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Electrochimica Acta 46 (2001) 3525–3534

ELECTROCHIMICA Acta

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Anodic oxidation of methane at noble metal electrodes: an 'in situ' surface enhanced infrared spectroelectrochemical study

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Received 28 February 2001; received in revised form 6 June 2001

Abstract

The mechanism of electrooxidation of methane at 25 °C in 0.5 M $HClO_4$ on the noble metal electrodes Pt, Au, Pd, Ru and Rh has been investigated by 'in situ' infrared spectroscopy. The final product of oxidation was found to be CO_2 in all cases. Using the technique of surface enhanced infrared absorption spectroscopy and deuterated water solutions, it has been possible to detect the presence of adsorbed intermediates such as CO and –CHO (or –COOH) for the first time. The infrared signal enhancement observed could be accounted for by considering the increase in the surface area of the electrodeposited metals as indicated by the cyclic voltammograms. Pt and Ru appear to have the highest, and Au the lowest, electrocatalytic activity among the metals studied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Methane; Noble metals; Anodic oxidation; Spectroelectrochemical study; Surface enhanced infrared spectroscopy

1. Introduction

The need for new power sources which minimize environmental pollution has spurred a renaissance in the further development of fuel cells for electric vehicle propulsion and for electricity generating power stations [1]. Fuel cell devices have proven their utility in aerospace applications where hydrogen has been used as fuel. However, problems with the storage of hydrogen in tanks or as metal hydrides, as well as costs, have prevented the commercial use of fuel cells for other more widespread applications. Methane and methanol are among the most simple and readily available organic compounds that can be used as fuel and are hence of great interest for use in fuel cell devices. Methanol is attractive because it can be obtained from renewable sources, such as corn and other agricultural products. Its electrochemical oxidation has therefore been extensively studied [2,3]. Little work has been done on methane as a fuel cell feedstock. Recent discovery of methane hydrate deposits under the ocean floor and the Arctic permafrost suggests that they are a potentially enormous resource that could fuel the 21st century and the third millennium [4]. There is thus a great economic incentive to develop a fuel cell device that could effectively utilize methane.

So far, because of its high stability, the use of methane as fuel has been limited to high temperature fuel cells, i.e. molten carbonate and solid oxide [5], after reforming into hydrogen and carbon monoxide mix-

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PII: S0013-4686(01)00649-1

tures [6]. There have been efforts to oxidize methane directly in low temperature fuel cells [7–9]. Recently, Berthelot et al. [10] showed that electrooxidation of methane could be carried out in a polymer electrolyte membrane fuel cell using high surface area electrodes with Pt and dispersed Pt–Ru as electrocatalysts. They reported that different products resulted from the use of the two different electrodes, i.e. carbon dioxide was produced in the case of Pt and methanol resulted when using Pt–Ru. Attempts to determine the mechanism of electrooxidation of methane from purely electrochemical studies have also been made [11,12]. Hsieh and Chen interpreted the results of their polarization measurements in acidic sulfate electrolyte at 80 °C by postulating the formation of intermediates from adsorbed CH_3 [11]. Sustersic et al. suggested the formation of adsorbed intermediates such as CO_2 and COH from their cyclic voltammetry (CV) studies in 1 N H_2SO_4 solution at 60 °C [12]. In the present work, we provide 'in situ' infrared spectroscopic evidence that unequivocably establishes for the first time the nature of some of the intermediates involved in the oxidation of CH_4. The technique of surface enhancement of the IR signal by electrodeposition was found particularly useful in enabling the detection of weak signals from the intermediates.

2. Experimental

The IR spectroelectrochemical cell and spectrometer have been described previously [13]. The cell was fitted with a flat CaF_2 window (25 mm diameter × 4 mm thick) to admit the IR radiation. The Fourier transform infrared (FTIR) spectrometer was a Bruker model IFS 66v with a liquid nitrogen-cooled MCT detector. The working electrodes were in the form of discs about 8 mm in diameter and 0.5–2 mm thick. They were attached to the end of a glass tube holder using epoxy, then polished with successive grades of alumina powder down to 0.3 μm, and rinsed thoroughly. The counter electrode consisted of a coil of Pt wire, while a hydrogen electrode was used as reference (RHE). The electrolyte was 0.5 M $HClO_4$; it was prepared from a suprapure material and ultrahigh purity water (Millipore-Milli Q). The solution was deaerated by bubbling ultrapure nitrogen gas (Air Liquide, quality U). The methane used was also obtained from Air Liquide (Alphagaz, purity N55). It was adsorbed on the electrodes by bubbling through the electrolyte solution for 1–3 h while the potential of the electrode was held at a certain value. 'In situ' IR spectra were obtained by either one of three techniques: (1) linear potential sweep-Fourier transform infrared spectroscopy (LPS-FTIRS); (2) potential difference infrared reflectance spectroscopy (PDIRS); and (3) subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy (SNIFTIRS). In the LPS-FTIRS technique [14], the potential of the electrode is scanned at 1 mV/s and interferograms are taken at regular intervals, say 100 mV. The interferograms are co-added and converted into reflectances, which are then ratioed to that of a reference in order to obtain spectra (transmittance). The second method (PDIRS) is very similar to the first one except that instead of scanning the potential at a very slow rate, it is stepped from an initial value (the reference) to a higher value and interferograms are collected for preset periods of accumulation at each potential [15]. It has the advantage that long counting periods could be employed to collect the spectra and thus improve on the signal to noise ratio. In the SNIFTIRS technique [16], the potential is modulated between two values while interferograms are taken at each potential and then co-added. Surface enhancement of the IR signal on Pt was carried out by platinization of the electrode following the procedure of Bjerke et al. [17]. Surface enhanced infrared absorption spectroscopy (SEIRAS) studies on Ru and Pd were carried out by electrodeposition of the metal on ruthenium disc and glassy carbon (GC) substrates, respectively. The conditions used for electrodeposition were similar to those outlined by Tian et al. [18] for surface enhanced Raman spectroscopy (SERS), but with some modifications. Thus, our solutions consisted of 0.01 M $PdCl_2$ in 0.1 M KCl for Pd plating and 0.01 M $K_2RuCl_5 \cdot xH_2O$ in 0.1 M KCl for Ru deposition. Moreover, the latter was carried out at a potential of − 0.2 V versus RHE for 5 min rather than the conditions used by Tian et al. [18]. The roughening procedure prescribed by Weaver and coworkers [19] was also used in an attempt to obtain SEIRAS on Au. In all cases, following electrodeposition, the electrodes were rinsed thoroughly with water before transfer to the IR spectroelectrochemical cell. All electrochemical and infrared spectroscopic measurements were carried out at ambient temperature.

3. Results

Fig. 1 shows cyclic voltammograms of Pt before (solid line) and after adsorption of methane (broken line) at 0.26 V while bubbling for 2 h in 0.5 M $HClO_4$. It is evident that the hydrogen adsorption–desorption peaks are suppressed partially which indicates the presence of an adsorbed species covering the electrode surface. There is an increase in current during the anodic scan which presumably corresponds to the oxidation of the adsorbed species. Fig. 2 shows 'in situ' IR spectra of the Pt disc electrode obtained by LPS-FTIRS. The technique allows the monitoring of the products or intermediates of an electrode reaction as a function of applied potential. From Fig. 2, for example, the appearance of a band at 2345 cm^{-1} is associated with the production of CO_2 due to the electrooxidation of CH_4. There is some indication of the presence of a band due to CO at about 2020 cm^{-1}. The positive-going band at about 1650 cm^{-1} is due to water which is presumably consumed in the oxidation process. However, the anticipated increase in the intensity of the band with potential is difficult to discern because of the poor signal to noise ratio. There is also a broad band at about 1750 cm^{-1} which may be due to some dissolved acidic, aldehydic, or ketonic species bearing a –CO moiety. We were unable to observe a band that we could attribute to adsorbed CH_4 or other surface species using conventional FTIR spectroscopy. We therefore resorted to the use of the SEIRAS technique by electrodeposition of Pt on the Pt (will be referred to as platinized Pt) disc electrode [17]. Along with the use of deuterated water, D_2O, to shift the position of the water bands (especially the band at around 1640 cm^{-1}), the resulting signal enhancement is then sufficient to observe the very weak signals due to the intermediates adsorbed on the surface. Fig. 3 shows LPS-FTIR spectra obtained 'in situ' following adsorption of CH_4 on the surface of a platinized Pt electrode. (Note that the reference for the spectrum is taken at 1.46 V so that the bands are inverted, i.e. going up rather than going down.) Bands at about 1719 and 2027 cm^{-1} are evident due to the presence of the carbonyl moiety of a –CHO (aldehyde) or –COOH (acid) intermediate and CO, respectively. A band at 2345 cm^{-1} due to CO_2 could also be expected but the OD stretching bands due to HDO and D_2O solution species which occurs in the same region are very intense to effectively mask the signal due to CO_2. The presence of the adsorbed species on the electrode surface is further confirmed in a SNIFTIRS experiment. Fig. 4 shows the results of such a measurement. Again, bands at 1706–1713 and about 1994–2031 cm^{-1} (pseudo-derivative in shape due to modulation) are observed. FTIR spectroelectrochemical studies of Au, Pd, Ru, and Rh also showed the production of CO_2 from the oxidation of CH_4. To obtain better sensitivity the SEIRAS technique was employed as far as practicable using the electrodeposition technique. Fig. 5 shows cyclic voltammograms of a smooth Ru electrode (solid line) compared to that of ruthenium electrodeposited (ruthenized) on a Ru disc (broken line). The considerable increase in current is evident and is presumably due to the increased surface area of the electrodeposited electrode. Fig. 6 shows PDIR spectra on the smooth Ru disc as a function of potential following the adsorption of CH_4. A band at 2345 cm^{-1} is observed due to the production of CO_2. The upward-going band at about 1650 cm^{-1} is presumably due to water; there also appears to be a downward-going band at about 1600 cm^{-1}. For the ruthenized Ru electrode, an additional band is observed at about 2047 cm^{-1} which is assigned to adsorbed CO (Fig. 7). There are other bands in the spectral region from 1550 to 1850 cm^{-1}. Adsorption and oxidation of CH_4 on smooth polycrystalline Pd showed only the production of CO_2. The use of Pd electrodeposited on GC to obtain IR surface enhancement, allowed the observation of a band at 2025 cm^{-1} due to CO. CO_2 at 2345 cm^{-1} and an unknown species at about 1600 cm^{-1} were observed on both smooth and roughened polycrystalline Au electrodes, as illustrated in Fig. 8. In Table 1 we summarize the main results of spectroelectrochemical experiments on the various metals which we have studied. We have included data obtained on the use of GC as a substrate in order to serve as a reference for comparing the results on palladium electrodeposited on GC. It was also of interest to see the behavior of a non-catalytic surface for methane electrooxidation, in comparison with noble metals which are generally regarded as electrocatalytically active.

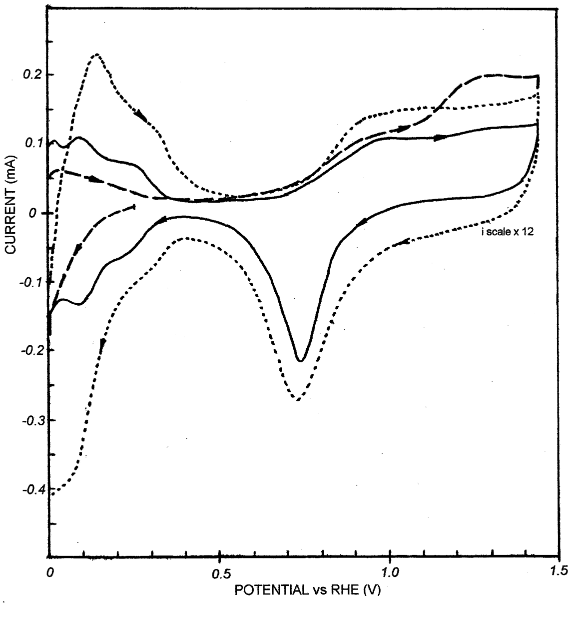

Fig. 1. Cyclic voltammograms of Pt in 0.5 M $HClO_4$ deaerated solution (solid line) and after bubbling CH_4 through the solution for 2 h (broken line) at 0.26 V; cyclic voltammogram of platinized Pt (dotted line); scan rate = 100 mV/s.

4. Discussion

4.1. Adsorption and oxidation of methane on Pt

Most of the studies on the electrochemical oxidation of methane have been conducted at temperatures above ambient because of the molecule's relative inertness and

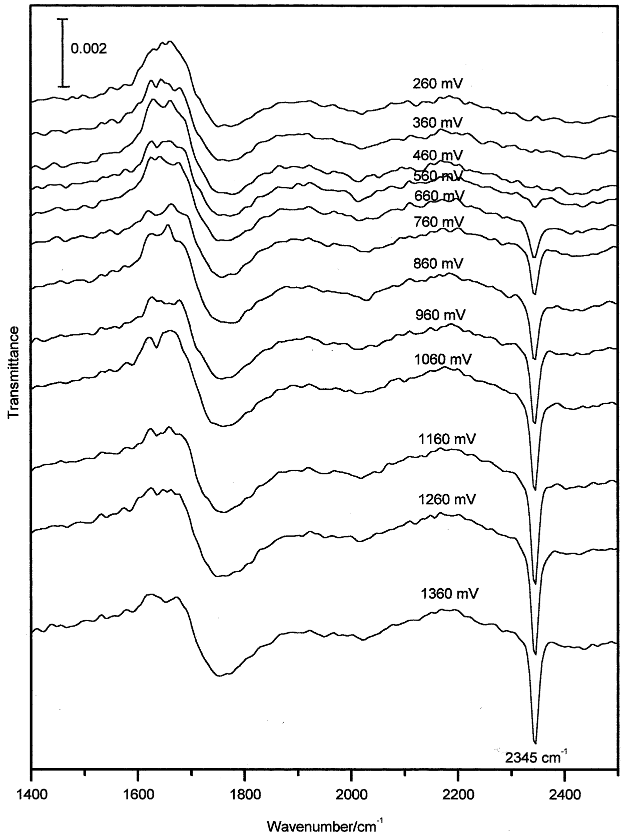

Fig. 2. 'In situ' LPS-FTIR spectra from a Pt disc electrode as a function of potential following adsorption of CH_4 at 0.16 V for 45 min (referenced to reflectance at 0.16 V).

difficulty to activate. The effective utilization of methane in fuel cells has therefore been confined so far to temperatures above 500 °C [20]. Without doubt, there is great economic incentive to find an electrocatalyst which would activate methane at room temperature. The complete anodic oxidation reaction involved is normally given as

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 8H^+ + 8e^- \quad E^\circ = 0.146\ \text{V} \quad (1)$$

It is easy to see from the above equation that the reaction cannot be a simple one, since it involves water as a co-reactant and requires the transfer of eight electrons. A catalytic electrode with activity for the adsorption of CH_4 and water (or OH_{ads}) is thus essential in order to effectively use methane in fuel cells.

The adsorption and subsequent anodic oxidation of CH_4 on Pt at temperatures above ambient have been established by a number of workers using various electrochemical techniques [8,11,12]. From these measurements, attempts have been made to deduce the nature of the adsorbed species on the electrode surface and proposals made on the mechanism of the electrooxidation process. Thus, Marvet and Petrii [21] have suggested that the equilibrium potentials observed upon adsorption of CH_4 on the platinized Pt in H_2SO_4 solutions is due to the dehydrogenation of CH_4 resulting in a shift of the electrode potential to the hydrogen region. From a study of the charge associated with the electrooxidation of the adsorbed species, they suggested that the latter contains an HCO entity. Niedrach and Tochner [9] have likewise suggested a C_1 oxygenated hydrocarbon species to be the intermediate in the anodic oxidation of CH_4 and C_2H_6 from an interpretation of the results of their potentiodynamic measurements in phosphoric acid electrolyte. Hsieh and Chen [11] proposed a mechanism involving the dissociative adsorption of CH_4 forming adsorbed CH_3 whose further conversion to an intermediate constitutes the rate determining step in the overall process of oxidation to CO_2. The mechanism was found to be consistent with the authors' results of the polarization measurements in acid sulfate electrolyte at 80 °C. Sustersic et al. [12] postulated the adsorption of two types of species, COH (or COOH) and CO, in order to explain their potentiodynamic measurements in 1 N H_2SO_4 solution at 60 °C. Needless to say, structural information from the spectroscopic measurements are essential in order to confirm any of the mechanisms that have been proposed. Berthelot [22] has attempted to make such measurements on the carbon-supported noble metal catalysts and their mixtures. However, the spectra were often not of sufficiently high signal to noise ratio to give definitive assignments of the bands to various species.

Our CV results (Fig. 1, broken line) are consistent with those obtained by others, although the anodic wave associated with the oxidation process is not as well defined at 25 °C as those observed at higher temperatures [8]. The first scan after bubbling CH_4 through the solution shows partial suppression of hydrogen adsorption indicating the presence of another species on the electrode surface. A search for the vibrational bands of adsorbed CH_4 or CH_3, did not yield any spectrum. From our own measurements on pure CH_4, bands could be expected at about 3016 and 1304 cm^{-1}, corresponding to the C–H stretching vibrational mode and the H–C–H bending mode, respectively. The absence of such bands might indicate that the adsorbed CH_4 quickly dissociates to some other species which in turn reacts with water (or OH) to form a CO-containing surface intermediate. This would be consistent with

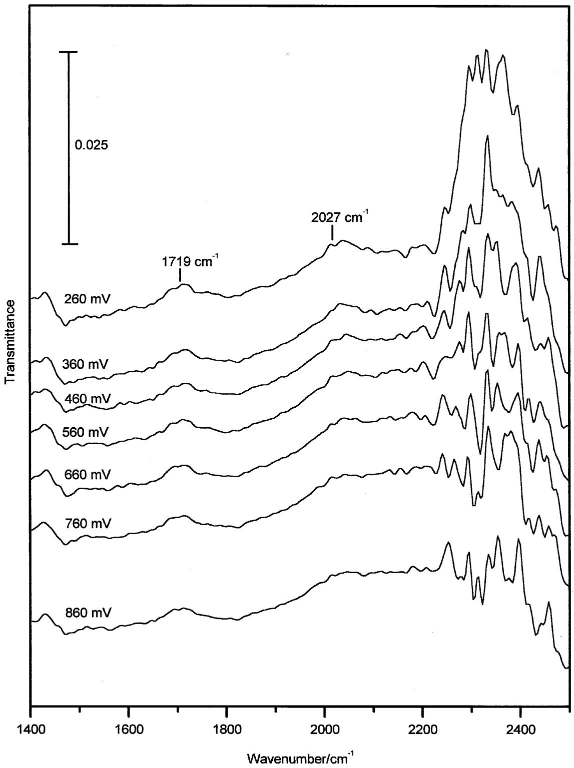

Fig. 3. 'In situ' LPS-FTIR spectra from a platinized Pt in 0.5 M $HClO_4$ with D_2O; CH_4 adsorbed at 0.26 V for 1 h (referenced to reflectance at 1.46 V).

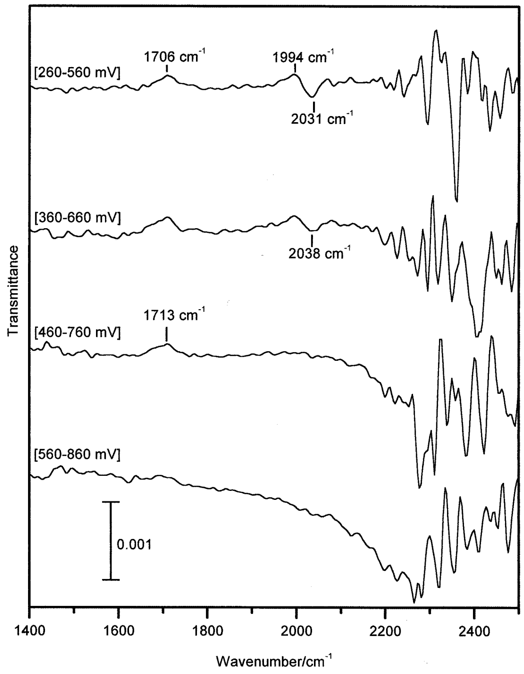

Fig. 4. 'In situ' IR spectra from a platinized Pt in 0.5 M $HClO_4$ with D_2O obtained by the SNIFTIRS technique; CH_4 adsorbed at 0.26 V for 2 h; modulation potentials indicated in brackets.

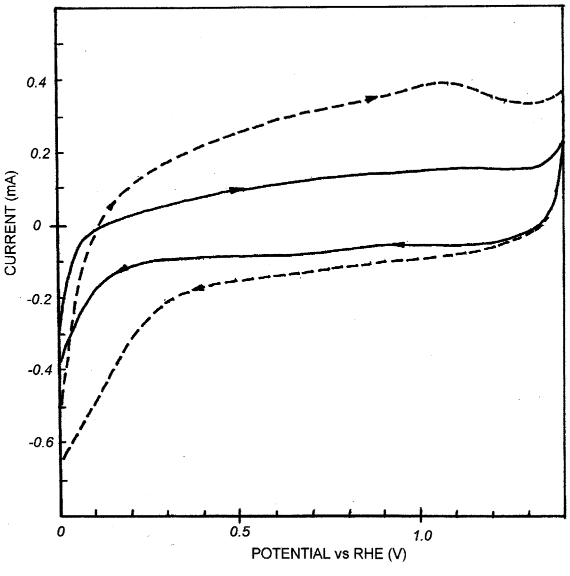

Fig. 5. Cyclic voltammograms of a polycrystalline Ru disc electrode (solid line) and a ruthenized Ru electrode (broken line) in 0.5 M $HClO_4$ solution; scan rate = 100 mV/s.

a fast dehydrogenation step as Marvet and Petrii [21] have suggested. However, Hsieh and Chen's [11] proposal on the adsorption of CH_3 cannot be confirmed.

Our LPS-FTIRS study showed the formation of CO_2 starting at about 500 mV, as indicated by the appearance of a band at 2345 cm^{-1} and possibly also CO at about 2020 cm^{-1} (Fig. 2). The use of SEIRAS with platinized Pt [17] provided for increased sensitivity. With the use of deuterated water as solvent, we found bands at about 1730 and 2027 cm^{-1} (Fig. 3). We assign the former to the vibration of a CO moiety in a –CHO (aldehyde) or –COOH (acid) species; the 2027 cm^{-1} band is due to the CO adsorbed on the Pt surface. The width of the CO band is rather broad and may be due to the presence of linearly bonded CO (commonly designated as CO_L, with the C atop the Pt) as well as bridge-bonded CO (or CO_B). These species generally give vibrational frequencies at about 2050 and 1950 cm^{-1}, respectively [23]. There may also be contribution to line broadening due to the heterogeneity of the surface sites on the polycrystalline Pt electrode. Most interestingly, the bands are already observed at 260 mV (Table 1) which suggest that they are likely to be intermediates in the conversion of CH_4 to CO_2. The reality of these bands was confirmed by SNIFTIRS measurements as a function of potential and with a modulation amplitude of 300 mV. Fig. 4 shows spectral bands at about 1706 and 2030 cm^{-1} with relatively good signal to noise ratio.

The results which we have obtained so far tend to support theories suggested by earlier workers [9,11,12,21], remarkably made on the basis of the electrochemical measurements alone, that CH_4 adsorbs dissociatively on the Pt surface and that a C_1 oxygenated hydrocarbon species is formed on anodic oxidation of CH_4. There have been mechanistic models proposed [22,24] to explain the anodic oxidation of CH_4. Bagotzky et al. [24] have suggested a generalized chemisorption scheme wherein the oxidation of a simple organic molecule involves a series of dehydrogenation steps and reaction with adsorbed OH radicals. The latter provides the essential step to introduce the oxygen into the hydrocarbon chain and the CO moiety. Berthelot [22] has similarly found CO_2 to be the principal product of CH_4 electrooxidation on Pt and has proposed a number of steps involved in the oxidation of C^{-4} in CH_4 to C^{+1} in CHO and subsequently from C^{+2} in CO to C^{+4} in CO_2. Hydrogenated free radicals,

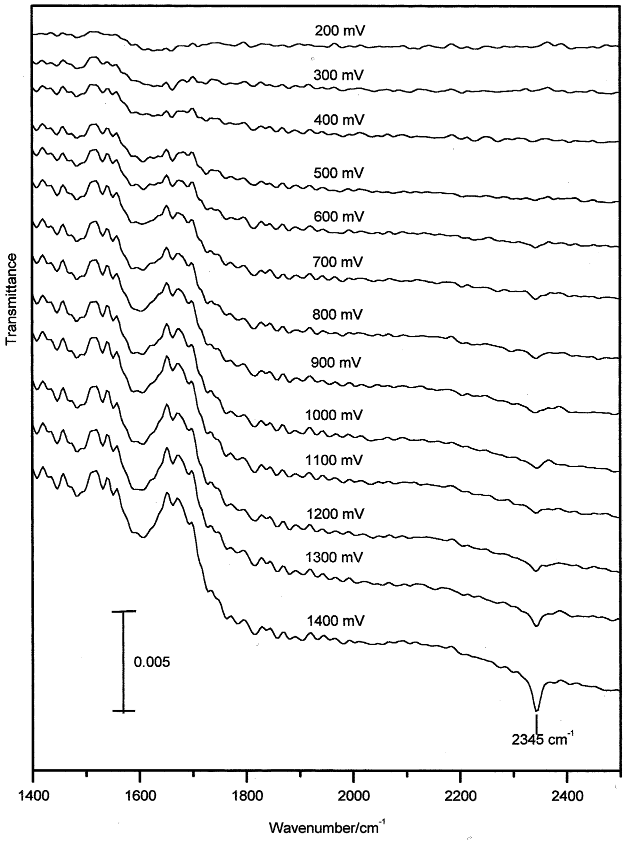

Fig. 6. 'In situ' PDIR spectra from a Ru disc electrode; CH_4 adsorbed at 0.1 V for 2 h (referenced to reflectance at 0.1 V).

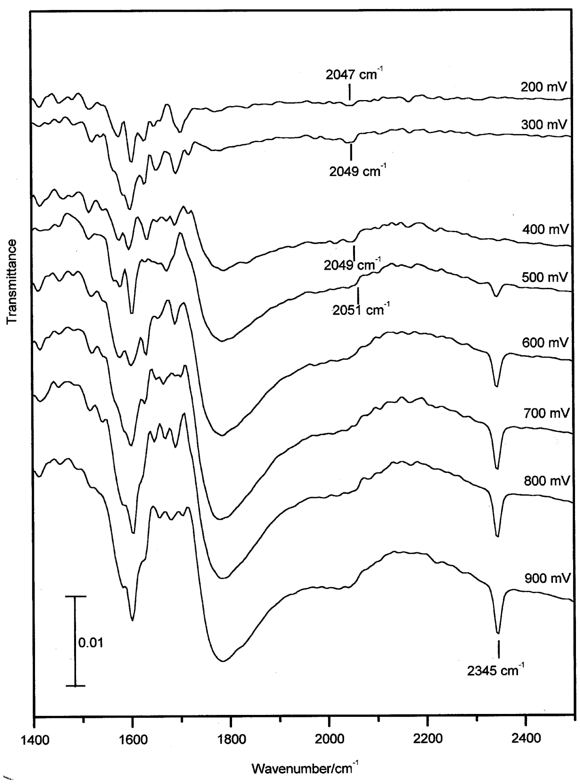

Fig. 7. 'In situ' PDIR spectra from a ruthenized Ru electrode; CH_4 adsorbed at 0.1 V for 2 h (referenced to reflectance at 0.1 V).

as well as C_1 alcohols, and acids have been postulated as intermediates formed. The detection of these species spectroscopically has eluded us so far. Our observation on the presence of CO and –CHO (or –COOH) at relatively low potentials (0.26 V) does suggest the involvement of a hydroxylated species (H_2O or OH_{ads}) early in the dissociation/oxidation reaction of CH_4. This is rather surprising. CO and –CHO are the same species that have been observed in the anodic oxidation of methanol. The formation of CHO should normally precede that of CO and –COOH. We are unable to distinguish between –CHO and –COOH at this time. The simultaneous observation of –CHO and CO may be suggestive of two different oxidation pathways, e.g.

$$CH_4 + H_2O \Leftrightarrow (CHO)_{ads} + 5H^+ + 5e^- \qquad (2)$$

$$CH_4 + H_2O \Leftrightarrow (CO)_{ads} + 6H^+ + 6e^- \qquad (3)$$

Still, such mechanisms will involve the simultaneous transfer of five or six electrons and this is deemed highly improbable. Even the further oxidation of adsorbed CO and CHO species to CO_2 would require three and two electrons, respectively, i.e.

$$(COH)_{ads} + H_2O \Leftrightarrow CO_2 + 3H^+ + 3e^- \qquad (4)$$

$$(CO)_{ads} + H_2O \Leftrightarrow CO_2 + 2H^+ + 2e^- \qquad (5)$$

In any case, it is most likely that other intermediates are involved in the multiple steps and further elucidation of the mechanism of CH_4 oxidation will have to await the identification of these species. It is also apparent that the discovery of the intermediates would require even better sensitivity in the technique being used. We are trying to explore the use of differential electrochemical mass spectroscopy to see if other reaction products could be identified and also to further confirm the results obtained in the present work.

4.2. *Investigations on other noble metals*

Studies on the oxidation of CH_4 at Au, Pd, Rh and Ru electrodes showed that the activity of the metals toward the electrooxidation process varies significantly as can be discerned from the spectroelectrochemical data presented in Table 1. CO_2 has been observed as the main oxidation product for all. From the value of the potential at which CO_2 is first observed, it can be surmised that Pt and Ru are the most effective electrocatalysts. The low activity of Au, wherein the appearance of CO_2 is first observed by IR at 0.9 V, was not unexpected. It is consistent with the results obtained by others on the high anodic potential at which CO oxidation occurs on Au in acid solutions [25,26]. We also observe a band at about 1600 cm^{-1} in the case of Au and Ru electrodes. This frequency is too low to be assigned to some –CO moiety or water; we have no satisfactory explanation for its origin at this time. Interestingly for comparison, GC shows the highest overpotential and can be said to have no electrocatalytic activity for the anodic oxidation of CH_4. Ru appears to have a slightly higher activity for the production of CO_2 than Pd. CO has been found as an intermediate in the case of Pt, Ru and Pd, where increased detection sensitivity has been possible using SEIRAS. Attempts to detect –CHO or –COOH on electrodeposited Ru and Pd using SNIFTIRS and with D_2O solutions did not yield definitive results.

4.3. *Utility of the SEIRAS technique*

It is worthwhile to point out here the utility of the SEIRAS technique because it has not been as widely recognized as the corresponding SERS technique. Hatta et al. [27] first applied the SEIRA technique to the study of the electrochemical interface. Osawa et al. [28] subsequently studied the SEIRA effect more extensively. The enhancement factors obtained in SEIRA are not as high as for SERS, but they are nevertheless sufficient to allow for the identification of weak signals. A comparison of the intensity of the CO bands at about 2027 cm^{-1} in Figs. 2 and 3 suggests an enhancement of

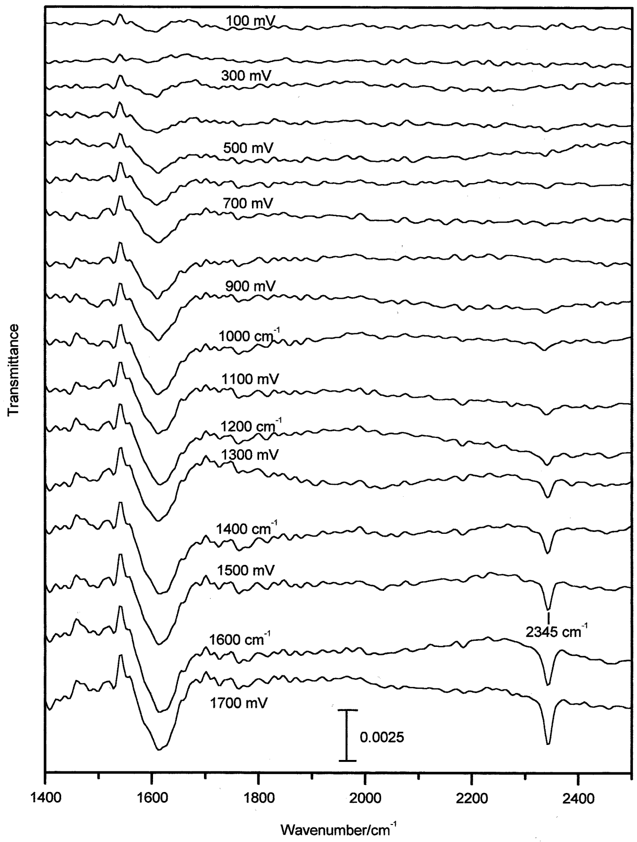

Fig. 8. 'In situ' LPS-FTIR spectra from a smooth Au electrode; CH_4 adsorbed at 0.0 V for 1 h (referenced to reflectance at 0.0 V).

about ten times have been obtained by electrodeposition in the present work. This maybe accounted for by the increased surface area of the electrodeposited material. One can see this from a comparison of the current–potential curves for the platinized Pt (dotted line) with that of the smooth Pt disc (full line) in Fig. 1. The magnitude of the currents for the former is nearly about 20 times higher than for the Pt disc electrode. The shape of the cyclic voltammogram is very similar. The increase in current is obviously a result of the increased surface area of the electrodeposited material. A similar increase accompanied the electrodeposition of Ru on a ruthenium disc electrode. The difference in the magnitudes of the currents for the two electrodes (Fig.

Table 1
Summary of spectroelectrochemical results

Metal electrode	Adsorption potential (V)	Time (h)	Potential (V) at which product first observed	Product	Type of experiment
Pt	0.16	0.75	0.56	CO_2	LPS-FTIRS
Pt/Pt (in D_2O)	0.26	1.0	0.26	–CHO, CO	LPS-FTIRS
Pt/Pt (in D_2O)	0.26	2.0	0.26	–CHO, CO	SNIFTIRS
Ru	0.1	2.0	0.6	CO_2	PDIRS
Ru/Ru	0.1	2.0	0.5	CO	PDIRS
Pd	0.3	1.0	0.8	CO_2	LPS-FTIRS
Pd/GC	0.3	3.0	0.6	CO	LPS-FTIRS
Rh	0.1	1.0	0.7	CO_2	LPS-FTIRS
Au	0.0	1.0	0.9	CO_2	LPS-FTIRS
GC	0.1	3.0	1.3	CO_2	LPS-FTIRS

5) is again mainly due to the increased surface area associated with the higher roughness factor for the ruthenized electrode. The same could be said for the Pd electrodeposited on GC. Thus, it does not appear necessary to use a model of plasmon resonance at the surface of the very small metal islands or particles as have been generally invoked by others [17,27,28]. This is not to say that such a phenomenon does not exist or is not operative here also. Attempts were made to utilize the SEIRA effect on gold by roughening the electrode surface in KCl solution following the procedure used by Weaver and coworkers [19] to obtain SERS. However, these have not been successful. Surprisingly, we found no increase in the surface area of the electrode following the roughening procedure. It appears therefore not unreasonable to find no SEIRA in the case of Au. It can be argued that maybe the length scale involved in SERS is not the same as for SEIRAS. It is rather difficult to accept since Ataka et al. [29] have effectively utilized the SEIRA effect on the electrodeposited Au for their investigations on potential dependent water reorientation at the electrode/electrolyte interface. Finally, we might mention here that we have not attempted to optimize the electrodeposition conditions, as well as the morphology and size of the electrodeposited metals. Further gain in enhancement factors could possibly result from such a study. Suffice it to say, that we found the SEIRAS technique to be a most useful adjunct in infrared spectroscopy and the method of electrodeposition is particularly convenient for the preparation of appropriate electrode materials.

5. Conclusions

The spectroscopic identification of the products of chemisorption and oxidation of methane at noble metal electrodes has been carried out using infrared spectroscopy, with and without surface enhancement via the electrodeposition of the metal. In all cases, the final product observed was CO_2. CO and –CHO (or –COOH) have been identified as reaction intermediates on Pt, presumably arising from the dissociative adsorption of CH_4 at the electrode surface with concomitant reaction with water. The mechanism of oxidation appears to be similar to that of methanol in that CO and –CHO (or –COOH) are produced. The associated problem of electrode poisoning will therefore have to be dealt with. Activation of methane at room temperature is nevertheless possible using noble metals as electrocatalysts. The most active appears to be Pt and Ru. It would be interesting, in future work, to examine the effect of alloying (e.g. Pt–Ru and Pt–Pd) on the electrocatalytic activity. The effect of temperature on the rates and mechanisms of CH_4 electrooxidation should also be worthwhile to study and would be of great practical importance for the development of a commercially viable fuel cell system. Finally, the role of water continues to pose a most interesting fundamental question that remains unanswered to date.

Acknowledgements

The financial support of the Université de Poitiers and the CNRS-UMR 6503 are gratefully acknowledged. One of us (C.A.M.) thanks Professor C. Lamy for support during a sabbatical year that made this work possible.

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