text{CH}_3\text{OH}$$

(4)

It is evident that the process considered is very sensitive to water presence. It is reported [33] that the polarization curve in the double-layer potential range in $10^{-4}$ - $10^{-1}$ M water solutions does not change when compared to that in absence of water but a sharp decrease of the rate of methanol oxidation is observed at higher potential values (in the range between 0.5 and 1.0 V vs. SCE). On further water concentration increase a maximum of methanol electrooxidation is outlined. The peak current increases, while its potential shifts towards lower potential values with the water concentration increase until it reaches the value of 1 mol l$^{-1}$.

The comparative consideration of methanol electrooxidation in water absence and presence reveals the role of OH- and CO-like species in the oxidation route as well as the effect of the surface composition of PtAu bimetallic systems in modeling their reactivity towards surface intermediates oxidative removal. The aim of the present communication is to address these features in highly concentrated methanol solutions where they are expected to be even better outlined.

**EXPERIMENTAL**

The experiments were conducted in 0.5 M solution of H$_2$SO$_4$ in dried CH$_3$OH and 0.5 M solution of H$_2$SO$_4$.
in CH₃OH:H₂O in a ratio of 1:1. The alcohol (Merck) was of purity greater than 99.9% and the water content was less than 0.003%. The acid (Merck) was analytical grade. They were used without further purification or drying. The aqueous solutions were prepared with bidistilled water. Three-electrode electrochemical cells providing an inert atmosphere (99.999 % N₂ was purged prior to the recording of each curve) were used but the effect of some moisture from the air could not be excluded in absence of a glove box.

The electrocatalytic behavior of Pt and PtAu alloy electrodes of bulk composition of 20, 40, 60 and 80 at. % was studied. Pt and Au plate counter electrodes were used. Pt wire was used a reference electrode in the experiments run in 0.5 M solution of H₂SO₄ in dry CH₃OH. Because of the presence of some water content the polarization curve recorded in this solution showed a sharp current decrease determined by hydrogen evolution and anodic maxima attributed to methanol electrooxidation. The hydrogen evolution potential value was accepted equal to 0 V referred to RHE. The experiments in the second electrolyte mixture were carried out using Ag/AgCl (saturated KCl) reference electrode. All potential values cited in the text refer to RHE. The true electrode surface of the working electrodes was determined at room temperature prior to each experiment in a cell containing 0.5 M aqueous solution of H₂SO₄. The conventional procedure used was based on recording a cyclic voltammogram in the range from 0.050 V to 1.550 V with a scan rate of 0.100 V s⁻¹ and subsequent estimation of the charge required for oxygen coverage reduction at Pt and the alloy α₁-phase rich in Pt [34 for an example] as well as that for oxygen coverage reduction at the alloy α₂-phase rich in Au (the behavior of these phases present at the alloy surface is analogous to that of Pt and Au, correspondingly, in respect to electrooxidation/reduction processes). The values were corrected for the double-layer charging and then referred to the charges of reduction of the monolayer Pt and Au oxide coverage, i.e. 0.420 mC cm⁻² and 0.386 mC cm⁻² [35 and references therein], correspondingly. The working electrode surface had to be pretreated because of the fouling observed. The latter was well expressed at temperatures higher than 298 K. An additional cell containing 0.5 M aqueous solution of H₂SO₄ was used for electrodes surface pretreatment. The preliminary experiments carried out showed the validity of the following potential-time program: oxidative removal of the strongly adsorbed species through the application of a constant potential value of 2.0 V for 180 s; reductive removal of any oxidation products and/or oxides deposited on the surface during this period through the application of a constant potential value of 0 V for 120 s, cycling within the range between these two values with a scan rate of 10V s⁻¹ for additional 10 min, cycling within the range of the real electrode surface determination (0.050 V -1.550 V) with a scan rate of 0.100 V s⁻¹ for 15 min.

Cyclic voltammetry was applied varying the potential ranges studied and the scan rate applied. Conventional electrochemical equipment was used.

The experiments were run at four temperature values in the interval from 293.2 K to 323.2 K.

RESULTS AND DISCUSSION

The voltammetric profiles presented in Fig. 1 illustrate the behavior of Pt in 0.5 M H₂SO₄ in CH₃OH and the effect of N₂ bubbling through the solution. It is seen that two anodic maxima, A₁ and A₂, are outlined on positive- and negative-going scan, respectively. They are attributed to methanol electrooxidation in this medium containing obviously some traces of water. Unlike the picture in aqueous solution the peak current of A₂ is always greater than that of A₁ even in presence of N₂ bubbling which leads to general current decrease. The latter effect can be attributed to forced convection which

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**Fig. 1. Two voltammetric profiles recorded at Pt in 0.5 M H₂SO₄ in CH₃OH at a scan rate of 0.050 V s⁻¹ in absence (1) and presence (2) of N₂ bubbling through the solution (297.3 K).**
transports the reaction intermediates away from the electrode. Such competition between diffusion, convection and oxidation is observed at high flow rates of aqueous methanol solutions of high concentrations [9].

The experimental results referring to Pt behavior in this medium show that methanol electrooxidation occurs via CO_ads formation which results in electrode surface fouling. The alloy electrocatalysts studied are not so susceptible to blocking by these adsorbed species. Fig. 2 shows that the application of subsequent scanning in the potential range of methanol oxidation at a PtAu alloy results in current increase providing to record a reproducible voltammetric profile. This is observed even in case of low surface content of the equilibrium α_2-phase rich in Au. As expected the latter increase leads to currents decrease and to a change of the peak current densities ratio, i.e. the peak current density of A1 becomes greater than that of A2. The comparison of the Fig. 2(a) and Fig. 2(b) illustrates these considerations. The anodic process investigated competes with oxide coverage formation and CO_ads oxidative removal. This is valid not only for Pt but to a certain extent for PtAu alloy electrodes as well. Fig. 3(a) compares the basic voltammetric profile recorded at a PtAu alloy to two negative-going scans obtained on scan reversal at the peak potential of A1 (scan 1) and at a potential value referring to the current minimum following A1 (scan 2). It is evident that scan 1 goes through a maximum slightly higher than A1, while scan 2 is characterized by a spike much higher than A2. The comparison of the form of the scans considered and the magnitude of the corresponding current densities indicates that oxygen coverage reduction proceeding in both cases is superimposed by CO_ads oxidation under the conditions of scan 2 recording. This explanation is in correspondence with the fact [36] that CO oxidizes approximately between 0.8 V and 1.3 V (vs. RHE) at polycrystalline Au and at ca 1.1 V (vs. RHE) at Pt-modified Au substrates. It is worth adding that the value pointed out varies depending on the Pt coverage and the corresponding particles size. The comparison of the negative-going scans presented in Fig. 3(b) provides further evidence. It is seen that the arrest at the potential reversal value which leads to an increase of the surface oxide coverage results in A2 shifting to less positive values and hence to a decrease of the corresponding peak current density because of hampering of CO_ads oxidation.

It is well recognized that the numerical value of the Tafel slope b depends on the mechanism of the electrode process and the experimental determination of this parameter is one of the most important tools in its elucidation [37,38]. The estimation of b is usually based on the dependence of E vs. log j in correspondence with the Tafel equation

$$E = E_r + a \pm b \log j$$  \hspace{1cm} (5)

where E is the electrode potential, E_r is the reversible potential, j is the current density, while a is a parameter, containing the exchange current density. The procedure
requires the recording of a voltammetric profile at a scan rate of 0.002 Vs\(^{-1}\) and the measurement of the values of \(E\) and \(j\) in the range of the very initial current increase connected with the anodic process considered. The value of \(b\) can be also determined using the linear dependence of the peak potential value on the logarithm of the scan rate applied in accordance with \([36, 37]\).

\[
E_p = E^o + b \left[ 0.52 - \frac{1}{2} \log \left( \frac{b}{D} \right) - \log k^o + \frac{1}{2} \log v \right] \quad (6)
\]

where \(E^o\) is the formal potential, \(D\) is the diffusion coefficient, while \(k^o\) is the standard heterogeneous rate constant. Eq.(6) refers to an irreversible anodic wave and its application in this case is justified because of the overall irreversibility of the process investigated. The fit of the experimental data to Eq. (5) and Eq. (6) gives regression lines with a coefficient of correlation higher than 0.995. Figs. 4 and 5 illustrate some of the dependences obtained. It is worth noting (see Fig.4) that the values of \(b\) referring to A1 do not depend on the equation used. The comparative consideration of the values obtained shows that those obtained in presence of water traces (0.5 M \(\text{H}_2\text{SO}_4\) in \(\text{CH}_3\text{OH}\)) are much higher than the values obtained in aqueous solutions. For an example, \(b = 0.257 \text{ Vdec}^{-1}\) for Pt at room temperature, while for most of the alloys it is slightly higher than that. The Tafel slope found for the process at the alloy containing 20 at. % of Au is the only exception as it is equal to 0.179 Vdec\(^{-1}\). Besides, the potential range where the Tafel equation is obeyed is limited when compared to that observed in presence of water. These results agree well with the data reported in studying absolute methanol electrooxidation \([32]\). The values of \(b\) referring to A2 recorded in 0.5 M \(\text{H}_2\text{SO}_4\) in \(\text{CH}_3\text{OH}\) depend on the equation used. Those obtained at room temperature with application of the Tafel equation are of the order of 0.052 V dec\(^{-1}\) and hence are very close to that widely accepted for the surface oxide removal which is a prerequisite for methanol oxidation proceeding. The values estimated on the ground of Eq.(6) are of the order of 0.116 Vdec\(^{-1}\) (compare the slopes of the lines in Fig 5). They are very close to that found for methanol electrooxidation in aqueous solutions. This can be attributed to the electrode surface activation resulting from oxide reduction and hence the favored \(\text{CO}_\text{ads}\) oxidation \([39\text{ and references therein}]\).

It is found that the temperature increase results in Tafel slope values decrease. This effect cannot be precisely followed in case of A2 as the range of application
Fig. 4. Illustration of Tafel slope determination on the ground of E vs. log \( j \) (a) and \( E_p \) vs. log \( v \) (b) in case of a PtAu alloy electrode of bulk composition of 60 at. % of Au (14.4 % surface content of \( \alpha_2 \)-phase). The data presented refer to the anodic process taking place on positive-going scan in 0.5 M \( \text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{OH} \) at 298.0 K.

Fig. 5(a). Illustration of Tafel slope determination on the ground of E vs. log \( j \) in case of PtAu alloy electrodes of bulk composition of 40 at. % of Au (10.0 % surface content of \( \alpha_2 \)-phase) and 60 at. % of Au (14.4 % surface content of \( \alpha_2 \)-phase). The lines are designated as 1 and 2, respectively. The data presented refer to the anodic process taking place on negative-going scan in 0.5 M \( \text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{OH} \) at 299.3 K and 298.0 K, correspondingly.

Fig. 5(b). \( E_p \) vs. log \( v \) in case of Pt (1) and a PtAu alloy electrode of bulk composition of 60 at. % of Au (14.4 % surface content of \( \alpha_2 \)-phase). The data presented refer to the anodic process taking place on negative-going scan in 0.5 M \( \text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{OH} \) at 297.3 K and 298.0 K, correspondingly.

of Eq. (5) becomes extremely limited, while electrode surface fouling observed on temperature increase hampers to follow the scan rate effect on anodic peak potential as required by Eq. (6). The temperature effect on the Tafel slope values referring to A1 is illustrated in Fig. 6. It shows that the temperature increase brings about \( b \) values decrease to ca 0.10 Vdec\(^{-1}\) in case of 0.5 M \( \text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{OH} \) (Fig. 6a) and to ca 0.06 Vdec\(^{-1}\) in 0.5 M \( \text{H}_2\text{SO}_4 \) in \( \text{CH}_3\text{OH} : \text{H}_2\text{O}= 1:1 \) (Fig. 6b). The data presented can be explained taking into consideration the competition [40] between the parallel and consecutive reaction steps of water molecules destructive chemisorptions, methanol oxidation involving various adsorbed species and \( \text{CO} \) oxidative removal. In addition, the effect of (bi)sulfate adsorption should not be overlooked especially in the solutions under investigation. The anion-platinum interactions are found [41] as important in determining the methanol oxidation rate as is the surface geometry of the Pt catalyst. It precedes in general or occurs in parallel with methanol oxidation affecting the
overall process. It is reported [11, 42, 43] that at Pt(111) it leads to a more prominent role of the direct pathway, while on all other single-crystal Pt surfaces it seems to block the formation of soluble intermediates. However, it does not preclude the presence of water in the adsorption layer [44, 45]. The b values reached at the highest temperature studied in presence of water traces (Fig. 6a), the formation of soluble intermediates as illustrated in Fig. 1 and the electrode surface fouling observed suggest that methanol decomposes to CO via O-H bond scission. In fact, the solution considered does not provide multiple coordination sites for methanol adsorption and hence the alcohol interacts with the surface by O-H bond scission to produce CH_{3}O_{ads}[42,43] and HCOO_{ads}[46-48]. These adsorbed species can be oxidized to CO_{2} but they also imply the existence of formic acid in the solution. It is estimated [49, 50] that formaldehyde is formed even in presence of only two adjacent water molecules. In fact formaldehyde and formic acid have been reported to be among the primary species formed [4,41,42]. The presence of formic acid in the solution considered is further experimentally verified by the curves presented in Fig. 7. The latter illustrates the superimposition of a cyclic profile typical for the alloy containing 60 at.% of Au in 0.5 M H_{2}SO_{4} in CH_{3}OH and that recorded subsequently upon addition of formic acid to the solution. It is seen that even without any stirring the profile obtained in presence of formic acid follows the basic one. This is very well outlined in the range of A1.

The data presented in Fig. 6(b) suggest that the reaction which becomes in fact the rate determining step is that of CO_{ads} oxidative removal. It is well recognized [40] that methanol electrooxidation produces mainly formaldehyde and formic acid at high methanol concentrations at smooth Pt but formate (or formic acid) may also be a precursor for the formation of adsorbed CO [51,Eq.16]. It has to be noted that the transition from nonaqueous to concentrated aqueous environment results in adsorbed CO formation and CO_{2} evolution [52]. The oxidation reaction considered proceeds in a solution of a very high methanol concentration and therefore the amount of water providing oxygenated species for CO oxidative stripping is relatively small. The temperature increase diminishes further this amount as the latter refers mainly to interfacial water molecules only hydrogen-bonded to CO_{ads}[53]. The explanation suggested appears plausible taking into consideration the b values obtained for most of the electrodes at higher temperatures. They are close to 0.07 Vdec^{-1}, i.e. to that of the Tafel slope of CO coverage oxidation [54,55]. A further insight to the mechanism of the process taking place in this medium is provided by the profile presented in Fig. 8. It is recorded at a scan rate of 0.002 Vs^{-1} at an alloy containing 80 at. % of Au. In this particular case Au surface content is equal to 46.0% and the temperature is 327.65 K. The form of A2 is the most striking feature of the figure discussed. It includes four well outlined spikes followed by a broad peak. This peculiar form of the profile illustrates the consecutive
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scission of the three C-H bonds and the subsequent removal of the last H atom to leave CO$_{ads}$ on the electrode surface. It has to be pointed out that this pathway of methanol decomposition is in full correspondence with Scheme 1 of methanol oxidation presented in ref.[11]. In fact, the solution composition, the temperature and the electrode surface structure in this case are successfully interrelated to illustrate the proceeding of reactions 1, 2, 3 and 5 in Scheme 1 [11] which is found fairly complete and consistent picture of methanol oxidation mechanism on Pt. The explanation provided is additionally supported by the b values found at room temperature. They are very close to 0.120 Vdec$^{-1}$ which is attributed [41] to C-H scission as a rate determining step of methanol oxidation at Pt(111).

The data presented in Fig. 6 require further consideration as they illustrate the general trend of the temperature effect on Tafel slope values variation. It is seen that some of the points referring to the PtAu alloys studied are quite scattered. This could be explained by the effect of the alloy surface composition as methanol electrooxidation pathways are structure sensitive [11, 40-42 are some of the numerous investigations in the field]. It is now recognized [56] that the low activity of Pt for methanol oxidation is attributed to its inability to dissociate non-hydrogen bonded water molecules co-adsorbed with CO to produce adsorbed OH species required for CO and methanol oxidation at low potentials. Gold is virtually inactive towards methanol oxidation in an acidic medium and is not helpful for removing CO$_{ads}$ on Pt surface [51, 57]. It is further specified [58] that Au is not interesting for the preparation of active Pt-based bimetallic alloys devoted to methanol oxidation because the alloying results in (i) Pt antisegregation and hence in Pt sites reduction; (ii) Au as well as Pt d-band center shifts determining the poor abilities for adsorption of OH species and stronger adsorption of CO-like species, correspondingly. It is important to add that methanol can undergo [59] decomposition on gold in acidic media to yield chemisorbed fragments that are commonly claimed to be reactive intermediates in transition-metal electrocatalytic systems. But the key requirement is the availability of oxygen-donor coadsorbates with which the chemisorbed intermediates can be converted to CO$_2$ and other products. Regardless of all that there are studies which report electrocatalytic activity of AuPt/C catalysts [20, 21, 60] and of even small amounts of Pt on gold substrates [36] for methanol oxidation. It is claimed that the electron exchange between Au and Pt promotes the formation of active oxygen species on Pt or that the major methanol oxidation pathway is altered by alloying Au with Pt. The results obtained in this study show that a certain decrease of the apparent activation energy of methanol electrooxidation is observed in both media.

Fig. 7. Juxtaposition of a typical cyclic profile (1) recorded at a scan rate of 0.050 Vs$^{-1}$ on PtAu alloy electrode of bulk composition of 60 at.% of Au in 0.5 M H$_2$SO$_4$ in CH$_3$OH at 297.3 K and subsequently recorded profile (2) on introduction of 0.5 ml of HCOOH without any stirring.

Fig. 8. A cyclic profile recorded at a scan rate of 0.002 Vs$^{-1}$ on PtAu alloy electrode of bulk composition of 80 at.% of Au in 0.5 M H$_2$SO$_4$ in CH$_3$OH:H$_2$O=1:1 at 327.65 K. The surface composition of the electrode is 46.0%.
studied. The effect is better outlined in presence of water traces only. Besides, that referring to the anodic process determining A1 is the greatest. The dependences of the apparent activation energy on the bulk composition of the alloys used are shown in Fig. 9. It is worth noting that the surface composition of the alloys varies. It cannot be set in advance or kept constant by a specific pretreatment of the electrode surface. Some regulations in this respect can be achieved by using Pt-Au nanoparticles deposited on a given substrate but following strict requirements concerning the structure and the morphology of the electrode surface as the effect of the latter is very strong. Then perhaps it can be experimentally verified that the data reported in this study illustrate not only that alloying changes the electrode surface structure and its susceptibility to poisonous intermediates but alters to a certain extent the pathway followed in methanol oxidative transformation. In any case it is preferable to use PtAu bimetallic systems instead of Pt in carrying out experiments in non-aqueous media containing methanol. The electrode surface fouling will be certainly decreased.

CONCLUSIONS

The electrochemical experiments carried out in 0.5 M H$_2$SO$_4$ in CH$_3$OH and in 0.5 M H$_2$SO$_4$ in CH$_3$OH:H$_2$O=1:1 using Pt and PtAu bimetallic systems of varying bulk and surface composition show that the water presence affects the methanol decomposition pathway. O-H bond scission occurs preferably in the first medium leading to formation of formaldehyde and formic acid, while sequential C-H rupture takes place in the second one where the water molecules can reorient in a compact way to serve as a precursor of the oxygen species required. The apparent activation energy of the process is found to decrease with Au bulk increase till about 60 at. %. The effect is better outlined in presence of water traces which implies that PtAu bimetallic electrode systems should be preferred when compared to Pt in experiments carried out in non-aqueous media containing methanol. It can be generally concluded that the amount of water present controls the pathway of methanol oxidative transformation, while alloying favors predominantly the kinetics of the process through its effect on the surface susceptibility to poisonous intermediates.

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